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Preface

This handbook features selected articles from the 7th edition of *ULLMANN'S Encyclopedia of Industrial Chemistry*, including newly written articles that have not been published in a printed edition before. True to the tradition of the ULLMANN'S Encyclopedia, polymers and plastics are addressed from an industrial perspective, including production figures, quality standards and patent protection issues where appropriate. Safety and environmental aspects which are a key concern for modern process industries are likewise considered.

More content on related topics can be found in the complete edition of the ULLMANN'S Encyclopedia.

About ULLMANN'S

ULLMANN'S Encyclopedia is the world's largest reference in applied chemistry, industrial chemistry, and chemical engineering. In its current edition, the Encyclopedia contains more than 30,000 pages, 15,000 tables, 25,000 figures, and innumerable literature sources and cross-references, offering a wealth of comprehensive and well-structured information on all facets of industrial chemistry.

1,100 major articles cover the following main areas:

- Agrochemicals
- Analytical Techniques
- Biochemistry and Biotechnology
- Chemical Reactions
- Dyes and Pigments
- Energy
- Environmental Protection and Industrial Safety
- Fat, Oil, Food and Feed, Cosmetics
- Inorganic Chemicals
- Materials
- Metals and Alloys
- Organic Chemicals
- Pharmaceuticals
- Polymers and Plastics
- Processes and Process Engineering
- Renewable Resources
- Special Topics

First published in 1914 by Professor Fritz Ullmann in Berlin, the *Enzyklopädie der Technischen Chemie* (as the German title read) quickly became the standard reference work in industrial chemistry. Generations of chemists have since relied on ULLMANN'S as their prime reference source. Three further German editions followed in 1928–1932, 1951–1970, and in 1972–1984. From 1985 to 1996, the 5th edition of ULLMANN'S Encyclopedia of Industrial Chemistry was the first edition to be published in English rather than German language. So far, two more complete English editions have been published in print; the 6th edition of 40 volumes in 2002, and the 7th edition in 2011, again comprising 40 volumes. In addition, a number of smaller topic-oriented editions have been published.

Since 1997, *ULLMANN'S Encyclopedia of Industrial Chemistry* has also been available in electronic format, first in a CD-ROM edition and, since 2000, in an enhanced online edition. Both electronic editions feature powerful search and navigation functions as well as regular content updates.

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Symbols and Units

Symbols and units agree with SI standards (for conversion factors see page XI). The following list gives the most important symbols used in the encyclopedia. Articles with many specific units and symbols have a similar list as front matter.

Symbol	Unit	Physical Quantity
a_B		activity of substance B
A_r		relative atomic mass (atomic weight)
A	m^2	area
c_B	mol/m^3, mol/L (M)	concentration of substance B
C	C/V	electric capacity
c_p, c_v	$J\,kg^{-1}\,K^{-1}$	specific heat capacity
d	cm, m	diameter
d		relative density (ϱ/ϱ_{water})
D	m^2/s	diffusion coefficient
D	Gy (=J/kg)	absorbed dose
e	C	elementary charge
E	J	energy
E	V/m	electric field strength
E	V	electromotive force
E_A	J	activation energy
f		activity coefficient
F	C/mol	Faraday constant
F	N	force
g	m/s^2	acceleration due to gravity
G	J	Gibbs free energy
h	m	height
$\hbar$	$W{\cdot}s^2$	Planck constant
H	J	enthalpy
I	A	electric current
I	cd	luminous intensity
k	(variable)	rate constant of a chemical reaction
k	J/K	Boltzmann constant
K	(variable)	equilibrium constant
l	m	length
m	g, kg, t	mass
M_r		relative molecular mass (molecular weight)
n_D^{20}		refractive index (sodium D-line, 20 °C)
n	mol	amount of substance
N_A	mol^{-1}	Avogadro constant ($6.023 \times 10^{23}\,mol^{-1}$)
P	Pa, bar*	pressure
Q	J	quantity of heat
r	m	radius
R	$JK^{-1}\,mol^{-1}$	gas constant
R	Ω	electric resistance
S	J/K	entropy
t	s, min, h, d, month, a	time
t	°C	temperature
T	K	absolute temperature
u	m/s	velocity
U	V	electric potential

Symbols and Units (Continued from p. IX)

Symbol	Unit	Physical Quantity
U	J	internal energy
V	m^3, L, mL, μL	volume
w		mass fraction
W	J	work
x_B		mole fraction of substance B
Z		proton number, atomic number
α		cubic expansion coefficient
α	$Wm^{-2}K^{-1}$	heat-transfer coefficient (heat-transfer number)
α		degree of dissociation of electrolyte
[α]	10^{-2}deg cm^2g^{-1}	specific rotation
η	Pa·s	dynamic viscosity
θ	°C	temperature
ϰ		c_p/c_v
λ	$Wm^{-1}K^{-1}$	thermal conductivity
λ	nm, m	wavelength
μ		chemical potential
ν	Hz, s^{-1}	frequency
ν	m^2/s	kinematic viscosity (η/ϱ)
π	Pa	osmotic pressure
ϱ	g/cm^3	density
σ	N/m	surface tension
τ	Pa (N/m^2)	shear stress
φ		volume fraction
χ	Pa^{-1} (m^2/N)	compressibility

*The official unit of pressure is the pascal (Pa).

Conversion Factors

SI unit	Non-SI unit	From SI to non-SI multiply by
Mass		
kg	pound (avoirdupois)	2.205
kg	ton (long)	9.842×10^{-4}
kg	ton (short)	1.102×10^{-3}
Volume		
m^3	cubic inch	6.102×10^{4}
m^3	cubic foot	35.315
m^3	gallon (U.S., liquid)	2.642×10^{2}
m^3	gallon (Imperial)	2.200×10^{2}
Temperature		
°C	°F	°C ×l.8 + 32
Force		
N	dyne	1.0×10^{5}
Energy, Work		
J	Btu (int.)	9.480×10^{-4}
J	cal (int.)	2.389×10^{-1}
J	eV	6.242×10^{18}
J	erg	1.0×10^{7}
J	kW·h	2.778×10^{-7}
J	kp·m	1.020×10^{-1}
Pressure		
MPa	at	10.20
MPa	atm	9.869
MPa	bar	10
kPa	mbar	10
kPa	mm Hg	7.502
kPa	psi	0.145
kPa	torr	7.502

Powers of Ten

E (exa)	10^{18}	d (deci)	10^{-1}
P (peta)	10^{15}	c (centi)	10^{-2}
T (tera)	10^{12}	m (milli)	10^{-3}
G (giga)	10^{9}	μ (micro)	10^{-6}
M (mega)	10^{6}	n (nano)	10^{-9}
k (kilo)	10^{3}	p (pico)	10^{-12}
h (hecto)	10^{2}	f (femto)	10^{-15}
da (deca)	10	a (atto)	10^{-18}

Abbreviations

The following is a list of the abbreviations used in the text. Common terms, the names of publications and institutions, and legal agreements are included along with their full identities. Other abbreviations will be defined wherever they first occur in an article. For further abbreviations, see page IX, Symbols and Units; page XVII, Frequently Cited Companies (Abbreviations), and page XVIII, Country Codes in patent references. The names of periodical publications are abbreviated exactly as done by Chemical Abstracts Service.

abs.	absolute
a.c.	alternating current
ACGIH	American Conference of Governmental Industrial Hygienists
ACS	American Chemical Society
ADI	acceptable daily intake
ADN	accord européen relatif au transport international des marchandises dangereuses par voie de navigation interieure (European agreement concerning the international transportation of dangerous goods by inland waterways)
ADNR	ADN par le Rhin (regulation concerning the transportation of dangerous goods on the Rhine and all national waterways of the countries concerned)
ADP	adenosine 5′-diphosphate
ADR	accord européen relatif au transport international des marchandises dangereuses par route (European agreement concerning the international transportation of dangerous goods by road)
AEC	Atomic Energy Commission (United States)
a.i.	active ingredient
AIChE	American Institute of Chemical Engineers
AIME	American Institute of Mining, Metallurgical, and Petroleum Engineers
ANSI	American National Standards Institute
AMP	adenosine 5′-monophosphate
APhA	American Pharmaceutical Association
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
ATP	adenosine 5′-triphosphate
BAM	Bundesanstalt für Materialprüfung (Federal Republic of Germany)
BAT	Biologischer Arbeitsstofftoleranzwert (biological tolerance value for a working material, established by MAK Commission, see MAK)
Beilstein	Beilstein's Handbook of Organic Chemistry, Springer, Berlin – Heidelberg – New York
BET	Brunauer – Emmett – Teller
BGA	Bundesgesundheitsamt (Federal Republic of Germany)
BGB1.	Bundesgesetzblatt (Federal Republic of Germany)
BIOS	British Intelligence Objectives Subcommittee Report (see also FIAT)
BOD	biological oxygen demand
bp	boiling point
B.P.	British Pharmacopeia
BS	British Standard
ca.	circa
calcd.	calculated
CAS	Chemical Abstracts Service
cat.	catalyst, catalyzed
CEN	Comité Européen de Normalisation
cf.	compare
CFR	Code of Federal Regulations (United States)
cfu	colony forming units
Chap.	chapter
ChemG	Chemikaliengesetz (Federal Republic of Germany)
C.I.	Colour Index
CIOS	Combined Intelligence Objectives Subcommitee Report (see also FIAT)
CLP	Classification, Labelling and Packaging
CNS	central nervous system
Co.	Company
COD	chemical oxygen demand
conc.	concentrated
const.	constant
Corp.	Corporation
crit.	critical
CSA	Chemical Safety Assessment according to REACH
CSR	Chemical Safety Report according to REACH
CTFA	The Cosmetic, Toiletry and Fragrance Association (United States)
DAB	Deutsches Arzneibuch, Deutscher Apotheker-Verlag, Stuttgart
d.c.	direct current
decomp.	decompose, decomposition
DFG	Deutsche Forschungsgemeinschaft (German Science Foundation)
dil.	dilute, diluted

DIN	Deutsche Industrienorm (Federal Republic of Germany)
DMF	dimethylformamide
DNA	deoxyribonucleic acid
DOE	Department of Energy (United States)
DOT	Department of Transportation – Materials Transportation Bureau (United States)
DTA	differential thermal analysis
EC	effective concentration
EC	European Community
ed.	editor, edition, edited
e.g.	for example
emf	electromotive force
EmS	Emergency Schedule
EN	European Standard (European Community)
EPA	Environmental Protection Agency (United States)
EPR	electron paramagnetic resonance
Eq.	equation
ESCA	electron spectroscopy for chemical analysis
esp.	especially
ESR	electron spin resonance
Et	ethyl substituent ($-C_2H_5$)
et al.	and others
etc.	et cetera
EVO	Eisenbahnverkehrsordnung (Federal Republic of Germany)
exp (. . .)	$e^{(\ldots)}$, mathematical exponent
FAO	Food and Agriculture Organization (United Nations)
FDA	Food and Drug Administration (United States)
FD&C	Food, Drug and Cosmetic Act (United States)
FHSA	Federal Hazardous Substances Act (United States)
FIAT	Field Information Agency, Technical (United States reports on the chemical industry in Germany, 1945)
Fig.	figure
fp	freezing point
Friedländer	P. Friedländer, Fortschritte der Teerfarbenfabrikation und verwandter Industriezweige Vol. 1–25, Springer, Berlin 1888–1942
FT	Fourier transform
(g)	gas, gaseous
GC	gas chromatography
GefStoffV	Gefahrstoffverordnung (regulations in the Federal Republic of Germany concerning hazardous substances)
GGVE	Verordnung in der Bundesrepublik Deutschland über die Beförderung gefährlicher Güter mit der Eisenbahn (regulation in the Federal Republic of Germany concerning the transportation of dangerous goods by rail)
GGVS	Verordnung in der Bundesrepublik Deutschland über die Beförderung gefährlicher Güter auf der Straße (regulation in the Federal Republic of Germany concerning the transportation of dangerous goods by road)
GGVSee	Verordnung in der Bundesrepublik Deutschland über die Beförderung gefährlicher Güter mit Seeschiffen (regulation in the Federal Republic of Germany concerning the transportation of dangerous goods by sea-going vessels)
GHS	Globally Harmonised System of Chemicals (internationally agreed-upon system, created by theUN, designed to replace the various classification and labeling standards used in different countries by using consistent criteria for classification and labeling on a global level)
GLC	gas-liquid chromatography
Gmelin	Gmelin's Handbook of Inorganic Chemistry, 8th ed., Springer, Berlin – Heidelberg –New York
GRAS	generally recognized as safe
Hal	halogen substituent (−F, −Cl, −Br, −I)
Houben-Weyl	Methoden der organischen Chemie, 4th ed., Georg Thieme Verlag, Stuttgart
HPLC	high performance liquid chromatography
H statement	hazard statement in GHS
IAEA	International Atomic Energy Agency
IARC	International Agency for Research on Cancer, Lyon, France
IATA-DGR	International Air Transport Association, Dangerous Goods Regulations
ICAO	International Civil Aviation Organization
i.e.	that is
i.m.	intramuscular
IMDG	International Maritime Dangerous Goods Code
IMO	Inter-Governmental Maritime Consultive Organization (in the past: IMCO)
Inst.	Institute
i.p.	intraperitoneal
IR	infrared
ISO	International Organization for Standardization
IUPAC	International Union of Pure and Applied Chemistry
i.v.	intravenous

Kirk-Othmer	Encyclopedia of Chemical Technology, 3rd ed., 1991–1998, 5th ed., 2004–2007, John Wiley & Sons, Hoboken
(l)	liquid
Landolt-Börnstein	Zahlenwerte u. Funktionen aus Physik, Chemie, Astronomie, Geophysik u. Technik, Springer, Heidelberg 1950–1980; Zahlenwerte und Funktionen aus Naturwissenschaften und Technik, Neue Serie, Springer, Heidelberg, since 1961
LC_{50}	lethal concentration for 50 % of the test animals
LCLo	lowest published lethal concentration
LD_{50}	lethal dose for 50 % of the test animals
LDLo	lowest published lethal dose
ln	logarithm (base e)
LNG	liquefied natural gas
log	logarithm (base 10)
LPG	liquefied petroleum gas
M	mol/L
M	metal (in chemical formulas)
MAK	Maximale Arbeitsplatzkonzentration (maximum concentration at the workplace in the Federal Republic of Germany); cf. Deutsche Forschungsgemeinschaft (ed.): Maximale Arbeitsplatzkonzentrationen (MAK) und Biologische Arbeitsstofftoleranzwerte (BAT), WILEY-VCH Verlag, Weinheim (published annually)
max.	maximum
MCA	Manufacturing Chemists Association (United States)
Me	methyl substituent ($-CH_3$)
Methodicum Chimicum	Methodicum Chimicum, Georg Thieme Verlag, Stuttgart
MFAG	Medical First Aid Guide for Use in Accidents Involving Dangerous Goods
MIK	maximale Immissionskonzentration (maximum immission concentration)
min.	minimum
mp	melting point
MS	mass spectrum, mass spectrometry
NAS	National Academy of Sciences (United States)
NASA	National Aeronautics and Space Administration (United States)
NBS	National Bureau of Standards (United States)
NCTC	National Collection of Type Cultures (United States)
NIH	National Institutes of Health (United States)
NIOSH	National Institute for Occupational Safety and Health (United States)
NMR	nuclear magnetic resonance
no.	number
NOEL	no observed effect level
NRC	Nuclear Regulatory Commission (United States)
NRDC	National Research Development Corporation (United States)
NSC	National Service Center (United States)
NSF	National Science Foundation (United States)
NTSB	National Transportation Safety Board (United States)
OECD	Organization for Economic Cooperation and Development
OSHA	Occupational Safety and Health Administration (United States)
p., pp.	page, pages
Patty	G.D. Clayton, F.E. Clayton (eds.): Patty's Industrial Hygiene and Toxicology, 3rd ed., Wiley Interscience, New York
PB report	Publication Board Report (U.S. Department of Commerce, Scientific and Industrial Reports)
PEL	permitted exposure limit
Ph	phenyl substituent (—C_6H_5)
Ph. Eur.	European Pharmacopoeia, Council of Europe, Strasbourg
phr	part per hundred rubber (resin)
PNS	peripheral nervous system
ppm	parts per million
P statement	precautionary statement in GHS
q.v.	which see (quod vide)
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals (EU regulation addressing the production and use of chemical substances, and their potential impacts on both human health and the environment)
ref.	refer, reference
resp.	respectively
R_f	retention factor (TLC)
R.H.	relative humidity
RID	réglement international concernant le transport des marchandises dangereuses par chemin de fer (international convention concerning the transportation of dangerous goods by rail)
RNA	ribonucleic acid
R phrase (R-Satz)	risk phrase according to ChemG and GefStoffV (Federal Republic of Germany)
rpm	revolutions per minute
RTECS	Registry of Toxic Effects of Chemical Substances, edited by the National Institute of Occupational Safety and Health (United States)
(s)	solid

SAE	Society of Automotive Engineers (United States)
SAICM	Strategic Approach on International Chemicals Management (international framework to foster the sound management of chemicals)
s.c.	subcutaneous
SI	International System of Units
SIMS	secondary ion mass spectrometry
S phrase (S-Satz)	safety phrase according to ChemG and GefStoffV (Federal Republic of Germany)
STEL	Short Term Exposure Limit (see TLV)
STP	standard temperature and pressure (0°C, 101.325 kPa)
T_g	glass transition temperature
TA Luft	Technische Anleitung zur Reinhaltung der Luft (clean air regulation in Federal Republic of Germany)
TA Lärm	Technische Anleitung zum Schutz gegen Lärm (low noise regulation in Federal Republic of Germany)
TDLo	lowest published toxic dose
THF	tetrahydrofuran
TLC	thin layer chromatography
TLV	Threshold Limit Value (TWA and STEL); published annually by the American Conference of Governmental Industrial Hygienists (ACGIH), Cincinnati, Ohio
TOD	total oxygen demand
TRK	Technische Richtkonzentration (lowest technically feasible level)
TSCA	Toxic Substances Control Act (United States)
TÜV	Technischer Überwachungsverein (Technical Control Board of the Federal Republic of Germany)
TWA	Time Weighted Average
UBA	Umweltbundesamt (Federal Environmental Agency)
Ullmann	Ullmann's Encyclopedia of Industrial Chemistry, 6th ed., Wiley-VCH, Weinheim 2002; Ullmann's Encyclopedia of Industrial Chemistry, 5th ed., VCH Verlagsgesellschaft, Weinheim 1985–1996; Ullmanns Encyklopädie der Technischen Chemie, 4th ed., Verlag Chemie, Weinheim 1972–1984; 3rd ed., Urban und Schwarzenberg, München 1951–1970
USAEC	United States Atomic Energy Commission
USAN	United States Adopted Names
USD	United States Dispensatory
USDA	United States Department of Agriculture
U.S.P.	United States Pharmacopeia
UV	ultraviolet
UVV	Unfallverhütungsvorschriften der Berufsgenossenschaft (workplace safety regulations in the Federal Republic of Germany)
VbF	Verordnung in der Bundesrepublik Deutschland über die Errichtung und den Betrieb von Anlagen zur Lagerung, Abfüllung und Beförderung brennbarer Flüssigkeiten (regulation in the Federal Republic of Germany concerning the construction and operation of plants for storage, filling, and transportation of flammable liquids; classification according to the flash point of liquids, in accordance with the classification in the United States)
VDE	Verband Deutscher Elektroingenieure (Federal Republic of Germany)
VDI	Verein Deutscher Ingenieure (Federal Republic of Germany)
vol	volume
vol.	volume (of a series of books)
vs.	versus
WGK	Wassergefährdungsklasse (water hazard class)
WHO	World Health Organization (United Nations)
Winnacker-Küchler	Chemische Technologie, 4th ed., Carl Hanser Verlag, München, 1982-1986; Winnacker-Küchler, Chemische Technik: Prozesse und Produkte, Wiley-VCH, Weinheim, 2003–2006
wt	weight
$	U.S. dollar, unless otherwise stated

Frequently Cited Companies (Abbreviations)

Air Products	Air Products and Chemicals
Akzo	Algemene Koninklijke Zout Organon
Alcoa	Aluminum Company of America
Allied	Allied Corporation
Amer. Cyanamid	American Cyanamid Company
BASF	BASF Aktiengesellschaft
Bayer	Bayer AG
BP	British Petroleum Company
Celanese	Celanese Corporation
Daicel	Daicel Chemical Industries
Dainippon	Dainippon Ink and Chemicals Inc.
Dow Chemical	The Dow Chemical Company
DSM	Dutch Staats Mijnen
Du Pont	E.I. du Pont de Nemours & Company
Exxon	Exxon Corporation
FMC	Food Machinery & Chemical Corporation
GAF	General Aniline & Film Corporation
W.R. Grace	W.R. Grace & Company
Hoechst	Hoechst Aktiengesellschaft
IBM	International Business Machines Corporation
ICI	Imperial Chemical Industries
IFP	Institut Français du Pétrole
INCO	International Nickel Company
3M	Minnesota Mining and Manufacturing Company
Mitsubishi Chemical	Mitsubishi Chemical Industries
Monsanto	Monsanto Company
Nippon Shokubai	Nippon Shokubai Kagaku Kogyo
PCUK	Pechiney Ugine Kuhlmann
PPG	Pittsburg Plate Glass Industries
Searle	G.D. Searle & Company
SKF	Smith Kline & French Laboratories
SNAM	Societá Nazionale Metandotti
Sohio	Standard Oil of Ohio
Stauffer	Stauffer Chemical Company
Sumitomo	Sumitomo Chemical Company
Toray	Toray Industries Inc.
UCB	Union Chimique Belge
Union Carbide	Union Carbide Corporation
UOP	Universal Oil Products Company
VEBA	Vereinigte Elektrizitäts- und Bergwerks-AG
Wacker	Wacker Chemie GmbH

Country Codes

The following list contains a selection of standard country codes used in the patent references.

AT	Austria
AU	Australia
BE	Belgium
BG	Bulgaria
BR	Brazil
CA	Canada
CH	Switzerland
CS	Czechoslovakia
DD	German Democratic Republic
DE	Federal Republic of Germany (and Germany before 1949)*
DK	Denmark
ES	Spain
FI	Finland
FR	France
GB	United Kingdom
GR	Greece
HU	Hungary
ID	Indonesia
IL	Israel
IT	Italy
JP	Japan*
LU	Luxembourg
MA	Morocco
NL	Netherlands*
NO	Norway
NZ	New Zealand
PL	Poland
PT	Portugal
SE	Sweden
SU	Soviet Union
US	United States of America
YU	Yugoslavia
ZA	South Africa
EP	European Patent Office*
WO	World Intellectual Property Organization

*For Europe, Federal Republic of Germany, Japan, and the Netherlands, the type of patent is specified: EP (patent), EP-A (application), DE (patent), DE-OS (Offenlegungsschrift), DE-AS (Auslegeschrift), JP (patent), JP-Kokai (Kokai tokkyo koho), NL (patent), and NL-A (application).

Periodic Table of Elements

element symbol, atomic number, and relative atomic mass (atomic weight)

1A	"European" group designation and old IUPAC recommendation																0
1	group designation to 1986 IUPAC proposal																**18**
IA	"American" group designation, also used by the Chemical Abstracts Service until the end of 1986																VIIIA
1	2A											3B	4B	5B	6B	7B	2
H	**2**											**13**	**14**	**15**	**16**	**17**	**He**
1.0079	IIA											IIIA	IVA	VA	VIA	VIA	4.0026
3	4											5	6	7	8	9	10
Li	**Be**											**B**	**C**	**N**	**O**	**F**	**Ne**
6.941	9.0122											10.811	12.011	14.007	15.999	18.998	20.180
11	12	3A	4A	5A	6A	7A	8	8	8	1B	2B	13	14	15	16	17	18
Na	**Mg**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
22.990	24.305	IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB	26.982	28.086	30.974	32.066	35.453	39.948
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	**Ca**	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Ga**	**Ge**	**As**	**Se**	**Br**	**Kr**
39.098	40.078	44.956	47.867	50.942	51.996	54.938	55.845	58.933	58.693	63.546	65.409	69.723	72.61	74.922	78.96	79.904	83.80
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	**Sr**	**Y**	**Zr**	**Nb**	**Mo**	**Tc***	**Ru**	**Rh**	**Pd**	**Ag**	**Cd**	**In**	**Sn**	**Sb**	**Te**	**I**	**Xe**
85.468	87.62	88.906	91.224	92.906	95.94	98.906	101.07	102.91	106.42	107.87	112.41	114.82	118.71	121.76	127.60	126.90	131.29
55	56		72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	**Ba**		**Hf**	**Ta**	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**	**Hg**	**Tl**	**Pb**	**Bi**	**Po***	**At***	**Rn***
132.91	137.33		178.49	180.95	183.84	186.21	190.23	192.22	195.08	196.97	200.59	204.38	207.2	208.98	208.98	209.99	222.02
87	88		104	105	106	107	108	109	110	111	112	113	114	115	116		118
Fr*	**Ra***		**Rf***	**Db***	**Sg**	**Bh**	**Hs**	**Mt**	**Ds**	**Rg**	**Cn**	**Uut**[a]	**Fl**	**Uup**[a]	**Lv**		**Uuo**[a]
223.02	226.03		261.11	262.11													

[a] provisional IUPAC symbol

57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
La	**Ce**	**Pr**	**Nd**	**Pm***	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
138.91	140.12	140.91	144.24	146.92	150.36	151.97	157.25	158.93	162.50	164.93	167.26	168.93	173.04	174.97
89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Ac*	**Th***	**Pa***	**U***	**Np***	**Pu***	**Am***	**Cm***	**Bk***	**Cf***	**Es***	**Fm***	**Md***	**No***	**Lr***
227.03	232.04	231.04	238.03	237.05	244.06	243.06	247.07	247.07	251.08	252.08	257.10	258.10	259.10	260.11

* radioactive element; mass of most important isotope given.

Part 1

Fundamentals

Ullmann's Polymers and Plastics: Products and Processes
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Plastics, General Survey, 1. Definition, Molecular Structure and Properties

ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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1. Introduction

Plastics are commercially used materials that are based on polymers or prepolymers. The name plastics refers to their easy processibility and shaping (Greek: *plastein* = to form, to shape). Plastics and polymers, also termed macromolecules (Greek: *macro* = large), are not synonyms. Polymers or prepolymers are raw materials for plastics; they become plastics only after processing. The same polymers may be used as plastics or as fibers, paints, rubbers, coatings, adhesives, thickeners, surfactants, and ion-exchange membranes. Properties of polymers are engineered by varying the molecular architecture or the formulation, combining them with different materials in multicomponent and multiphase systems. Typically, plastics contain additives that are needed to enhance their stability and to tune their properties. Unparalleled by any other material, polymers are exceptional regarding their attractive combination of facile processing with low mass and high versatility in terms of properties, applications, flexible choice of feedstocks, and recycling. The system integration of functional polymers represents the key to the development of advanced technologies with applications ranging from lightweight engineering to packaging, construction, aerospace and automotive industries, as well as biomedical engineering. Whereas most plastics are passive, advanced functional plastics are rendered interactive and capable of responding to environmental stimuli. Today, highly cost-, resource-, eco-, and energy-efficient polymers play a prominent role in sustainable development of advanced materials and technologies.

1.1. Polymers

1.1.1. Fundamental Terms [1–16]

The term polymer refers to macromolecules composed of many units (Greek: *poly* = many, *meros* = parts). As first proposed by HERMANN STAUDINGER in 1920, who was awarded the Nobel Price of Chemistry for his groundbreaking concept in 1953, macromolecules consist of many atoms, usually a thousand or more, thereby having high molar masses. Prior to STAUDINGER, the term polymer was not related to high molar mass. For example, benzene was originally called a polymer which was "polymerized" from three acetylene molecules. What is now called a polymer consists of molecules with hundreds and thousands of such units; it was therefore termed "high polymer" in the ancient literature. The term polymer carries with it the connotation of molecules composed of many equal "mers", such as the ethylene units

in polyethylene, $R'(CH_2CH_2)_nR''$. The number n of monomer units in the polymer molecule is called the degree of polymerization X. There are, however, many polymer molecules (especially biopolymer molecules) with very different types of monomers per molecule, such as protein molecules $H(NH–CHR–CO)_nOH$ with up to 20 different R substituents. In accordance with STAUDINGER's view, a less constraining and more general term for polymer molecule is thus macromolecule. However, there is no sharp dividing line with respect to the number of units per molecule between macromolecules and low molar mass compounds. In principle, linear thermoplastic polymers are considered polymers when entanglement occurs, thus accounting for the viscoelastic properties typical for polymeric thermoplastics.

It was HERMANN STAUDINGER who recognized that polymers in industry and in nature are synthesized according to the same blueprint. Similar to pearls in a pearl necklace, monomer molecules are linked together by covalent bond formation. In the early days of polymer sciences and engineering, all polymers were bio-based, because efficient synthetic polymerization processes were not at hand. Prominent examples of biopolymers include proteins, polynucleotides, *cis*-1,4-polyisoprene as natural rubber, polysaccharides (carbohydrates) with cellulose as the most abundant polymer and major component of biomass. Wood is a composite of two biopolymers, i.e., cellulose and lignin. As pointed out by STAUDINGER and others, most silicates are inorganic polymers derived by polymerization of silicic acid and its derivatives. Some of these naturally occurring polymers are used by man without further chemical transformation (e.g., cellulose for paper and cardboard). Yet, the chemical transformation of natural polymers with retention of their chain structures leads to solution and even melt processable semisynthetic materials, for example, cellulose acetates from cellulose. Chains of other natural polymers are cross-linked before commercial use. Examples are the hardening of casein (a protein) by formaldehyde to produce galalith (plastic) or the vulcanization of *cis*-1,4-polyisoprene (natural rubber) to afford an elastomer.

Today, most polymers are synthesized chemically from synthetic monomers. Examples include the preparations of polyethylene from ethylene, poly(vinyl chloride) from vinyl chloride, nylon 6 from ε-caprolactam, or nylon 66 from adipic acid and hexamethylenediamine. Whereas the majority of monomers are derived from oil and gas in petrochemistry, the progress in biotechnology and the quest for green economy are stimulating the production of bio-based synthetic monomers, such as butadiene, ethylene, propene, acrylic acid, glycol, and lactic acid in biorefineries using biomass as feedstock. Some industrial polymers result from the chemical conversion of other synthetic polymers, for example, poly(vinyl alcohol) from poly(vinyl acetate). In contrast to natural polymer syntheses and biotechnology, most large scale commercial synthetic polymers are produced in the absence of water either in bulk or gas phase. Moreover, compared to biopolymers, synthetic polymers, including the synthetic bio-based polymers derived from renewable feedstocks, are much easier to tailor with respect to their molar mass distribution, short- and long-chain branching and stereochemistry, thus meeting the demands of polymer melt processing and polymer applications. In contrast to protein synthesis, where polypeptide chains are produced with identical molar mass and comonomer sequence distribution, is rather problematic to produce thermoplastics with shear thinning resulting from long chain branching and multimodal molar mass distribution with enzyme-catalyzed reactions.

1.1.2. Nomenclature [1, 5, 17–19]

The nomenclature of individual polymers and plastics is as confusing as their classification according to properties. Various systems of nomenclature are used simultaneously. Abbreviations and acronyms abound, sometimes with different meanings for the same letter combinations and other times without explanation. In addition, many thousands of trade names are used worldwide for plastics, fibers, elastomers, and polymeric additives. Furthermore, a polymer from a certain

company may come in many different grades depending on the processibility and application, sometimes up to 100 per polymer type. Some of these grades may even bear different trade names for various applications. The following nomenclature systems are commonly used for polymers.

Long-known Natural Polymers often have Trivial Names. Examples are cellulose, the polymeric sugar (-ose) of the plant cell; casein, the most important protein of milk and cheese (Latin: *caseus* = cheese); nucleic acids, the acids found in the cell nucleus; catalase, a catalyzing enzyme.

Synthetic Polymers are often Named after Their Monomers. Polymers of ethylene thus lead to polyethylene, styrene to polystyrene, vinyl chloride to poly(vinyl chloride), and lactic acid to a polylactic acid. This "polymonomer" nomenclature has the disadvantage that the constitution of monomeric units of the polymer molecules is not identical with the constitution of the monomers themselves. For example, the polymerization of ethylene, $CH_2{=}CH_2$, leads to $\sim(CH_2{-}CH_2)_n\sim$, a saturated compound and thus a polyalkane, not an unsaturated "ene" as the name polyethylene may suggest. The polymerization of lactams (cyclic amides) does not give macromolecules with intact lactam rings in the polymer chains but gives open-chain polyamides, etc. This polymonomer scheme is also ambiguous if a monomer can lead to more than one characteristic unit in a polymer. An example is acrolein, $CH_2{=}CH(CHO)$, which can polymerize via the ethylenic double bond to give $\sim[CH_2{-}CH(CHO)]_n\sim$, via the aldehyde group to $\sim[O{-}CH(CH{=}CH_2)]_n$, or via both to give six-membered rings in polymer chains.

For trade purposes, certain polymer names may denote not only homopolymers but also copolymers, contrary to what the "chemical" names imply. For example, the copolymers of ethylene with up to 10% butene-1, hexene-1, or octene-1 are known as linear low-density polyethylenes (LLDPEs). The commonly used chemical names of plastics thus often do not indicate the true chemical structure of the monomeric units of the polymers on which they are based.

Polymers are often Named after Characteristic Groups in Their Repeating Units. Polyamides are thus polymers with amide groups –NHCO– in their repeating units; for example $\sim[NHCO(CH_2)_5]_n\sim$ = polyamide 6 = nylon 6 = poly(ε-caprolactam). Other examples are polyesters with ester groups –COO– or polyurethanes with urethane groups –NH–CO–O– in the chains. A disadvantage is that this naming scheme is identical with that of organic chemistry where a polyisocyanate denotes a low molar mass compound with more than one isocyanate group per molecule [e.g., $C_6H_3(NCO)_3$]. A macromolecular polyisocyanate would thus be a polymer with many intact isocyanate groups per chain, for example, poly(vinyl isocyanate) $\sim[CH_2{-}CH(NCO)]_n\sim$. The polyisocyanates of polymer chemistry, on the other hand, possess polymerized isocyanate groups as, for example, in $\sim(NR{-}CO)_n\sim$. Such compounds are unfortunately also often called polyisocyanates.

IUPAC Names. IUPAC recommends the use of constitutive names, similar to those used in inorganic and organic chemistry. The nomenclature of low and high molar mass inorganic molecules follows the additivity principle; those of low molar mass organic molecules the substitution principle. The nomenclature of organic macromolecules is a hybrid of both principles: The smallest repeating units are thought of as biradicals according to the substitution principle; then their names are added according to the additivity principle, put in parentheses, and prefixed with "poly." Names of repeating units are written without spaces between words. The polymer $\sim[O{-}CH_2]_n\sim$ from formaldehyde, $H_2C{=}O$, is thus called poly(oxymethylene), abbreviated as POM. The polycondensation of ethylene glycol $HO{-}CH_2{-}CH_2{-}OH$ with terephthalic acid $HOOC{-}(p\text{-}C_6H_4){-}COOH$ leads to a polymer $\sim[O{-}CH_2CH_2{-}O{-}OC(p\text{-}C_6H_4)CO]_n\sim$ with the systematic name poly(oxyethyleneoxyterephthaloyl). The trivial names of this polymer are poly(ethylene terephthalate) and poly(ethylene glycol terephthalate). It is also known as PET

(an acronym) or PETP (an abbreviation) in the plastics literature, by the acronym PES in the fiber literature, and as PETE for recycling purposes.

With exception of POM, IUPAC names are rarely used in the plastics literature. They are however important for systematic searches in *Chemical Abstracts* and other literature services.

1.2. Plastics

1.2.1. Fundamental Terms [20–56]

Early plastics resembled natural resins. Natural resin refers mainly to oleoresins from tree sap but is also used for shellac, insect exudations, and mineral hydrocarbons (→ Resins, Natural). Early plastics were thus sometimes called synthetic resins. The word resin is today occasionally used for any organic chemical compound with medium to high molar mass that serves as a raw material for plastics (for a definition of the term resin according to current standards, see → Resins, Synthetic). Resin is not to be confused with rosin, which refers to mixtures of C_{20} fused-ring monocarboxylic acids, such as pine oil, tall oil, and kauri resin. Rosin is the main component of naval stores (→ Resins, Natural).

Plastics are usually divided into two groups according to their hardening processes. Those that yield solid materials by simple cooling of a polymer melt (a physical process) and soften while being heated are called *thermoplastics*. *Thermosets*, on the other hand, harden through chemical cross-linking reactions between polymer molecules; when heated, they do not soften but decompose chemically (→ Thermosets). The shaping of a thermoplastic is thus a reversible process: The same material can be melted and processed again. A thermoset cannot be remelted and reshaped; its formation is irreversible.

Thermoplastics are normally composed of fairly high molar mass molecules because many physical properties effectively become molar mass independent only above a certain molar mass enabling chain entanglement. Examples are melting temperatures and the moduli of elasticity. Other properties, however, increase with increasing molar mass and entanglement (e.g., melt viscosities).

Thermosets are usually generated from fairly low molar mass polymers, called oligomers (science) or prepolymers (industry). Oligomers containing functional endgroups are named telechelics, and telechelics containing polymerizable endgroups are termed macromonomers. High molar masses are unnecessary here because chemical reactions between prepolymer molecules lead to an interconnection of these molecules (cross-linking or advancement, respectively) and thus to a giant molecule with 100% conversion of the prepolymer. Prepolymers are thus thermosetting materials and become true thermosets only after the hardening reaction.

Plastics are usually divided into four groups: Commodity plastics (also called standard plastics or bulk plastics), engineering plastics (sometimes referred to as technical plastics or technoplastics), high-performance plastics, and functional plastics (or specialty plastics). A commodity, engineering, or high-performance plastic may have many different applications, whereas a functional plastic has one very specific application. Polyethylene, a commodity plastic, may according to its type or grade be used for containers, as packaging film, as agricultural mulch, etc. Poly(ethylene–co–vinyl alcohol) with a high content of vinyl alcohol units, on the other hand, is a functional plastic that is used only as an oxygen barrier resin. Other functional plastics are employed in optoelectronics, as resists, as piezoelectric materials, etc. Functional plastic is not synonymous with functional polymer or functionalized polymer, because the latter terms refer to polymers with functional chemical groups (i.e., groups with specific chemical reactivities).

Commodity plastics are manufactured in great amounts at low cost; hence, the terms bulk plastics or standard plastics. Engineering plastics possess improved mechanical properties and improved dimensional stability as compared to commodity plastics. Such improved properties may be higher moduli of elasticity, higher heat distortion temperature, smaller cold flows, higher impact strengths, etc. Engineering plastics are also often defined as those thermoplastics that maintain dimensional stability and

most mechanical properties above 100 °C or below 0 °C. High-performance plastics, on the other hand, are engineering plastics with even more improved mechanical properties.

No sharp dividing lines exist between commodity plastics and engineering plastics on the one hand or engineering plastics and high-performance plastics on the other; nor are there generally agreed upon property levels beyond which polymers are designated as engineering or high-performance plastics. The three groups of plastics, in general, include the following:

Commodity Plastics. Poly(vinyl chloride), abbreviated as PVC, high density polyethylene (HDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), very low density polyethylene (VLDPE), isotactic polypropylene (PP), polystyrene (PS), polystyrene foam as expanded polystyrene (EPS) and poly(ethylene terephthalate) (PET).

Engineering Plastics. Polypropylene (PP), poly (ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), polyamides (aliphatic, amorphous, aromatic) (PA), polycarbonate (PC), polyoxymethylenes (POM), poly(methyl methacrylate) (PMMA), some modified polystyrenes such as styrene–acrylonitrile (SAN) and acrylonitrile–butadiene–styrene (ABS) copolymers, and high-impact polystyrenes (HIPS), as well as various blends such as poly (phenylene oxide)–polystyrene (PPO–PS), polyoxymethylene–polyurethane (POM–PUR), polypropylene –poly(ethylene-co-propene-co-diene) rubber (PP–EPDM), and polycarbonate–ABS (PC–ABS).

High-Performance Plastics. Liquid crystal-line polymers (LCPs), polyetheretherketone (PEEK), various polysulfones, polyimides, fluoropolymers, etc.

Some thermosets are also classified as engineering or high-performance plastics. In general, thermosets are, however, considered a separate group of plastics. They comprise alkyd (→ Alkyd Resins), phenolic (→ Phenolic Resins), and amino resins (→ Amino Resins) (melamine and urea resins), epoxides (epoxies) (→ Epoxy Resins), unsaturated polyesters (including so-called vinyl esters) (→ Polyester Resins, Unsaturated), polyurethanes (→ Polyurethanes), and allylics (→ Allyl Compounds).

1.2.2. Designations [57–61]

The plastics trade and technical literature indulges in trivial names, abbreviations, and acronyms. Acetal polymer is, for example, the name given to polymers with $–OCH_2–$ as the major repeating unit. Polymers of methacryl esters $\sim[CH_2–C(CH_3)(COOR)]_n\sim$ are known as methacrylics (or often only acrylics), but polyacrylonitrile $\sim[CH_2–CH(CN)]_n\sim$ is not considered an "acrylic" in the plastics literature (the textile literature calls it an acrylic fiber). Styrenics comprise homopolymers of styrene as well as copolymers of styrene with other monomers. Nylon, originally a protected trade name, is now a generic term for polyamides, especially aliphatic ones.

Abbreviations often have more than one meaning (Tables 1–4): PBT may, for example, denote poly(butylene terephthalate), but it is also used for poly(*p*-phenylenebenzbisthiazole). Exhaustive lists of commonly used abbreviations of polymers and additives as recommended by various organizations have been compiled [61].

Tables 1–4 give the recommendations for abbreviations of names of thermoplastics and thermosets by ASTM/ANSI (American Society for the Testing of Materials/American National Standards Institute [D 1600–86 a]), DIN (German Industrial Standards [7728]), ISO (International Standardization Organization [1043 – 1986 (ε)]), IUPAC (International Union of Pure and Applied Chemistry). "Other" means other abbreviations used in the field but not recommended by ASTM, DIN, ISO, or IUPAC. The recommended abbreviations are often neither identical with those of fibers of the same chemical structures nor with those of elastomers containing the same monomer units; some of these also deviate from those recommended for recyclable plastics. Several abbreviations have different meanings in either two or more of the ASTM, DIN, ISO and IUPAC systems and/or the technical literature.

The abbreviations are in part based on the poly (monomer) nomenclature, i.e., on the names of

Table 1. Polymers by chain polymerization (addition polymerization), copolymerization, polycondensation (condensation polymerization), and polyaddition which are characterized by abbreviations based on the poly(monomer) nomenclature

Polymers of	ASTM	DIN	ISO	IUPAC	Other
Acrylester+acrylonitrile+butadiene	ABA	A/B/A			
Acrylester+acrylonitrile+styrene	ASA	A/S/A	A/S/A		
Acrylester+ethylene	EEA#		E/EA		EAA
Acrylic acid	PAA				PAS#
Acrylonitrile	PAN	PAN		PAN	
Acrylonitrile+butadiene	PBAN				
Acrylonitrile+butadiene+methyl methacrylate+styrene					MABS
Acrylonitrile+butadiene+styrene	ABS	ABS	ABS	ABS	ABS
Acrylonitrile+ethylene-propene-diene+styrene		A/EPDM/S		AES	
Acrylonitrile+methyl methacrylate	AMMA	A/MMA	A/MMA		
Acrylonitrile+styrene	SAN	SAN	SAN	SAN	PSAN
Acrylonitrile+styrene+chlorinated polyethylene		A/PE-C/S			
Adipic acid+hexamethylenediamine	PA 6.6	PA 66	PA 6.6	PA 6.6	
Adipic acid+tetramethylene glycol					PTMA
Allyldiglycol carbonate	ADC				
p-Aminobenzoic acid					PAB
Aminotriazol					PAT
11-Aminoundecanoic acid		PA 11			
Azelaic anhydride					PAPA
Bisphenol A+phosgene	PC#	PC#	PC#	PC#	
Bitumen+ethylene				ECB	
Butadiene+methyl methacrylate+styrene		MBS			
Butadiene+styrene (thermoplastic)	SB	S/B	S/B	S/B	PASB
Butene-1	PB	PB	PB		BT
Butyl acrylate		PBA		PBA	
Butylene glycol+terephthalic acid	PBT	PBT	PBT		PTMT
Butyl methacrylate					PBMA
ε-Caprolactam	PA 6	PA 6	PA 6	PA 6	
Chlorotrifluoroethylene	PCTFE	PCTFE	PCTFE	PCTFE	
Chlorotrifluoroethylene+ethylene					ECTFE
Cresol+formaldehyde	CF	CF	CF	CF	
1,4-Cyclohexanedimethylol+terephthalic acid					PCDT
Diallyl chloroendate (=diallyl ester of 4,5,6,7,7-hexachlorobicyclo-[2,2,1]5-heptane-2,3-dicarbonic acid	PDAC				
Diallyl fumarate	PDAF				
Diallyl isophthalate	PDAIP				
Diallyl maleate	PDAM				
Diallyl phthalate	PDAP	PDAP	PDAP	PDAP	DAP
1,4-Dichlorobenzene+disodium sulfide	PPS	PPS			
2,6-Dimethylphenol+oxygen	POP				PPO™
Dodecanolactam (laurolactam)	PA 12	PA 12	PA 12	PA 12	
Ethyl acrylate					PEA
Ethyl acrylate+ethylene		E/EA			EEA#
Ethylene	PE	PE	PE	PE	PL
Cross-linked polymer		VPE			XLPE
High-density polymer	HDPE	PE-HD	PE-HD		
Low-density polymer	LDPE	PE-LD	PE-LD		
Low-density polymer, linear	LLDPE				
Medium density polymer	MDPE				
Ultra-high molar mass polymer	UHMW-PE				
Ethylene+methyl acrylate+vinyl chloride		VC/E/MA	VC/E/MA		
Ethylene+methyl methacrylate	EMA	E/MA			
Ethylene+propene		E/P	E/P		PEP
Ethylene+propene (+diene)		EPDM			
Ethylene+tetrafluoroethylene	ETFE	E/TFE			
Ethylene+vinyl acetate	EVA	E/VA	EVA		VAE
		E/VAC	E/VAC		
Ethylene+vinyl acetate+vinyl chloride		VC/E/VAC	VC/E/VAC		
Ethylene+vinyl chloride		VC/E	VC/E		
Ethylene glycol					PEG
Ethylene glycol+maleic anhydride	UP#				

Ethylene glycol+terephthalic acid (ester)	PET	PET	PETP	PETP	PETE
Fast crystallizing polymer					CPET
Oriented polymer					OPET
Ethylene oxide	PEO	PEOX	PEOX	PEO	
Formaldehyde (or trioxane)	POM[#]	POM[#]	POM[#]	POM[#]	
Formaldehyde+furan	FF				
Formaldehyde+melamine	MF	MF	MF	MF	
Formaldehyde+melamine+phenol		MPF	MPF		
Formaldehyde+phenol	PF	PF	PF	PF	
Formaldehyde+urea	UF	UF	UF	UF	
Furfural+Phenol	PFF				
Hexafluoropropene+tetrafluoroethylene	FEP	FEP	FEP		
Hexamethylenediamine+sebacic acid		PA 610			PA 6.10
p-Hydroxybenzoic acid	POB				PHB[#]
3-Hydroxybutyric acid					PHB[#]
2-Hydroxyethylmethacrylate					PHEMA
Isobutene	PIB	PIB	PIB	PIB	IM
Laurolactam (dodecanolactam)	PA 12	PA 12	PA 12	PA 12	
Linseed oil, epoxidized		ELO	ELO		
Maleic anhydride+ styrene	SMA	S/MA			
Methacrylimide		PMI			
Methyl acrylate					PMA
Methyl acrylate+vinyl chloride		VC/MA	VC/MA		
Methyl α-chloromethacrylate	PMCA				
Methyl methacrylate	PMMA	PMMA	PMMA	PMMA	
Methyl methacrylate+vinyl chloride			VC/MMA		
1,4-Methylpentene	PMP	PMP	PMP		TPX
α-Methylstyrene		PMS			PAMS
α-Methylstyrene+styrene	SMS	S/MS	S/MS		
Octyl acrylate+vinyl chloride		VC/OA	VC/OA		
Perfluoroalkoxyalkane	PFA	PFA			
Phosphoric acid					PPA[#]
Propene	PP	PP	PP	PP	
Oriented polymer					OPP
Oriented biaxially					BOPP
Propene+tetrafluoroethylene (alt.)					TFE-P
Propylene oxide	PPOX	PPOX	PPOX		
Soybean oil, epoxidized		ESO	ESO		
Styrene	PS	PS	PS	PS	
Expanded (foamed) polymer					EPS
High-impact polymer					HIPS
Impact resistant polymer	SRP	IPS			
Oriented polymer					OPS
Tetrafluoroethylene	PTFE	PTFE	PTFE	PTFE	
Tetrahydrofuran					PTHF
Polymer with hydroxy endgroups					PTMEG
Triallyl cyanurate	PTAC				
Trifluoroethylene				P 3 FE	
Trioxane (+comonomers)	POM[#]	POM[#]	POM[#]	POM[#]	
Vinyl acetate	PVAC	PVAC	PVAC	PVAC	PVA
Vinyl acetate+vinyl chloride	PVCA	VC/VAC	VC/VAC		
N-Vinylcarbazole	PVK	PVK	PVK		
Vinyl chloride	PVC	PVC	PVC	PVC	PCU, V
Polymerized in bulk					M-PVC
Polymerized in emulsion					E-PVC
Polymerized in suspension					S-PVC
Polymer as flexible film					FPVC
Polymer as oriented film					OPVC
Polymer as rigid film					RPVC
Vinyl chloride and vinylidene chloride		VC/VDC	VC/VDC		
Vinyl fluoride	PVF	PVF	PVF	PVF	
Vinylidene chloride	PVDC	PVDC	PVDC	PVDC	
Vinylidene fluoride	PVDF	PVDF	PVDF	PVDF	
Vinyl methyl ether					PVME
N-Vinylpyrrolidone	PVP	PVP	PVP		

[#] Abbreviation with more than one meaning.

Table 2. Abbreviations for polymers named after a characteristic polymer group

Characteristic group	ASTM	DIN	ISO	IUPAC	Other
Amide	PA	PA	PA	PA	
Amide, aromatic	PARA				
Metal coated films	PA**				
Saran coated films	PA*				
Amide–imide	PAI	PAI			
Aryl amide	PARA				
Aryl sulfone					PAS#
Benzimidazole					PBI
Carbodiimide					PCD
Carbonate, aromatic	PC#	PC#	PC#	PC#	
Epoxide (epoxy)	EP	EP	EP	EP	
Glass-fiber reinforced					GEP
Epoxide–ester			EPE		
Ester, saturated		SP			
Ester, thermoplastic	TPES				
Metallized polymer film					MPE
Ester, unsaturated	UP#	UP#	UP#	UP#	
Glass fiber reinforced					FRP
Ester–alkyd	PAK				
Ester–ether (thermoplastic elastomer)	TEEE				
Ester–imide	PEI				
Ether–block-amide	PEBA	PEBA			
Etheretherketone	PEEK				
Ether–imide		PEI			
Ether sulfone	PES	PES			
	PESU				
Imide	PI	PI			
Isocyanurate		PIR			
Parabanic acid					PPA#
Phenylene ether	PPE	PPE			
Phenylene sulfone	PPSU	PPSU	PPSU		PSU
Silicone	SI	SI	SI		
Sulfone	PSUL	PSU			
Urethane	PUR	PUR	PUR	PUR	
Thermoplastic	TPUR				
Thermoset	TSUR				

* Saran coated polymer film.
** Metallized polymer film.
# Abbreviation with more than one meaning.

the monomers used in the manufacture of polymers, sometimes, however, without a prefix "P" for "poly" (Table 1). The names of monomers for copolymers are given in alphabetical order without regard to their prevalence.

Other abbreviations are based on characteristic groups of polymers (Table 2) or indicate polymers synthesized by chemical transformation of base polymers (Table 3). Special abbreviations apply to blends, reinforced polymers, etc., (Table 4).

Special properties of polymers are symbolized by up to four additional letters. These letters are arranged after the symbol for the base polymer according to ISO and DIN; in the technical literature, they are, however, commonly placed in front of the base symbol, following ASTM. DIN recommends the following letters for special properties: C = chlorinated; D = density; E = expanded, expandable; F = flexible, liquid; H = high; I = impact resistant; L = linear, low; M = molar mass, average (mean), molecular; N = normal, novolac; P = plasticized; R = raised (enhanced), resol; U = ultra, plasticizer-free (unplasticized); V = very; W = mass (weight); X = cross-linked. The technical literature also uses BO = biaxially oriented and O = oriented (usually in one direction).

Companies have long used internal classification systems, and the military has issued plastics specifications. An industry-wide classification system for thermoplastic

Table 3. Abbreviations for polymers produced by chemical transformation of other polymers

Resulting polymer	ASTM	DIN	ISO	IUPAC	Other
Carboxymethyl cellulose	CMC	CMC	CMC	CMC	
Carboxymethyl hydroxyethyl cellulose					CMHEC
Casein, cross-linked with formaldehyde	CS	CS	CS	CS	
Cellulose, as Cellophan	C				
Ditto, coated with Saran	C*				
Cellulose acetate	CA	CA	CA	CA	
Cellulose acetobutyrate	CAB	CAB	CAB	CAB	
Cellulose acetopropionate	CAP	CAP	CAP	CAP	
Cellulose nitrate	CN	CN	CN	CN	NC
Cellulose plastics, unspecified	CE				
Cellulose propionate	CP	CP	CP	CP	
Cellulose triacetate	CTA	CTA			TA
Ethyl cellulose	EC	EC	EC	EC	
Hydroxyethyl cellulose					HEC
Hydroxypropyl cellulose					HPC
Hydroxypropyl methyl cellulose					HPMC
Methyl cellulose		MC			
Polyethylene, chlorinated	CPE	PE-C	PEC		
Chlorosulfonated	CSM				CSR
Poly(ethylene-co-vinyl alcohol)		E/VAL			EVAL
					EVOH
Polypropylene, chlorinated		PPC			
Polyvinyl alcohol	PVAL	PVAL	PVAL	PVAL	PVOH
Polyvinyl butyral	PVB	PVB	PVB		
Polyvinyl chloride, chlorinated	CPVC	PVC-C	PVCC		PC#, PeCe
Polyvinyl formal	PVFM	PVFM	PVFM	PVFM	

* Saran coated polymer film.

materials introduced by ISO is based on an alphanumeric "line call-out," a special code (see below) [57, 58]. A material is characterized by several data blocks that indicate its composition and certain property data or ranges. These property data refer to essential criteria. Since different thermoplastics have different applications, property data are restricted to different "leading properties" for each type of thermoplastic.

The property data covered by this classification scheme are thus not comprehensive. Rather, various plastics types are characterized by one to three sets of leading criteria, selected from

- Chemical structure data, such as content of vinyl acetate (VAC) or acrylonitrile units (AN), isotacticity (IT), or density (D) as a measure of branching
- Molar mass data, such as intrinsic viscosity (IV) or Fikentscher's K value (FK)
- Bulk density (BD)
- Rheological data, such as melt flow rate (MFR) (melt flow index)

Table 4. Abbreviations for blends, reinforced polymers, etc

Resulting polymer	ASTM	DIN	ISO	IUPAC	Other
Elastomers, thermoplastic					
Containing ester and ether groups	TEEE				
Olefin-based	TEO				
Styrene-based	TES				
Epoxide, glass-fiber reinforced					GEP
Plastic, carbon-fiber reinforced		KEK			CFP
Glass-fiber reinforced					GFK
Man-made fiber reinforced					CFK
Metal fiber reinforced					MFK
Poly(acrylonitrile-co-styrene)+chlorinated polyethylene	ACS				
Sheet molding compound					SMC
with high glass fiber content					HMC

- Thermal data, such as Vicat temperature (VT) or torsional stiffness temperature (TST)
- Mechanical properties, such as modulus of elasticity (*E*), tensile stress at 100% strain (TS), shore hardness (SH), or impact strength (notched) (ISN)

The following leading criteria are used:

Polyethylene	D, MFR
Polypropylene	I, MFR
Polystyrene and acrylonitrile-styrene copolymers	VT, MFR
Styrene-butadiene, acrylonitrile-butadiene-styrene, and acrylonitrile-styrene-acrylic acid copolymers	VT, MFR, ISN
Ethylene-vinyl acetate copolymers	VAC, MFR
Poly(vinyl chloride)	IV, FK, BD
Poly(vinyl chloride), unplasticized	VT, E, ISN
Poly(vinyl chloride), plasticized	TS, SH, TST
Polyamides	IV, E
Polycarbonates	IV, MFR, E
Poly(methyl methacrylate)	IV, VT
Poly(ethylene terephthalate)	IV

The standard designation of a thermoplastic material consists of a description block, a standard number block, and a series of data blocks.

Designation Block. The designation block gives the type of material (e.g., thermoplastic, molding, etc.).

Standard Number Block. *Data block 1.* The standard number block consists of the number of the ISO (or DIN or other national) standard, followed by a hyphen and data block 1. This data block contains the abbreviation of the chemical name of the material [e.g., PE = polyethylene, PVC = poly(vinyl chloride)]. This may be followed by analytical data, such as the vinyl acetate content of ethylene–vinyl acetate copolymers (EVAC). However, these are not the exact analytical data but rather code numbers for the range (called "cell") in which this material can substitute for a similar one. Separated by a hyphen, supplemental information on this material may be given (e.g., H = homopolymer, P = plasticized, U = unplasticized, E = polymerized in emulsion).

Data block 2. may contain up to four letters that give qualitative information. The first letter denotes the intended application (e.g., B = blow molding, G = general purpose, P = paste resin, Y = textile yarn). The following one to three letters can code up to three essential additives or supplemental information, for example, A = antioxidant, D = powder (dry blend), L = light and weather stabilizer, S = slip agent.

Data Block 3. Quantitative information about the designated properties is contained in data block 3. The encoding of these data is different for each plastic material and each testing standard. For example, the code 20 – D 050 in data block 3 for a polyethylene tested according to DIN 16 776 means a material with a density of 0.918 g/cm^3 (cell 020) and a melt flow rate of 4.2 g/min (cell 050) measured at 190 °C under a load of 2.16 kg (D). On the other hand, a third data block 22 – 030 for a polyamide 12 means a polymer with an intrinsic viscosity of 210 cm^3/g (cell 22) and a modulus of elasticity of 280 MPa (cell 030). The definition of the cells can be found in special cell tables.

Data block 4. gives information about the type and content of fillers or reinforcing materials; these codes are independent of the types of polymers. The first letter gives the type of filler, for example, C = carbon or G = glass. The second letter indicates the shape of the filler (e.g., F = fiber, S = sphere). The letters are followed by a code for the mass content of the filler; 15 for the range 12.5–17.5 wt %, 60 for the range 57.5–62.5 wt %.

Data block 5. is reserved for specifications based on individual agreements between supplier and customer. It may code additional requirements, restrictions, or supplemental information.

A thermoplastic may thus carry the designation "Molding material DIN 7744-PC, XF, 55–045, GF 30," which indicates a polycarbonate (PC) with no special indication of its application (X) but with special burning characteristics (F), an intrinsic viscosity in a coded range of 55 (here for [η] = 56 cm^3/g), and a melt flow rate of 5.5 g/(10 min) (coded as 045), which contains 30% (30) of glass (G) fibers (F).

A designation system similar to the above ISO–DIN system has been recommended by ASTM [59, 60]. A typical ASTM designation,

for example, would read "Molding material ASTM D-4000 PI 000 G 42 360"; this material is a polyimide (PI). Because no individual property table has been specified for polyimides, the cell table G of ASTM D-4000 has been used to characterize the properties of PI. This particular cell table identifies five different properties by designating cell limits to the five digits following the letter G. The first digit characterizes the minimum tensile strength, here "4", which according to cell table G means at least 85 MPa. The second digit gives the cell value for the flexural modulus (here "2" for 3 500 MPa). The third digit denotes the Izod impact strength (50 J/m →"3"), and the fourth digit the heat deflection temperature (300 °C→"6"). The fifth digit is undetermined; the "0" indicates an unspecified property.

1.3. History of Plastics [13–16, 62–67]

The first plastics were prepared long before their macromolecular nature was discovered. Decorative coatings based on polymers, such as egg white or blood proteins were used in the cave paintings of Altamira, Spain, as early as 15 000 B.C. Later painting methods utilized gelatin and polymers resulting from naturally drying vegetable oils. The use of these materials resulted from the eternal desire of artists for easy-to-handle materials that give an optimal artistic effect and have infinite stability.

These requirements were not restricted to surface coatings, which are two dimensionally applied plastics. Cow horns were used in the Middle Ages to prepare windows for lanterns and intarsia in wood. To this purpose, the horns had to be flattened by steaming, a very difficult process. The flattened horns also tended to curl up after a while. An early, easy-to-process substitute for natural horn was reported by the Bavarian monk WOLFGANG SEIDEL (1492–1562); it undoubtedly derived from far older recipes. This imitation horn was based on the protein casein, the white material from skim milk. Casein was extracted from skim milk with hot water, treated with warm lye, and shaped while being warmed; the desired shape was then fixed by immersion in cold water. Unknown inventors later discovered that the addition of inorganic fillers increased the mechanical stability of this early thermoplastic. The same material was used later for children's building blocks by the German aviation pioneer OTTO LILIENTHAL (1848–1896) and his brother GUSTAV. In 1885 a patent based on the same physical process was granted to the American EMERY EDWARD CHILDS. The properties of these plastics were improved markedly by the chemical reaction of casein with formaldehyde, as described in 1897 by the German inventors WILHELM KRISCHE and ADOLF SPITTELER. The resulting thermoset was called galalith (Greek: *gala* = milk, *lithos* = stone); it is still used today for haberdashery.

Another early thermoset used natural rubber as the raw material. In 1839, the American CHARLES GOODYEAR discovered the cross-linking (vulcanization) of natural rubber to an elastomer by sulfur under the action of "white lead" (basic lead carbonate) and heat. His brother NELSON used larger amounts of sulfur and in 1851 invented ebonite, a hard, black thermoset.

The first fully synthetic thermoset was invented in 1906 by the Belgian-born American chemist LEO H. BAEKELAND, who heated various phenols with formaldehyde under pressure and produced insoluble hard masses. These "bakelites" were recognized in 1909 as excellent electrical insulators and thus became one of the foundations of the modern electrical industry. BAEKELAND was not the first to prepare phenolic resins though; they were first observed by ADOLF VON BAEYER in 1872. BAEYER'S substances were merely resinous materials, and BAEKELAND'S "heat and pressure" process was necessary before commercially useful materials could be produced.

The first *semisynthetic thermoplastics* originated from cotton. Cotton fibers consist of cellulose; they have been used by man since prehistoric times. Because cotton is relatively easily grown, many attempts have been made to improve its textile properties. The Englishman JOHN MERCER discovered in 1844 that the treatment of cotton with aqueous solutions of caustic soda (sodium hydroxide) leads to fibers with increased strength, higher luster, and improved dyeability. The Frenchman L. FIGUIER demonstrated in 1846 that cellulose paper was strengthened in a manner similar to cotton when it was treated with sulfuric acid. In

1853 W. E. GAINE received an English patent for the same process, which delivered a parchment-like material. An English patent by THOMAS TAYLOR described the formation of very resistant materials from layers of paper sheets by the combined action of zinc chloride and pressure. These products were called "vulcanfiber" because they resembled the vulcanization products of natural rubber.

Mercerized cotton, artificial parchment, and vulcanized paper result from physical transformations of cellulose. If, however, cellulose materials are treated not by sulfuric acid alone but by a mixture of sulfuric and nitric acids, a chemical reaction to cellulose nitrate (nitrocellulose, gun cotton) occurs. This chance discovery by the German CHRISTIAN FRIEDRICH SCHÖNBEIN in 1846 paved the way for the invention of the first semisynthetic thermoplastic. In 1862 ALEXANDER PARKES found an easy method for processing cellulose nitrate into thermoplastic masses by the addition of castor oil, camphor, and dyes. The manufacture of the resulting "parkesine" was difficult, however, and production ceased in 1867. The use of alcoholic solutions of camphor by DANIEL W. SPILL was equally unsuccessful. In 1869, a patent was granted to the American JOHN WESLEY HYATT for the use of camphor without camphor oil or alcohol. The resulting "celluloid" is generally considered the pioneering thermoplastic [66].

Other early, fully synthetic thermoplastics have a far longer history, albeit not as industrial materials. Polymers of formaldehyde were found by JUSTUS VON LIEBIG in 1839; yet extensive scientific investigations by HERMANN STAUDINGER in the 1920s and 1930s and major industrial development work by Du Pont and Celanese were necessary before it became an engineering plastic in 1956.

Vinyl chloride was synthesized by H. V. REGNAULD in 1838, who also observed the formation of resins. Vinyl chloride was polymerized by KLATTE in Germany and OSTROMUISLENSKY in England in 1912, but not until 1931 was the first poly(vinyl chloride) produced commercially in Germany by I. G. Farben.

Styrene was discovered by a chemist called NEUMAN as reported in W. NICHOLSON'S 1786 *Dictionary of Practical and Theoretical Chemistry*. The conversion of styrene to a solid mass was discovered by E. SIMON in 1839, who considered it a styrene oxide. A. W. VON HOFMANN and J. BLYTH showed in 1845 that the alleged styrene oxide was an isomer of styrene; they called it metastyrene. It was however only in 1920 that the polymeric nature of polystyrene was recognized by H. STAUDINGER; it was first produced commercially by I. G. Farben (Germany) in 1930.

A highly branched polyethylene is found in nature as the "mineral" elaterite. Lightly branched synthetic polyethylene was first obtained in 1933 by high-pressure polymerization of ethylene at ICI (England); its commercial production began in 1939. Linear polyethylenes were first synthesized in 1953 by low-pressure polymerization using catalysts based on transition metals (ZIEGLER), chromium oxide (Phillips Petroleum), and molybdenum oxide (Standard Oil of Indiana). For the first time, NATTA employed ZIEGLER's catalysts to polymerize α-olefins, such as propene, thus producing solid, crystalline stereoregular polymers. The commercial production of isotactic polypropylene (PP) began in Italy, Germany, and the United States in 1957. The use of these catalysts and the availability of inexpensive feedstocks from petroleum refining led to rapid growth of the polymer industry. Progress in heterogeneous polymerization catalysis enabled morphology control in olefin polymerization, thus producing spherical pellet-sized polyolefin particles without requiring pelletizing extrusion.

1.4. Economic Importance [68–73]

The rapid growth of plastics production is a result of three factors: (i) growth of world population with surging demand for cost-, resource-, eco-, and energy-efficient advanced materials, (ii) average increase in standard of living, and (iii) replacement of metal, wood, ceramics, and environmentally less friendly materials by plastics. The growth pattern may be economy driven [determined by the price of materials (substitutes); shortages (substitution), or governmental regulations; or technology driven (determined by technological requirements, internal knowhow, and accidental discoveries). At present, the expected declining

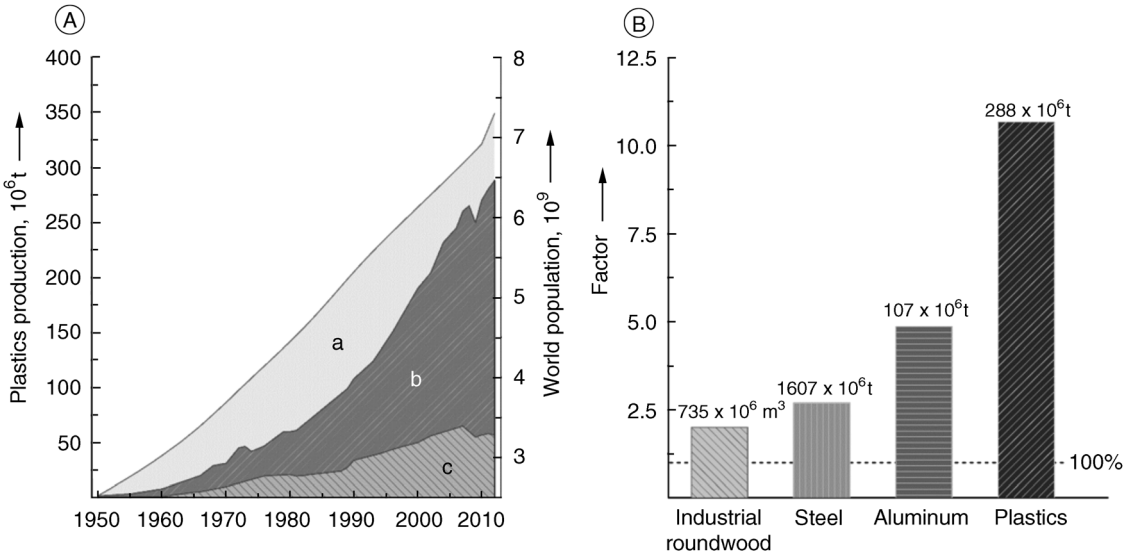


Figure 1. A) Growth of world plastics production and world population (data taken from [73, 74]); B) Production growth (1970–2012) of other materials
a) Population Growth; b) World plastic production; c) European production

supply of fossil resources, and public concerns relating to global warming and climate change, are stimulating the quest for polymers based on renewable resources. The world population grew from 2.532×10^9 in 1950 to 7.159×10^9 in 2014, and is expected to reach 9×10^9 in 2050. Because more people aspire the high living standards of the Western World, the rapid growing world population is accompanied by a surging demand for polymeric materials. Hence, the world plastics production (approximately equal to consumption) climbed from 0.6 kg per capita (1950) to ca. 42 kg per capita in 2014 (see Fig. 1).There are great differences in plastics consumption between various countries: Whereas plastic production is slowing down in Europe, it continues to grow rapidly in Asia and India.

According to a survey conducted by PlasticsEurope (the association of plastics manufacturers in Europe) in 2012, the European plastics industry producers, plastics converters, and plastics machinery with more than 62 000 companies accounted for approximately 1.4 million jobs in the European Union's 27 member states and had a combined turnover of around 3×10^9 Euro. By 2014, the world plastics production will pass the 300×10^6 t/a mark. In 2012, China was the leading plastics producer with 23.9% share of the world plastics production, followed by the rest of Asia, including Japan, (20.4%), Europe (20.4%), NAFTA (19.9%), Middle East/Africa (7.2%). In 2013, the world's plastic consumption was close to 300×10^6 t, of which commodity polymers, such as PE, PP, PVC, PS, and PET claim a major share of around 80% (Fig. 2). The growth of the plastics production during the first decade of the 21st century is unparalleled by any other class of materials including wood, aluminum and steel (Fig. 1). Close to half of the world's plastics production

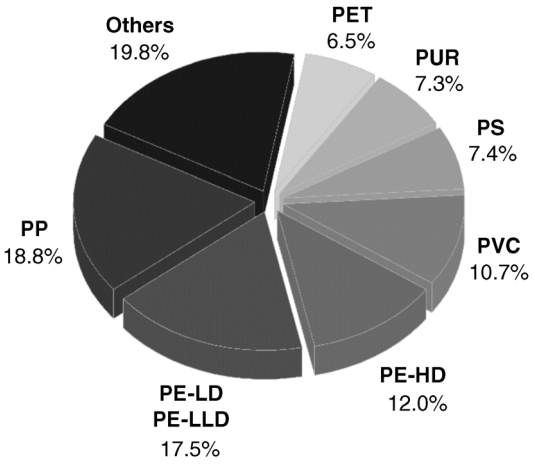


Figure 2. Industrially important polymers [73]

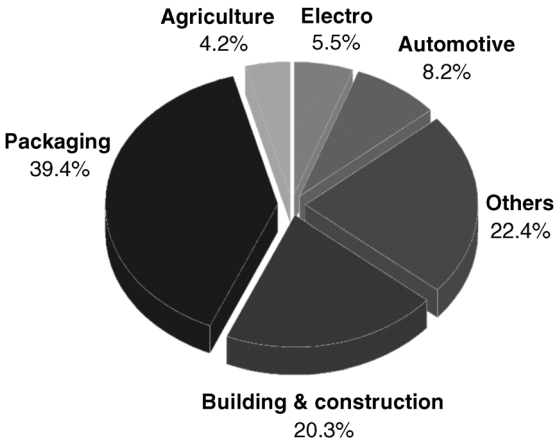


Figure 3. Application areas of plastics [73]

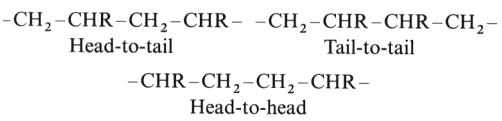
are polyolefins, such as PE and PP. Plastics serve the needs of a variety of markets (Fig. 3). In 2012, the largest plastic application area in Europe was packaging (39.4%), followed by building and construction (20.3%), automotive (8.2%), electrical and electronics (5.2%), agricultural applications (4.2%), and other diversified sectors (22.4%) including consumer and household products, furniture, sports, safety, as well as medical applications (see Fig. 3). Today, plastics wastes are recognized as very valuable source of raw materials and energy. Upon thermal treatments, commodity plastics are converted back into oil and gas, thus substituting fossil resources. In 2012, the plastics recycling and energy recovery reached 61.9% in Europe. The recycling of plastics and polymer products, ranging from lightweight engineering to membranes for water purification, offer great prospects for sustainable development, protecting resources, such as oil and water, for future generations, reducing carbon footprint, and securing the supply of energy and food.

2. Molecular Structure of Polymers [1–12]

2.1. Constitution

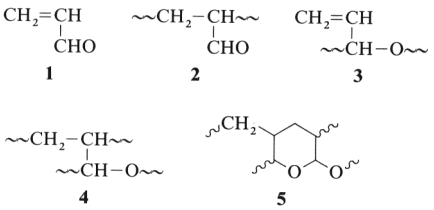
2.1.1. Homopolymers

A homopolymer is defined as a polymer derived from one type of monomer. The term homopolymer thus refers to the origin of the monomers in a polymer and not to the actual constitutional units. The polymerization of a monomer CH_2=CHR leads to constitutional units –CH_2CHR–. These units may be connected to each other not only in head-to-tail positions but also in head-to-head and tail-to-tail arrangements:



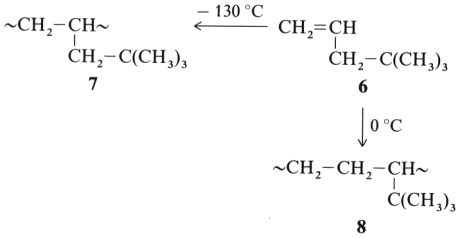
The proportion of head-to-head regioisomeric units increases with decreasing size of substituents R and with reduced resonance stabilization of the growing species. Free-radical polymerization of vinyl acetate [CH_2=CH($OOCCH_3$)] leads to 1–2%, of vinyl fluoride (CH_2=CHF) to 6–10%, and of vinylidene fluoride (CH_2=CF_2) to 10–12% tail-to-tail connections. Head-to-head connection is detrimental to thermal stability, because the steric hindrance of the substituents reduces the bond strength of the C–C bonds.

Monomer molecules can also polymerize to a lesser or greater extent via "wrong" groups. The amount of such isomeric units depends on the constitution of the monomer and the mode of polymerization. Acrolein (**1**), for example, polymerizes free radically via the carbon–carbon double bond (**2**) and the aldehyde group (**3**); it forms branched (**4**) or cross-linked units and even intramolecular rings (**5**) from two units of (**4**):



Monomers may also isomerize during polymerization, especially cationic polymerization. 4,4-Dimethyl-pentene-1 (**6**) polymerizes at low temperature (≈ −130 °C) via the carbon–carbon double bond (**7**), but at higher

temperature (≈ 0 °C) leads to a "phantom polymer" (**8**) with three carbon atoms per monomeric unit:



Irregular structures may also be created by chain-transfer reactions to polymer molecules (see Chap. 3); these reactions lead to branched polymers.

The groups at the ends of polymer chains are not shown, in part because they are often unknown and in part because their structure does not influence most of the polymer properties. End groups may be initiator or catalyst residues or groups that are generated by transfer reactions. These groups rarely affect mechanical properties; they may, however, negatively influence the thermal or photochemical stability of polymers.

2.1.2. Copolymers

Copolymers are generated from more than one type of monomer; they are called bipolymers, terpolymers, quaterpolymers, etc., according to the number of monomer types. The copolymerization of ethylene (CH_2=CH_2) and propene [CH_2=CH(CH_3)] thus leads to the bipolymer poly(ethylene-*co*-propene). Polymers of butadiene (CH_2=CH–CH=CH_2) with 1,4-units –CH_2–CH=CH–CH_2– and 1,2-units –CH_2–CH(CH=CH_2)– are not called copolymers because they are generated from only one monomer type. Rather, they are pseudocopolymers, such as the ones that result from partial saponification of poly(vinyl acetate), ~[CH_2–CH($OOCCH_3$)]$_n$~ to a pseudocopolymer with vinyl acetate units and vinyl alcohol units –CH_2–CH(OH)–. Thus, the term copolymer does not refer to the chemical structure of the resulting polymer, but to the monomers from which it derives.

The succession of monomeric units in copolymer chains is known as their sequence. Monomer units "a" and "b" alternate in *alternating copolymers* (Table 5), which are limiting cases of periodic copolymers ~(abb)$_n$~, ~(aabb)$_n$~, ~(abc)$_n$~, etc.

The sequence of monomeric units in *statistical copolymers* is determined by the statistics of copolymerization (Markov statistics of zeroth, first, etc., order). *Random copolymers* are special cases of statistical copolymers: The sequence follows Bernoulli statistics (i.e., zeroth-order Markov statistics).

Graded copolymers (i.e., tapered copolymers) exhibit a compositional gradient along the chain: One chain end is enriched in "a" units, the other in "b" units. *Block copolymers* are extreme cases of such graded copolymers; they consist of blocks of homosequences that are joined via their ends. Linear multiblock copolymers with short blocks are called *segment(ed) copolymers*. In *graft copolymers*, "b" blocks are connected to "a" chains via center monomeric units.

Copolymers poly(A-co-B) of monomers A and B possess properties quite different from blends of homopolymers A and B.

Table 5. Types of copolymers from monomers A, B, and C (monomeric units are characterized by lower-case letters)

Name	Structure	Shorthand name
Copolymer without specified squende	~(a/b)~	poly(A-co-B)
Statistical copolymer (example)	~a-b-b-b-a-a-b-a-a-a-a-b~	poly(A-stat-B)
Random copolymer (with Bernoulli statistics of sequence)	ditto	poly(A-ran-B)
Alternating copolymer	~a-b-a-b-a-b-a-b-a-b-a-b~	poly(A-alt-B)
Periodic copolymer	~a-b-b-a-b-b-a-b-b-a-b-b~	poly(A-per-B-per-B)
	~a-b-c-a-b-c-a-b-c-a-b-c~	poly(A-per-B-per-C)
Diblock copolymer	~a . . . . . .a-b . . . . . .b~	poly(A)-block-poly(B)
Triblock copolymer	~a . . . . . a-b . . . . . b-c . . . . . c~	poly(A)-block-poly(B)-block-poly(C)
Graft copolymer	~a-a-a .....a-a-a .....a~ (b$_m$, b$_n$)	poly(A)-graft-poly(B)

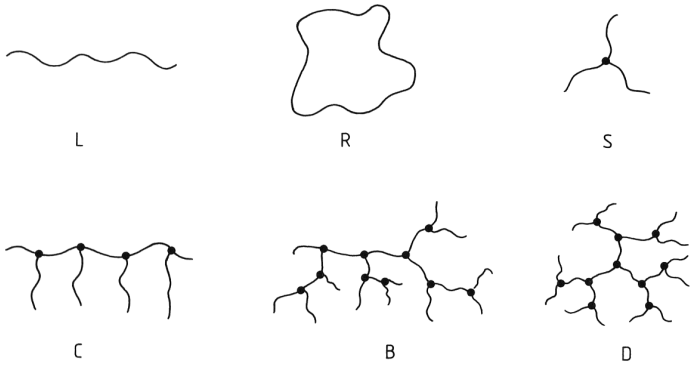


Figure 4. Schematic representation of linear and branched marcomolecules
L = Linear (unbranched) chain in almost extended state; R = ring molecule; S = starlike molecule with three subchains, C = comblike molecule with four branching points of functionality 3; B = randomly branched chain with subsequent branching; D = dendrimer with three-functional branch points and three generations of subchains

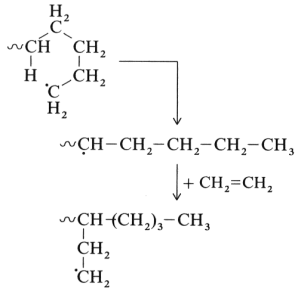
2.1.3. Branched Polymers

Open chains of the type R–m_n–R exhibit the simplest structures. They possess *n* monomeric "m" units and two R end groups. They are also called linear chains (Fig. 4, L) because of their one-dimensional connectivity or their unbranched structures and because they were originally (and wrongly) assumed to be completely extended (stretched out). Spiropolymers and ladder polymers (see below) are also linear polymers because they are not "branched" in the macromolecular sense.

Cyclic polymers (ring polymers; Fig. 4, R) consist of linear polymer molecules that are joined via their ends. They do not have end groups and are not called macrocycles because that term is traditionally reserved for "big rings" of ca. 15–20 chain atoms.

Branched polymers contain branch points that connect three or more subchains (sometimes called subunits). The following types of branched polymers are distinguished:

1. *Star polymers* possess one branching point from which three or more subchains radiate (Fig. 4, S).
2. *Dendrimers* (dendritic polymers) are treelike star polymers in which the subchains are themselves starlike branched (Fig. 4, D). They are also called cascade polymers (because of the cascade-like sequence of branching points), isotropically branched polymers, or isobranched polymers (because each generation of newly added monomer molecules is "isotropically" arranged around the central core), or much more poetically, starburst polymers. Whereas ideal dendrimers require tedious multistep syntheses, a more industrially viable synthesis is to produce less perfect cascade macromolecules, which are known as hyperbranched polymers.
3. *Comb polymers* have "long" side chains, whose chemical structures usually differ from those of the main chains (Fig. 4, C). The term *graft copolymer* refers to comb polymers into which branches have been introduced by subsequent grafting onto a primary chain. Comb polymers whose side chains exhibit liquid crystalline (LC) behavior are called LC side-chain polymers.
4. *Randomly branched polymers* have a random distribution of branching points (Fig. 4, B); the subchains may be further branched (Christmas tree branching) or not. Short-chain and long-chain branching are distinguished. *Short-chain branches* are often generated by intramolecular transfer reactions, for example, the butyl side chain of polyethylene is formed during free-radical polymerization of ethylene:



Long-chain branches are usually generated by intermolecular transfer reactions. In the

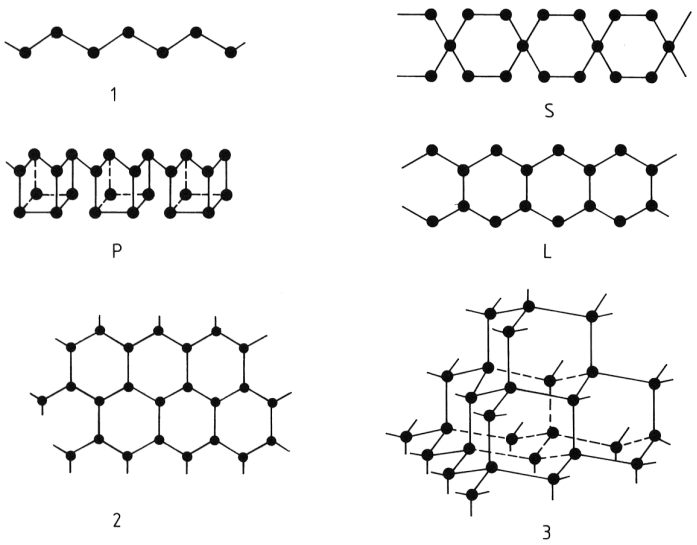
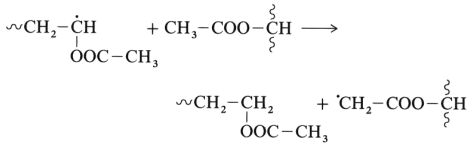


Figure 5. Schematic representation of some ordered chain assemblies
1 = Catena polymer in all-*trans* conformation; S = Spiro polymer; P = Pearl-stringlike polymer; L = Ladder polymer; 2 = Phyllo polymer; 3 = Tecto polymer

polymerization of vinyl acetate, side-chain radicals formed by transfer reactions may initiate the polymerization of additional vinyl acetate monomers.



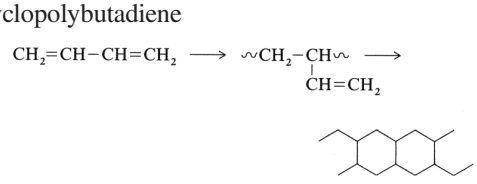
Such side-chain radicals are also formed by radical transfer from certain initiator radicals. Side chains introduced by the inherent structure of a (co)monomer are not called branches in polymer science. Neither linear poly(vinyl acetate) nor the low-crystallinity, low-density polymers formed by copolymerization of ethylene with small amounts of α-olefins (butene-1, hexene-1, octene-1) are considered branched; the latter are known as linear low-density polyethylenes. Although short-chain branching significantly reduces melting temperature and crystallinity of polyethylene, as reflected by reduced density, the incorporation of a few long chain branches greatly improves melt processing, such as shear thinning and melt strengthening in blow molding of polyolefin films.

2.1.4. Ordered Chain Assemblies

Two or more chains may also be joined at more than two points by chemical bonds in an ordered way. The chains are thought to be fully extended for classification purposes; a distinction is made among one-, two-, and three-dimensional assemblies or, according to IUPAC, among catena (Fig. 5, 1), phyllo (Fig. 5, 2) and tecto (Fig. 5, 3) compounds.

Linear polymers are catena polymers in this nomenclature because the fully extended chains extend in only one direction (Fig. 5, 1). Spiro polymers possess two chains with connecting atoms shared by both of them (Fig. 5, S).

Ladder polymers consist of two chains joined by bonds in regular intervals (Fig. 5, L); they are also called double-strand polymers. Such ladder polymers are generated by first forming a linear chain with pendant side groups that are subsequently polymerized. An example is the polymerization of 1,3-butadiene to 1,2-polybutadiene with subsequent cyclization to cyclopolybutadiene



Ladder polymers may also be synthesized by two-step polycondensation or polyaddition reactions; in general, however, only fairly short ladderlike units are formed in this way (see below). One-step ladder syntheses are very rare. Polymerization of the silicon analogue of

cubane, $(C_6H_5)_8Si_8O_{12}$, does not lead to a ladder polymer of type L in Figure 5 but to a pearl-string-like polymer P (Fig. 5, P). Many silicates are ladder polymers or double-ladder polymers.

Phyllo polymers are also called layer or parquet polymers (Fig. 5, 2). Graphite and the silicates montmorillonite, bentonite, and mica are well-known examples. Cell walls of bacteria consist of bag-shaped polymers (i.e., layer polymers). Diamond and quartz are examples of tecto polymers (Fig. 5, 3). Two-dimensional carbon polymers, consisting of planar honeycomb-like sp^2-hybridzed carbons, are known as graphene which is equivalent to a single carbon layer of the graphite lattice.

2.1.5. Unordered Networks

Multifunctional oligomer and polymer molecules can be interconnected via chain groups or end groups to cross-linked polymers (networks). The cross-linking points must be at least trifunctional; that is, the cross-linkable groups must be at least bifunctional. The cross-linking bridges between chains can be short or long; the distribution of cross-linking points, at random or in clusters. Both chemical and physical bonds can be employed for cross-linking; chemically and physically cross-linked polymers are thus distinguished.

Chemical Networks. The structure of chemical networks depends on the relative amount of cross-linking sites and the state of the reactants during the cross-linking reaction. The network structure is to a first approximation independent of the chemical structure of the cross-linking sites. The relative amount of cross-linking sites determines the cross-link density. Light cross-linking does not change the mobility of chain segments between cross-links, and the resulting networks behave as elastomers if the chain segments are above the glass transition temperature. Networks with strong cross-linking or chain segments below the glass transition temperature are employed for thermosets.

Networks are fairly *homogeneous* with respect to the distribution of cross-links if they are prepared by polymerization in bulk or from homogeneous solutions and if the corresponding linear chains are soluble in their own monomers or in the applied solvent (Fig. 6, HN). Inhomogeneous networks are formed if phase separation occurs during polymerization; for example, if the low molar mass polymers generated early are insoluble in the applied solvent or the remaining monomer. The resulting *macroreticular networks* exhibit cavities (Fig. 6, MN).

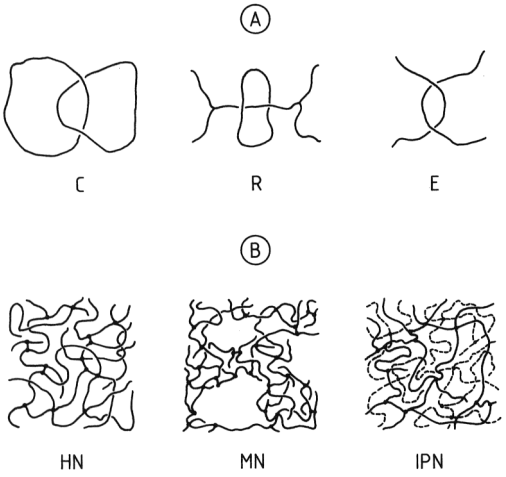


Figure 6. Schematic representation of cross-linked polymers
A) Physical cross-links; B) Chemical networks
C = catenane; E = entanglement; HN = homogeneous network; IPN = interpenetrating network; MN = macroreticular network; R = rotaxane
Reprinted with permission by Hüthig and Wepf Publ., Basel [5]

In principle, two chemically different networks poly (a) and poly (b) can coexist independently of each other in interpenetrating networks (IPNs). In reality, these networks are not molecularly interdispersed; rather, each network forms interconnected domains with higher cross-link densities. Semi-interpenetrating networks consist of cross-linked poly (a) in uncross-linked poly (b).

Chemical cross-links are in most cases irreversible. These cross-linked polymers do not dissolve in solvents. With an increase in temperature, subchains decompose rather than revert to the original monomers. Chemically reversible cross-linked networks are being investigated because they would be of value in the recycling of thermosets.

Physical Networks. Physically cross-linked polymers, on the other hand, are in most cases reversibly cross-linked. Examples are

microdomains in block copolymers, ion clusters in ionomers, or even crystallites in partly crystallized polymers. Physically cross-linked polymers often dissolve in suitable solvents.

Entanglements (Fig. 6, E) behave under strain as physical cross-links because the two chains cannot diffuse away rapidly enough; the chains disentangle, however, if sufficient time is allowed. Catenanes (Fig. 6, C) and rotaxanes (Fig. 6, R) have irreversible physical cross-links. Catenanes consist of two intertwined rings. Such structures are well known for deoxyribonucleic acids; they have also been observed for some synthetic polymers. Rotaxanes are rings on chains that are sealed on both ends by branched or cross-linked structures in such a way that the ring cannot slip out. Such structures are suspected to exist in some cross-linked polydimethylsiloxanes.

2.2. Molar Masses and Molar Mass Distributions

Molar masses of polymers can be varied over a wide range; they may extend from several hundreds to several millions, albeit not for every polymer type. The molar mass ranges used industrially depend on the limitations of the available polymerization procedures, the restrictions imposed by processing methods, and the desired properties of the plastics.

Presently available polymerization methods all employ statistical approaches to initiation and propagation of growing chains, as well as to termination and transfer, where applicable. The resulting polymer molecules thus show a distribution of molar masses; they are not molecularly uniform, and the experimentally determined molar masses represent averages. Synthetic copolymers are, in addition, nonhomogeneous with respect to the distribution of different types of monomer units; they are polydisperse with respect to both constitution and molar mass.

In contrast, biopolymers are synthesized via matrix polymerization. Many (if not all) biopolymers are monodisperse in their biological environments: Each macromolecule of a polymer has the same constitution and the same molar mass. Examples are nucleic acids and enzymes. Upon isolation from living cells and further processing, some degradation may occur. Industrially employed celluloses thus exhibit molar mass distributions.

Starburst dendrimers are synthetic polymers that are molecularly uniform. Their molecular homogeneity approaches that of isotopic distributions in atoms and molecules. It is caused by a self-limitation of molecular growth due to surface crowding after a certain number of growth generation steps [75].

2.2.1. Molar Mass Average

Many polymer properties depend on the type and range of molar mass distributions. In many cases, molar mass averages are determined instead, in part because it is experimentally easier and in part because a number is simpler to grasp than a function.

The averages employed in polymer science are usually arithmetic averages. The polymer molecules of size i (degree of polymerization X_i, molar mass M_i) are counted according to their statistical weight g_i, which may be their mole fraction $x_i \equiv n_i/\Sigma_i n_i$, their mass fraction $w_i \equiv m_i/\Sigma_i m_i = x_i M_i/M_n$, or their z-fraction defined as $Z_i \equiv z_i/\Sigma_i z_i = w_i M_i/M_w = x_i M_i^2/(M_n M_w)$. The number-, mass-, and z-average molar masses are defined as

$$\overline{M}_n \equiv \Sigma_i x_i M_i = \frac{\Sigma_i w_i}{\Sigma_i (w_i/M_i)}$$

$$\overline{M}_w \equiv \Sigma_i w_i M_i = \frac{\Sigma_i x_i M_i^2}{\Sigma_i x_i M_i}$$

$$\overline{M}_z \equiv \Sigma_i Z_i M_i = \frac{\Sigma_i w_i M_i^2}{\Sigma_i w_i M_i} = \frac{\Sigma_i x_i M_i^3}{\Sigma_i x_i M_i^2}$$

Each of these three average moments is essentially a single moment of the distribution of molar masses present. There are, however, molar mass averages that are composed of more than one moment, for example, molar masses from sedimentation and diffusion coefficients for certain types of molecular shapes and solvent interactions.

2.2.2. Determination of Molar Mass

Number-Average Molar Masses. Many methods exist for the determination of molar masses. Most important for the number-average molar mass is *osmometry*, which measures the osmotic pressure Π of polymer solutions at various

polymer concentrations c against the solvent. Solution and solvent are separated by a semipermeable membrane that is permeable to the solvent but not to the polymer molecules.

Older osmometers determined osmotic pressure in true thermodynamic equilibrium, which was reached only after days and weeks because large volumes of solvent had to be moved through the membrane. Modern osmometers compensate for the increase in pressure difference between solution and solvent caused by the flow of solvent into the solution chamber via a servomechanism by a change of solvent pressure; equilibrium pressures are established after 10–30 min. Reduced osmotic pressures, Π/c, determined at various concentrations, are extrapolated to zero concentration to give the number-average molar mass according to the van't Hoff equation, $\overline{M}_n = RT\left[\lim_{c\to 0}(\Pi/c)\right]$. Number-average molar masses may be determined by osmometry in the range of 10^4 g/mol (lower limit of semipermeability of membranes) to ca. 10^6 g/mol (upper limit of sensitivity).

Mass-average molar masses are determined mainly via static *light scattering* of dust-free dilute solutions. Modern instruments measure the so-called Rayleigh ratio $R_o = K \cdot c \cdot \overline{M}_{w,app}$, at very low angles relative to the incident light beam, where K is an optical constant and $M_{w,\,app}$ an apparent mass-average molar mass that is calculated from R_o, c, and K. Values of $K \cdot c/R_o$ are measured at various polymer concentrations and extrapolated to zero concentration. The limiting value $\lim_{c\to 0}\ (K \cdot c/R_o)$ delivers the inverse mass-average molar mass, $1/\overline{M}_w$. Molar masses from several hundred to several million grams per mole can be determined by light scattering, the upper limit being given by experimental problems, such as multiple scattering. If measurements are performed over a wide range of scattering angles, important additional information about the radii of gyration of the molecules can be gained from the angular dependence of the Rayleigh ratio.

The *viscometric method* is fast and simple and therefore the most often applied method. From solvent viscosity η_o and viscosities η of dilute solutions of various concentrations c (measured at low shear rates), reduced viscosities (i.e., viscosity numbers) are calculated via $\eta_{red} = (\eta - \eta_o)/(\eta_o \cdot c)$. The reduced viscosities are extrapolated to zero concentration to give the *intrinsic viscosity* (limiting viscosity number) $[\eta]$ (DIN recommends the symbol J_o). This quantity has the physical unit of a specific volume because the concentration c is measured as mass per volume. The recommended units are milliliters per gram (cubic centimeters per gram), but data in 100 mL/g are still found in the literature; in the older literature, $[\eta]$ was given as Z_η in liters per gram.

Intrinsic viscosities measure the volume occupied by 1 g polymer at $c \to 0$, that is, the specific volumes (inverse densities) of isolated polymer molecules. Because molecular density varies with size for most molecule shapes, intrinsic viscosities can be used to measure molar masses for a homologous series of polymer molecules.

The viscosity increment η_i of unsolvated, compact spheres is, according to EINSTEIN:

$$\eta_i = (\eta - \eta_o)/\eta_o = (5/2)\phi = (5/2)(N_A V_H c/M)$$

where N_A is the Avogadro number, ϕ the volume fraction, $V_H = \rho_H/m$ the hydrodynamic volume, ρ_H the density, and m the mass of a sphere. Hard spheres from the same material have the same density. Because $m \sim M$ and $\eta_i/c \approx [\eta]$, intrinsic viscosities of spheres are independent of their molar masses (i.e., $[\eta] = K \cdot M^0$).

The hydrodynamic densities of other particle shapes, such as rods and coils change, however, with the molar mass

$$[\eta] = K \cdot M^a \qquad (1)$$

The exponent $a = 2$ for rigid rods of infinite length. Theory and experiment indicate a value of $a = 1/2$ for random coils in the unperturbed state (see below); this is a limiting case for very flexible chains in theta solvents. A theta solvent is a solvent being at a temperature at which a polymer adopts the theta state, i.e., where coil molecules are in their unperturbed state with a Gaussian distribution of segments (no excluded volumes). A theta solvent is a thermodynamically bad solvent. Theory predicts $a = 0.764$ for nondraining coils of high molar mass in thermodynamically good solvents (Fig. 7). Experimentally, values of $0.5 < a < 0.764$ are often found for flexible chains (such as most

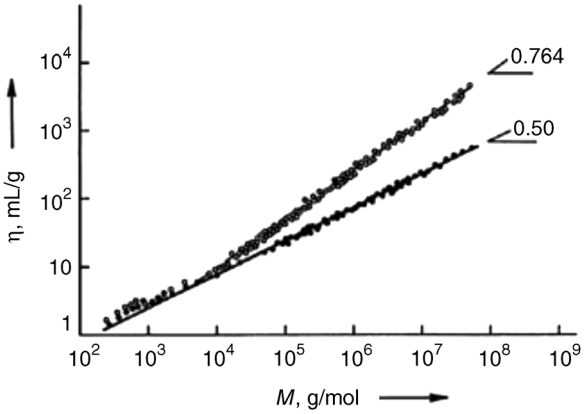


Figure 7. Molar mass dependence of intrinsic viscosities of flexible, coillike molecules: polystyrene in the theta solvent cyclohexane at 34.5°C (●) and in the thermodynamically good solvent benzene at 25°C (○)
The slopes at high molar masses adopt the theoretical values of 0.764 (good solvent) and 0.500 (theta solvent)

thermoplastics in solution) because their molar masses are not high enough for the assumptions of the theory to be fulfilled.

Wormlike molecules may adopt values of $0 < a < 2$ because they resemble spheres and ellipsoids at low molar masses, rigid rods at medium ones, and random coils at very high molar masses. This behavior is found for stiff molecules such as the double helices of deoxyribonucleic acids in aqueous solutions or certain poly(α-amino acids) in helicogenic solvents (see Chap. 5).

Viscometry delivers a peculiar molar mass average, such as can be derived from Equation (1):

$$\overline{M}_n = ([\eta]/K)^{1/a} = \left(K^{-1} \cdot \Sigma_i w_i [\eta]_i\right)^{1/a} = \left(\Sigma_i w_i M_i^a\right)^{1/a}$$

Numerical values of viscosity-average molar masses $\overline{M}_\eta$ lie between number and mass averages for $0 < a < 1$ and become identical with mass averages if $a = 1$.

2.2.3. Molar Mass Distributions

The types and characteristic parameters of molar mass distributions of polymers are determined thermodynamically or kinetically by the synthesis conditions and, to a smaller extent, by the processing of plastics. The molar mass distributions are mathematically described by distribution functions, which may be discontinuous (discrete) or continuous and differential or integral (cumulative) (Fig. 8). In these functions, polymer molecules of size i (molar mass M_i, degree of polymerization X_i) are considered according to their statistical weights, which may be mole fractions x_i, mass fractions w_i, etc.

All molar mass distributions are discrete, because successive polymer molecules of a homologous series differ from each other by a degree of polymerization of 1 and the molar mass M_u of one monomeric unit. The discrete distribution functions can normally be replaced by continuous ones because so many different degrees of polymerization exist, and the difference in molar masses between molecules with M_i and M_{i+1} is small compared to the average molar mass.

The various types of distribution functions are usually named after their discoverers. The *Schulz–Zimm distribution* function derives from processes in which reactive chains add other monomer or polymer molecules until the chains are deactivated. Such deactivation processes may be chain termination reactions (chain polymerization, polyelimination) or the decrease of reactivity by lowering of temperature (polycondensation, polyaddition). The mass fraction of polymer molecules with degree of polymerization X_i is given by

$$w_i = \frac{(k/\overline{X}_n)^k \cdot X_i^k \cdot \exp(-kX_i/\overline{X}_n)}{\Gamma(k+1)} \qquad (2)$$

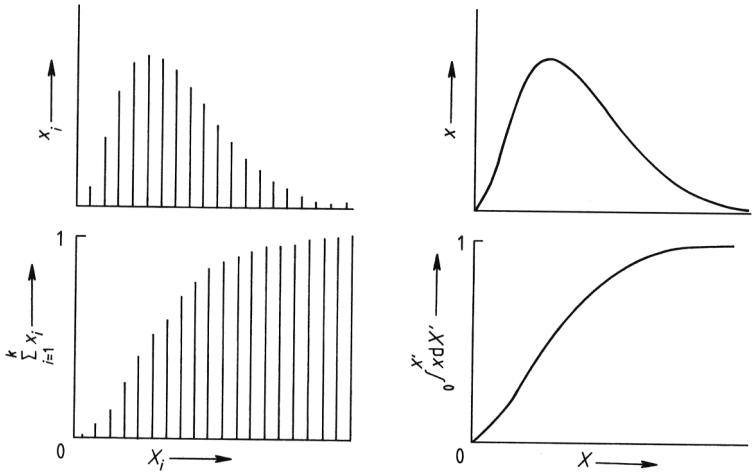


Figure 8. Distributions of mole fractions x of degrees of polymerization X
Left: discontinuous (discrete); right: continuous; top: differential; bottom: integral (cumulative)
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where k is the degree of coupling of chains (e.g., $k = 2$ for recombination of two growing chains to one dead chain and $k = 1$ if two growing chains react by disproportionation to two dead chains) and γ ($k = 1$) the gamma function of ($k = 1$). This function is called *Schulz–Flory* or *Flory distribution* for the special case of $k = 1$ (polycondensation, radical chain polymerization with termination by disproportionation). Equation (2) reduces for $k = 1$ and high degrees of polymerization to

$$w_i = (1/\overline{X}_n)^2 \cdot X_i \cdot [1 - (1/\overline{X}_n)]^{xi}$$

The various average degrees of polymerization are connected via

$$\overline{X}_n/k = \overline{X}_w/(k+1) = \overline{X}_z/(k+2)$$

Poisson distributions are formed if a constant number of chains starts to grow simultaneously and if monomer molecules are added to the chains at random and independent of previous additions. The mass fraction of molecules of degree of polymerization X_i is given by

$$w_i = \frac{X_i \cdot (\overline{X}_n - 1)^{X_i - 1} \cdot [\exp(1 - \overline{X}_n)]}{(X_i - 1)!(\overline{X}_n)}$$

and the interrelationship between the various averages by

$$\overline{X}_w/\overline{X}_n = 1 + (1/\overline{X}_n) - (1/\overline{X}_n)^2$$

The ratio of mass to number average approaches 1 at infinitely high molar masses. The Poisson distribution is thus a very narrow distribution, in contrast to the Schulz–Zimm distribution where the ratio $\overline{X}_w/\overline{X}_n$ equals 2 for $k = 1$ and 3/2 for $k = 2$.

The Schulz–Zimm distribution is a special case of the *Kubin distribution*, an empirical, generalized exponential distribution (GEX distribution) with three empirical, adjustable parameters γ, ε, and β:

$$w_i = \frac{\gamma \cdot \beta^{(\varepsilon+1)/\gamma} \cdot X_i^{\varepsilon} \cdot \exp(-\beta X_i^{\gamma})}{\Gamma[(\varepsilon+1)/\gamma]}$$

This expression converts to the Schulz–Zimm distribution if $\gamma = 1$, $\varepsilon = k$, and $\beta = k\,\overline{X}_n$. The Kubin distribution also includes the *Tung distribution* ($\varepsilon = \gamma - 1$) and the logarithmic normal distribution ($\gamma = 0$; $\varepsilon = \infty$), both of which frequently describe molar mass distributions of polymers from Ziegler–Natta polymerizations. The Kubin distribution is a very adaptable distribution because it contains a

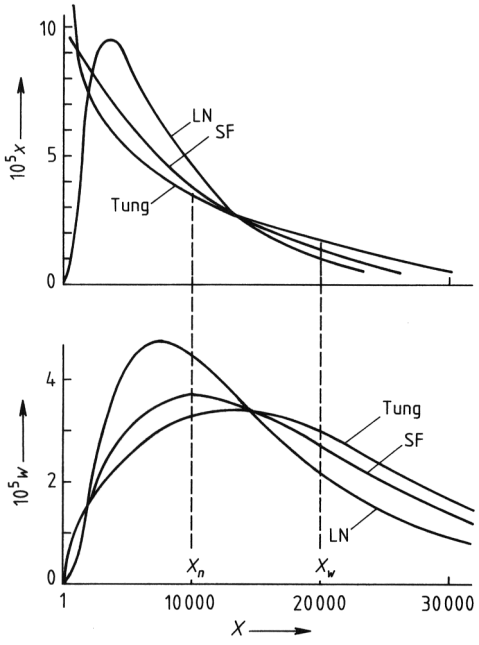


Figure 9. Continuous differential distributions of degrees of polymerization X for a) the logarithmic normal distribution (LN); b) the Schulz–Flory distribution (SF); and c) the Tung distribution (Tung), shown as distributions of mole fractions (top) and corresponding mass fractions (bottom) for a polymer with $\overline{X}_n = 10\,000$ and $\overline{X}_w = 20\,000$
The Poisson distribution is so narrow that it is practically identical with the vertical line for $\overline{X}_n = 10\,000$.
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"stretched exponential" (i.e., a variable X with an exponent γ in the exponential term).

Some of these distribution functions are compared in Figure 9. Note that only the logarithmic normal distribution shows a maximum in the distribution of mole fractions and that none of the maxima in the distributions of the mass fractions correspond to simple molar mass averages.

2.2.4. Determination of Molar Mass Distributions

Molar mass distributions can be determined by preparative *fractionation* of polymers from solutions because the various species of a polymer-homologous series exhibit small differences in solubility. Fractionation occurs upon change of temperature or addition of a nonsolvent. The molar masses of the resulting fractions are determined in separate experiments. Fractionations are inexpensive but time consuming.

The method of choice for the fast determination of molar mass distribution is *size exclusion chromatography* (SEC), also being referred to as gel permeation chromatography (GPC). Dilute polymer solutions are placed on the top of a column filled with a porous carrier. Low molar mass molecules can enter the pores, but high molar mass molecules cannot. Medium-sized molecules enter with difficulty and remain for shorter times than low molar mass molecules. Higher molar masses are thus eluted first, and elution curves are observed that give the concentration of eluted molecules as a function of the eluted volume V_e. The maximum of the elution curve is called the retention volume.

The retention volumes depend on the SEC system (carrier, solvent, temperature) and the polymer being investigated. The carrier may consist of rigid porous materials (e.g., porous glass beads) or swollen, cross-linked polymers (e.g., cross-linked polystyrenes or dextrans). In the latter case, the method is called gel permeation chromatography (synthetic polymers) or gel filtration (biopolymers).

Retention volumes are constant below and above certain molar masses of the polymers (Fig. 10). The volume V_o at lower molar masses gives the total volume available for the flow of solvent; the volume V_i at upper molar masses

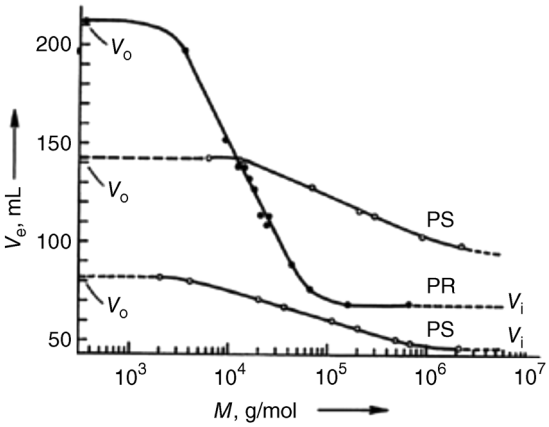


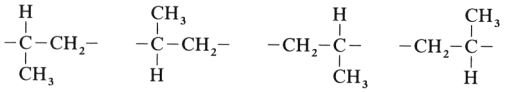
Figure 10. Molar mass dependence of elution volumes V_e
a) Coil-like linear polystyrenes PS with two different SEC columns from cross-linked polystyrenes; b) Various spheroidal proteins PR with cross-linked dextran
V_o = total volume; V_i = interstitial volume

indicates the interstitial volume between carrier particles. Polymer molecules can thus be separated only in the range $V_i < V_e < V_o$, where V_e is the elution volume.

Elution volumes depend to a first approximation on the logarithms of molar masses (Fig. 10). A function $V_e = K \cdot \ln M$ is thus often used to determine unknown molar masses with the help of a constant K derived from calibrations with narrow-distribution polystyrene standards. This procedure does not give absolute molar masses because polystyrenes and test polymers with the same molar masses possess different chromatographically effective volumes. A frequently used "universal" calibration method thus employs a function $V_e = f(\log [\eta] \cdot M)$ because $[\eta]$ measures the specific hydrodynamic volume of the solute molecules and $[\eta] \cdot M$ has the physical unit of a molar volume.

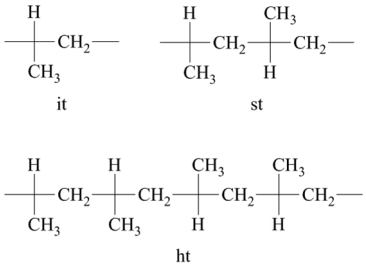
2.3. Configurations

Polymers with symmetric repeating units, such as $-CH_2-CH_2-(-CH_2-CH_2-)$, $-CH_2-CF_2-$, and $-NH-CO(CH_2)_5-$ do not possess configurational isomers. Such isomers do exist, however, for polymer molecules with nonsymmetric repeating units, such as $-CH(CH_3)-CH_2-$(polypropylene) and $-NH-CO-CH(CH_3)-$(polyalanine). Polypropylene, for example, has two configurational repeating units **9** and **10** with two different monomeric units each:



9a **9b** **10a** **10b**

The configurational units **9a** and **9b** are enantiomeric; they belong to the same constitutional unit $-CH(CH_3)-CH_2-$. The configurational units **9a** and **10a**, on the other hand, are based on two different constitutional units. Several configurational units may be joined to give steric repeating units; the three simplest steric repeating units for polypropylene are



The repetition of these units leads to polymer chains that are called isotactic (it), syndiotactic (st), and heterotactic (ht). A heterotactic unit ht in a polymer chain consists of three monomeric units (the first or last three of ht), but the repetition of such ht-triads does not lead to a completely heterotactic polymer ht because it would consist of alternating heterotactic and syndiotactic triads. Whether **9a** or **10a** is used as the simplest configurational repeating unit is immaterial because infinitely long polypropylene chains of **9a** differ from those of **10a** only by the orientation of these units.

The term tacticity thus refers to the relative arrangements of configurational units in a chain. Relative configurations are classified by starting at one end of the polymer chain and considering the configuration around a central atom relative to the preceding one. This classification is different from that of the absolute configuration of organic chemistry where the configuration of each central atom is determined relative to the ligand with the lowest seniority.

The substituents R of isotactic polymer molecules are always "on the same side" if these molecules are shown in Fischer projections or in other stereo formulas with hypothetical *cis* conformations of the chains. In stereo formulas based on *trans* conformations, ligands are only on the same side for isotactic molecules consisting of two chain atoms per monomeric unit (Fig. 11), that is $\sim(CHR-CH_2)\sim$.

Real polymer chains of the types $\sim CHR\sim$, $\sim CHR-CH_2\sim$, $\sim X-CHR-CH_2\sim$, etc., contain configurational mistakes; they are neither 100% isotactic nor 100% syndiotactic. The tacticity of such chains is expressed by the

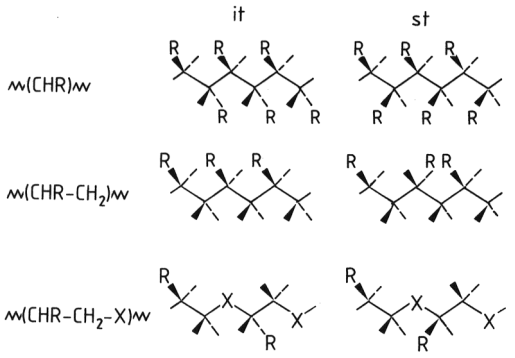


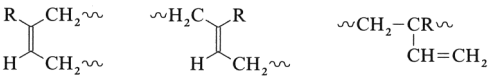
Figure 11. Isotactic (it) and syndiotactic (st) polymers with monomeric units –CHR–, –CHR–CH_2–, and –CHR–CH_2–X– in *trans* conformations
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fraction X_J of their isotactic or syndiotactic diads, triads, etc. A diad consists of two monomeric units, a triad, of three; etc. Each monomeric unit of a polymer chain belongs to two tactic diads, three tactic triads, four tactic tetrads, and so on. Figure 11 thus shows five diads, four triads, three tetrads, etc., for ~CHR~. The sum of the mole fractions of all J-ads of given J must equal 1 ($x_i + x_s \equiv 1, x_{ii} + x_{is} + x_{si} + x_{ss} \equiv 1$, etc.), where i = isotactic diad, s = syndiotactic diad, ii = isotactic triad of two isotactic diads, etc. The mole fraction of isotactic diads is given by the mole fraction of isotactic triads plus 1/2 of the mole fraction of the sum of the two heterotactic triads, that is, $x_i = x_{ii} + (1/2)(x_{is} + x_{si})$, etc. The number-average sequence length of isotactic sequences is thus given by $(X_{\dagger})_n = 2\, x_i/(x_{is} + x_{si})$.

The presence and/or fraction of tactic J-ads can be investigated by a number of experimental methods. 2D-NMR spectroscopy allows absolute determination of the types of J-ads and their amounts up to pentads, whereas conventional high-resolution NMR spectroscopy requires prior knowledge of the J-ad type by X-ray crystallography or other methods. Infrared spectroscopy detects only diads, whereas crystallinity, solubility, glass and melt temperatures, and chemical reactions may or may not indicate the presence of shorter or longer tactic sequences.

Highly isotactic polymers can be produced by Ziegler–Natta polymerization of α-olefins (e.g., it-polypropylene or it-polybutene-1). Special Ziegler–Natta catalysts lead to st-polypropylene and st-polystyrene; these syndiotactic polymers have no commercial use thus far. Highly syndiotactic polymers are also generated by most very low-temperature free-radical polymerizations of vinyl and acryl monomers. Conventional vinyl and acryl polymers are, however, synthesized at ambient temperature or above, and consist, at best, of slightly syndiotactic polymers; in general, they are considered atactic polymers.

Polymers with different geometric isomerism are also tactic. Depending on the configuration of the chain segments relative to the double bonds in the chain *cis*-tactic (ct) and *trans*-tactic (tt) structures are distinguished. The ct structure of 1,4-polyprenes[~ $(CH_2-CR{=}CH-CH_2)_n$ ~] from the polymerization of 1,3-dienes $CH_2{=}CR-CH{=}CH_2$ via both double bonds corresponds to an E isomer; the tt structure, to a Z isomer. If the polymerization proceeds via one double bond only, 1,2-polydienes are formed that may be isotactic, syndiotactic, atactic, etc.



2.4. Conformations

2.4.1. Microconformations

Rotations of atoms or groups of atoms around single bonds create spatial arrangements called conformations (organic chemistry) or microconformations (macromolecular chemistry). The sequence of these microconformations determines the shape of the macromolecule, i.e., the macroconformation (in statistical mechanics, the configuration).

In principle, an infinite number of conformations are possible around each single bond. In practice, certain positions are energetically preferred; only these are called (micro)conformations. In two joined tetrahedrons, such as ethane (H_3C-CH_3), two extremes of energetically different positions are possible: The staggered

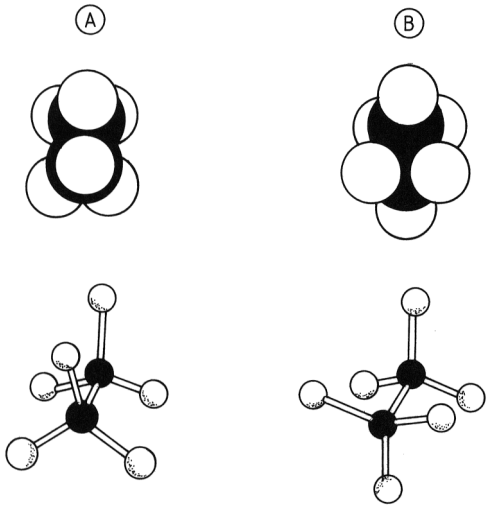


Figure 12. Microconformations of ethane
A) Eclipsed position (*cis* or synperiplanar); B) Staggered position (*trans* or antiperiplanar)
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position corresponds to a minimum of energy and the eclipsed position to a maximum of energy if repulsive forces are prevalent (Fig. 12). On rotation by 360° around the C−C axis, three energetically equivalent eclipsed and three energetically equivalent staggered positions may be occupied as the three H atoms bound to the same C atom ("bonded atoms") are equivalent. Small molecules, such as ethane, can be considered as definite species in conformations with energy minima; they are called conformers, rotamers, or rotational isomers.

The number of types of conformers increases if the three bonded atoms are not equivalent, for example, in butane ($CH_3-CH_2-CH_2-CH_3$) (one CH_3 group and two H atoms bonded to each carbon atom participating in the central C−C bond). In polymer chains, one of the bonded atoms is never equivalent because it is part of the chain; in polyethylene (∼ CH_2-CH_2 ∼), the bonded atoms are two H atoms and the chain. There are two energetically different eclipsed positions (*cis* and *anti*) and two energetically different staggered ones (*trans* and *gauche*). Each *gauche* and each *anti* position can occur in two spatially different positions that are energetically equivalent (plus and minus) if two of the three bonded atoms are equivalent. These (micro)conformers have different names in macromolecular and in organic chemistry (Fig. 13).

All eclipsed positions are sterically hindered in polymer chains and therefore only *trans* and *gauche* positions must be considered. The conformational energy is the energy difference between the energies of the *trans* and *gauche* conformations. Activation energy (potential energy) is necessary to overcome the rotational barrier between *trans* and *gauche* conformations. This rotational barrier increases with decreasing length of the central bond and with increasing number and increasing size of bonded atoms. Its value is, for example, 12.1 kJ/mol for the C−C bonds in polyethylene chains ∼$(CH_2-CH_2)_n$∼ but only 2.1 kJ/mol for the CH_2-CO bonds in polyester chains with units ∼$CH_2-CO-O-CH_2$∼. Because these bond energies can easily be overcome by thermal energy, (hindered) rotations are possible around the chain bonds and the molecules may adopt many chain conformations (Section 2.4.3). Isolated aliphatic polyester

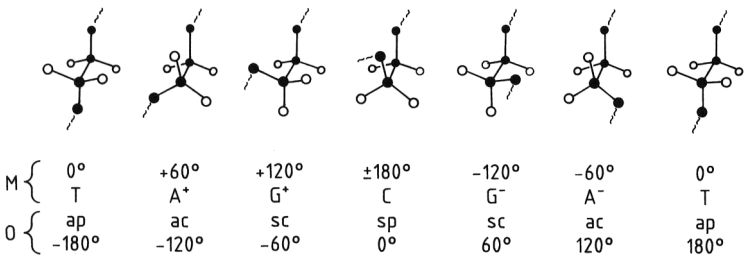


Figure 13. Chain conformations and their names and symbols in macromolecular (M) and organic (O) chemistry
• Chain atoms; ○ substituents; T = *trans*, A = *anti*; G = *gauche*; C = *cis*; ap = antiperiplanar; ac = anticlinal; sc = synclinal; sp = synperiplanar

chains $\sim OOC(CH_2)_x\sim$ (with $x > 3$) are thus more flexible than carbon chains; such polymers are used as polymeric plasticizers.

Two different types of flexibility are distinguished. A chain molecule is said to be *statically flexible* if it possesses many accessible conformational minima. *Dynamic flexibilities* are characterized by low barriers between conformational minima.

2.4.2. Conformations in Ideal Polymer Crystals

A regular sequence of microconformations leads to regular macroconformations of polymer chains. The chains are linearly extended; the end-to-end distance is commonly called the contour length r_{cont} of the chain (this term originally referred to the contour of the chain along the individual chain bonds). Chains in all-*trans* microconformations are said to be fully extended (e. g., the chain in Fig. 5, 1).

Polyethylene crystallizes ideally in an all-*trans* conformation because the shortest distance between nonbonded hydrogen atoms (0.254 nm) is greater than the sum of the van der Waals radii of H atoms (0.24 nm). The size of substituents R in isotactic poly(α-olefins) $[\sim(CH_2-CHR)_n\sim]$, however, forces the microconformation around each second chain bond to adopt a *gauche* position (see Fig. 13). All *gauche* conformations must be alike for steric reasons; conformational diads G^+G^- and G^-G^+ are forbidden (Fig. 13). The chain thus adopts either a . . . $TG^+TG^+TG^+$ . . . or a $TG^-TG^-TG^-$ . . . macroconformation, i.e., it becomes helical. The number of monomeric units per complete turn is determined mainly by the size of the immediate substituents. it-Polypropylene $\sim[CH_2-CH(CH_3)]_n\sim$ has three propene units per one turn (3_1 helix, Fig. 14 A), it-poly(4-methylpentene-1) (P4MP) $\sim(CH_2-CH[CH_2CH(CH_3)_2])_n\sim$ has seven units per two turns (7_2 helix = 3.5 helix, Fig. 14 B), and poly(3-methylbutene-1) (P3MB) has four units per one turn (4_1 helix, Fig. 14 C). The conformational angles are not necessarily the ideal ones of 0° for *trans* and 120° for *gauche* as found for it-polypropylene; they are rather −13°/110° for P4MP and −24°/96° for P3MB. Conformational positions with deviations up to ± 30° from the ideal conformational angles are still named after the ideal microconformations.

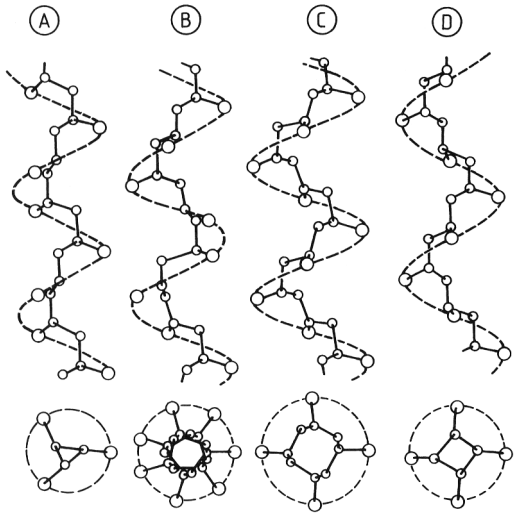


Figure 14. Helix types of poly(α-olefins) $\sim CH_2-CHR\sim$ A) 3_1 Helix; B) 7_2 Helix; C), D) Different types of 4_1 helices Reprinted with permission by Societa Italiana di Fisica, Bologna, from [76]

The R substituents of syndiotactic vinyl polymers $[\sim(CH_2-CHR)_n\sim]$ are farther apart than those of their isotactic counterparts (see Fig. 11). In general, *trans* conformations thus have the lowest energy in those st-polymers where only repulsive forces operate. Attractive forces, such as intramolecular hydrogen bonds between neighboring OH groups in poly(vinyl alcohol) $(\sim[CH_2-CH(OH)]_n\sim$, PVAL), lead to different conformational sequences: Isotactic PVAL exists in all-*trans* conformations, whereas syndiotactic PVAL forms helices.

Chain atoms with free electron pairs lead to *gauche* effects. The chains of crystallized polyoxymethylene $[\sim(O-CH_2)_n\sim]$ exist in all-*gauche* conformation (9_5 helix). Polyoxyethylene $[\sim(O-CH_2-CH_2)_n\sim]$ and polyglycine $[\sim(NH-CO-CH_2)_n\sim]$, on the other hand, possess the conformational sequence TTG. The resulting 7_2 helices of polyglycine are stabilized by intramolecular hydrogen bonds between the first, fourth, seventh, etc., peptide bonds of a chain.

Polypeptides $[\sim(NH-CO-CHR)_n\sim]$ are based on chiral monomeric units. An L-polymer may thus form two different helices: A right-handed and a left-handed one. These helices are diastereomers with different energy contents. In general, one "handedness" is preferred over the

other in polymers with chiral base units. Poly(L-α-amino acids) generally form right-handed helices, whereas poly([*S*]-α-olefins) and most polysaccharides from D-sugars exist as left-handed ones.

2.4.3. Conformations in Polymer Solutions

Helices can survive melting and dissolution processes only if the helical structure is stabilized by intramolecular attractive forces. Examples are the hydrogen bonds in helices of poly(α-amino acids) or hydrogen bonds plus base stacking in double helices of deoxyribonucleic acids. These forces may be so strong that the molecules decompose rather than melt on heating. A delicate balance between intramolecular bonding and solvation of substituents is necessary to preserve helical structures in solution; examples are poly(α-amino acids) in helicogenic solvents.

Helices that are generated in crystals by packing of chains whose microconformations originate from repulsive forces do not survive the melting process intact. Each macromolecule can form many macroconformers that equilibrate rapidly. Only very short helical sequences in very low concentrations may thus exist in melts.

Two extreme cases must be considered for the dissolution of polymers. Only weak interactions (or none at all) exist between monomeric units of apolar polymers and apolar solvent molecules. Conformational changes are thus entropy driven; the sequence of microconformations is irregular, and the polymer molecule adopts the macroconformation of a coil.

In apolar enantiomeric polymers in apolar solvents, long conformational sequences are conserved, although fast conformational transformations from left- to right-handed helices and vice versa may occur in enantiomeric polymers. On average, few microconformations are converted into other ones. These helical sequences may be stabilized by association processes.

Polar solvents, on the other hand, interact strongly with polar polymers; these solvents cause strong changes in microconformations. Because the ligands around each chain bond can adopt various microconformations and these microconformations can change rapidly; a given macromolecule may exist in time in many macroconformations, similar to those of simple apolar polymers in apolar solvents:



Figure 15. Electron micrograph of the double helix molecules of deoxyribonucleic acid chains showing two-dimensional random coils
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A polymethylene [$\sim(CH_2)_n\sim$] with degree of polymerization $n = 20\ 001$ possesses 20 000 chain bonds, each of which can adopt three microconformations: *trans*, *gauche* (plus), and *gauche* (minus). According to statistics, such chain can exist in $3^n = 3^{20\ 000} \approx 10^{9542}$ different macroconformations. Conversely, a collection of chains may have many macroconformations at any given time. None of these macroconformations adopts a simple geometric shape, not even instantaneously. Rather, the chains form rapidly changing coil structures that can be made visible by electron microscopy as two-dimensional projections of the three-dimensional coil shape for chains of sufficiently long chain diameter (Fig. 15).

2.4.4. Unperturbed Coils

The instantaneous shapes of coils cannot be determined by presently known methods. Their radius of gyration can be measured, however, by light scattering, small-angle X-ray scattering, and small-angle neutron scattering. The end-to-end distances of coiled linear chains can be modeled for various types of chains and calculated for individual chains via the rotational isomeric state method.

The simplest model is that of a freely jointed chain (no fixed bond angles) that assumes infinitely thin segments without interactions. The mean square end-to-end distance, r_∞^2, of such a coil is given by the

number N of its unspecified segments with segment lengths b:

$$\langle r_{oo}^2 \rangle = N \cdot b^2$$

Real chains possess fixed bond angles τ between chain atoms and finite torsion (or dihedral) angles θ ($\theta = 0°$ for *trans* conformations). The mean square end-to-end distance for such a chain in the unperturbed state (zero net polymer−polymer and polymer−solvent interactions) is given by

$$\langle r_o^2 \rangle = N \cdot b^2 \cdot \left(\frac{1-\cos\tau}{1+\cos\tau}\right) \cdot \left(\frac{1+\cos\theta}{1-\cos\theta}\right)$$

$$\langle r_o^2 \rangle = N \cdot b^2 \cdot \left(\frac{1-\cos\tau}{1+\cos\tau}\right) \cdot \sigma^2$$

The factor σ is called the *hindrance parameter* or steric factor. Often the hindrance parameter and the bond angle are combined to give the *characteristic ratio* C_N:

$$C_N = \langle r_o^2 \rangle / (N^2 \cdot b^2) = (1-\cos\tau) \cdot (1+\cos\tau)^{-1} \cdot \sigma^2$$

The characteristic ratio becomes approximately constant for chains with more than 100 atoms. A chain can also be characterized by its *Kuhn length* L_K, which can be calculated from its unperturbed mean square end-to-end distance, its degree of polymerization, and the effective length b_{eff} of monomeric units (i.e., length of units in chain direction projected on a plane; $r_{cont} = X \cdot b_{eff} = N_K \cdot L_K$)

$$\langle r_o^2 \rangle = N_K \cdot L_K^2$$

End-to-end distances can rarely be measured directly. They are however related to the experimentally accessible radii of gyration s via

$$\langle s_o^2 \rangle = \langle r_o^2 \rangle / 6$$

This relationship applies to all chains with random flight statistics (e.g., unperturbed chains and freely jointed chains). It is not valid for perturbed chains (Section 2.4.5).

Coil densities are very low (Fig. 15). The volume fraction of monomeric units is, for example, only 0.012 at the center of gyration for a polyethylene chain with a molar mass of 1.19×10^6 g/mol; 99.8% of the space of these polyethylene coils is occupied by solvent molecules (in very dilute solutions) or by units of other polymer chains (in melts).

A chain in a melt cannot distinguish between its own segments and segments of other chains. Because the interactions between the segments of various chains are also the same, such chains adopt their unperturbed dimensions, which has been confirmed by small-angle neutron scattering. Most of the coil volume is filled by segments of other chains to avoid space. Chains of sufficient length may thus become entangled, which manifests itself in properties, such as diffusion and melt viscosity.

2.4.5. Perturbed Coils

Coils adopt their unperturbed dimensions in melts or in certain solvents at certain temperatures (so-called theta solvents). In such theta solvents, polymer−solvent and polymer−polymer interactions cancel each other and the chain behaves as if it is infinitely thin. In thermodynamically good solvents, polymer−solvent interactions dominate and the coil is swollen. The volume requirements of such coils must thus lead to interpenetrations by other coils even at very low concentrations. Because segments are not infinitely thin, however, a part of the total space is excluded for segments of other chains (and also for other segments of the same chain).

2.4.6. Wormlike Chains

Real polymer chains are not totally flexible. Their finite thickness and the partially hindered rotation around chain bonds prevent them from adopting all possible positions in space. Such chains can be described by the model of the wormlike chain (Kratky–Porod model).

The characteristic parameter of this model is the *persistence length* a. This parameter is defined as the average of the projection of the end-to-end-distance of an infinitely long and infinitely thin chain in the direction of the first segment. It can be calculated from the radius of

gyration and the conventional contour length via

$$\langle s_o^2 \rangle = a^2\{(y/3) - 1 + (2 - y) - (2/y^2)[1 - \exp(-y)]\}$$

where $y = r_{cont}/a$. For flexible chains, it is related to the unperturbed radius of gyration via

$$\langle r_o^2 \rangle/6 = \langle s_o^2 \rangle = a \cdot r_{cont}/3 = a \cdot N_K \cdot L_K/3$$

For infinitely stiff chains,

$$\langle s_o^2 \rangle = a^2 \cdot y^2/12 = (r_{cont})^2/12$$

which is an infinitely stiff chain, behaves like an infinitely thin rod. Wormlike chains thus describe the whole transition from rodlike molecules (small y) to random coils (large y). The model is strictly valid for infinitely thin chains, but the error produced by this assumption is negligible if the persistence length is much greater than the chain diameter.

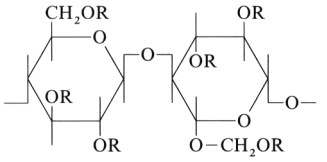
3. Polymer Manufacture

3.1. Raw Materials [78]

The raw materials for most industrially used plastics are synthetic polymers and prepolymers; only a few are derived from naturally occurring polymers or monomers. The overwhelming majority of polymers for plastics are organic materials; very few are semiorganics (i.e., inorganic polymer chains with organic substituents). Raw materials for polymers include biomass, such as wood and fossil resources, such as coal, petroleum, natural gas, and gases supplied by fracking. In view of the increasing energy demand and the limited fossil resources, an important objective is to substitute fossil resources by renewable ones. Another important strategy aims at direct chemical fixation of carbon dioxide to produce monomers and polymers directly from carbon dioxide without endangering food supply.

3.1.1. Wood

Wood (→ Wood) is a naturally occurring composite of oriented cellulose fibers in a continuous matrix of cross-linked lignin; it is plasticized by water and "foamed" by air (vacuoles). The water content varies from 40–60% for green wood to 10–20% for air-dried wood. Solids include cellulose (42%); hemicelluloses (28–38%); lignin (19–28%); and proteins, resins, and waxes (2–3%), depending on the type and age of the plant. Most of the wood is used directly as fuel or for construction purposes, but one-sixth is converted into wood pulp or cellulose pulp for the manufacture of paper, cardboard, or rayon. A very small amount of wood is filled with monomers that are subsequently polymerized to give polymer wood.



Repeating unit (cellobiose) of cellulose (R=H) and cellulose derivatives

Cellulose pulp is chemically transformed into cellulose derivatives (→ Cellulose; → Cellulose Esters; → Cellulose Ethers):

- 2,5-Acetate with 2,5 acetate groups, R = $OOC-CH_3$, per glucose residue (fibers, cigarette filters)
- Cellulose triacetate with three acetate groups per glucose residue (fibers)
- Cellulose acetobutyrate with R=29–6 mol % acetyl and 17–48 mol% butyryl groups (a thermoplastic for tubes, packaging)
- Cellulose nitrate ($R-NO_2$; various degrees of substitution; gun cotton, films, lacquers, celluloid)
- Cellulose ethers with $R-CH_3$, C_2H_5, $CH_2CH_2OR^1$, or $CH_2-CHOR^2-CH_3$, where R^1 may be $CH_2CH_2OR^1$ or CH_2CH_2OH and $R^2-CH_2-CHOR^2-CH_3$ or $CH_2-CHOH-CH_3$ (thickeners, binders, suspension agents, injection molding materials, etc.)

Huge amounts of *lignin sulfonates* (→ Lignin) are generated during wood pulp production, most of which are burned. Small amounts are used for street pavement, as binders for foundry sand, or as drilling agents, and even smaller amounts as raw materials for organic intermediates (→ Lignin). Degradation products of lignin have been utilized for the synthesis of ion-

exchange resins and other polymers. Lignocellulose of forestry and agricultural wastes represents an attractive source of glucose as a renewable feedstock for biorefineries without competing with food production. In biorefineries glucose is converted into a variety of monomers including lactic acid, butadiene, acrylic acid, and even ethylene and propene.

3.1.2. Coal

Coals (→ Coal) are polymerized and partly cross-linked hydrocarbons with average compositions between $C_{75}H_{140}O_{56}N_2S$ (peat) and $C_{240}H_{90}O_4NS$ (anthracite). They were the primary raw materials for acetylene-based monomers during the first half of the 20th century but have since been replaced in most countries by oil and natural gas as monomer sources.

Coals deliver coke and coal tar. A number of aliphatic monomers are produced from coke via acetylene, such as chloroprene, various vinyl monomers, acrylonitrile, and hexamethylenediamine. Coal tar delivers aromatics, such as benzene, xylene, phenol, and phthalic anhydride, which lead subsequently to polystyrene, phenolic resins, and glyptal resins, to name a few.

3.1.3. Natural Gas and Fracking

Natural gas (→ Natural Gas) is a gas with a high proportion of aliphatic hydrocarbons. European gas is rich in methane, whereas American and Saudi Arabian gases are relatively rich in higher hydrocarbons. Natural gas is processed to synthesis gas, ethylene, and acetylene. These gases are used to produce a variety of monomers for polymers. The increasing exploitation of fracking enables the production of hydrocarbons which offer great potential as cost-effective alternative to crude oil.

3.1.4. Petroleum

Petroleum (crude oil) (→ Oil Refining) is the main feedstock for monomers. It consists of 95–98% hydrocarbons and 2–5% oxygen, nitrogen, and sulfur compounds. The hydrocarbons are largely aliphatic, partly naphthenic, and to a small extent aromatic, depending on the source. Petroleum distillation leads to saturated hydrocarbons (gas, naphtha, gasoline, kerosene, diesel fuel, heating oil, etc.). For monomer production, these hydrocarbons are subsequently cracked to mixtures of olefins that are fractionated by distillation. The resulting compounds are used as such or are converted further into the desired monomers.

The polymer industry is a major petrochemical customer: About 60% of the cracking and subsequent products of naphtha are used to produce polymers (ca. 50% for plastics—elastomers, ca. 10% for fibers).

3.1.5. Other Renewable Resources and Biorefineries [79–83]

Vegetable oils are a relatively large source of raw materials. They have high hydrocarbon content and consist of mixtures of fatty acid triglycerides and are usually subdivided into drying oils with high linolenic and linoleic acid content, semidrying oils with high linoleic and oleic acid content, and nondrying oils with high oleic acid content (→ Fats and Fatty Oils). Some oils are used directly for paints; others are chemically converted into monomers.

Castor oil is converted into methyl ricinoleate, which is thermally cracked into methyl undecenate and heptanal. Methyl undecenate is the raw material for 11-aminoundecanoic acid, which is subsequently polycondensed to form polyamide 11. Alkali scission of castor oil or ricinoleic acid produces sebacic acid, a monomer used to prepare polyamide PA6,10. Moreover, castor is propoxylated and end-tipped with ethylene oxide in order to produce polyols, thus enabling the formation of polyurethanes containing up to 30 wt % renewable resources.

Soybean oil is converted by a series of chemical reactions into the methyl ester of the C_{10} amino acid $H_2N(CH_2)_9COOCH_3$, which is the monomer for PA 10. The plant *Crambe abyssinica* contains about 55% of erucic acid, which leads to the C_{13} amino acid and subsequently to PA 13 ($\sim[NH(CH_2)_{12}CO]_n\sim$).

Corn husks and other agricultural waste are rich in *pentosans*, which can be converted into tetrahydrofuran and further into polytetrahydrofuran

$[HO(CH_2CH_2CH_2CH_2O)_nH]$, which serves as a soft block in certain polyurethanes. Moreover, epoxidized soybean oil is produced in large scale and employed as plasticizers for PVC.

Other Natural Oils. Although the production of polymers based upon soybean oil feedstocks may compete with food production, other nonfood oils, such as linseed and tung oil are attractive intermediates for plant-oil based polymers.

Bio-Based Monomers from Biorefineries. Progress made in biotechnology and in the production of biofuels is stimulating the development of new processes for exploiting biomass conversion in biorefineries as intermediates for bio-based plastics. In principle, there are three different strategies for biomass conversion (i) biomass-to-liquid conversion, (ii) biorefining exploiting glucose, bioethanol, glycerol, and plant oils as raw materials, and (iii) direct catalytic liquefaction and hydrothermal carbonization of biomass. Figure 16 gives an overview on the different strategies to produce bio-based monomers. Similar to the Fischer–Tropsch chemistry in coal-to-liquid conversion, biomass is converted by partial oxidation into syngas consisting of a mixture of carbon monoxide and hydrogen, which serves as feedstock for monomer production. This is a rather energy intensive process that is sensitive to catalyst poisoning by biomass components. A more energy-efficient process is the biotechnological conversion of glucose, preferably gained from nonfood sources, such as lignocellulose from agricultural and forestry wastes, into ethanol and a variety of other monomers, such as glycols and lactic acid. Bioethanol is readily converted into ethylene by splitting off water. In addition, butadiene and propene can be produced from bioethanol. In biodiesel production, vegetable oils are converted in their methyl ester by transesterification of oils with methanol. The byproduct glycerol can be converted into a variety of monomers including epichlorhydrin, acrylic acid, and polyols (see Fig. 16).

Whereas biomass-to-liquid conversion is energy intensive, the catalytic direct conversion of biomass into diesel represents another attractive green route to renewable oil. In this process, plastics wastes as well as biomass can be employed as carbon source. In the third approach, entire plants can be converted into coal by hydrothermal carbonization. This is an exothermic process that operates at much lower temperature than the Fischer–Tropsch process. This renewable coal obtained by hydrothermal biomass carbonization is an attractive feedstock

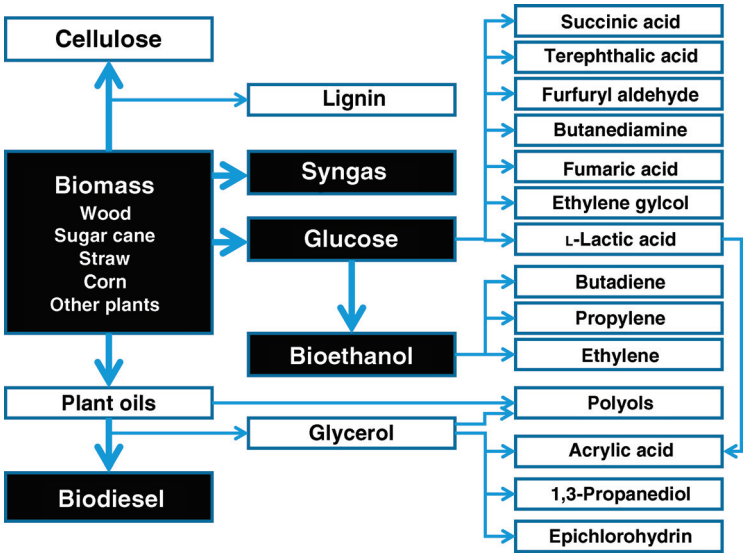


Figure 16. Biorefineries and biobased monomers

for catalytic liquefaction and production of renewable oil.

Carbon dioxide that is emitted by power plants, is the energy sink in combustion processes. Activation and chemical fixation of carbon dioxide requires energy, which can be supplied from renewable resources, thus enabling chemical energy storage of excess energy from wind and solar power plants. In contrast to traditional conversion of carbon dioxide into carbon monoxide and hydrogen by reduction with coal at very high temperatures, oil and gas are produced by electrochemical reduction of carbon dioxide in water. However, this process is not yet feasible for the production of monomers on industrial scale. Another more viable approach exploits the direct conversion of carbon dioxide with reactants, such as epoxides with a high energy content. Thus cyclic carbonates as well as linear aliphatic polycarbonates are available. Polyfunctional cyclic carbonates serve as intermediates for the formation of green polyurethanes without requiring phosgene or isocyanates.

3.2. Polymer Syntheses: Overview [84]

3.2.1. Classifications

Polymers may be synthesized from monomers by polymerization or from other polymers by chemical transformations. The nomenclature and classification of these reactions have grown and changed with the times; they are not very systematic and are sometimes confusing.

All reactions of small monomer molecules to macromolecules are called *polymerizations*. Polymerizations are classified according to the:

- Origin of polymers (bio and chemical polymer synthesis)
- Chemical structure of monomers (vinyl polymerizations, diene polymerizations, ring-opening polymerizations, etc.)
- Chemical structure of resulting polymers (linear, branching, cross-linking, isomerizing, cyclopolymerization, etc.)
- Relative composition of monomers and monomer units (addition, condensation, etc.)
- Formation of low molar mass byproducts (polycondensation)
- Type of polymerization initiation (thermal, catalytic, photochemical, enzymatic, etc.)
- Type of propagating species (free radical, anionic, cationic, polyinsertion, etc.)
- Type of mechanism (chain growth, step growth, living, controlled, catalytic, etc.)
- Reaction media (bulk, solution, emulsion, suspension, mesophase, etc.)
- State of matter (gaseous, homogeneous, heterogeneous, super critical, etc.)

The resulting four types of polymerization can be depicted schematically as

$$P_n + P_m \rightarrow P_{n+m}$$ Polyaddition

$$P_n + M \rightarrow P_{n+1}$$ Chain polymerization

$$P_n + P_m \rightarrow P_{n+m} + L$$ Polycondensation

$$P_n + M \rightarrow P_{n+1} + L$$ Polyelimination

where M denotes monomer; P_n, P_m, P_{n+m}, P_{n+}, denote polymers and L leaving molecules (e.g., water in polyesterifications of diacids and diols).

The names of three of these four types have been used with different meanings by different researchers since the 1930s. The following discussion thus centers on the present nomenclature recommendations by IUPAC.

Chain-Growth Polymerization. Polymer chains grow by repeated addition of monomer molecules M to polymer molecules P_i, consisting of *i* monomeric units m, an initiator end group R, and an "active center ∗," without the formation of leaving molecules:

$$R(m_n)m^* + M \rightarrow R(m_{n+1})m^*$$

An example is the polymerization of vinyl monomers (CH_2=CHR) by chain carriers Y∗, which may be free radicals $Y^{\cdot}$, anions Y^-, or cations Y^+:

$$Y{-}CH_2{-}CHR^* + CH_2{=}CHR \rightarrow Y{-}CH_2{-}CHR{-}CH_2{-}CHR^*$$

A *living polymerization* is a chain polymerization consisting only of fast initiating reactions (Y∗ + CH_2=CHR → Y $-CH_2-$CHR∗) and propagation reactions

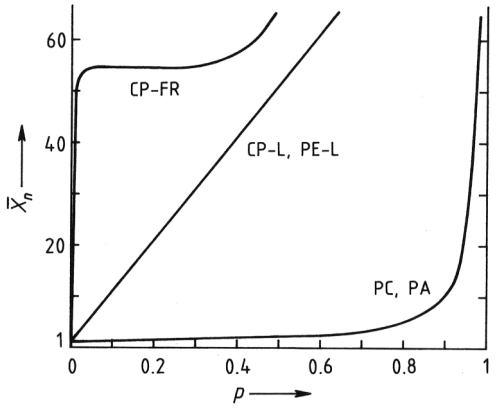


Figure 17. Change of number-average degree of polymerization $\overline{X}_n X^-$ with the extent of reaction of functional monomer groups p for living chain polymerizations CP−L and living polyeliminations PE−L (with initial monomer−initiator ratio 100 : 1 mol/mol), free-radical chain polymerizations CP−FR with gel effect (schematic for high initiator concentrations), and equilibrium polycondensations PC and polyadditions PA (numerically exact)

$[Y-(CH_2-CHR)_n* + CH_2=CHR \rightarrow Y-(CH_2-CHR)_{n+1}*]$ without termination of the growing chains and without side reactions. In such reactions, the degree of polymerization is directly proportional to the conversion u of monomer molecules or p of functional groups, respectively (Fig. 17, curve CP−L). An example is the polymerization of styrene $CH_2=CH(C_6H_5)$ by the butyl anion $C_4H_9^-$ from butyllithium, LiC_4H_9.

The variation of the degree of polymerization with monomer conversion is quite different for *radical polymerizations*, such as the polymerization of styrene by benzoyloxy radicals $C_6H_5COO^{\cdot}$ from the thermal decomposition of dibenzoyl peroxide, $C_6H_5COO-OOCC_6H_5$. Radicals are here formed successively and not "at once" as are the butyl anions in living polymerizations. Growing polymer chains are terminated by reaction with other radicals (recombination, disproportionation). Many side reactions may occur because of the high and fairly indiscriminate reactivity of radicals. Depending on reaction conditions, the degree of polymerization may remain constant (primarily at low conversions) or increase with monomer conversion (so-called gel effect, also referred to as autoacceleration or Trommsdorff effect) (Fig. 17, curve CP−FR). Whereas in living chain-growth polymerizations all chain ends are active during polymerization, in controlled polymerization reactions there is a rapid equilibrium between temporarily inactive ("dormant") chain ends and active chain ends. Similar to living polymerization, controlled chain-growth polymerizations afford narrow molar mass distribution, first order polymerization kinetics, and a degree of polymerization which is proportional to conversion.

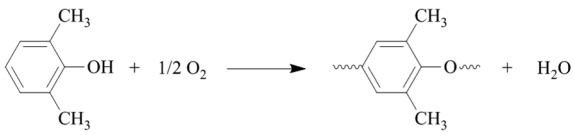
Chain-growth polymerizations have generally been called *addition polymerizations* in the literature. Addition polymerization is not to be confused with polyaddition (see below).

Condensative Chain-Growth Polymerization is the name recommended by IUPAC for a polymerization by repeated addition of monomer molecules with elimination of low molar mass molecules L; this polymerization has thus also been called *polyelimination* [5]:

$$R(m_n)m^* + M \rightarrow R(m_{n+1})m^* + L \quad (3)$$

Biological polymerizations to polysaccharides seem to proceed exclusively through polyeliminations. Cellulose of cotton, for example, is formed by polymerization of guanosine diphosphate D-glucose attached to a lipid matrix. The reaction proceeds via insertion of the glucose moiety into the chain with elimination of guanosine diphosphate.

Synthetic polymers are rarely formed by polyelimination. Examples are the polymerizations of α-amino acid *N*-carboxyanhydrides Leuchs anhydrides) and the "oxidative polymerization" of 2,6-dimethylphenol to polyphenylene oxide (PPO, PPE):



Polycondensation [85]. The step-growth polymerization, known as polycondensation, proceeds by reaction between molecules of all degrees of polymerization (not just between a polymer molecule and a monomer molecule as in chain polymerization and polyelimination) resulting in the formation of low molar mass molecules

as byproducts. Many polymers with hetero atoms in the chains are generated by polycondensation. An example is the polycondensation of 11-aminoundecanoic acid to polyamide 11:

$$n\,H_2N(CH_2)_{10}COOH \rightarrow H[NH(CH_2)_{10}CO]_nOH + (n-1)H_2O \quad (4)$$

In these reactions, dimers ($n = 2$) are formed first, which then react to form tetramers ($n = 4$), etc. The reaction is thus statistical with respect to the size of the molecules to which the functional groups are attached. The degree of polymerization of the polymer is a number average $\overline{X}_n$ over all degrees of polymerizations of the polymer molecules.

All amino groups have the same chance to react if their reactivity is independent of molecule size. The reaction of amino groups attached to molecules with higher molar mass adds, however, considerably more to the increase of the degree of polymerization than the reaction of lower molar mass molecules: The degree of polymerization snowballs with increasing extent of reaction of functional groups (Fig. 17, PC). High conversion of functional groups and no side reactions are prime requirements for achieving high molar mass in step-growth polymerization. Molar mass is controlled either by adjusting the conversion of functional groups or by adding monofunctional chain terminating agents. The term polycondensation was used in the past as a synonym for condensation polymerization. The latter term included both the current concepts of polycondensation and polyelimination (condensative chain polymerization).

Polyaddition. This is a polymerization by reaction among molecules of all degrees of polymerization but without the formation of low molar mass byproducts. The number-average degree of polymerization of the resulting polymers varies with the extent of reaction of functional groups in the same way as it does in polycondensation. An example of polyaddition is the polymerization of diisocyanate with diol to form polyurethane:

$$n\,OCN{-}R{-}NCO + n\,HO{-}R' - OH \rightarrow OCN(R{-}NH - CO - O - R'O)_nH \quad (5)$$

These polymerizations have also been called "polyadduct formations." Polyaddition is not to be confused with addition polymerization, the term used in the literature for chain-growth polymerization.

3.2.2. Functionality

The functionality of monomers is essential for controlling polymer constitution. (e.g., see Eq. 3). When difunctional monomers, such as divinylbenzenes $CH_2{=}CH{-}C_6H_4{-}CH{=}CH_2$, are added to the chain-growth polymerization of styrene, first branching and later cross-linking takes place. The second vinyl group of a divinylbenzene possesses, however, a different reactivity after polymerization of the first one. The two reactivities may differ so strongly in certain ionic polymerizations of divinylbenzenes that linear polymers, and not cross-linked ones, result (e.g., in the cationic polymerization of 1,4-divinylbenzene by acetyl perchlorate in dichloromethane).

The isocyanate group $-N{=}C{=}O$ of diisocyanates can react with hydroxy groups of diols to produce linear polyurethanes by step-growth polyaddition (Eq. 5). It may, however, undergo a chain-growth polymerization to form polyisocyanates via the polymerization of the N=C double bond

$$n\,R{-}N = C = O \rightarrow (NR - CO)_n$$

It should be noted that isocyanates react with urethane to afford branching via allophanate groups (Eq. 6)

$$\sim NH{-}CO{-}O\sim + O{=}C{=}N\sim \longrightarrow \sim NH{-}CO{-}\underset{\wr}{N}{-}CO{-}O\sim \quad (6)$$

The functionality f of polymer molecules is given by the functionality f_o of the monomer molecules and the number X of mers if no intramolecular rings are formed between functional groups.

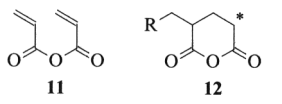
$$f = 2(f_o - 1) + (X - 2)(f_o - 2) = 2 + X(f_o - 2)$$

A monomer with functionality $f_o = 3$ thus gives a dimer ($X = 2$) with a functionality $f = 4$ and a 100-mer ($X = 100$) with a functionality $f = 102$. Because the molecule needs to be bifunctional only for the formation of linear molecules, the "extra" functionalities lead to

interconnections between various molecules (branching) and thus finally to cross-linked, "infinitely large" molecules.

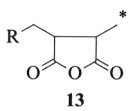
3.2.3. Cyclopolymerizations

Polymerizations of multifunctional molecules may proceed not only intermolecularly to produce branched and cross-linked molecules but also intra/intermolecularly with the formation of rings in chains. These polymerizations are called cyclopolymerizations. They occur especially with monomers having carbon−carbon double bonds in the 1,5- or 1,6-position. An example is acrylic anhydride (**11**), $CH_2{=}CH{-}CO{-}O{-}OC{-}CH{=}CH_2$, which polymerizes free-radically even at high monomer concentrations to soluble polymers with 90–100% six-membered (**12**) and five-membered (**13**) ring structures, and only 0–10% "linear" monomeric units **14** (R symbolizes a polymer chain and ∗ an active chain end):

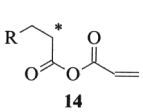


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3.3. Chain-Growth Polymerization

Chain-growth polymerization and polyelimination (condensative chain polymerization) agree in their polymerization kinetics, molar mass distributions, etc., if similar polymerization mechanisms are compared. They differ in the formation of low molar mass byproducts and thus in the design of industrial polymerization reactors.

3.3.1. Thermodynamics

Polymerizations occur only if their molar standard Gibbs energies ΔG_p^o are negative. Because the Gibbs energy

$$\Delta G_p^o = \Delta H_p^o - T \cdot \Delta S_p^o = -RT \cdot \ln K \qquad (7)$$

is determined by both the polymerization enthalpy ΔH_p^o and the polymerization entropy ΔS_p^o, four different cases are possible:

Case 1. Both enthalpy and entropy are negative; the entropy term $-T \cdot \Delta S_p^o$ becomes more positive with increasing temperature. At a certain temperature, the enthalpy and entropy terms balance each other; no polymerization to high molar mass molecules is possible above this *ceiling temperature*. Oligomers, however, may be formed at the ceiling temperature, because polymerization equilibria consist of a series of consecutive equilibria between monomer and growing chains of different degrees of polymerization.

Case 1 is the most common case. It is found for monomers with polymerizable double and triple bonds, such as C=C, C=O, C=S, or C=N. The polymerization entropies of such monomers are practically determined only by the loss of translational entropy; they are thus almost independent of the chemical structure of the monomers. The polymerization enthalpy of α-olefins $CH_2{=}CHR$ is influenced little by resonance stabilization and is practically independent of the size of the substituent R. Steric hindrance, however, strongly decreases the polymerization enthalpy of 1,1-disubstituted compounds $CH_2{=}CRR'$. Styrene and α-methylstyrene, have practically the same polymerization entropies (-105 J K^{-1} mol^{-1}) but very different polymerization enthalpies (-71 vs. -35 kJ/mol, respectively) for the polymerization of liquid monomers to condensed polymers. The ceiling temperatures in bulk are 303 °C (styrene) and 60 °C (α-methylstyrene), (i.e., the latter cannot be homopolymerized to high molar mass compounds above 60 °C).

σ-Bonds are opened and formed again in ring-opening polymerization of cyclic monomers. Differences of bond energies in monomers and polymers are thus practically zero, and the polymerization enthalpy is determined by delocalization and strain energies. Polymerization enthalpies are very negative for ring-opening polymerization of three-membered rings, increase to about zero for five- or six-membered rings, drop again to negative values, and return almost to zero for very large rings. The polymerization entropies of very small rings are very negative due to the release of rotational entropy

upon polymerization. They become less negative with increasing ring size.

Case 2. The polymerization enthalpy is negative (or zero) and the polymerization entropy positive. Polymerization is possible at all temperatures in this rare case, the polymerization of cyclooctamethyltetrasiloxane being an example.

Case 3. The polymerization enthalpy is positive (or zero) and the polymerization entropy is negative. No polymerization is possible at any temperature. This case seems to apply to the polymerization of acetone.

Case 4. Both polymerization enthalpy and polymerization entropy are positive. A *floor temperature* exists below which no polymerization is possible. This rare case is fulfilled for the polymerization of tightly packed cyclic monomers, such as cyclooctasulfur or oxacycloheptane (oxepane) since the number of rotatory degrees of freedom increases strongly upon polymerization to open chains.

Polymerization enthalpies and entropies are influenced by the state of monomers and polymers (gaseous, liquid, crystalline, etc.), the physical interaction between reactants themselves or reactants and solvents, and pressure. Especially important for industrial polymerizations is the fact that most (but not all, see above) chain polymerizations are exothermic. The heat of polymerization can be considerable: Adiabatic polymerization of gaseous ethylene to crystalline polyethylene would result in a temperature increase of 1 800 K for complete monomer conversion. Polymerization reactors must be designed in such a way that the heat of polymerization can be removed rapidly because, otherwise, inhomogeneous charges may result or the reactor may even explode.

3.3.2. Free-Radical Polymerizations [86]

Free-radical polymerizations are initiated and propagated by free radicals. Such polymerizations are relatively insensitive to impurities in the reaction mixture and fairly easy to control. They are thus the methods of choice for the industrial production of plastics if the monomers can be subjected to free-radical polymerizations. This is true for ethylene and many ethylene derivatives: Most commodity plastics are thus obtained from free-radical polymerizations (Table 6).

Other industrial polymers formed by free-radical homopolymerizations include poly(vinyl acetate) (for coatings and adhesives), poly(acryl ester) (for adhesives), polyacrylamide (for thickeners), polyacrylonitrile (for fibers), polychloroprene (for elastomers), poly(acryl acid) (for thickeners), and poly(*N*-vinylpyrrolidone) (for various applications).

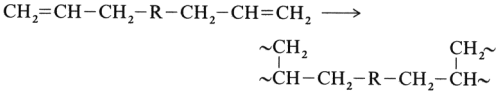
Table 6. Plastics by free-radical chain-growth polymerizations*

Monomers	Polymerization in						Monomeric units
	Gas phase	Bulk	Suspension	Emulsion	Solution	Precipitation	
Living polymerization							
p-Xylylene	+						$-CH_2-(p\text{-}C_6H_4)-CH_2-$
Irreversible polymerization to linear or slightly branched polymers							
Ethylene		+	+	(+)	(+)	(+)	$-CH_2-CH_2-$
Styrene		+	+	(+)	(+)		$-CH_2-CH(C_6H_5)-$
p-Methylstyrene			+	+			$-CH_2-CH(p\text{-}CH_3C_6H_4)-$
Vinyl acetate		(+)	(+)	+	(+)		$-CH_2-CH(OOCCH_3)-$
Vinyl chloride	+	(+)	(+)	+	(+)		$-CH_2-CHCl-$
Vinyl fluoride		+					$-CH_2-CHF-$
Vinylidene fluoride			+	+			$-CH_2-CF_2-$
Trifluorochloroethylene			+				$-CF_2-CFCl-$
Tetrafluoroethylene			+				$-CF_2-CF_2-$
Methyl methacrylate		+	+	+	+		$-CH_2-C(CH_3)(COOCH_3)-$
Cross-linking polymerization							
Diallyl phthalate		+					see Equation (7)

* + = major processes; (+) = minor processes.

Other industrial polymers by free radical homopolymerizations include poly(vinyl acetate) (for coatings and adhesives), poly(acryl ester) (for adhesives), polyacrylamide (for thickeners), polyacrylonitrile (for fibers), polychloroprene (for elastomers), poly(acrylic acid) (for thickeners), and poly(*N*-vinyl pyrrolidone) (for various applications).

Polymerizations may be carried out in the gas phase, bulk, suspension, emulsion, solution, or under precipitation. Most monomers are bifunctional; they lead to linear or slightly branched polymers and thus to thermoplastics. Thermosets obtained from free-radical homopolymerizations include bis- and trimethacrylates as well as diallyl and triallyl compounds that cross-link under polymerization conditions:



where R may be $COO(CH_2)_2O(CH_2)_2OOC$ [diethylene glycol bis(allyl carbonate], *o*-$C_6H_4(COO)_2$ (diallyl phthalate), or *m*-$C_6H_4(COO)_2$ (diallyl isophthalate). Other allyl compounds are used as cross-linking comonomers (diallyl fumarate, diallyl maleate, triallyl cyanurate).

Most free-radical polymerizations follow the kinetics of true chain reactions. In initiating (start) reactions (Eq. 9), radicals $R^\bullet$ are formed by the decomposition (Eq. 8) of initiator molecules I, that react with monomer molecules M. The resulting polymeric free radicals add further monomer molecules in the propagation reaction (Eq. 10) until the growing polymer radicals are terminated by recombination (Eq. 11) or disproportionation (Eq. 12) with other polymer radicals or by addition of initiator radicals (Eq. 13):

$$I \rightarrow 2\,R^\bullet \tag{8}$$

$$R^\bullet + M \rightarrow R - M^\bullet \tag{9}$$

$$R - M^\bullet + M \rightarrow R - M - M^\bullet, \text{etc.} \rightarrow R - M_{n-1} - M^\bullet \tag{10}$$

$$R - M_{n-1} - M^\bullet + {}^\bullet M - M_{m-1} - R \rightarrow R - M_{n+m} - R \tag{11}$$

$$R - M_{n-1} - M^\bullet + {}^\bullet M - M_{m-1} - R \rightarrow R - M_{n-2} - M = M + X - M_m - R \tag{12}$$

$$R - M_{n-1} - M^\bullet + R^\bullet \rightarrow R - M_n - R \tag{13}$$

In Equation (12), X is an atom or a group that is transferred from the ultimate monomeric unit of one polymer radical to another polymer radical, for example, the H atom in the reaction

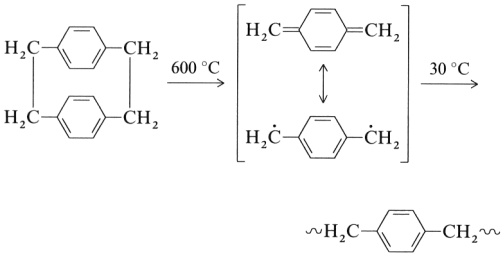
$$CH_2 - C^\bullet HR + {}^\bullet CHR - CH_2 \rightarrow CH_2 - CH_2R + CHR = CH_2$$

These reactions are kinetically classified as termination reactions and not as transfers because they lead to dead chains. The term "transfer" is rather reserved for chemical transfers that generate new propagating radicals, such as

$$CH_2 - C^\bullet HR + AX \rightarrow CH_2 - CH_2\,RX + A^\bullet \tag{14}$$

Initiation. Free-radical polymerizations can be initiated thermally by thermal initiators, by redox initiators, by photoinitiators, or electrolytically.

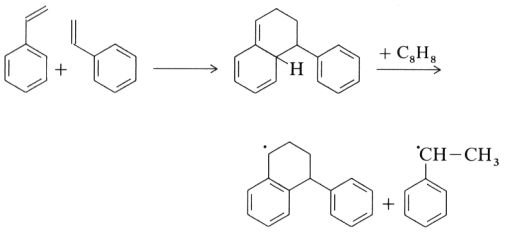
Thermal initiation is utilized in the polymerization of *p*-cyclophane to poly(*p*-xylylene):



Propagation proceeds by addition of biradicals of various sizes i.e., by polyaddition and not by chain polymerization. The resulting polymer is cross-linked because radicals also attack methylene groups, which generates more than two radical sites per reactant and thus cross-linking sites. The reaction is utilized for the formation of thin coatings.

Styrene is the only monomer that is polymerized commercially by thermal initiation through monoradicals. The primary Diels–Alder adduct of two styrene molecules

reacts with another styrene molecule to give two different starter radicals:



Only relatively small amounts of styrene are, however, polymerized commercially by this method. Most styrene polymerizations, like many other commercial free-radical polymerizations, are started by radicals from *thermal initiators*. These thermal initiators dissociate homolytically into two radicals at elevated temperature, usually 60–80 °C. For the bulk polymerization of styrene, high-temperature initiators, such as 1,2-dimethyl-1,2-diethyl-1,1-diphenylethane or vinylsilane triacetate are preferred. For styrene polymerization in suspension, dibenzoyl peroxide (BPO) ($C_6H_5CO-O-O-OCC_6H_5$) and *tert*-butyl perbenzoate [$C_6H_5CO-O-O-C(CH_3)_3$] are used.

Many other bulk polymerizations employ diisopropyl peroxydicarbonate (IPP), which decomposes according to

$$(CH_3)_2CHO-COO-OOC-OCH(CH_3)_2 \rightarrow 2(CH_3)_2CHO-COO^{\bullet}$$

Water-soluble initiators, such as dipotassium persulfate ($K_2S_2O_8$) and certain redox initiators are used in emulsion polymerizations. *Redox initiators* generate radicals by reaction of a reducing agent with an oxidizing agent (e.g., $Fe^{2+} + H_2O_2$). These systems need far less activation energy for the formation of radicals, and polymerization can thus be initiated at low temperature.

Photochemical initiations are utilized for the production of lithographic plates (→ Imaging Technology, 3. Imaging in Graphics Art) and for hardening lacquers but not in the manufacture of plastics. *Electrolytic polymerizations* find applications in the coating of metal sheets by plastics.

Only initiator radicals are formed at the early stages of free-radical polymerizations. These radicals are successively converted into monomer radicals by addition of initiator radicals to monomer molecules and into polymer radicals by further addition of monomers. At the same time, some polymer radicals are removed by termination reactions. Finally, a steady state is established in which as many radicals are formed as are removed by termination. This state of constant total radical concentration (ca. 10^{-8} mol/L) is in general observed within seconds at monomer conversions of 10^{-2}–10^{-4}%.

Propagation. Monomer molecules are usually added head-to-tail to growing polymer radicals:

$$CH_2-CHR^{\bullet} + CH_2=CHR \rightarrow CH_2-CHR-CH_2-CHR^{\bullet}$$

Tail-to-tail additions also occur (see Section 2.1).

Free-radical polymerizations lead in general to atactic or predominantly syndiotactic polymers. The syndiotacticity increases with decreasing polymerization temperature.

Termination. Termination reactions by recombination, disproportionation, and (at higher initiator concentrations) addition of initiator radicals, cannot be avoided. Because initiator radicals and thus also polymer radicals are formed successively and are deactivated at random by different termination reactions, distributions of molar masses are formed. The width of these distributions is given by the relative proportion of the different types of termination reactions.

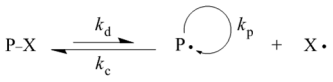
Chain Transfer. The transfers of radicals to monomers, solvents, and initiators terminate polymer chains and generate others (Eq. 14). The ratios of rate constants k_{tr} of transfer to rate constants k_p of propagation are called transfer constants, $C_{tr} = k_{tr}/k_p$; at 60 °C they possess values between ca. 2×10^{-6} for the transfer of polystyryl radicals to benzene and 5 700 for the transfer of poly(vinyl acetate) radicals to carbon tetrabromide.

Chain transfers often lead to new radicals that have approximately the same reactivity as the disappearing ones. In this case, the rate of polymerization is not decreased by chain transfer, but the degree of polymerization is lowered. Certain transfer agents with high transfer

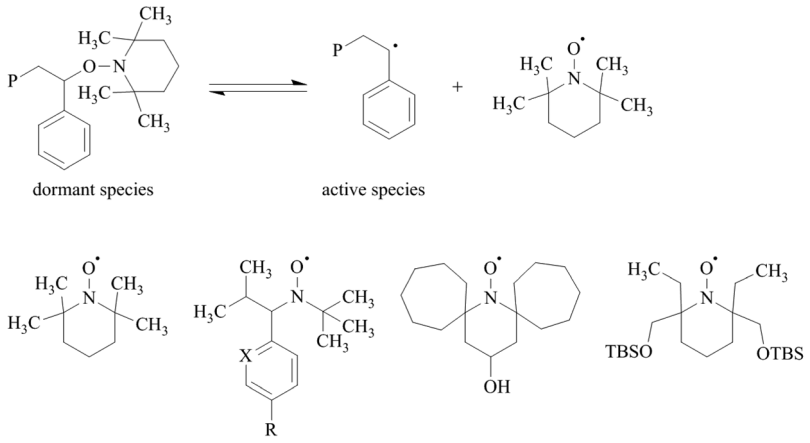
constants (such as thiols) are thus often employed to regulate molar mass.

Inhibition and retardation occur if the new radical is more sluggish in adding monomers than the transferring polymer radical. In the case of *inhibition*, stable radicals are formed by chain transfer reactions. Typically, inhibitors, such as methylhydroquinone, are added. Moreover, retardation is observed when chain transfer to nonionic allyl monomers generates resonance-stabilized allyl radicals. The addition of monomer molecules to these radicals produces radicals that are more stabilized by resonance than their precursors and thus do not start a polymer chain. The polymerization of noncharged monoallyl monomers thus leads to oligomers with degrees of polymerization of ca. 10–20.

Controlled Radical Polymerization [87, 88]. Reversible deactivation is the key feature of controlled radical polymerization. Unlike living polymerization, the free radicals at the chain end are rendered temporarily inactive ("dormant"). Because there is a rapid equilibrium between free radical and dormant sites, controlled radical polymerization exhibits all features typical for living polymerization, i.e., the degree of polymerization is proportional to conversion and the rate of polymerization follows first order kinetics. The reversible trapping of free radicals prevents undesirable chain termination by recombination and disproportionation.



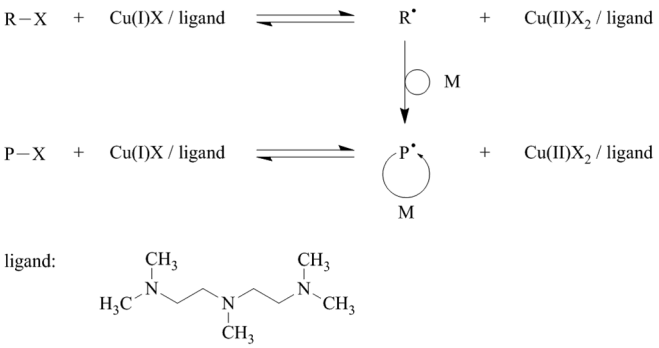
By using controlled radical polymerization techniques, it is possible to synthesize block-, graft-, and star copolymers as well as polymers with narrow molar mass distribution and well-defined end group functionalities. In *nitroxide-mediated controlled radical polymerization* (NMRP), stable nitroxide free radicals, such as (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) radicals are added to a free radical polymerization. Immediately after the nitroxide radical traps the free radial at the polymer chain end, thermal bond cleavage reinitiates chain growth by free radical polymerization. Because free radicals are temporarily trapped, the polymerization rate and monomer conversions are lower than in a living anionic polymerization.

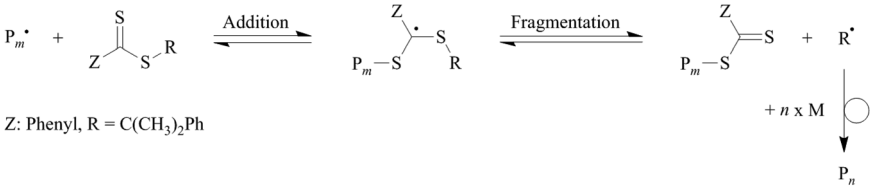


In *atom transfer radical polymerization* (ATRP) organic halides react with redox metals, such as Cu^+, to produce organic free radicals via transfer of the halogen atom. This free radical at the chain end is temporarily terminated by transfer of the halogen, accompanied by changing of the oxidation state resulting from electron transfer of the redox metal. Although copper is

preferred for ATRP, various other redox transition metals can be employed. The addition of ligands is required to prevent precipitation of the metal complex.

In *reversible addition chain tranfer polymerization* (RAFT) the polymer free radical adds to a thiocarbonyl group of dithioesters, dithiocarbamate or dithiocarbonates, forming a free radical that undergoes fragmentation to form a polymer radical and thiocarbonyl group.





Polymerization Kinetics of Free Radical Polymerization. Initiator radicals are generated by initiator decomposition (Eq. 15) with a rate of $2f \cdot k_d \cdot [I]$ where f is the radical yield (i.e., the fraction of radicals that start the polymerization). Initiator radicals disappear in the start reaction with a rate of $k_{st}[P]\,[M]$. In the steady state, as recognized by BODENSTEIN, the polymer radical concentration is constant. Hence, the rate of the start reaction equals the rate of the termination reaction(s), thus $R_{st} = R_t$, and for terminations through deactivation by other polymer radicals,

$$d[P]/dt = R_{st} - R_t = 2f \cdot k_d \cdot [I] - k_t[P]^2 = 0 \quad (15)$$

Because monomer is practically consumed only by the propagation reaction with a rate of $R_p = -d[M]/dt = k_p[P]\,[M]$, the propagation rate at diminishing initiator consumption is obtained from Equation (16)

$$R_p = -d[M]/dt = k_p(2f \cdot k_d/k_t)^{1/2} \cdot [I]_o^{1/2}[M] \quad (16)$$

The polymerization rate is directly proportional to the monomer concentration; bulk polymerization is thus always faster than solution polymerization. Because the kinetic chain length is equivalent to R_p/R_t, the degree of polymerization increases with increasing monomer concentration. Because ethylene has rather low reactivity, as reflected by its low k_p value, high pressure (i.e., high monomer concentration) and high temperature are required for achieving free radical ethylene polymerization. Due to inter- and intramolecular chain transfer reactions, the

resulting polyethylene chains contain long- and short-chain alkyl branches. Whereas small amounts of long chain branches account for shear thinning during melt processing, the incorporation of short chain propyl- and butyl-branches impairs crystallization and lowers the polyethylene density. Therefore, high pressure free radical polymerization produces low density polyethylene (LDPE).

A "self-acceleration" of the polymerization and a concomitant increase of both the polymerization rate and degree of polymerization are observed at higher monomer conversion, especially in bulk and in concentrated solutions. This so-called gel-effect, also known as the Trommsdorff effect, is caused by a changing diffusion control of the termination by mutual reaction of two polymer radicals (i.e., a decrease of termination reactions), which in turn comes from an increasing entanglement of polymer chains. Because neither the rate of the initiator decomposition nor the rate of monomer addition is affected by increasing entanglements, and only the termination is slowed down, the Bodenstein steady-state principle does not apply anymore. Hence, both overall polymerization rates and molar masses simultaneously increase. This autoacceleration broadens molar mass distributions. Owing to the drastically reduced heat transfer at high viscosity, the autoacceleration can cause severe increase of temperature and even explosions, resulting from pyrolysis of polymers and gas evolution at temperatures above 400 °C. The addition of chain transfer agents, such as alkylthiols reduces molecular masses, thus preventing viscosity buildup and autoacceleration.

Cross-Linking Polymerization. Free-radical chain polymerizations are employed commercially in the manufacture of diallyl thermosets and in styrene–divinylbenzene copolymerizations for polymer beads. Primary macromolecules produced at very low monomer conversions are almost linear and carry pendant polymerizable groups. The likelihood of an attack at these groups increases with increasing mass average molar mass. Branched molecules are formed that convert to cross-linked polymers at the gel point. Monomer conversion at the gel point cannot at present be predicted theoretically for such free-radical polymerizations.

Process Engineering. Free-radical polymerizations may be performed in the gas phase, in bulk, solution, emulsion, suspension, or under precipitation (Table 6). Each method has advantages and disadvantages.

Bulk Polymerizations. Industrial bulk polymerizations are performed in *liquid monomers*, occasionally with the addition of 5–15 vol% solvent as a polymerization aid. The process leads to very pure products. However, much heat is generated per unit volume and, in addition, by the Trommsdorff effect. Local overheating may cause multimodal molar mass distributions, branching, polymer degradation, discoloring, or explosion. Bulk polymerizations are thus often terminated at 40–60% monomer conversion. The remaining monomer is distilled and recovered. Alternatively, polymerizations may be performed in two steps: First in large batch reactors, then in thin layers. Residual monomer is usually removed by steam.

Suspension polymerization is a "water-cooled" bulk polymerization. Water-insoluble monomers are suspended as small droplets of 0.001–1 cm diameter with the help of suspending agents, such as water-soluble polymers. The polymerization is initiated by oil-soluble initiators. The droplets are converted by polymerization into pearls; thus the process is also called *pearl polymerization*. The addition of protective colloids, such as water-soluble polymers, affords steric stabilization of the formed polymer particles and prevents their agglomeration. Suspension polymerization allows easy control of the reaction and delivers the polymer as easy-to-handle beads. A disadvantage is the cost of water removal and cleaning, along with the sometimes deleterious effects of incorporated suspension agents. The average size of spherical polymer particles decreases with increasing stirring speed. Prominent applications of styrene pearl polymerization include the formation of polystyrene pellets containing pentane as foaming agent and the production of cross-linked polystyrene beads that are sulfonated to produce polymeric cation exchange resins for water deionization.

Emulsion Polymerization. In emulsion polymerizations, water-insoluble monomers are solubilized in water by micelles of surfactant molecules (4–10 nm diameter); the monomers are also suspended in a few droplets (ca. 1 000 nm diameter). Water-soluble initiators decompose into radicals that travel through the water to the micelles where polymerization begins. Polymerization takes place in this micellar reaction compartment, referred to as polymer *latex*. Diffusion of monomer from the droplets to the latex replenishes the monomer that has been used up by reaction in the micelles. The average diameter of these latex particles is 500–5 000 nm. Each latex particle contains just one free radical, which is terminated when another initiator radical enters the latex particle; this remains dormant until a new initiator radical initiates the growth of a new chain. Because the reaction volume is very small in micelles (and in growing latex particles), termination reactions are rare, and polymerization proceeds in a quasi-living manner, leading to much higher molar masses than bulk polymerization. In terms of reaction control, emulsion polymerizations have advantages similar to suspension polymerizations. In addition, they offer higher polymerization rates by redox initiators and higher molar masses (which can be regulated by transfer agents). Emulsion polymerization is applied to produce homo- and copolymers based upon styrene, butadiene, vinyl chloride, vinyl acetate, acrylates as well as tetrafluoroethylene. The resulting latex can furthermore be used directly for producing water-borne paints, adhesives, and coatings forming corrosion resistant polymer films when water vaporizes and the polymers entangle.

Gas-phase polymerizations can be initiated photochemically. Each growing particle contains only one radical and the polymerization is thus quasi-living. The polymerization rate is determined by the rate of monomer adsorption in the precipitating particles and later by monomer diffusion to the occluded polymer radicals. The resulting polymers are very clean.

Solution polymerizations decrease polymerization rates by monomer dilution and allow easy removal of the heat of polymerization. Solvents are, however, costly to remove, and the process is used only if the resulting polymer solutions can be used directly or if monomers and polymers decompose in melts.

3.3.3. Anionic Polymerizations [89]

Anionic polymerizations are initiated by bases, such as alkali metals, alkoxides, amines, phosphines, Grignard compounds, and sodium naphthalene, very often in solution. The initiators dissociate "instantaneously" into the initiating species. These dissociations and the subsequent start reactions need little activation energy; anionic polymerizations thus often proceed with high speed even at −100 °C.

The initiating species and the growing macroions are rarely completely dissociated into anions and counterions. They are rather in equilibrium with various types of ion pairs (nondissociated species, contact ion pair, solvent-separated ion pair, free ions plus associates of these species). The type and amount of initiating species strongly affect the polymerization rates and the tacticity of polymers.

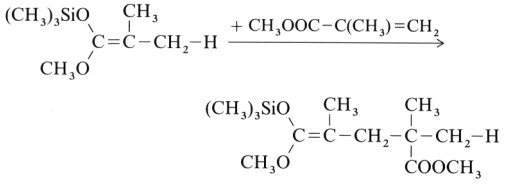
The initiating species are present in their effective concentrations at the beginning of polymerization; they are not formed one after another as in free-radical polymerization. Termination reactions are fairly rare if protons are absent. Hence, anionic polymerizations are often "living." Very low initiator concentrations are required for living polymerizations to high molar masses (see Section 3.2.1); however, high monomer–initiator ratios are difficult to control and may lead to low polymerization rates. In general, polymers from living polymerizations have very narrow molar mass distributions of the Poisson type if diffusion effects are avoided during the mixing of monomer and initiator solutions.

Contrary to traditional living polymerizations, a variety of controlled anionic polymerizations have been developed. Key feature is a rapid equilibrium between active and dormant endgroups. For example, in *group transfer polymerization (GTP)* there is a rapid equilibrium between inactive silyl ketene acetals and

Table 7. Industrial anionic homopolymerizations

Monomer	Repeating unit	Application
Butadiene	$\sim CH_2-CH=CH-CH_2\sim$	elastomer (1,4-*cis*)
Isoprene	$\sim CH_2-C(CH_3)=CH-CH_2\sim$	elastomer (1,4-*cis*)
Methyl cyanoacrylate	$\sim CH_2C(CN)\,(COOCH_3)\sim$	adhesive
Formaldehyde	$\sim O-CH_2\sim$	engineering plastics
Ethylene oxide	$\sim O-CH_2-CH_2\sim$	thickener
Glycolide	$\sim O-CO-CH_2\sim$	surgical threads
ε-Caprolactone	$\sim O-CO-(CH_2)_5\sim$	polymer plasticizer
ε-Caprolactam	$\sim NH-CO-(CH_2)_5\sim$	fiber, thermoplastic
Lauryllactam	$\sim NH-CO-(CH_2)_{11}\sim$	fiber, film
Hexamethylcyclotrisiloxane	$\sim O-Si(CH_3)_2\sim$	elastomer

enolate anions, catalyzed by nucleophilic catalysts ($[(CH_3)_3SiF_2]^-$, $[HF_2]^-$, CN^-, etc.):



Very few anionic polymerizations are employed for the production of thermoplastics, most notably those of formaldehyde, ε-caprolactam (also used in reaction injection molding), and laurolactam (Table 7). Anionic polymerizations are, however, the method of choice for the syntheses of block copolymers, such as thermoplastic elastomers, e.g., polystyrene–block–polybutadiene–block–polystyrene (SBS).

3.3.4. Cationic Polymerizations [90]

Three groups of monomers can be polymerized cationically: (i) Olefin derivatives CH_2=CHR with electron-rich double bonds, (ii) monomers with double bonds containing heteroatoms or heterogroups Z (e.g., CH_2=Z), and (iii) rings with heteroatoms. Initiators are Brønsted acids (perchloric acid, trichloroacetic acid, trifluoromethanesulfonic acid, etc.); Lewis acids ($AlCl_3$, $TiCl_4$, $SnCl_4$, etc.) with "coinitiators", such as water; and carbenium salts (acetyl perchlorate, tropylium hexachloroantimonate, etc.). The propagating macrocations are thermodynamically and kinetically unstable. They attempt to stabilize themselves by addition of nucleophilic species, which leads to very fast polymerization on one hand and to a host of transfer and termination reactions on the other. Very few monomers are thus polymerized cationically on an industrial scale (Table 8). Prominent examples include polyisobutene and poly(isobutene-co-isoprene) rubber.

3.3.5. Ziegler–Natta [91–95], ROMP [96] and ADMET [97] Catalysis

Ziegler–Natta polymerization catalysis involves a chain-growth polymerization on Ziegler catalysts, comprising a vast group of transition-metal compounds activated with main group metal alkyls, preferably aluminum alkyls. Today, in line with pioneering

Table 8. Industrial cationic polymerizations

Monomer		Application**
Name	Structure*	
Isobutene	$CH_2=C(CH_3)_2$	elastomers, adhesives, VI improvers
Vinyl ethers	CH_2=CHOR	adhesives, textile aids, plasticizers
Formaldehyde	$CH_2=O$	engineering plastic
Ethyleneimine	c-($NHCH_2CH_2$)	paper additive, flocculant
Tetrahydrofuran	c-[$O(CH_2)_4$]	soft segment for polyurethanes or polyether–ester elastomers

* c = cyclo.
** VI = viscosity index.

advances at Phillips using activator-free silica supported Cr(III) catalysts, a variety of cationic transition metal alkyls containing weakly coordinating counterions are available that do not require the addition of main group metal activators. Because monomers are inserted into the transition metal alkyl bonds, this catalytic polymerization is named polyinsertion. In older literature, polyinsertions are also referred to as coordination polymerizations or anionic–coordination polymerizations, although coordination of a monomer to an initiator need not lead to a Ziegler–Natta type of polymerization catalysis. Whereas free-radical polymerization of ethylene requires temperatures above 150 °C and pressures well above 1 000 bar and produces branched low-density polyethylenes, catalytic ethylene polymerization takes place at ambient temperature and pressure below 10 bar, thus producing linear high density polyethylene. Short chain branches are introduced by copolymerization of ethylene with α-olefins. Stereospecific catalytic diene polymerization produces highly stereoregular poly(*cis*-1,4-isoprene) and poly(*cis*-1,4-butadiene) as synthetic alternative to natural rubber. Both KARL ZIEGLER and GIULIO NATTA were awarded the Nobel Prize for Chemistry in 1963, honoring their groundbreaking research, which paved the way for the industrial production of polyolefins. Half of the annual world production of polymers is based on this process.

Typical Ziegler catalysts for industrial polymerizations of olefins, such as ethylene, propene are shown in Table 9. Metallocenes and post-metallocene complexes have been developed since the early 1980s to produce tailor-made polyolefins in which the molecular architectures of polyolefins are tuned as a function of the molecular architectures of the catalytically active transition metal complexes. Traditionally, Ziegler catalysts are multi-site catalysts that contain different catalytically active sites and produce polymer chains with different molecular masses and molar-mass dependent comonomer sequence distribution. In contrast, modern single-site catalysts, which are based on metallocene and post-metallocene complexes, contain a single type of catalytically active site and give much more uniform polymers; molecular mass and molar-mass independent comonomer incorporation can be controlled easily.

Homogeneous catalysts are used in solution polymerization forming elastomers, such as ethylene–propene copolymers, which can contain a small amount of nonconjugated dienes, such as ethylidene norbornene as cross-linking sites. Slurry polymerizations, in which polymers precipitate during polymerization, require heterogeneous catalysts in order to prevent reactor fouling. Incorporating active transition metal alkyl sites on high surface area supports boosts catalyst activity and enables control of both polyolefin molecular architectures and polyolefin particle morphologies. In slurry polymerizations, most soluble catalysts produce small submicron dustlike polyolefin particles, thus causing severe reactor fouling and handling problems. Owing to fragmentation of supported catalysts during slurry polymerization (see Fig. 18), much larger micron-sized polyolefin particles are formed, which prevent reactor fouling. Moreover, spherical supported catalysts produce spherical pellet-sized polyolefin particles,

Table 9. Important industrial polymerizations with transition-metal catalysts

Monomer	Initiator	Application
Ethylene	$MgX_2/TiY_4/AlR_3$ (X = Cl, R, OR; Y = Cl, R, OR); (post)metallocene (Ti, Zr, Hf, Fe, Co), halfsandwich (Ti) and Cr(III) catalysts supported on silica	thermoplastic (HDPE, LLDPE)
Propene	$MgCl_2$/1,3-diether/$TiCl_4/AlR_3$; (post)metallocene (Ti, Zr, Hf) supported on silica	thermoplastic (PP)
Ethylene+propene+nonconjugated diene	Metallocene and halfsandwich catalysts, $VOCl_3/R_2AlCl$	elastomer (EPDM)
Butadiene	Co-, Ni-, Nd-, Sm-, Ln-catalysts, (post)metallocene and halfsandwich catalysts,	elastomer
Isoprene	Ti-, Co-, Ni-, Nd-, Sm-, Ln-catalysts, (post)metallocene and halfsandwich catalysts	elastomer
Butene-1	$MgCl_2$/1,3-diether/$TiCl_4/AlR_3$; (post)metallocene (Ti, Zr, Hf) supported on silica$TiCl_3$–Et_2AlCl	thermoplastic

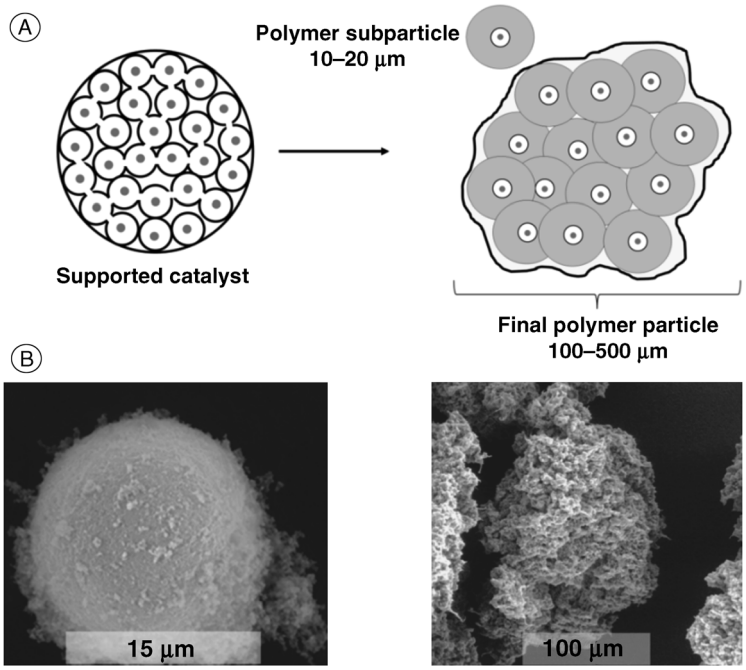


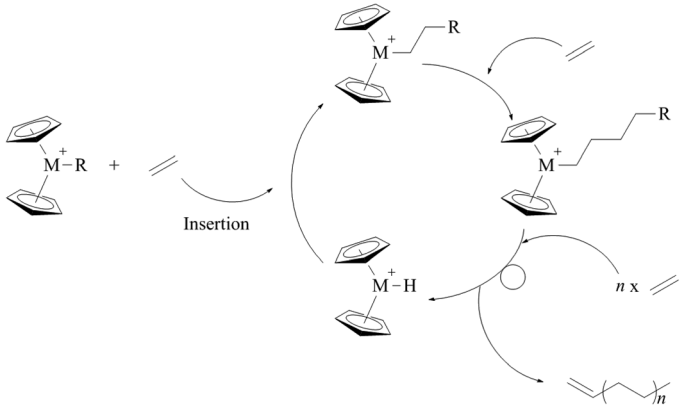
Figure 18. Morphology control in catalytic olefin polymerization by fragmentation of catalyst particles during polymerization A) Fragmentation of catalyst particle; B) Scanning Electron Microscope image of a catalyst particle (left) and a polyethylene particle (right)

thus eliminating the need for pelletizing extrusion.

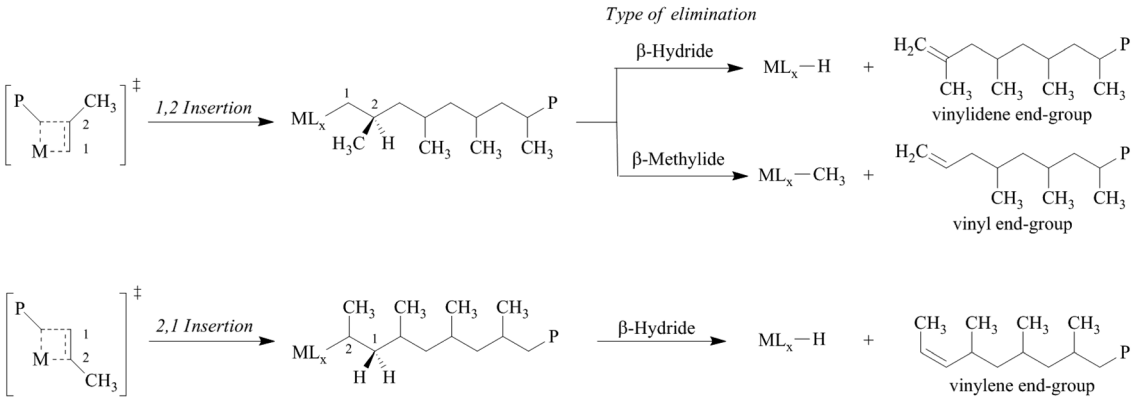
The development of highly active and stereoselective supported catalysts was essential for enabling solvent-free gas phase and liquid pool olefin polymerization. The choice of the support materials and the selection of supporting strategies depend on the selected transition metal component. Because $MgCl_2$ has the same crystal structure as $TiCl_3$, it can substitute inactive bulk $TiCl_3$ that does not have vacant coordination sites. Hence, $MgCl_2$ supported titanium catalysts, activated with aluminum alkyls, afford orders of magnitude higher catalyst activities. In propene polymerization, the addition of small amounts of Lewis bases, such as 1,3-diethers promotes high stereospecifity, leading to the formation of highly isotactic polypropylene. Most (post)metallocene and chromium catalysts are preferably immobilized on high surface area silica supports.

Breakthroughs in catalyst and process technologies have greatly simplified olefin polymerization. With catalyst activities exceeding 1 000 kg polyolefin/g Ti, the titanium content in the polyolefin is below 1 ppm. Hence, catalyst residues can be left in the polymers, i.e., the catalyst does not need to be removed by extraction or by adsorber beds typical for early catalysts generations. Furthermore, highly energy- and resource-efficient polymerization in gas phase and bulk eliminates the need for organic solvents as polymerization media and for their recycling. Because of the excellent control of molecular mass and stereoregularity, polyolefin purification by solvent extraction of low molecular mass polyolefin waxes and atactic polypropylene is no longer required. Employing fossil and renewable feedstocks, such as oil, gas and even bioethanol in environmentally friendly and highly energy-efficient catalytic polymerization processes meets the demands of green chemistry. As hydrocarbon resins, polyolefins preserve oillike energy content. They are readily recycled by remolding and serve as valuable source of energy and "renewable oil", produced by thermal degradation of polyolefins.

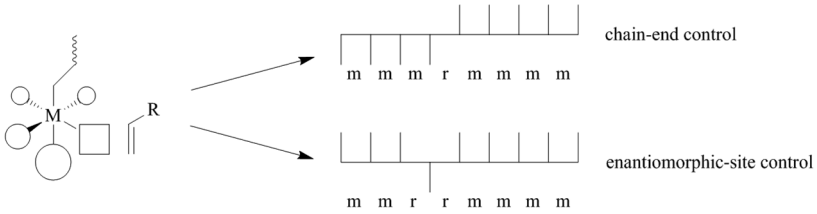
The basic reaction mechanisms and the correlations between the architectures of catalytically active transition metal complexes and polyolefin architectures are quite well understood. As illustrated below for olefin polymerization on a cationic metallocene alkyl catalyst, the olefin forms a π-complex with the transition metal prior to insertion into the transition metal carbon bond. After repeated insertion β-hydride elimination terminates the polymer chain, thus forming vinyl-terminated polyethylene. The resulting transition metal hydride is the catalytically active intermediate, which adds to an olefin and starts the growth of a new polyethylene chain. Additionally, hydrogen can be added to control molecular mass by chain transfer that involves hydrogenation of the transition metal alkyls and formation of a transition metal hydride, which subsequently adds to the ethylene.



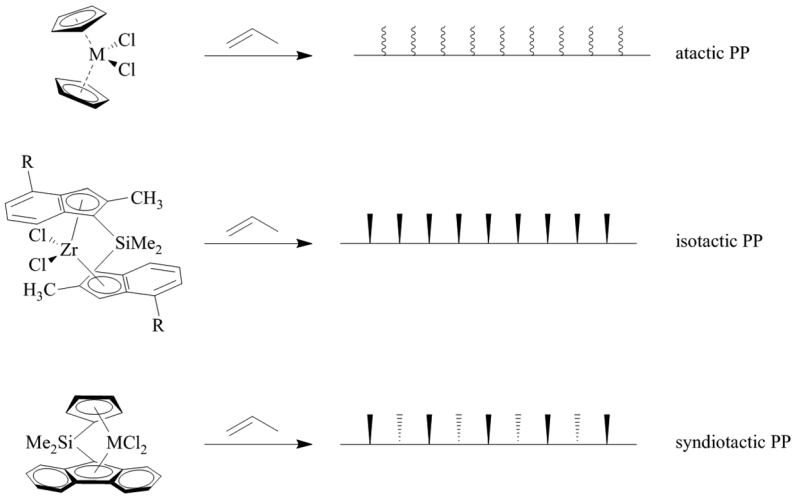
The regioselectivity in α-olefin and the polyolefin constitution is governed by the insertion type. Whereas 100% of 1,2- or 2,1-insertion exclusively afford head-to-chain polyolefins, lower regioselectivity accounts for head-to-head enchainment in the polyolefin backbone. Most α-olefins are polymerized by 1,2-insertion in highly regioselective catalytic polymerization. The insertion type is identified by end group analysis of poly(α-olefins), taking into account chain termination by β-hydride as well as β-methylide transfer.



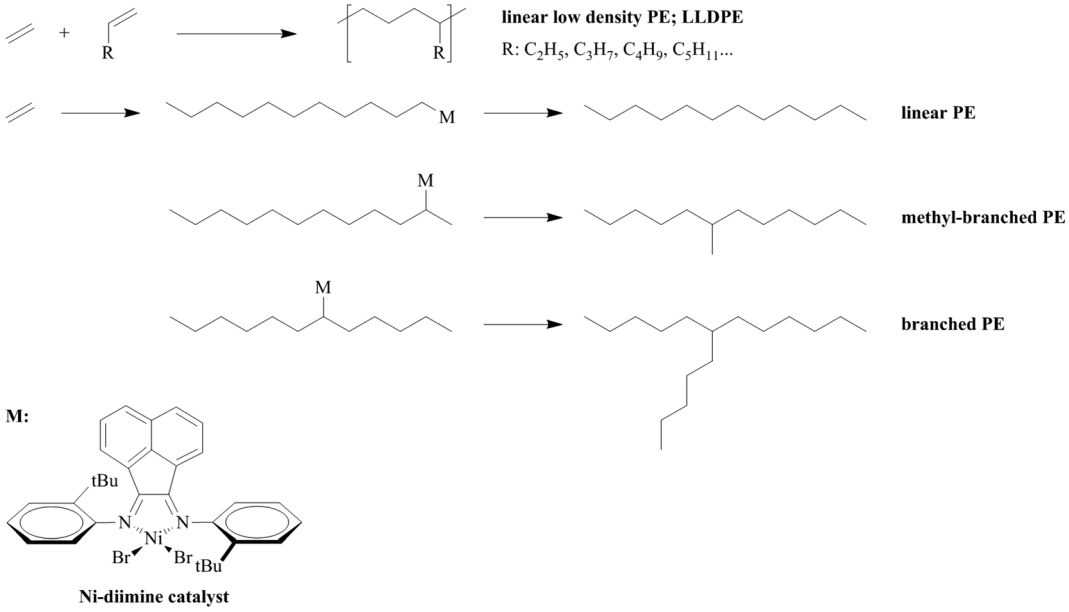
The stereospecificty of α-olefin polymerization is governed either by the configuration of transition metal complex (enantiomorphic site control) or by that of the asymmetric carbon atom of the monomeric unit at the chain end (chain end control). When a false insertion occurs, the resulting change of configuration is isolated in the case of enantiomorphic site control but is perpetuated in the case of chain end control (see below, m denotes meso, r denotes racemic). The analysis of polyolefin microstructures reveals that for most catalysts the chirality of the transition metal accounts for the control of the stereoregularity.



The ability of catalysts to control the stereochemistry of poly(α-olefins) and polydienes makes Ziegler–Natta polymerization catalysis industrially extremely useful. Propene, for example, polymerizes cationically to highly branched, atactic, low molar mass polymers that do not crystallize and have low glass transition temperatures. They can be used only as hotmelt adhesives and lubricants. Ziegler–Natta polymerization catalysis (Table 9) leads, however, to stereoregular polymers with high melting temperatures. Isotactic polypropylenes find extensive use as thermoplastics. Stereoblock polypropylenes can be engineered to produce thermoplastic elastomers containing highly flexible amorphous and rigid crystalline segments. The structure of single-site metallocene catalysts can be varied to produce virtually any kind of poly(α-olefin) microstructure industrially:



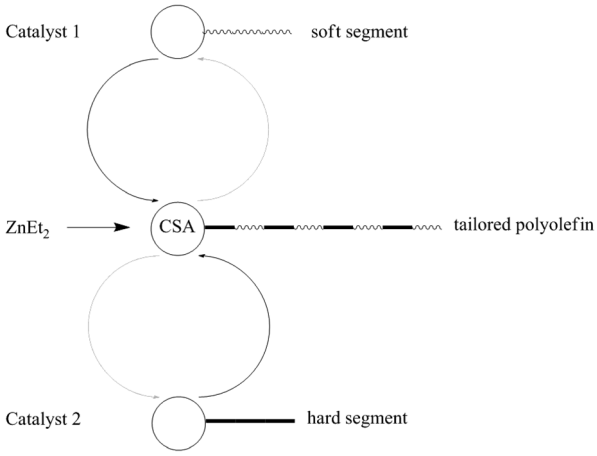
Similar to free radical polymerization, short and long chain branches are readily introduced by catalytic olefin polymerization. With increasing α-olefin comonomer incorporation, both crystallinity and density of polyethylene decrease. Whereas high density linear polyethylene (HDPE) is attractive for producing pipes, linear low density polyethylene (LLDPE) is highly flexible and has lower density, thus meeting the demands of packaging applications. A small amount of long chain branching promotes shear thinning and melt strengthening, which is beneficial to blow molding of films. At a high degree of branching, polyethylene is rendered amorphous and elastomeric. In principle, there are two synthetic strategies for branching of polyolefins: (i) Copolymerization of ethylene with various α-olefins, and (ii) branching homopolymerization of ethylene according to the "chain walking" mechanism. In chain walking, the catalytically active transition metal alkyl travels up and down the polymer chain via repeated β-hydride elimination followed by addition of the transition metal hydride to the resulting double bond. Whereas titanium catalysts form linear polyethylene chains, branching ethylene homopolymerization takes place on postmetallocene complexes, such as cationic alkyl Ni diimine. Alkyl Pd diimine complexes produce high molecular mass highly branched amorphous polyethylenes. Because Pd metal alkyl travels up and down the main chain and side chains, branches are formed.



In the early days of catalyst development, the multisite nature of catalysts accounted for the formation of rather complex copolymer compositions in slurry polymerizations. Frequently, the α-olefin comonomer was predominantly incorporated in low molar mass waxlike fractions. More uniform copolymer compositions are obtained in high temperature solution polymerization operating at temperatures above 130 °C. In the past, very different catalyst systems were developed for producing HDPE, LLDPE, and EP(D)M rubbers. Since the 1980s, the development of single-site catalysts based upon metallocene, post-metallocene, and

constrained geometry half-sandwich complexes has revolutionized the industrial synthesis of branched polyethylenes. As a function of the ligand framework, it is possible to control molecular mass independent incorporation of α-olefins into polyethylene backbone to produce LLDPE as well as very low density polyethylenes and elastomers by the same catalyst. Moreover, improved reactivity enables the efficient copolymerization of polyethylene vinyl endgroups, thus producing long chain branched polyethylene.

In a chain shuttling solution process, zinc alkyls transfer polymer chains between catalytically active sites producing exclusively linear polyethylene or ethylene−1-octene copolymers. As a consequence, block copolymers are obtained that contain alternating rigid HDPE segments and elastomeric poly(ethylene-co-1-octene) segments. Such block copolymers are attractive as thermoplastic elastomers.



CSA: chain shuttling agent Et_2Zn-P

Although single-site catalysts afford uniform polyolefins, it is highly desirable to tailor polyolefins with broad molecular mass distributions and preferred incorporation of branches exclusively into the ultrahigh molar mass fraction. This greatly improves shear thinning during melt processing. Moreover, small amounts of slightly branched ultrahigh molar mass poylolefins function as "tie molecules" bonding together polyethylene crystallites and significantly improve the fatigue resistance and durability of polyethylene pipes. Two strategies are exploited: (i) Ethylene polymerization in cascade reactors, and (ii) ethylene polymerization in a single reactor using multi-site catalysts, prepared by incorporating different single-site catalysts on the same support (see Fig. 19). In cascade reactors, ethylene is polymerized in the absence and the presence of hydrogen to control molar mass dstribution. The addition of α-olefin as comonomer selectively branches UHMWPE without affecting HDPE.

In multi-site catalysis, different catalytically active complexes that produce high and low molecular mass polyethylenes are incorporated on the same support, thus enabling simultaneous production and blending of both polyolefins. Reactor blend formation is advantageous compared to blends prepared by conventional melt compounding, especially with respect to dispersion problems due to the high viscosity of ultrahigh molecular mass

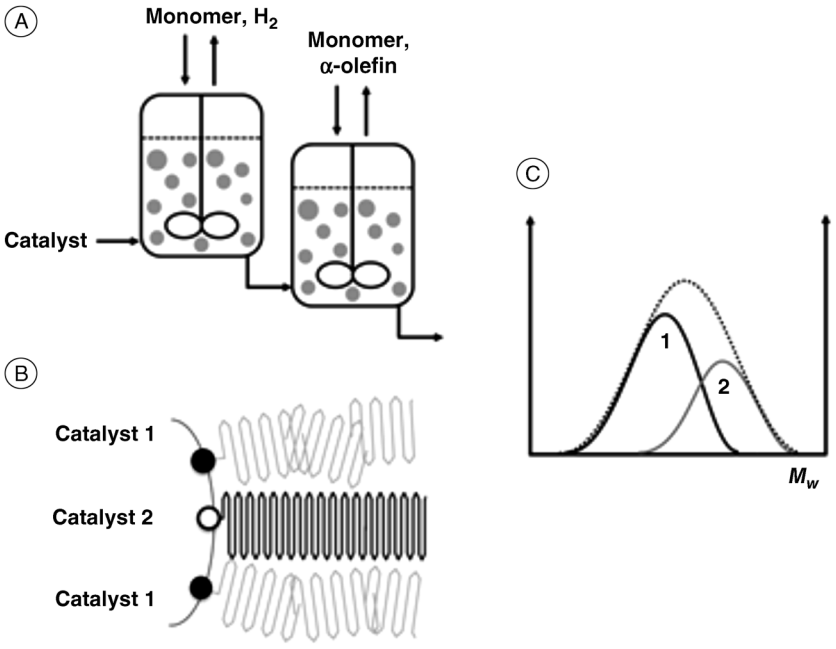
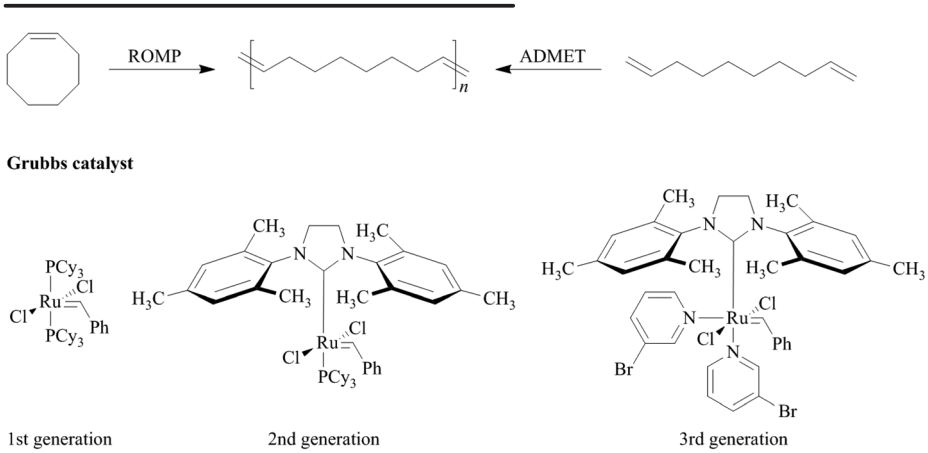
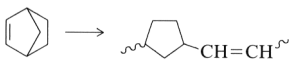


Figure 19. A) Reactor cascades; B) Multi-site catalysts producing reactor blends of HDPE with ultrahigh molecular mass polyethylene (UHMWPE); C) Polyolefin with bimodal molar mass distribution containing UHMWPE (2)

polyolefins and rubbers. The reactor blend formation of HDPE with UHMWPE (see Fig. 19) is the key to self-reinforcing polyethylene (see Section 11.2.4). The reactor granule technology, which combines liquid pool propene homopolymerization with subsequent propene–ethylene copolymerization in a gas phase reactor, incorporates EPM rubber phases directly into the matrix of the PP granules (Catalloy technology). Most conventional Ziegler and related catalyst systems polymerize cyclic olefin, such as cyclopentene via 1,2 polymerization, thus linking together cyclic hydrocarbons by covalent bonds to form rigid polymers. In contrast, transition carbene complexes enable ring-opening polymerization of cyclic olefins to produce flexible polyalkenamers. Catalytic intermediate of this ring-opening metathesis polymerizations (ROMP) are metallcylobutanes formed by cycloaddition of carbene complexes to cycloolefins.



Metatheses reactions are exchange and disproportionation reactions of double bonds, mainly carbon−carbon double bonds in olefins and cycloolefins. A low molar mass example is the metathesis of pentene-2 to butene-2, pentene-2, and hexene-3 (in the ratio 1 : 2 : 1) by the catalyst system $WCl_6-C_2H_5AlCl_2-C_2H_5OH$. Stable carbene complexes are at hand for metathesis reaction and ROMP. Industrially, cyclooctene, norbornene, and dicyclopentadiene are polymerized by ROMP. Cyclooctene gives polyoctenamer $\sim CH{=}CH-(CH_2)_6\sim$; both the *cis* and the *trans* isomers are elastomers (→ Rubber, 6. Sythesis by Radical and Other Mechanisms). Norbornene polymerizes to a thermoplastic polymer that is plasticized with mineral oil to give an elastomer (→ Rubber, 6. Sythesis by Radical and Other Mechanisms). Dicyclopentadiene is polymerized by reaction injection molding (RIM) processes to produce rigid engineering materials.



In *acyclic diene metathesis polymerization* (ADMET), the polycondensation of a variety of nonconjugated linear dienes, such as 1,5-headiene, affords polyenes. Using functional nonconjugated diene monomers, ADMET enables precise control of the spacer length between two branches, whereas conventional copolymerization process affords broad distributions. Unlike industrial Ziegler catalysts, Ru carbene complexes are tolerant to polar groups, thus enabling the formation of polyolefins with polar groups attached as side chains.

3.3.6. Copolymerizations [98]

Copolymerizations are joint polymerizations of two or more monomers; they were also called interpolymerizations in the older literature. In the simplest case, both active chain ends ∼a∗ and ∼b∗ react irreversibly with the two monomers A and B:

$$\sim a^* + A \rightarrow \sim a - a^*; R_{aA} = k_{aA}[a^*][A]$$

$$\sim a^* + B \rightarrow \sim a - b^*; R_{aB} = k_{aB}[a^*][B]$$

$$\sim b^* + A \rightarrow \sim b - a^*; R_{bA} = k_{bA}[b^*][A]$$

$$\sim b^* + B \rightarrow \sim b - b^*; R_{bB} = k_{bB}[b^*][B]$$

Four rates R_{ij} and four rate constants k_{ij} are to be considered in this terminal model, which corresponds to Markov first-order statistics. At high molar masses, monomers are consumed only by the four propagation reactions. The relative monomer conversion is given by

$$\frac{-d[A]/dt}{-d[B]/dt} = \frac{R_{aA} + R_{bA}}{R_{bB} + R_{aB}} = \left(\frac{k_{bA} + k_{aA}([a^*]/[b^*])}{k_{bB} + k_{aB}([a^*]/[b^*])}\right) \cdot \frac{[A]}{[B]} = \frac{d[A]}{d[B]}$$

The ratios of rate constants of homopropagations and cross-propagations are called copolymerization parameters

$$r_A \equiv k_{aA}/k_{aB};\ r_B \equiv k_{bB}/k_{bA}$$

Five different cases can be distinguished for each copolymerization parameter:

$r = 0$	The rate constant of homopropagation is zero; the active center adds only the other monomer.
$r<1$	The other monomer is added preferentially.
$r = 1$	Both monomers are added in the same amounts.
$r > 1$	The own monomer is added preferentially but not exclusively.
$r = \infty$	No copolymerization, only homopolymerization.

Depending on the relative numerical value of the two copolymerization parameters, five different types of copolymerization can be distinguished (Table 10).

In general, one of the monomers is consumed preferentially during copolymerization ($r_A \neq r_B$). This drift of copolymer composition can be avoided if the more reactive monomer is fed into the reactor according to its consumption. A conversion-independent polymer composition also results if copolymerization is performed under azeotropic conditions, which are defined by

$$d[A]/d[B] \equiv [A]/[B]$$

Table 10. Types of copolymerization of monomers A and B

Types	Copolymerization parameters				
	Azeotropic		Nonazeotropic		
	r_A	r_B	r_A	r_B	$r_A r_B$
Alternating	0	0	0	> 0	0
Statistical	< 1	< 1	$< 1/r_B$	> 1	< 1
Ideal	1	1	$1/r_B$	$1/r_A$	1
Block forming	> 1	> 1	$> 1/r_B$	< 1	> 1
Blend forming	∞	∞	∞	< ∞	∞

i.e., the relative rate of monomer consumption equals the ratio of monomer concentrations at any time: The monomer and the polymer compositions do not drift with the progress of polymerization.

This equation is a special case of the Lewis–Mayo equation, which describes the instantaneous composition of the copolymer as a function of the ratio of instantaneous monomer concentrations:

$$\frac{d[A]}{d[B]} = \frac{1 + r_A([A]/[B])}{1 + r_B([B]/[A])} = \frac{x_a}{x_b}$$

All types of copolymerization can in principle occur with the same monomer pair if various initiators are used. All copolymerizations of styrene and methyl methacrylate shown in Figure 20 are, for example, statistical. The free-radical-initiated copolymerization is, however, azeotropic, and the cationic and anionic ones are nonazeotropic. Initiation by $Et_3Al_2Cl_3$ and traces of oxygen leads to almost alternating copolymers, whereas cationic polymerization generates long styrene sequences and anionic polymerization produces long methyl methacrylate ones. The sequence length determines many polymer properties, most notably glass and melting temperatures.

Ionic copolymerizations very often lead to long block sequences, whereas free-radical copolymerizations tend in general to produce more random copolymers. Free-radical copolymerizations are thus the method of choice for industrial purposes if allowed by monomer structures (Table 11).

3.4. Polycondensations and Polyadditions [85]

3.4.1. Bifunctional Polycondensations

Polycondensations and polyadditions are generally divided into bifunctional reactions (two

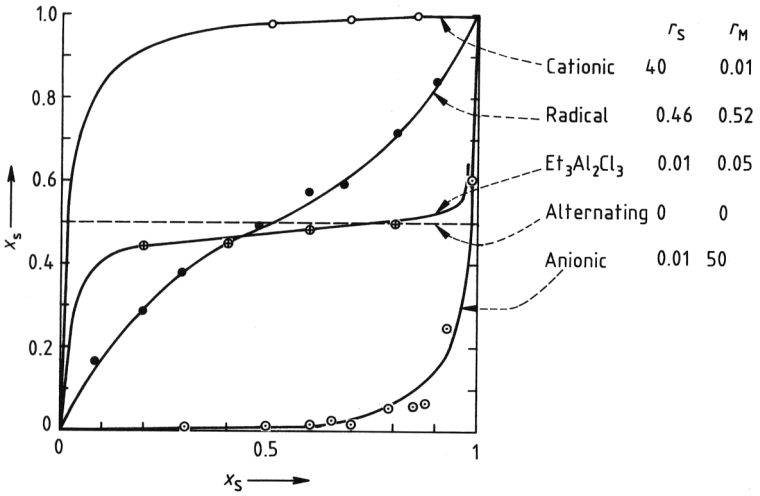


Figure 20. Instantaneous mole fraction x_s of styrene units in the polymer formed as a function of the instantaneous mole fraction x_s of styrene in the copolymerization of styrene with methyl methacrylate initiated by (○) cations; (●) free radicals; (⊕) $Et_3Al_2Cl_3$; (⊙) Anions
Solid lines: calculated with copolymerization parameters shown to the right; dotted line: theory for alternating copolymerizations.

Table 11. Industrial copolymerizations

Monomers	Polymerization	Application
Free radical, linear (or slightly branched)		
Ethylene + 10% vinyl acetate	bulk	shrink films
Ethylene + 10–35% vinyl acetate	bulk	thermoplastics
Ethylene + 35–40% vinyl acetate	under precipitation[a]	films
Ethylene + > 60% vinyl acetate	emulsion	elastomers
Ethylene + < 10% methacrylic acid	bulk	extrusion coating
Ethylene + trifluorochloroethylene		thermoplastics
Butadiene + styrene	emulsion	multipurpose elastomers
Butadiene + 37% acrylonitrile	emulsion	oil-resistant elastomers
Vinyl chloride + 3–20% vinyl acetate	solution[b]	Paints
Vinyl chloride + 15% vinyl acetate	solution[b]	Hi-fi records
Vinyl chloride + 3–10% propene	bulk	thermoplastics
Acryl esters + 5–15% acrylonitrile		oil-resistant elastomers
Acrylonitrile + 4% different monomers	under precipitation[c]	fibers with improved dyeability
Acrylonitrile + styrene		thermoplastics
Acrylonitrile + butadiene + styrene		thermoplastics
Tetrafluoroethylene + propene	emulsion	thermoplastics
Methacrylic acid + methacrylonitrile		hard foams (after cyclization)
Free radical, cross-linking		
Glycol methacrylate + 2–4% glycol dimethacrylate		contact lenses
Unsaturated polyesters + styrene or methyl methacrylate	bulk	glass-fiber-reinforced thermosets
Anionic		
Styrene + butadiene	solution	elastomers
Cationic		
Isobutene + 2% isoprene	solution	butyl rubber
Trioxane + ethylene oxide	solution	thermoplastics
Ethylene oxide + propylene oxide	solution	thickener, detergents
Ziegler–Natta polymerization		
Propylene oxide + nonconjugated dienes	solution	elastomers
Ethylene + propene + nonconjugated dienes		elastomers

[a] In *tert*-butanol.
[b] In acetone, 1,4-dioxane or hexane.
[c] In water.

functional groups per reactant) and multifunctional ones (three or more functional groups per monomer molecule). Bifunctional reactions lead to linear macromolecules; multifunctional ones, to branched and finally cross-linked polymers. Bifunctional reactions are further subdivided into AB reactions (e.g., that of $H_2N-R-COOH$) and AA/BB reactions (e.g., $H_2N-R-NH_2$ + HOOC−R'−COOH).

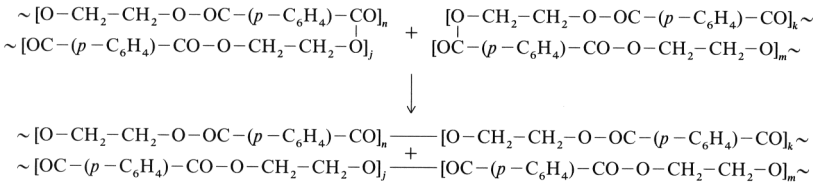
All reactants, from monomer to high polymer, may react to form macromolecules in bifunctional polycondensations and polyadditions. Only monomers are present at the beginning of the reaction; later, oligomers are present. If the reactivity of the functional groups is independent of molecule size, then the greater number of smaller molecules leads first to low molar mass polymers and only at high conversions to chemical compounds with high molar masses (see Fig. 17). In equilibrium, the number-average degree of polymerization of polymers from AB and stoichiometric AA−BB reactions is dictated by the extent of functional group reaction p:

$$\overline{X}_n = 1/(1-p)$$

At 50% conversion ($p = 0.5$), the number-average degree of polymerization of reactants is only 2 (this includes monomer molecules), and the number-average degree of polymerization of polymers ($2 < X_i < \infty$) is only 3. Industrial polycondensations rarely deliver number-average degrees of polymerization greater than 100–200 (i.e., $p = 0.99$–0.995 in equilibrium). The endgroups of these equilibrium polymers may condense further during processing by, e.g., extrusion or injection molding. The accompanying strong increase in viscosity is undesirable and these endgroups are therefore blocked against further polycondensation

by "sealing" them with monofunctional reagents.

Equilibria are established not only by retroreactions (reversal of polycondensations and polyadditions) but also by catalyzed exchange reactions between chain segments. In these trans reactions, number-average molar masses remain constant, but mass-average molar masses increase if the initial ratio of mass to number-average molar mass was smaller than dictated by equilibrium conditions. An example is the transesterification of poly(ethylene terephthalate):



Higher degrees of polymerization at lower extents of reaction can be obtained by irreversible "activated reactions" and especially by heterogeneous reactions of fast reacting monomers. An example is the Schotten–Baumann reaction of diamines in water with diacid dichlorides in chloroform, for example. A polyamide film is formed at the interface of the two solutions. Functional groups of this polymer are buried in the interior of the film; they cannot react with each other. Exchange reactions and retroreactions are also absent. Only surface groups can react; the resulting irreversible reaction leads to high molar masses. Industrially, this reaction is utilized for one of the two industrial syntheses of polycarbonates, i.e., from the sodium salt of bisphenol A and phosgene (Table 12).

Most industrial polycondensations are of the AA–BB type (Table 12); they can be described

Table 12. Industrially important linear AA–BB polycondensations following Equation (17)

Polymer	Chemical structure				Remarks
	A	V	W	B	
Poly(ethylene terephthalate)	H	$O(CH_2)_iO$	CO–*p*-Ph–CO	OH	$i = 2$ (ethylene) or
	H	$O(CH_2)_iO$	CO–*p*-Ph–CO	OCH_3	4 (butene)
Unsaturated polyesters	H	$O(CH_2)_2O$	CO–CH=CH–CO	$O_{1/2}$	from maleic anhydride (isomerizes mainly to fumaric acid residues)
Polycarbonate	H	O–*p*-Ph–$C(CH_3)_2$–*p*-Ph–O	CO	OC_6H_5	
	Na	O–*p*-Ph–$C(CH_3)_2$–*p*-Ph–O	CO	Cl	
Polyarylates	Na	O–Ar–O	CO–Ar–CO	Cl	different Ar
Poly(phenylene sulfide)	Na	S	*p*-Ph	Cl	
Polysulfides	Na	S	R	Cl	different R
Polysulfones	K	O–*p*-Ph–O	SO_2–*p*-Ph–O–*p*-Ph–SO_2	Cl	different V and W units
Polyamides	H	$NH(CH_2)_iNH$	$CO(CH_2)_jCO$	OH	PA 66 ($i = 6$; $j = 4$) PA 610 ($i = 6$; $j = 8$) PA 46 ($i = 4$; $j = 4$)
Polyetheretherketone	K	O–*p*-Ph–CO–*p*-Ph–O	*p*-Ph–CO–*p*-Ph	F	

Ar = aromatic residue; *p*-Ph = *para*-substituted phenylene group; R = organic residue.

by

$$n\,A-V-A+n\,B-W-B\rightarrow A-(V-W)_n-B+(2n-1)AB \quad (17)$$

where A− and B− are leaving groups, AB represents leaving molecules, −V− and −W− are monomeric units, and −V−W− are repeating units.

Industrial AB polycondensations are fairly rare. Examples are the formation of polyamide 11 (nylon 11) (Eq. 4), the polycondensation of carbodiimides

$$O=C=N-R-N=C=O\rightarrow R-N=C=N+CO_2$$

and the synthesis of certain polysulfones

$$C_6H_5O(p\text{–}C_6H_4)SO_2Cl\rightarrow$$

$$(p\text{–}C_6H_4)-O-(p-C_6H_4)-SO_2+HCl$$

3.4.2. Multifunctional Polycondensations and Hyperbranched Polymers [99]

Multifunctional polycondensations are condensation reactions with the participation of monomers having higher functionality ($f_o > 2$). At low conversions, branched molecules are formed with increasingly higher number of functional end groups per molecule (i.e., increased functionality f):

$$f = 2(f_o - 1) + (X - 2)(f_o - 2) = 2 + X(f_o - 2)$$

Only one such group is, however, needed to link two molecules; the probability of such a linkage thus increases dramatically with increasing degree of polymerization X. At a certain degree of conversion of functional groups, molecules are linked throughout the volume of the reactor. The viscosity increases strongly, and the mass-average molar mass of the cross-linked polymer approaches infinity at this "gel point." Not all reactants are linked at the gel point; some are still soluble up to high conversions. The number-average degrees of polymerization of reactants are thus fairly low at the gel point, usually in the range $10 < \overline{X}_n < 50$.

Knowledge of the gel point is technically very important. Polymers cannot, or can only with difficulty, be processed beyond the gel point and must thus be shaped before or during the cross-linking reaction. The gel point can be calculated from the functionality and relative amounts of reactive groups if intramolecular cyclizations are assumed absent. In practice, such cyclizations are often present and cross-linking occurs at higher extents of reaction than calculated. The theoretical calculations thus provide a safety margin.

Chemical cross-linking reactions are utilized for thermosets, certain leathers, and the preparation of elastomers from rubber. Thermosetting polycondensation reactions allow the hardening of phenol, amino, and alkyd resins. In the reaction of phenol(s) with formaldehyde, methylene, formal, and ether bridges are formed between the *ortho* and *para* positions of the phenols; the hardening of novolacs with hexamethylenetetramine (urotropin) also leads to imine structures (→ Phenolic Resins). Amino plastics result from the reaction of urea or melamine with formaldehyde (→ Amino Resins), and alkyd resins from multifunctional alcohols with bifunctional organic acids or their anhydrides (→ Alkyd Resins).

Homopolymerization of AB_n monomers and copolymerization of AB with B_n monomers, respectively, affords hyperbranched polymers. Due to their low entanglement, hyperbranched polymers have reduced viscosity compared to linear polymer. Moreover, they have very high end-group functionality and can be tailored for applications in thermoset resin formulations and drug carriers. Amphiphilic hyperbranched polymers are effective dispersing agents for pigments and various other particles.

3.4.3. Polyaddition

No leaving molecules have to be removed during polyadditions, an important advantage for process engineering. Practically all industrially important polyadditions are thus performed with thermosetting resins. Polyurethanes are formed from diisocyanates (or triisocyanates) and polyols (see Eq. 5 for diols). Polyurethane formation may be so rapid that cross-linking and shaping can be performed in

one step through reaction injection molding with short cycle times. Epoxides (epoxy resins) contain two or more epoxy groups per prepolymer molecule and are cured with either difunctional or multifunctional amines or with anhydrides of organic acids.

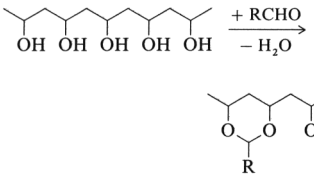
3.5. Polymer Reactions [100, 101]

3.5.1. Polymer Transformations

Several polymers are chemically transformed into industrially useful polymers by polymer-analogous reactions of their substituents (Table 13).

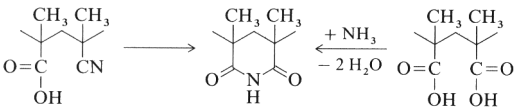
These reactions per group are chemically identical to their low molar mass analogues. They differ in the effect of side reactions, which do not lead to removable byproducts as in micromolecules but to "wrong" structures in the polymer chain. In most cases, such structures decrease the desired polymer properties. Polymer transformations that are prone to side reactions are thus generally avoided. This is one reason why only five types of polymer-analogous reactions are utilized commercially: Transesterification−saponification, chlorination−sulfochlorination, etherification, hydrogenation, and cyclization.

The reaction of poly(vinyl alcohol) with butyraldehyde leads to acetals. For statistical reasons, however, not all hydroxyl groups can be transformed:



The resulting poly(vinyl butyral) is used as an intermediate layer in safety glass and for wash primers.

Heating of methacrylic acid−methacrylonitrile copolymers with ammonia produces polymethacrylimide structures that are hard foams:



The thermal treatment and carbonization of polyacrylonitrile fibers represents the key to the industrial production of carbon fibers, which are highly attractive for reinforcement of thermosets and the formation of carbon-fiber reinforced polymers in lightweight engineering.

Table 13. Industrial polymer transformations (for ring formations see text)

Base units in primary polymer	Reagent	Conversion, %	Base units in final polymer	Application
$CH_2CH(OOCCH_3)$	ROH	98	CH_2-CHOH	thickener
$CH_2CH_2CH_2CH(OOCCH_3)$	CH_3OH	99	CH_2-CHOH/CH_2-CH_2	engineering plastics
Cellulose$-NHCOCH_3$	H_2O	?	Cellulose NH_2	paper additive
Cellulose OH	CH_3COOH	83–100	Cellulose $OOCCH_3$	fibers, films
Cellulose OH	HNO_3	67–97	Cellulose$-ONO_2$	plastics, fibers
Cellulose ONa	oxirane	53–87	Cellulose$-OCH_2CHRCH_3$	thickener
Cellulose OH	oxirane	100–400[a]	Cellulose$-OCH_2CH(OR')CH_3$	thickener
CH_2-CH_2	Cl_2	25–40[b]	CH_2-CHCl	elastomer
		>40[b]	$CH_2-CHCl/CHCl-CHCl$	impact improver for PVC
CH_2-CHCl	Cl_2	64[b]	$CH_2-CHCl/CHCl-CHCl$	adhesives, paints
CH_2-CH_2	Cl_2/SO_2	<42[b]; <2[c]		coatings
$CH_2CH=CHCH_2/CH_2-CHCN$	H_2	?	$(CH_2)_4/CH_2-CHCN$	elastomer
$CH_2-CH(C_6H_5)$	SO_3	low	$CH_2-CH(C_6H_4SO_3H)$	ion exchangers
$N=PCl_2$	RONa	?	$N=P(OR)_2$	elastomer

[a] Further reaction of primary reaction products may lead to more than one monomeric unit of reagent per hydroxyl group of cellulose.
[b] Chlorine content in %.
[c] Ether groups per glucose unit.

3.5.2. Block and Graft Formations [102]

Reactive chain ends can either initiate the polymerization of other monomers or couple with other preformed macromolecules to give block polymers:

$$A_n^* + mB \rightarrow A_nB_m^*$$

$$A_n^* + B_m^* \rightarrow A_nB_m$$

Both methods are used industrially with a variety of strategies for the synthesis of diblock polymers A_nB_m as compatibilizing agents for polymer blends, triblock polymers $A_nB_mA_n$ as thermoplastic elastomers, and various multiblock polymers for different purposes, especially for thermoplastic elastomers. Anionic living polymerizations are used for the syntheses of poly(styrene−block-butadiene−block-styrene) and poly(styrene−block-isoprene−block-styrene). Polycondensations serve for the preparation of multi[{poly(butylene terephthalate)}−block-poly{(polytetrahydrofuran)−terephthalate}], and various polyesteramide and polyetheramide segmented block polymers.

Graft copolymers result from the grafting of monomers on chemically different polymer chains. Grafts of isobutene−isoprene on polyethylenes, vinyl chloride on poly(ethylene-stat-vinyl acetate), ethylene−propene on poly(vinyl chloride), or styrene−acrylonitrile on saturated acryl rubber also yield thermoplastic elastomers.

3.5.3. Cross-Linking Reactions

Cross-linking of preformed polymers is used for vulcanizing unsaturated rubbers with sulfur, vulcanizing saturated rubbers with peroxides, hardening unsaturated polyester chains with styrene or methyl methacrylate via copolymerization, or tanning collagen with certain reagents to leather.

3.5.4. Degradation Reactions

Degradation of polymers is undesirable for their application and often desirable for their disposal after use. The term degradation includes the decrease in degree of polymerization with preservation of the chemical structure of monomeric units (depolymerization), the unwanted chemical transformation of some monomeric units with preservation of the degree of polymerization (decomposition), and a combination of both. The terms degradation, depolymerization, and decomposition are sometimes used with the same meaning as in this article, but other times with broader or more restricted meanings; no accepted usage exists.

Depolymerizations involve chain scissions. They are retroreactions (i.e., the reverse of chain polymerizations, polyeliminations, polycondensations, or polyadditions). Chain scissions may be at random as in retropolycondensations and retropolyadditions or may be unzipping reactions as in retro-chain polymerizations and retropolyeliminations.

Unzipping can occur only with activated chains above their ceiling temperatures, that is, with living polymers, chain ends comprising certain functional groups, or radical ends generated by a prior chain scission. Unzipping at higher temperature results in gaseous monomers that lead to voids in molded parts. This can be prevented or reduced by shorter sequence lengths of the unzippable polymer blocks. This strategy is utilized, for example, in the formation of acetal copolymers by copolymerization of trioxane (gives unzippable oxymethylene sequences $\sim OCH_2\sim$) with ethylene oxide (oxyethylene sequences $\sim OCH_2CH_2\sim$ do not unzip).

Decomposition can be caused by heat, light, oxygen, water, or other environmental agents as well as mechanical forces such as extensional flow, ultrasound, or a combination of these. It may lead to undesirable changes of mechanical, electrical, or optical properties. Unstabilized poly(vinyl chloride) $\sim(CH_2CHCl)_n\sim$ discolors on decomposition because HCl is eliminated and colored polyene sequences $\sim(CH{=}CH)_i\sim$ are formed. The polymer ultimately becomes brittle.

Decomposition is the primary degradation process in the pyrolysis of polymers, which

may be desirable (rocket fuels, waste disposal) or not (fires), and often produces toxic fumes or smoke at lower flame temperatures. The risk of pyrolysis is enhanced for polymers with branching points, electron-accepting groups, long methylene sequences, and all groups capable of forming five- or six-membered rings. Thermostability is enhanced by aromatic rings, ladder structures, fluorine as a substituent, and low hydrogen content. On heating above 400 °C, polyolefins degrade to form small molar mass hydrocarbons, which are equivalent to those obtained from fossil resources. This route to "renewable oil" from polyolefin wastes is attractive with respect to recycling and sustainability.

4. Plastics Manufacture [103]

4.1. Homogenization and Compounding

Polymerization reactors do not deliver polymers that can be used directly as raw materials for plastics. Polymer melts must be filtered; melts, powders, beads, pellets, and granulates must be degassed; and all particulates must be dried or conditioned to environmental surroundings. Beads from suspension polymerization are washed and polymer solutions concentrated.

Batchwise polymerizations often lead to slightly different products, which are mixed (blended) to guarantee customers polymer grades according to specifications (microhomogenization). Granulates and pellets are sometimes similarly blended by macrohomogenization.

Compounding is the mixing of polymers and additives. This process can be performed by adding single additives one at a time, by using additive systems, or by employing master batches. Additive systems are carefully adjusted mixtures of additives that are formulated to avoid mutually synergistic or antagonistic effects. Master batches are concentrates of additives in polymers; they facilitate the dosage of small amounts of additives.

The properties of compounds depend very much on the compounding process. Only heterogeneous compounds result when poly(vinyl chloride) is mixed with additives in regular mixers; these compounds cannot be processed directly to end-use products. High-performance mixers deliver free-flowing powders; these "dry blends" can be extruded and injection molded. Compounding is often carried out by specialized companies (compounders).

4.2. Additives [5, 104, 105] (→ Plastics, Additives)

4.2.1. Overview

Polymers are rarely used directly as materials. They do not fulfill per se all technological requirements and become commercially useful only after they have been mixed with certain additives. These additives average ca. 23% of the total mass of plastics but may range for individual plastics from 0.01% (packaging films for food) to 90% (barium ferrite-filled ethylene–vinyl acetate copolymers for magnetizable sealing strips). Polymer additives are to be distinguished from *polymer auxiliaries*; the former are added to polymers after the polymerization process, whereas the latter are used for the manufacture of polymers (e.g., polymerization catalysts, emulsifiers, initiators). The free-radical initiators used for the hardening of unsaturated polyesters are sometimes considered additives (added to the solution of unsaturated polyester molecules in monomers such as styrene) and sometimes auxiliaries (promoting the thermosetting reaction).

Additives are usually subdivided according to their application into process additives and functional additives. Process additives aid the processing of plastics by either stabilizing the chemical composition of polymers (processing stabilizers) or facilitating the processing itself (processing aids). Functional additives stabilize the chemical composition against attacks by environmental agents (stabilizing additives) or improve certain end-use properties (modifiers). Additives may also be classified according to their primary mode of action (chemical or physical). Some additives act in more than one way:

A filler or colorant may also be a nucleating agent for crystallization; a pigment may enhance discoloration, etc.

4.2.2. Chemofunctional Additives

Polymers can be attacked by oxygen and ozone during processing and use. The attack generates radicals that cause chain reactions to produce even more radicals. Ultimately, changed chemical compositions, degradation, or cross-linking occur. Oxidation is reduced if the accessibility of the oxidizable groups is limited or if radical formation is prevented. Oxygen diffusion into the polymer is slowed by certain coatings that act as mechanical barriers or by additives that diffuse into surface layers and are preferentially oxidized there.

Antioxidants (→ Antioxidants) prevent radical formation, at least during processing and for the targeted lifetime of the plastic. They are subdivided into deinitiators and chain terminators.

Deinitiators prevent the formation of radicals (i.e., preventive antioxidants) and are always used in combination with chain terminators (also called secondary antioxidants). They are further subdivided into peroxide deactivators, metal deactivators, and UV absorbers. Peroxide deactivators (tertiary amines, tertiary phosphines, sulfides) convert hydroperoxides into harmless compounds before they can form radicals. Metal deactivators are chelating agents that form inactive complexes with catalytically active metal species (mainly from Ziegler–Natta polymerizations).

Chain terminators, such as hindered phenols, amines, and anellated hydrocarbons, react with already formed radicals and terminate the kinetic chain (chain-breaking or primary antioxidants). A combination of deinitiators and chain terminators often leads to synergistic effects. Antagonistic effects are also known (e.g., with carbon black as filler).

Light-induced degradation reactions can be prevented by the reduction of light absorption or by the addition of *UV absorbers* and quenchers. Less light is absorbed by the plastic if the surfaces are reflective or if certain pigments are added (e.g., carbon black). Ultraviolet absorbers either convert the incident light into harmless infrared radiation or are transformed into other chemical compounds. Quenchers deactivate excited states and become excited themselves.

Heat stabilizers prevent chemical transformations of plastics at higher temperature; their main application is for the stabilization of poly(vinyl chloride) against HCl elimination during processing. PVC additives include HCl scavangers, such as metal stearates, metal oxides, and epoxidized soybean oil. PVC additives, such as dibutyltin dithiolate react with thermally labile allylic chloride and double bonds in the PVC backbone.

Flame retardants either prevent oxygen access to burning plastics by formation of nonburning gases or by "poisoning" radicals generated by the burning. Some plastics are self-extinguishing because either CO_2 (polycarbonates) or water vapor and a protecting carbon layer are formed (vulcanized fiber: a $ZnCl_2$-treated cellulose) during burning. Chlorine and bromine compounds generate radicals during burning; these radicals combine with radicals from the degradation of plastics and stop the kinetic chain. Phosphorus compounds are oxidized during the burning to nonvolatile phosphor oxides, which either form a protective layer or are converted by water into phosphorus acids that catalyze the elimination of water. Intumescent additives, such as ammonium polyphosphate, form a carbon form that serves as a thermal insulator.

The flammability of plastics is often characterized by the limiting oxygen index (LOI). The LOI value indicates the limiting value of the volume fraction of oxygen in an oxygen–nitrogen mixture that just allows the polymer to burn after ignition with a flame. Materials with LOI > 0.225 are called flame retardant; those with LOI > 0.27, self-extinguishing. Low LOI values (high flammabilities) are exhibited by polyoxymethylenes (0.14), polyolefins (0.17–0.18), saturated polyesters (0.20), and cellulose (0.20). High LOI values are exhibited by poly(vinyl chloride) (0.32), polybenzimidazole (0.48), and polytetrafluoroethylene (0.95). However, LOI values are not absolute measures of the flammability or combustibility of plastics because these

properties also depend on flame temperatures, heat capacities, heat conductivities, melting temperatures, and melt viscosities. The hazard of burning plastics is also determined by smoke formation and the toxicity of the evolving gases. In view of growing environmental and health concerns, halogenated flame retardants are gradually substituted by halogen-free flame retardants, such as $Al(OH)_3$ hydrate, $Mg(OH)_2$, and ammonium polyphosphate.

4.2.3. Processing Aids

Processing aids facilitate the processing of plastics by enhancing either transport rates to the processing machines, flow behavior in these machines, achievement of final properties during processing, or removal of shaped articles from the machines or from each other.

Easy-flow grades of powdered polystyrenes, for example, often contain 3–4% mineral oil, which forms a low-viscosity film on the surface of the particles and thus reduces friction in polar polymers; amphiphilic compounds such as metal stearates or fatty acid amides are used for this purpose. Such *external lubricants* also reduce the friction between polymer particles and the walls of the processing machine and the friction of polymer melts at such walls; they also prevent the cleavage of particles to smaller flow units. External lubricants are always incompatible with polymers and are thus found predominantly at polymer surfaces. They are related to *release agents*, which facilitate the separation of shaped articles from the tools (molds), and *slip agents*, which prevent the sticking together of shaped articles. Slip agents are thus sometimes also called lubricants.

Internal lubricants improve the flow behavior and homogeneity of polymer melts; they also reduce the Barus effect (see Section 7.3.2) and the melt fracture. Internal lubricants probably act by desegregating larger units (aggregates), which were probably formed during polymerization and are still present shortly after the melting of the polymer to a macroscopically homogeneous material. Typical internal lubricants are amphipolar compounds, e.g., modified esters of long-chain fatty acids.

Nucleating agents promote the crystallization of crystallizable polymers by generating many nuclei for crystallites. They prevent the formation of larger spherulites and thus improve the mechanical properties of plastics.

4.2.4. Extending and Functional Fillers [106–108]

Fillers are solid inorganic or organic materials. Some fillers are added mainly to improve the economics of expensive polymers; they are *extenders*. Extenders are usually particulate materials of corpuscular nature, such as chalk and glass spheres (aspect ratio ca. 1). Functional fillers improve certain properties, such as stiffness, strength, scratch resistance, electrical conductivity, crystallization rate, etc. Reinforcing fillers possess aspect ratios higher than 1; they may be short fibers, platelets (e.g., kaolin, talc, mica) (→ Reinforced Plastics), or long fibers (continuous filaments). Active fillers are sometimes subdivided into property enhancers (aspect ratio < 100) and true reinforcing fillers (aspect ratio > 100). No sharp dividing line exists between fillers and reinforcing agents, nor can the term "reinforcement" be unambiguously defined (e.g., it may denote an increase in breaking or impact strength or a decrease of brittleness).

A variety of fillers are used for plastics (-Table 14). Glass-fiber-reinforced polymers often carry the abbreviation GRP (or FRP); those reinforced by carbon fibers, CRP. Syntactic plastics are polymers reinforced with hollow glass spheres. The amounts of fillers added vary widely: In general, industry standards are about 30 wt % for thermoplastics and 60 wt % for thermosets. Fillers act very differently in polymers. Some fillers form chemical bonds with polymers; an example is carbon black, which acts as a chemical cross-linker in elastomers. Other fillers can adsorb polymers on their surfaces, i.e., physical bonds are introduced between fillers and polymers. On impact, adsorbed chain segments may take up energy and slip from the surface, which increases impact strength. Still other fillers act as nucleating agents in crystallizable polymers. Fillers furthermore constitute impenetrable walls to polymer coils. They restrict the number of conformational positions of chain segments near the filler surface; chains become less

Table 14. Fillers for thermoplastics (T), thermosets (D), and elastomers (E). For definition of other acronyms see Tables [1–4]

Filler	Application in	Concentration in %	Improved property
Inorganic fillers			
Chalk	PE, PVC, PPS, PB, UP	< 33 in PVC	price, gloss
Potassium titanate	PA	40	dimensional stability
Heavy spar	PVC, PUR	< 25	density
Talc	PUR, UP, PVC, EP, PE, PS, PP		white pigment, impact strength, plasticizer uptake
Mica	PUR, UP	< 25	dimensional stability, stiffness, hardness
Kaolin	UP, vinyls	< 60	demolding
Glass spheres	T, D	< 40	modulus of elasticity, shrinkage, compressive strength, surface properties
Glass fibers	T, D	< 40	fracture strength, impact strength
Fumed silica	T, D	< 3	tear strength, viscosity (increase)
Quartz	PE, PMMA, EP	< 45	heat stability, fracture
Sand	EP, UP, PF	< 60	shrinkage (decrease)
Al, Zn, Cu, Ni, etc.	PA, POM, PP	< 100	conductivity (heat and electricity)
MgO	UP	< 70	stiffness, hardness
ZnO	PP, PUR, UP, EP	< 70	UV stability, heat conductivity
Organic fillers			
Carbon black	PVC, HDPE, PUR, PI, PE, E	< 60	UV stability, pigmentation, cross-linking
Graphite	EP, MF, PB, PI, PPS, UP, PMMA, PTFE	< 50	stiffness, creep
Wood flour	PF, MF, UF, UP	< 5	shrinkage (decrease), impact strength
Starch	PVAL, PE	< 7	biological degradation

flexible, and tensile strengths and moduli of elasticity increase.

Due to the significant progress made in nanotechnology, a large variety of nanofillers have emerged since the mid-1990s. As compared to conventional filled polymers that contain micron-sized filler particles nanocomposites have nine orders of magnitude larger number of nanometer-scaled particles at the same volume fraction (Fig. 21). As a consequence, most polymers are allocated in nanocomposites at the nanofiller interface. Converting bulk polymers into interfacial polymers account for novel property profiles. The high surface area lowers considerably the percolation threshold required for particle network formation. This improves the electrical conductivity at much lower filler content. However, in view of the nanoparticle interactions, dispersion of nanoparticles is more difficult than micron-sized particles. Therefore, special processing technology and nanofiller surface modification are required. As illustrated in Figure 22, the nanofiller family

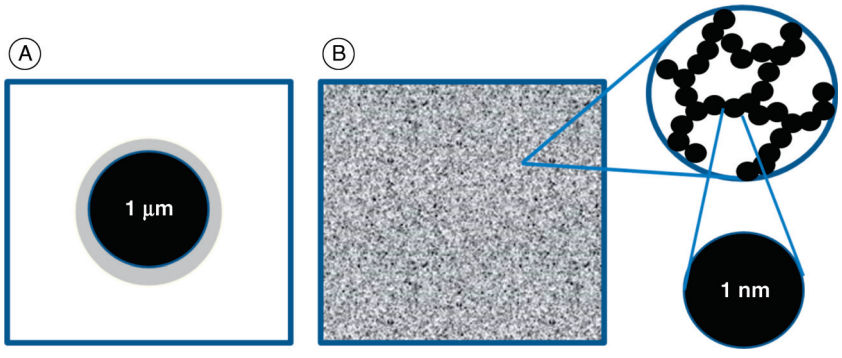


Figure 21. Different sized polymer composites containing the same volume fraction
A) One particle (1 µm) microfiller-sized fillers; B) 10^9 particles (1 nm) nanofiller with the same volume fraction like microfiller

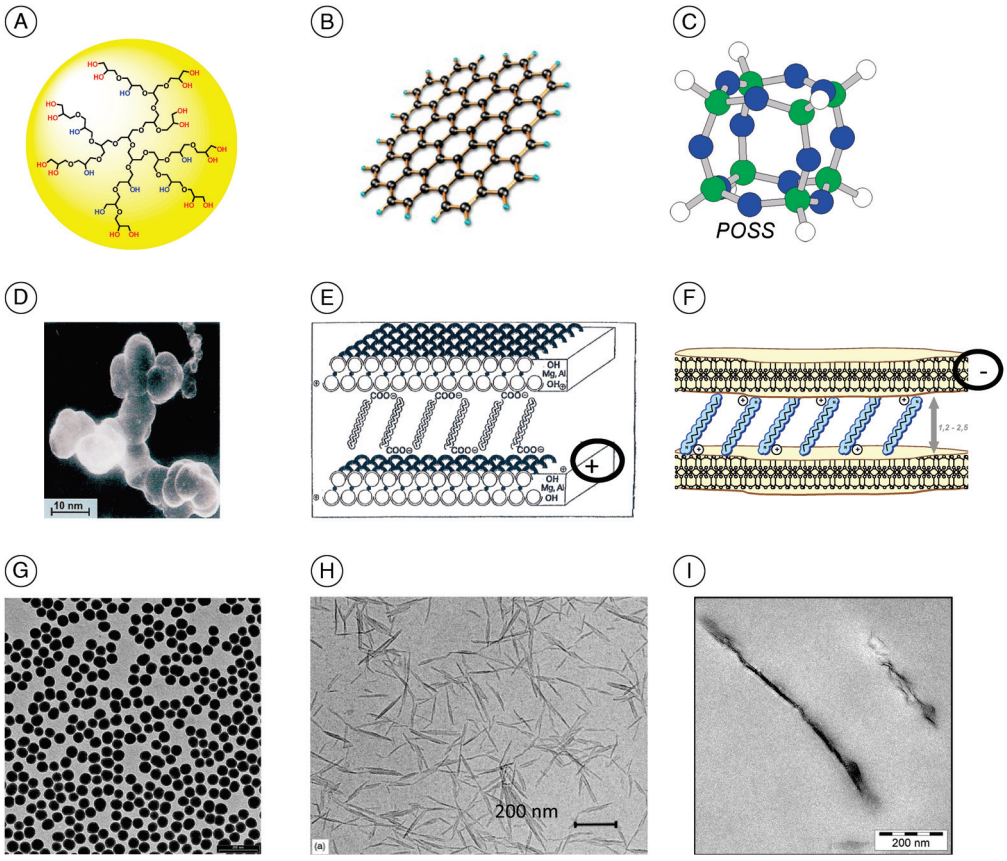


Figure 22. Different types of nanofillers
A) Nanomolecules; B) Molecular carbon; C) Molecular silica (POSS); D) Pyrogenic silica nanoparticles; E) Hydrotalcite; F) Organoclay; G) SiO_2 dispersion; H) Cellulose nanowhiskers; I) Graphene embedded in polypropylene

includes inorganic nanoparticles as well as organic–inorganic hybrid particles, among them dispersions of metal oxides and silicate nanoparticles with shapes varying from spheres to platelets and sheets. The smallest silica nanoparticles are polyhedral oligomeric silsesquioxanes (POSS), which are readily functionalized. The exfoliation of graphite affords graphene that consists of a honeycomb-like planar arrangement of sp^2 hybridized carbon atoms equivalent to a single layer of the graphite lattice. Other carbon allotropes, such as nanometer-scaled carbon particles ("conducting carbon black"), fullerenes, nano diamonds, and single- and multi-walled carbon nanotubes (CNT) are employed as nanofillers. Nanometer-sized carbon particles and especially carbon macromolecules render polymer nanocomposites electrically conductive without sacrificing optical clarity. Organophilic layered silicates ("organoclay") are obtained by cation exchange of the intergallery sodium cations of bentonite for alkyl ammonium. Alternatively, layered silicates with cationic layers, such as hydrotalcites are rendered organophilic by modification with long chain aliphatic carboxylates. As a function of the layered silicate modification and polymer processing conditions, either individual silicate layers are dispersed within the polymer matrix or the polymer is intercalated between silicates layers. The dispersion of sheetlike nanoparticles improves the barrier resistance of polymers. Going beyond wood flour, bio-

based nanofillers (cellulose whiskers, nanocellulose) are derived from cellulose by etching of the amorphous regions.

4.2.5. Plasticizers (→ Plasticizers) [109]

Plasticizers are added to polymers to improve their flexibility, processibility, or foamability. About 500 different types of plasticizers are marketed. They are generally low molar mass liquids; polymer plasticizers are used in much smaller amounts. Of all plasticizers for thermoplastics, 80–85% are used for poly(vinyl chloride); the most important plasticizers are di-2-ethylhexyl phthalate ("dioctyl phthalate," DOP) and dinonyl phthalate. The main plasticizer for elastomers is mineral oil; tires contain up to 40%. Polymer plasticizers are mainly aliphatic polyesters and polyethers. The former are prepared by polycondensation; they thus possess fairly broad molar mass distributions and also contain monomeric and oligomeric molecules. Because their number-average molar mass is low (ca. 4 000 g/mol), they are called oligomer plasticizers. Plasticization can also be achieved by copolymerization of the parent monomer with certain other monomers; this effect is called internal plasticization, in analogy to external plasticization by added high and low molar mass plasticizers.

External plasticizers are subdivided into primary and secondary ones. Primary plasticizers interact directly with chains by way of solvation. Secondary plasticizers are merely extenders; they can be used only in combination with a primary plasticizer. A certain plasticizer may thus be a primary or a secondary one, depending on the chemical constitution of the polymer. Mineral oils are, for example, primary plasticizers for polydienes but extenders for poly(vinyl chloride).

4.2.6. Colorants

Colorants are subdivided into dyes (soluble in polymer matrix) and pigments (insoluble). Textile fibers are dyed mainly with dyes. Pigments are preferred for plastics because they have a higher light-fastness and are more stable against migration than dyes. Colorants for plastics are dominated by titanium dioxide (60–65%) and carbon black (20%); only 2% are dyes.

Pigment particles generally possess diameters of 0.3–0.8 μm, which allows the pigmentation of films and fibers of > 20 μm thickness. Very thin films and fibers are colored exclusively by organic pigments because these can be ground to much smaller diameters than inorganic ones. The hiding power of pigments increases with increasing difference between refractive indices of pigment and polymer.

Pigments need not have a special affinity for polymers. They must be wettable by the polymer melt, however, which can be achieved by treating them with surfactants. The aggregation of pigments is mainly the result of air inclusions; it can be removed by the application of vacuum. Pigments can be metered into plastics via master batches (in plastics), color concentrates (in plasticizers), or electric charging of the surface of polymer particles in granulate mixers. Up to 1 wt % of pigment can be mixed in by the last method.

4.2.7. Blowing Agents

Foamed plastics (plastic foams, cellular plastics, expanded plastics) are blends of polymers with gases (→ Foamed Plastics). They may be rigid (glass transition or melting temperature higher than use temperature) or flexible; their cell structure can be open or closed. The gases may be air, nitrogen, carbon dioxide, fluorinated hydrocarbons, etc.

Plastic foams can be produced by mechanical means (whipping, stirring), physical methods (shock volatilization of liquids, washing-out of solids), or chemical foaming either by internal foaming during the polymerization or by external foaming with chemical blowing agents. Chemical blowing agents are chemical compounds that decompose at elevated temperature with release of gases. The most widely used agent for natural rubber is *N,N′*-azobisisobutyronitrile $(CH_3)_2C(CN)-N{=}N-C(CN)(CH_3)_2$ (AIBN); for plasticized PVC, *N,N′*-dinitroso dimethyl terephthalamide $CH_3-N(NO)-CO-(p\text{-}C_6H_4)-CO-N(NO)-CH_3$ (NTA); and for other plastics, 1,1′-azobisformamide $H_2N-CO-N{=}N-CO-NH_2$ (ABFA). Blowing agents are used in amounts of ca. 0.1% to eliminate sinks in injection

molding; 0.2–0.8% for injection-molded structural foams; 0.3% for extended profiles; 1–15% for vinyl plastisol foaming; and 5–15% for compression-molded foam products. Because of the depletion of the ozone layer, some fluorine-containing blowing agents were banned.

4.3. Processing [110–113]

There are many different types of processes to convert monomers, prepolymers, or polymers into plastics. In general, four procedures can be distinguished for processing raw materials into shaped plastics:

1. From monomers to polymers by direct polymerization with simultaneous shaping
2. From monomers by oligomerization to prepolymers, followed by simultaneous polymerization and shaping
3. From monomers by polymerization to polymers, followed by separate shaping
4. From monomers by polymerization to polymers, shaping to semifinished product, and finally to the end product

In all four cases, end products must sometimes be after-treated (degated, polished, etc.).

Procedure 1 has only one process step and should be the most economical. It is widely used for wire coatings and casting. However, technological problems are often encountered for shaped articles because the process involves the conversion of a low-viscosity liquid into a high-viscosity body. Because very high polymerization rates are required for this process to achieve high cycle times (phase sequences) in molding (i.e., number of articles produced per unit time), very few monomers, types of polymerization, and shaping methods are suitable. The method is utilized industrially in the RIM (reaction injection molding) process, mainly for the polyaddition of diisocyanates with polyols. The anionic polymerization of lactams and the Diels–Alder polymerization of dicyclopentadienes and related compounds are also suitable for RIM. In resin transfer molding (RTM), thermoset resins and curing agents are mixed together, injected, and cured in the mold.

Procedure 2 is typical for thermosets. Oligomerizations are conducted to conversions shortly before the gel point. Additives are added, and the final processing step consists of a simultaneous cross-linking polymerization and shaping. Typical processing methods include molding, compression molding, cavity compression molding (hot pressing), injection–compression molding, and resin transfer molding.

Procedure 3 is generally chosen for thermoplastics. Polymers from the polymerization process are isolated before shaping and stored (e.g., as granulate) for a shorter or longer period of time. The stored polymers must be dried before further processing; otherwise, steam produced at higher processing temperatures may lead to voids and cavities in shaped articles. After compounding, the plastic raw material must be weighed out accurately for each cycle in discontinuous processing procedures. The filling factor (= raw material density/bulk density) must be known.

The choice of a processing technique is influenced technically by the rheological properties of the material and the form or shape of the desired article. The cost of processing machines and the cycle time are economically important. Commodity articles are produced by casting, centrifugal casting, hot pressing, compression molding, coating, spraying, roll milling, extrusion, injection molding, blow molding, cold forming, press forming, calendering, stretch forming, blowing, extrusion blowing, sintering, fluidized-bed sintering, flame spraying, or hot blast sprinkling, and specialty articles by molding.

Procedure 4 is the method of choice for difficult-to-manufacture articles. Procedures, such as welding, stamping, cutting, forging, sawing, boring, turning, milling (in the metalworking sense), sintering, and baking are employed for both thermoplastics and thermosets. The surfaces of plastics are sometimes treated further for technical (surface hardness, friction) or aesthetic reasons (gloss, color) by polishing, painting, metallizing, coating, etc.

Whereas conventional processing requires molds or machining, in additive processing, also referred to as additives processing and solid

freeform fabrication, complex 3D objects are built by computer-assisted layer-by-layer assembly. Typically, 3D scanner or computer-assisted design are used to create virtual 3D objects, which are sliced and used to construct the real 3D objects layer by layer. Originally designed to serve the special needs of model making, tooling, and rapid prototyping, this mold-free fabrication is emerging as highly versatile processing technology for rapid manufacturing and digital 3D printing. Typical 3D printing technologies include stereolithography with laser-induced photopolymerization of acrylic monomers, selective laser sintering of metal, ceramic and polymer powders, fused deposition molding using 3D extrusion of thermoplastic filaments, and 3D printing by ink-jet printing of binders to bind together powder layers.

5. Supermolecular Structures (→ Plastics, Properties and Testing) [114–116]

Polymer properties are influenced not only by the chemical structure (constitution, molar mass, configuration, microconformation) but also by the physical structure of polymers. These structures may range from totally irregular arrangements of chain segments over shorter or longer parallelizations of chains, to voids and other defects in otherwise highly organized assemblies of polymer molecules. Two possible ideal structures exist in the solid state: Perfect crystals and totally amorphous polymers. Polymer molecules are perfectly ordered in ideal crystals. They convert at the thermodynamic melting temperature into melts, which ideally are totally disordered. Amorphous polymers can be viewed as frozen-in polymer melts. They are polymer glasses that convert to melts at the glass transition temperature.

5.1. Noncrystalline States

5.1.1. Structure

Isolated polymer coils possess approximately a Gaussian distribution of chain segments; their segment density decreases with increasing chain length. However, the macroscopic densities of polymer melts do not change with chain lengths if end group effects on small molar mass molecules are neglected. Coils must therefore overlap considerably in polymer melts. At the glass transition temperature, cooperative segmental movements freeze in, and the physical structure of the melt is conserved. Small-angle neutron scattering studies have shown that the radii of gyration of amorphous polymers are indeed essentially identical for their melts, glasses, and solutions in theta solvents.

The absence of long-range order in melts and amorphous polymers does not exclude the presence of short-range order in these states. Because of the persistence of polymer chains, a parallelization of short segments seems probable, as is found, for example, for alkanes according to X-ray investigation. This local order does not exceed 1 nm in each direction.

The packing of chain segments cannot be perfect. Amorphous polymers thus possess "free volumes", which are regions of approximately atomic diameters. The volume fraction of this free volume is ca. 2.5% at the glass transition temperature and is independent of polymer constitution. Polymer segments in melts can move more freely than in the glassy state; the densities of melts are thus higher than the densities of glasses at the same temperature.

5.1.2. Orientation

Polymer segments, polymer molecules, and crystalline domains may be oriented along the machine direction by drawing or other mechanical processes. The orientation of chain segments need not necessarily lead to crystallization, however. An example is injection-molded polystyrene, which shows optical birefringence due to the orientation of segments but no X-ray crystallinity.

The degree of orientation of segments or crystallites can be measured by wide-angle X-ray or small-angle light scattering, infrared dichroism, optical birefringence, polarized fluorescence, and ultrasound velocity. The orientation is usually characterized for each of the three directions *a*, *b*, and *c* by a *Hermans*

orientation factor f_i, where β is the angle between the draw direction and the principal axis of the segments:

$$f_i = (1/2)(3\cos^2\beta - 1)$$

The orientation factor becomes 1 for a complete orientation of that axis in the draw direction (β = 0°), −1/2 for a complete orientation perpendicular to the draw direction (β = 90°), and 0 for a random orientation.

Since methods to determine orientation factors are often expensive, time consuming, or difficult to perform, the easy-to-calculate *draw ratio* (length after drawing/length before drawing) is often used to characterize orientation. The draw ratio is, however, not a good measure of the degree of orientation because it depends on the history of the specimen. Drawing may also lead to viscous flow of the polymer without any orientation of segments and crystallites.

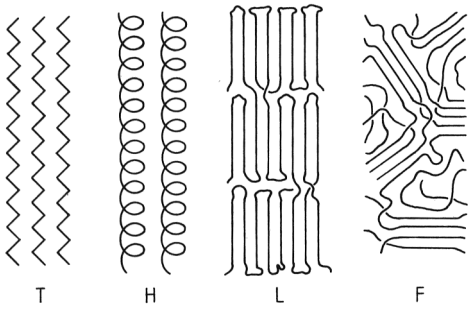


Figure 23. Schematic representation of crystalline polymers as extended chain crystals with chains in all-*trans* (T) or helical conformation (H), (L) lamellae of chains interconnected by tie molecules, and (F) fringed micelles. No bond angles are shown for H, L, and F.

5.2. Polymer Crystals [117, 118]

5.2.1. Introduction

Spheres and other geometrically simple entities can be arranged in crystal lattices irrespective of whether they are atoms, small molecules, large molecules such as enzyme, or latex particles. The centers of gravity of these entities occupy lattice sites that are regularly spaced in three dimensions. Lattices are called *superlattices* if the distances between lattice points significantly exceed atomic dimensions. The existence of three-dimensional order on the atomic level is called crystallinity.

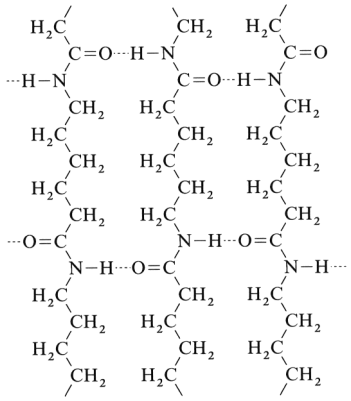
Chain molecules can also be arranged in crystal lattices. The whole chain may be completely parallel to other chains as in the case of truly extended chain crystals; the microconformation of the chain can be all *trans* or helical (Fig. 23), and the chains may have a directional sense as in polyamide 6 or an inversion center as in polyamide 66 (Fig. 24). In other cases, only sections of the chains may be parallel to each other, either sections of a single chain as in folded chain crystals or those of neighboring chains as in fringed micelles. These ordered segments form crystalline regions in otherwise less ordered (though not necessarily completely disordered) polymers.

Crystalline regions may be assembled into greater entities, which themselves may be more or less ordered. The types and degrees of order −disorder depend on external conditions such as temperature, pressure, cooling and heating rates, and presence of solvents. A variety of morphologies may thus exist for any crystallizable polymer [104], for example, spherical, platelet-like, fibrillar, and sheaflike structures of a polyamide 6 (Fig. 25).

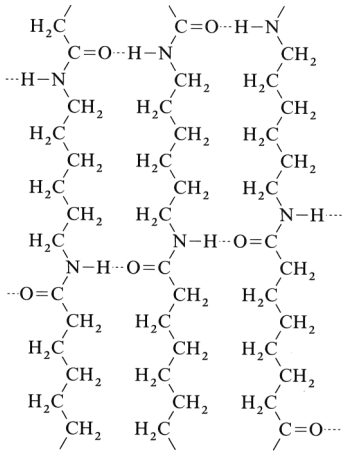
5.2.2. Crystal Structures

The unit cell describes the smallest, regularly repeating structure of a parallelepiped that generates a crystal by parallel displacements in three directions. The parallelepipeds are characterized by three lattice constants (distances between lattice points in three directions) and three lattice angles (Table 15).

Lattice constants reflect the microconformations of chains in crystal lattices. The *c*-direction is normally assigned to the chain direction; a value of $c = 0.254$ nm thus gives the distance between repeating units $-CH_2-CH_2-$ in all-*trans* conformation (bond distance 0.154 nm, bond angle 112°). The *c*-values in carbon chains that are nonmultiples of 0.254 indicate the presence of non-all-*trans* conformations (e.g., helical



PA 6



PA 66

Figure 24. Pleated-sheet structures of polyamides PA 6 (anticlinal) and PA 66 (isoclinal)

structures in it-polypropylene and it-polybutene-1). The *a* and *b* values reflect physical bonds (such as van der Waals or hydrogen bonds) that are longer than the chemical bonds in the *c*-direction. The anisotropy of bond lengths in the three spatial directions prevents the existence of cubic lattices for chain molecules. The other six lattice types are however found [hexagonal, tetragonal, trigonal, (ortho) rhombic, monoclinic, triclinic].

Most polymers form polymorphs (i.e., polymers of the same constitution and configuration can possess various energetically different crystal modifications). *Polymorphism* may be caused by different microconformations of polymer chains (e.g., polybutene-1) or by different packing of chains with identical chain conformations (e.g., it-polypropylene). Such differences can be generated by small changes in processing conditions (e.g., different crystallization temperatures) or by stretching.

Copolymers can furthermore show *isomorphism* if different monomeric units can replace each other without change of lattice structure. Isomorphism of chains is also possible if the two corresponding homopolymers have analogous crystal modifications, similar lattice constants, and the same helix types. An example is a mixture of the γ-modification of it-polypropylene and the modification I of it-polybutene-1 (Table 15). This phenomenon is sometimes also called allomerism. One company calls its crystalline copolymers from two or more olefinic monomers *polyallomers*, because the monomeric units are isomorphic.

5.2.3. Crystallinity

Perfect crystal lattices should give sharp X-ray reflections and sharp melting points. Polymers do not exhibit these features, even if they show a crystallike appearance in electron micrographs. In addition, X-ray patterns of polymers frequently exhibit continuous, diffuse scattering. These findings can be interpreted by either a one-phase model (voids in crystals) or a two-phase model (coexistence of completely crystalline and completely amorphous regions). Crystallinity is defined as the presence of three-dimensional order on the level of atomic dimensions.

In reality, segments are ordered to various degrees. Because most experimental methods are sensitive to different types and degrees of order, various "degrees of crystallinities" are found depending on the experiment. The degree of crystallinity is the fractional amount of crystallinity. Stretched poly(ethylene terephthalate) has, for example, a degree of crystallinity of 59% by IR spectroscopy, 20% by density determination, and 2% by X-ray diffraction.

5.2.4. Morphology

Earlier experimental findings were interpreted in terms of the two-phase model of partially crystalline polymers: The coexistence of

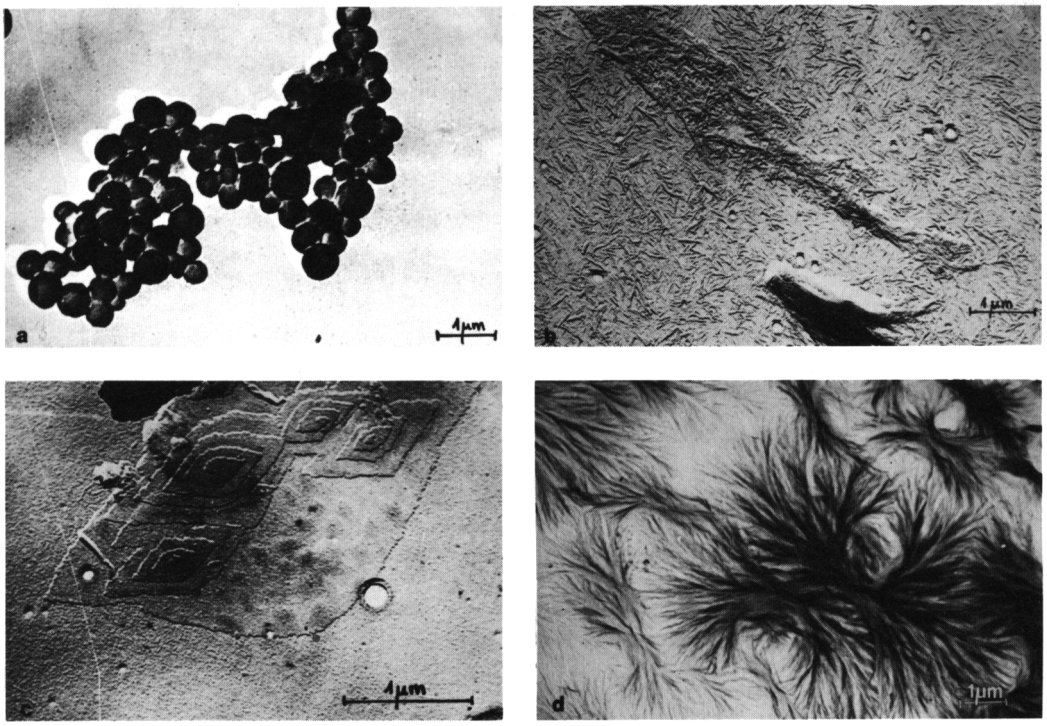


Figure 25. Electron micrographs of different morphologies of a polyamide 6
a) From a 260°C solution in glycerol quenched into 20°C glycerol; b) Same solution fast cooled (40 K/min); c) Same solution slowly cooled (1–2 K/min); d) Slow evaporation of formic acid solution at room temperature [119]

crystalline reflexes and amorphous halos in X-ray diagrams, the independence of X-ray short periodicities on molar masses, the disappearance of X-ray long periodicities with increasing molar masses, lower macroscopic densities than predicted by X-ray densities of unit cells, broad melting ranges, optical birefringence of oriented polymers, and heterogeneity of partially crystalline polymers against chemical reactions.

Table 15. Crystal structure of some polymers

Polymer			Lattice constants				Angles of unit cell			Helix type	Crystal system
			N_u	nm[a]	nm[b]	nm[c]	α°	β°	γ°		
PE		I[b]	2	0.742	0.495	0.254	90	90	90	2_1	R
		II[a b]	2	0.809	0.479	0.253	90	90	107.9	2_1	M
PP	st	8	1.450	0.560	0.74	90	90	90	2_1	R	
	it	α[b]	12	0.665	2.09	0.495	90	99.6	90	3_1	M
	it	β[b]	3	0.638	0.638	0.633	90	90	120	3_1	VI
	it	γ[b]	12	0.647	2.140	6.50	89	100	99	3_1	T
PB	it	I[b]	18	1.769	1.769	0.650	90	90	90	3_1	VI
		II[b]	44	1.485	1.485	2.060	90	90	90	11_3	IV
		III[b]	8	1.238	0.892	0.745	90	90	90	4_1	R

[a] N_u = Number of monomeric units per unit cell.
[b] Crystal modification.
[c] R = (ortho)rhombic; M = monoclinic; VI = hexagonal; T = triclinic; IV = tetragonal.

In 1957, however, three different groups found that rhombic platelets are obtained if very dilute solutions of polyethylene are cooled. Similar platelets of 5–20 nm thickness are now known from many other crystallizable polymers (e.g., see Fig. 25). Electron diffraction showed sharp reflections typical of single crystals and chain directions perpendicular to the surface of the platelets. Since the contour lengths of the chains are greater than the thicknesses of the platelets, chains must be folded back as shown in Figure 23, L.

Crystallization from polyethylene melts similarly shows stacked single crystals. These lamellae are 75–80% X-ray crystalline. After oxidation of the surface, a 100% crystalline material remains. The folds or the interface between lamellae must thus be "amorphous." Various models have been suggested for the surface layers: Loose folds with adjacent reentry of the chains, a switchboard-like structure, adsorbed chains not involved in chain folding, loose or entangled cilia (tangling chain ends), and crystal bridges composed of tie molecules (Fig. 26). Electron microscopy has shown that crystal bridges exist in crystallized mixtures of high and low molar mass polyethylenes. Such interlamellar connections are responsible for some remarkable properties of partially crystalline polymers (see below). Highly crystalline polymers result if tie molecules and surface layers are removed (e.g., by grinding); these fairly low molar mass materials are called microcrystalline polymers.

Crystallization of melts sometimes delivers spherical, polycrystalline entities (Fig. 27). These spherulites exhibit radial symmetry. They consist of lamellae with tangential chain axes (Fig. 28A); radial chain axes seem to be unknown (Fig. 28B). The formation of spherulites can be controlled by the crystallization temperature, the cooling rate, and the addition of nucleating agents.

Spherulites lead to opaque plastics if their diameters are greater than one-half the wavelength of incident light and their densities and

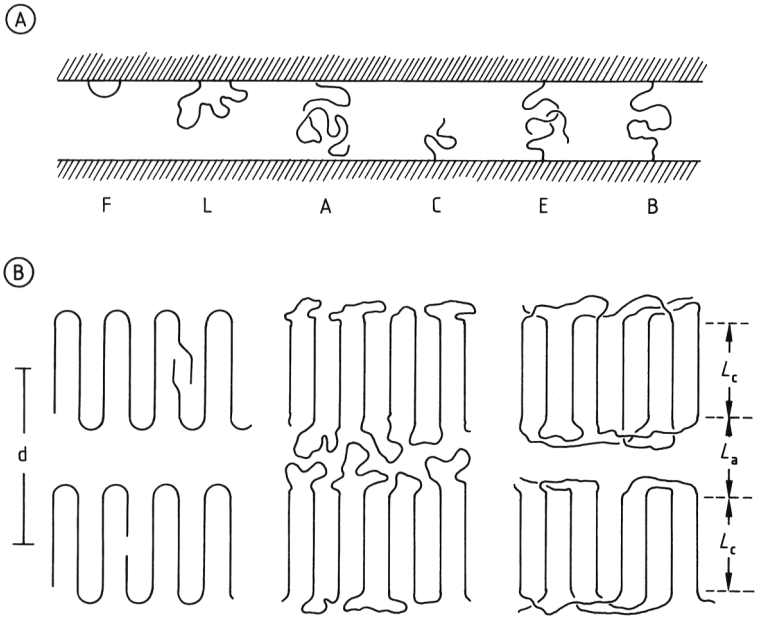


Figure 26. Models for the fine structure of lamellae of single crystals
A) Chains between two adjacent lamellae: F = sharp folds, L = loose loops, A = adsorbed chain, C = cilium, E = entangled cilium, B = crystal bridge or tie segment; B) Structures of lamellae: R=Regular lamellae with sharp folds, adjacent chain reentry, void from chain ends (below) and dislocation (above); L = lamellae with loose loops and adjacent reentry; S = switchboard model; d = crystallographic long period; L_c = thickness of lamella; L_a = thickness of "amorphous" surface layer ($d = L_c + L_a$)
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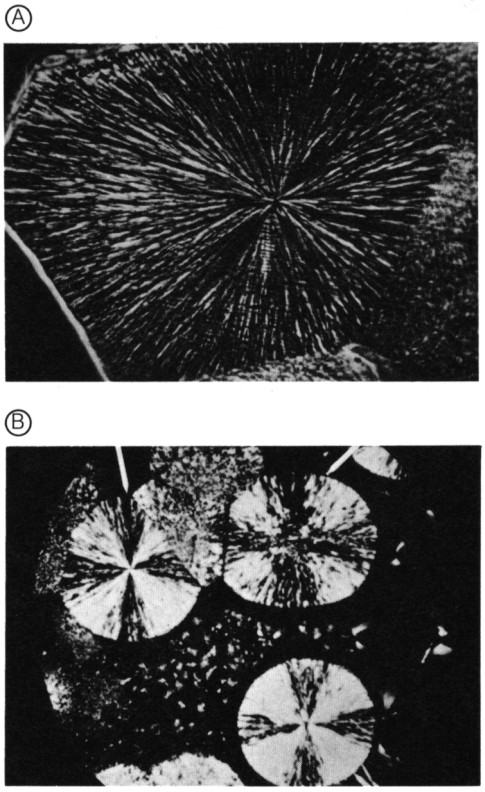


Figure 27. Spherulites of it-polypropylene under the phase contrast microscope (A) and the polarization microscope (B) [120]

refractive indices are different for crystalline and noncrystalline regions. The numbers and sizes of such spherulites are important for the fracture behavior of polymers.

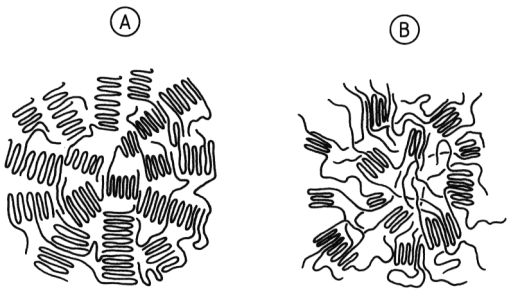


Figure 28. Schematic representation of spherulite structures
A) Tangential chain axes; B) Radial chain axes (hypothetical)
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Spherulites develop in a viscous environment if crystallization nuclei are present and if equal crystallization rates prevail in all three directions. Different crystallization rates exist in strongly stirred dilute solutions. Polymer chains then try to orient themselves along the flow gradients and crystallize in an extended (nonfolded) conformation. The resulting fibrils are organized in bundles with chains parallel to the fibril axes. These bundles act as nuclei–substrate for the epitaxial growth of the remaining chains. Since the shear rate is strongly reduced between bundles, crystallization leads to lamellae with folded chains whose axes are parallel to the fibril axes (Fig. 29). The

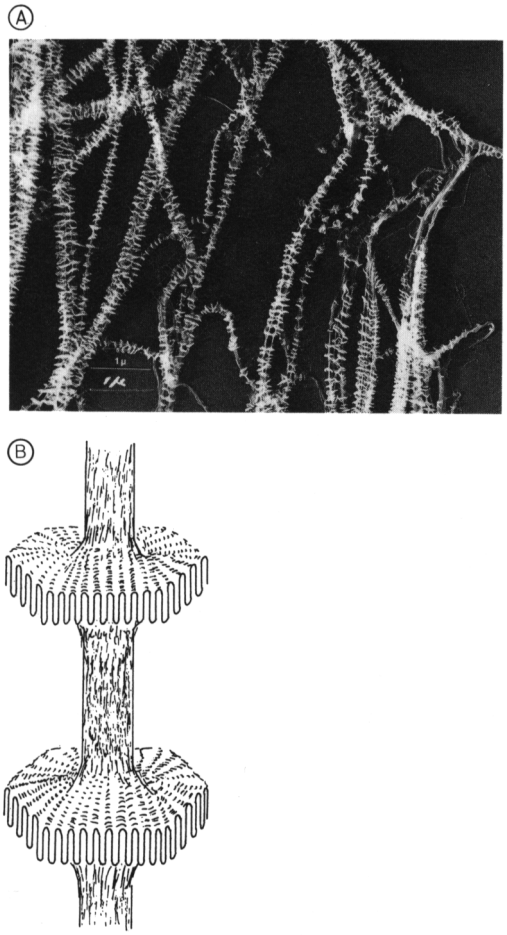


Figure 29. Shish kebab structures of linear polyethylene crystallized from rapidly stirred 5% solutions in toluene [76]
A) Electron micrograph; B) Schematic drawing of chain arrangements

resulting extended-chain structures are responsible for the remarkable properties of some ultraoriented polymers.

5.3. Mesophases and Liquid-Crystalline Polymers [121]

5.3.1. Introduction

Mesomorphic chemical compounds exhibit microscopic structures (mesophases) that are intermediate between crystals with long-range three-dimensional order and liquids without long-range order (Greek: *mesos* = middle, *morphe* = shape, form). Three types of mesophases are distinguished: Liquid crystals, plastic crystals, and condis crystals. Since liquid crystals were discovered first and are furthermore the most common of the three classes, the term mesophase is often used as a synonym for liquid crystal.

Liquid crystals (LCs) (→ Liquid Crystals for Display Application) possess a certain ordered structure like crystals, but they flow like liquids. *Thermotropic liquid crystals* exhibit this phenomenon in the pure state above a certain solid−mesophase transition temperature, where the solid may be a crystal or a glass. *Lyotropic liquid crystals* exhibit mesophase behavior in certain solvents above critical concentrations. Liquid crystalline behavior is present in both cases if the molecules contain "mesogens", that are short rodlike sections that comprise the whole molecule as in low molar mass LCs, or segments thereof as in polymer liquid crystals (LCPs). Mesogens are anisotropic; they are oriented with respect to their mesogen axes but not with respect to their positions.

Plastic crystals exhibit order of positions but disorder of orientations of molecules. They are found for certain spherical low molar mass molecules packed in cubic lattices (i.e., they are isotropic). The absence of strong attractive forces between molecules and the presence of slip planes lead to easy deformabilities of plastic crystals, sometimes even under their own weight. No polymers are known that form plastic crystals.

Condis crystals are *con*formationally *dis*ordered crystals containing several conformational isomers in more or less ideal crystalline positions with respect to position and orientation of segments (conformational isomorphs). An example is the hexagonal high-pressure phase of polyethylene extended-chain crystals. It is often difficult to determine whether polymer crystals are normal or condis crystals.

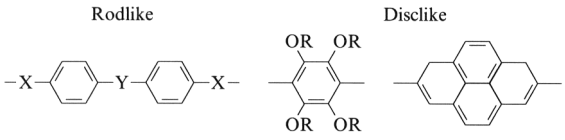
On cooling, thermotropic liquid crystals either crystallize or solidify to "mesomorphic glasses" with retention of their liquid crystal structures. These glasses do not carry special names, but since "liquid crystalline glass" and similar names are oxymorons, the terms "LC glass," "PC glass," and "CD glass" have been suggested for the three classes of mesomorphic materials. The LCPs are used mainly as LC glasses not as liquid crystals per se, except in processing.

Condensed matter can thus exist in several of the five possible classes of pure phases: Completely ordered crystal oC, mesomorphic glass mG, amorphous glass aG, ordered mesophase oM, and isotropic melt (liquid) iL. Seven types of biphasic materials exist: oC + mG, oC + aG, oC + oM, oC + iL, mG + aG, mG + iL, oM + iL, and three types of triphasic materials: oC + mG + aG, oC + mG + iL, oC + oM + iL. Because each class can be subdivided further, many physical structures (and thus properties) are possible for the same polymer.

Mesophasic polymers are characterized by domains of microscopic size (see below). "Microdomains" of similar size are also exhibited by certain block copolymers and, in much smaller sizes, by ionomers.

5.3.2. Types of Liquid Crystals

Liquid crystals and LC glasses are generated by rod- or disclike mesogens, which either comprise the whole molecule (as in low molar mass LCs) or sections of it (LCPs). Examples are



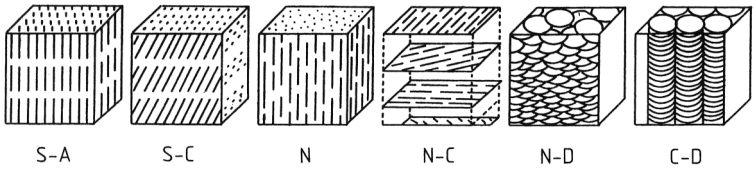


Figure 30. Schematic representation of mesogens in different types of mesophases
S = smectic (types A and C); N = nematic; N−C = nematic cholesteric; C−D = columnar discotic; N−D = nematic discotic
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where X = O, OOC, COO, etc.; Y = COO, *p*-C_6H_4, CH=CH, N=N, etc.; R = CO $(CH_2)_nCH_3$, etc.; and phenylene residues may be replaced by 1,4-cyclohexane rings. The lengths of polymer mesogens are often comparable to those of repeating units; they seem to be identical with respect to persistence lengths.

Rodlike mesogens are also called calamitic (Greek: *calamos* = reed) and disclike ones discotic. Calamitic liquid crystals are further subdivided into smectic, nematic, and cholesteric mesophases. Smectic LCs show fan-shaped structures under the polarization microscope; they feel like soaps (Greek: *smegma* = soap). Nematic LCs form threadlike schlieren (Greek: *nema* = thread). Cholesteric LCs exhibit beautiful reflective colors, which were first discovered with cholesterol.

The birefringence of LCs originates from the anisotropy of mesogens, which are more or less aligned in microscopic domains with diameters in the micrometer range. These alignments lead to different refractive indices parallel and perpendicular to the direction of polarization of incident light. The domains themselves are arranged randomly. The presence of birefringence however is not proof for the existence of mesogens; it may also result from higher-melting crystallites in partially molten polymers or from crystallites in partially molten polymers or from crystallites in gels or concentrated solutions.

Liquid crystals are turbid because their domains are anisotropic structures whose dimensions are greater than the wavelength of incident light. At a certain "clearing temperature," these domains melt to a transparent (isotropic) liquid.

The soaplike character of *smectic LCs* is due to two-dimensional, layerlike arrangements of mesogens (Fig. 30). At present, twelve different smectic types are known: Four with the average direction of the long axes perpendicular to layer planes and seven with tilted axes. Examples are type S-A with mesogens perpendicular to the layer planes; type S-B, the same but with perfect hexagonal packing of mesogens; type S-C, with mesogen axes at an angle to the planes, etc.

Nematic mesophases (Fig. 30, N) are one-dimensionally ordered. The principal axes of mesogens are more or less parallel to each other; the centers of mass are however distributed at random.

Cholesteric mesophases (Fig. 30, N−C) are observed only with chiral mesogens. They consist of layers of nematically ordered mesogens. These layers have a sense of rotation relative to each other due to the presence of chirality centers in mesogens. Cholesteric mesophases are thus screwlike nematics.

Discotic mesophases may exist in many different structures. The disclike mesogens are randomly arranged in nematic-discotic types (Fig. 30, N−D) but stacked like coins in columnar-discotic ones (Fig. 30, C−D).

5.3.3. Mesogens

Mesogens of polymers can be contained in main chains (MC-LCPs) or in side chains (SC-LCPs). Thermotropic MC-LCP glasses are used as engineering plastics; lyotropic MC-LCP glasses, for fibers. Thermotropic SC-LCPs are not used commercially at present but may find use in optical recording devices.

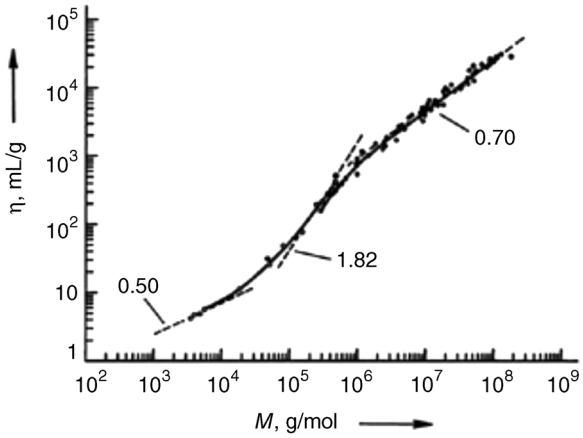


Figure 31. Molar mass dependence of intrinsic viscosities of wormlike chains
(○) Helices of poly(γ-benzyl-L-glutamate) (PLBG) in *N,N*-dimethylformamide at 25°C; (●) double helices of deoxyribonucleic acids in dilute aqueous NaCl solutions at 20°C. The two polymers are comparable because the helix diameters are similar (1.5 nm for PLBG, 2.0 nm for DNA). Numbers indicate exponents a in Equation (1)
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Mesogens usually constitute the whole molecule in low molar mass LC molecules. In macromolecules, this is true only for dissolved helices up to certain molar masses. Such helicogenic macromolecules are rigid rods at small molar masses but become coillike at very high degrees of polymerization (cf. the behavior of short and very long garden hoses). This behavior is demonstrated by the molar mass dependence of their intrinsic viscosities, which are measures of the molecule volume per unit mass (Fig. 31). Rodlike molecules are characterized by their axial ratio (aspect ratio) Λ (length/diameter).

All other polymer chains form either flexible or semiflexible coils in dilute solution or in their isotropic melts (see examples in Fig. 32). Semiflexible (wormlike) chains SF allow rotations around some of their chain bonds. The rodlike character of their segments is however preserved in melts or concentrated solutions if the chain axes remain linear or if the segment linearity can be restored by a crankshaft motion. Conjugated bond structures are helpful but not necessarily required for mesogens since, for example, 1,4-phenylene rings may be replaced by 1,4-cyclohexylene units.

Linear chain axes are present in poly(*p*-phenylene) (PPP) or poly(*p*-phenylene benzoxazole) (PBO). Crankshaft motions around the chain axes are possible in the conjugated chains of poly(*p*-phenylene vinylene) (PPV), the partially conjugated chains of poly (*p*-hydroxybenzoic acid) (PHB), and even in the nonconjugated poly(*p*-phenylene alkylenes) as long as even numbers of methylene groups are present between phenylene rings as in poly(*p*-phenylene ethylene). Semiflexible molecules are characterized by their persistence lengths a or their Kuhn lengths $L_K = 2\ a$.

Rodlike molecules and semiflexible molecules with long persistence lengths form many physical bonds between parallel chains. The total energy of such assemblies is so high that individual intramolecular chemical bonds rather than all of the physical bonds are broken upon heating: These molecules decompose instead of producing thermotropic mesophases. They may however form lyotropic mesophases in suitable solvents. An example is poly (*p*-phenylene bisbenzoxazole).

The "stiffness" of the chain segments can be removed or reduced by several means (Fig. 33). Bulky substituents prevent the parallelization of chains; they "frustrate" crystallization. Nonlinear chain elements (such as *ortho* and *meta* substituents) work in the same way. Flexible chain segments reduce the persistence lengths of the chains.

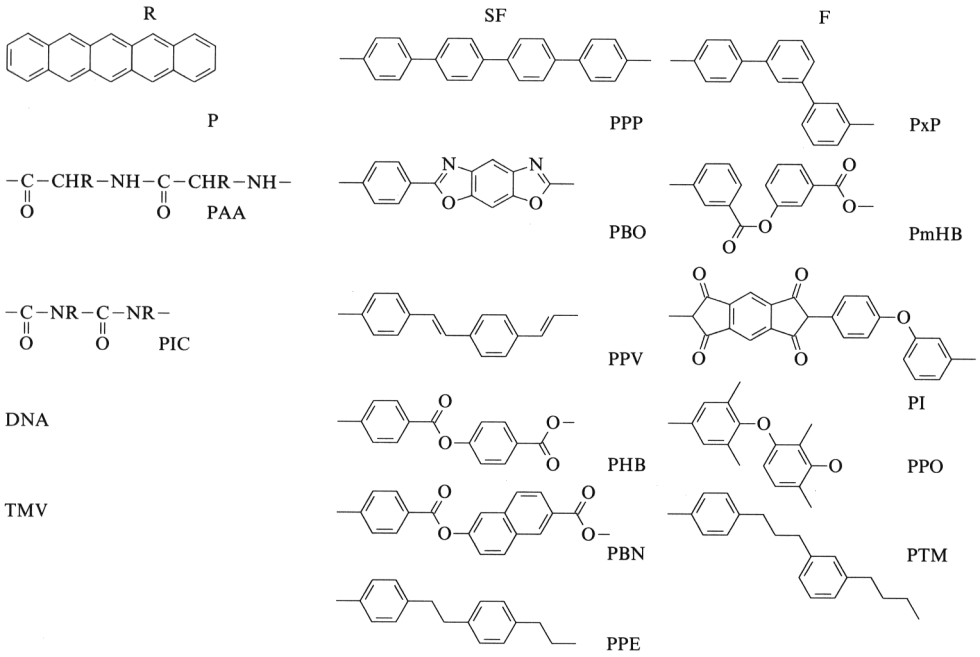


Figure 32. Examples of rodlike (R), wormlike or semiflexible (SF), and flexible (F) molecules and segments. See text for further explanation.
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5.3.4. Lyotropic Liquid-Crystalline Polymers

Molecule axes of low molar mass rodlike molecules are disordered in isotropic melts, whereas mesogen axes are more or less parallel to each other in nematic and smectic mesophases. Very short rods resemble spheroids. They can arrange themselves in various stable ways, but the parallel ordering need not be much more stable than other arrangements. Therefore, a critical axial ratio exists above which the simple geometric anisotropy is sufficient to stabilize a mesophase.

This critical axial ratio has been calculated with the lattice theory of polymer solutions as $\Lambda_{crit} \approx 6.42$. A geometric stabilization by

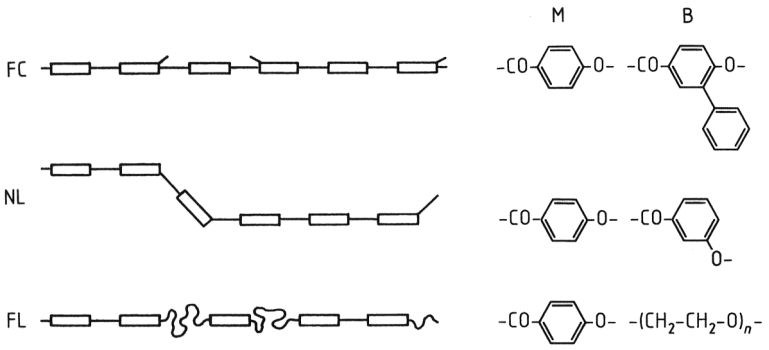


Figure 33. Flexibilization of rigid chain segments by frustrated crystallization (FC), nonlinear chains (NL), or flexible chain elements (FL); M = mesogen-forming monomeric units; B = stiffness-breaking units
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repulsion is insufficient for $\Lambda < \Lambda_{crit}$ and the mesogens must exert additional orientation-dependent attractive forces.

In solution, repulsive forces between mesogens can act only at sufficiently high mesogen concentrations. At a critical volume fraction, Φ_p^* phase separation occurs into a polymer-rich mesophase and a dilute isotropic phase. The dependence of Φ_p^* on Λ can be described to a first approximation by [122]

$$\Phi_p^* \approx 8(1 - 2L^{-1})/L \quad (18)$$

The axial ratio Λ is the molar mass-dependent true axial ratio of rodlike molecules (i.e., helices) and the molar mass-independent Kuhn length of semiflexible molecules. Equation (18) is remarkably well fulfilled for both helical and semiflexible molecules (Fig. 34). An exception is the tobacco mosaic virus, probably because of additional charge effects that are not considered by the theory.

Lyotropic mesophases are formed by the helices of tobacco mosaic virus ($c > 2\%$) and deoxyribonucleic acids ($c > 6\%$) in dilute aqueous salt solutions as well as by poly(α-amino acids) in helicogenic solvents, e.g., poly(γ-methyl L-glutamate) in dichloromethane–ethyl acetate (12 : 5) ($c > 15\%$).

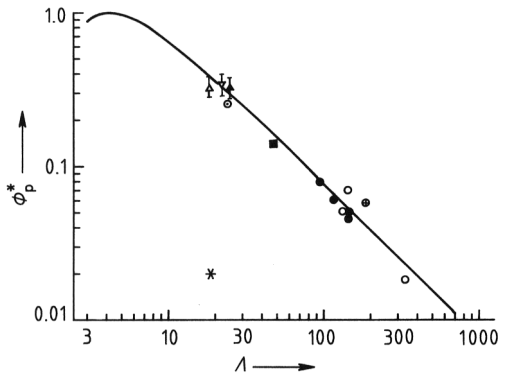


Figure 34. Critical volume fractions ϕ_p^* for phase separations of isotropic solution → nematic mesophase as function of Λ [i.e., the axial ratio of helical (rigid) molecules (circles) and the Kuhn length of semiflexible molecules (triangles, square)]
∗Tobacco mosaic virus; solid line: prediction of Equation (18)
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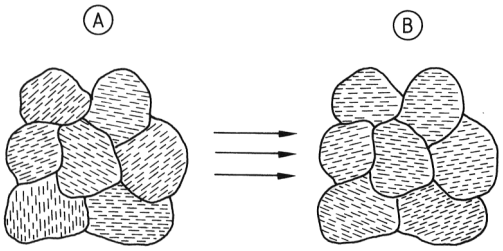
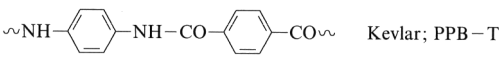


Figure 35. Alignment of mesogen axes upon shearing
A) Mesophase domains in liquid crystalline state at rest; B) During shearing or as LC glass with "frozen in sheared state"

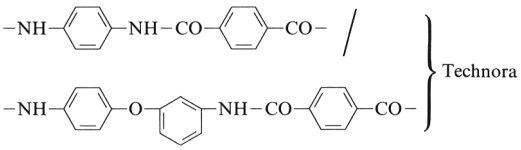
Hydroxypropyl cellulose (HPC) forms a cholesteric mesophase at room temperature in water at $w_{HPC} > 0.41$.

On shearing, mesophase domains become oriented with respect to the mesogen axes (Fig. 35). This alignment becomes frozen-in on rapid quenching of thermotropic LCs or by precipitation of lyotropic ones into baths (half-lifes of orientation between a few seconds and a few hundredths seconds). The resulting LC glasses possess good orientations of mesogen axes in the shear direction (e.g., fiber direction), high tensile strengths, and low extensibilities.

A number of LC fibers are produced commercially. Poly(*p*-phenylene terephthalamide) (PPB−T) was originally spun from concentrated sulfuric acid solutions, whereas chlorinated *N*-methyl pyrrolidine is now used:

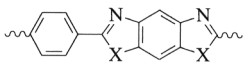


A similar copolyamide is also on the market



Even better LC fibers are produced from poly(*p*-phenylene-2,6-benzoxazoles) and poly(*p*-phenylene-2,6-benzthiazoles) (PBT), which

are spun from poly(phosphoric acid) solutions, at present on a bench scale. Both "*cis*" (shown) and "*trans*" (X and N exchanged at one ring) structures are known:

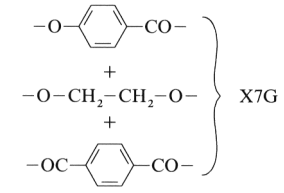


PBO (X = O); PBT (X = S)

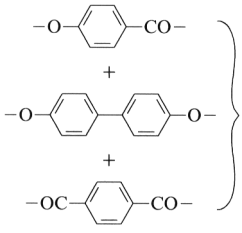
5.3.5. Thermotropic Liquid Crystal Polymers

Non-Newtonian shear viscosities of liquid crystal polymers drop drastically with increasing shear rates due to the orientation of mesogen axes upon shearing. Less energy is thus needed for processing thermotropic LCPs than isotropic thermoplastics. The high orientation times permit a freezing-in of the mesogen orientation in injection molding, for example. Because of the higher than usual moduli of elasticity and tensile strengths, such LCPs are also called *self-reinforcing polymers*.

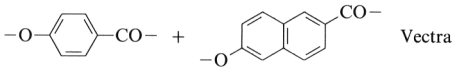
The first self-reinforcing polymer was the copolyester X7 G with 60 mol% *p*-hydroxybenzoyl and 40 mol% terephthaloyl glycol units. It is no longer produced because the less expensive glass-fiber-reinforced saturated polyesters possess similar properties. Xydar and Vectra are, however, industrially produced:



X7G



Xydar



Vectra

Polymeric side-chain LCs can serve for the thermooptical storage of information. A guided laser beam increases the temperature locally, whereupon phase transformations occur. The change of order can then be frozen-in on cooling below the glass transition temperature. The resolution is ca. 0.3 μm.

5.3.6. Block Copolymers [101]

Block copolymers consist of two and more blocks of constitutionally or configurationally different monomeric units (e.g., A_n-B_m, $A_n-B_m-A_n$). In most cases these blocks are thermodynamically or kinetically immiscible because their homopolymers A_n, B_m, etc., are not miscible. The demixing of block copolymers cannot proceed, however, to macroscopic phase separations because the blocks are chemically coupled. Similar blocks of different block copolymer molecules can thus only aggregate and form domains in a matrix of the other blocks. This phenomenon is called microphase separation.

Three different applications of block copolymers are known: Polymeric detergents, thermoplastic elastomers, and compatibilizers for blends. Polymeric detergents consist of hydrophilic and hydrophobic blocks. Examples are the multiblock copolymers from watersoluble ethylene oxide blocks $[-(OCH_2CH_2)_n-]$ and water-insoluble propene oxide blocks $-[OCH_2CH(CH_3)]_n-$. The hydrophobic blocks associate in water, which produces high viscosities.

A similar action is exerted by *compatibilizers* for nonmiscible blends of A_n and B_m polymers. These polymers are A_p-B_q diblock copolymers: The A_p block resides in the A_n phases and the B_q block in the B_m ones. Compatibilizers thus anchor the two types of phases (Fig. 36).

Thermoplastic elastomers [123] consist of tri- or multiblock copolymers. Triblock copolymers $S_n-B_m-S_n$ possess a soft center polybutadiene block$-B_m-$(glass transition temperature below use temperature) and two hard end polystyrene blocks S_n-(glass transition temperature above use temperature). Below certain *m/n* ratios, styrene blocks form spherical microdomains in a continuous matrix of

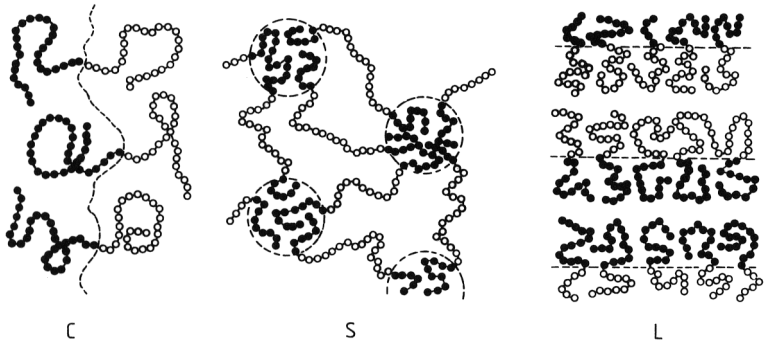


Figure 36. Arrangement of A_n blocks (with A units •) and B_m blocks (with B units ○) in diblock (C, L) and triblock copolymers (S)
C: compatibilizers at an interface - - -; S: spherical A_n domains in continuous matrix B_m; L: lamellae of A_n and B_m

butadiene blocks. These spherical domains thus act as cross-linking units in an elastomer (Fig. 36, S). The hard domains "melt" above their glass transition temperatures, and the block copolymers can then be processed like thermoplastics.

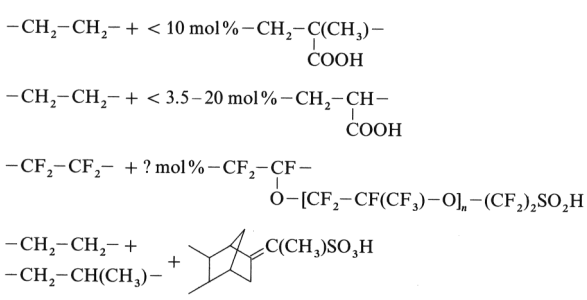
The morphology of *diblock copolymers* is governed mainly by the relative spatial requirements of the blocks. Both blocks, if independent, would form unperturbed random coils. If the unperturbed volumes of both blocks are of equal size, all A_n blocks would line up in one layer and all B_m blocks in another because the blocks are (1) coupled to each other and (2) incompatible. The A_n layer faces another A_n layer, where the A_n blocks are coupled to B_m blocks, etc. (Fig. 36, L). The diblock polymers thus form lamellae with a thickness of two coil diameters. Similar structures result for triblock polymers $A_r-B_m-A_r$, where $r = n/2$.

If the volume of the A_n blocks is much lower than the volume of the B_m blocks, then the A_n blocks can no longer be packed into layers without violating the demand for tightest packing or deviating from the shape of unperturbed coils. Both possibilities are energetically unfavorable, and the smaller A_n blocks thus cluster together and form spherical domains in a continuous matrix of the larger B_m blocks. If the A_n blocks are somewhat larger (but not big enough to form lamellae), then cylinders would result (Fig. 37).

A great number of thermoplastic elastomers of both the triblock and the multiblock type is known [70]. Their chemical structures range from $(styrene)_n-(butadiene)_m-(styrene)_n$ triblock copolymers to polyether–urethane multiblock polymers, ethylene–propene copolymer–polyolefin blends, polyether–esters, and graft copolymers of butyl rubber on poly- ethylenes.

5.3.7. Ionomers

Ionomers are copolymers from primarily hydrophobic monomers with small amounts of ionic comonomers. The ionic groups may be in the main chain or in substituents. Four different types of ionomers are produced commercially.



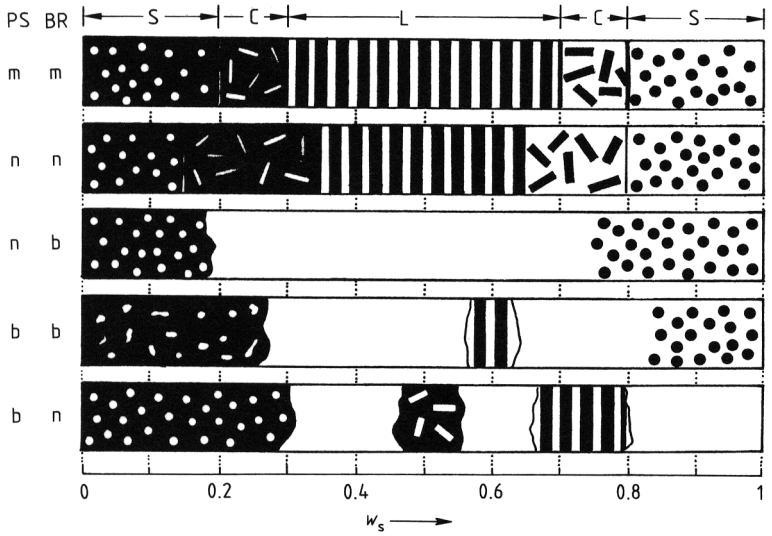


Figure 37. Morphology of styrene–butadiene diblock copolymers as a function of the mass fraction of the styrene units. White: polystyrene blocks (PS); black: polybutadiene blocks (BR). The block length distribution may be (m) molecularly homogeneous (theory), (n) narrow, or (b) broad
S = Spherical domains, C = cylinders (rods), L = lamellae (layers). Upper row: Predictions of Meier theory; rows 2–5: schematic after experimental results of many authors
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Surlyn, EEA, and Nafion are synthesized by direct copolymerization of the corresponding monomers. Thionic results from the postpolymerization sulfonation (< 5%) of the diene units (usually 5-ethylidene-2-norbornene) of the primary ethylene–propene–diene (EPDM) rubber. Both EEA and Nafion are used as acids, whereas Surlyn and Thionic are obtained by aftertreatment that leads to sodium or zinc salts.

The introduction of ionic groups into hydrophobic polymers leads to ion associations and subsequently to microphase separations. The ion association is controlled by the coordination number of the ions; that is, sodium ions with valence 1 and coordination number 6 are as good cross-linkers as zinc ions with valence 2. Cross-linking by ions does not occur via ion pairs but via clusters and domains of many ions. These ionic bonds dissociate at higher temperature, and the ionomers can then be processed like thermoplastics. At lower temperature, they behave either as thermoplastic elastomers (T_G of polymer segments lower than use temperature) or as "reversible" thermosets (T_G of segments higher than use temperature).

5.4. Gels

Chemically lightly cross-linked polymers swell upon addition of solvent to form gels. The maximum degree of swelling results from the attempt of segments located between cross-linking sites to attain their energetically most favored coil dimensions which in turn is counteracted by the elastic retraction due to cross-links. Physically cross-linked polymers behave in the same way if the physical cross-links (crystallites, ion clusters, etc.) survive the dissolution process.

The latter phenomenon is utilized in poly(vinyl chloride) pastes. The strong dipole–dipole interactions between C−Cl bonds leads to associations of chain segments which at room temperature resist dissolution by plasticizers such as phthalates, adipates, sebacates, or citrates. Heating of PVC with these plasticizers and subsequent cooling leads to gelation by formation of a lightly physically cross-linked network. Plasticized PVC thus behaves like an elastomeric material. The physical cross-links dissociate at higher temperature, and the resulting PVC

paste can be processed with extruders or roll mills.

5.5. Polymer Surfaces [124]

5.5.1. Structure

Outer layers of solid or liquid polymers do not exhibit, in contrast to air, water, metal surfaces, etc., the same average composition as the interiors of these polymers. Groups or segments with the lowest Gibbs interfacial energy will reside preferentially at the surface or interface. Surface structures may also be altered by chemical attack during processing or on prolonged use (e.g., by oxidation) or by physical processes such as transcrystallization.

This behavior can be studied by a wide variety of new spectroscopic methods, for example, the concentration of immediate surface groups by Fourier transform infrared spectroscopy (FT-IR); the composition of the upper 0.3–0.5 nm layer by ion scattering spectroscopy (ISS, LEIS); of the upper 1–10 nm by photoelectron spectroscopy [UPS, PE (S)], electron spectroscopy for chemical analysis (ESCA, XPES, XPS, IEE), and Auger spectroscopy (AES).

These methods have shown that poly-(2-vinylpyridine) and poly(4-vinylpyridine) have much more hydrophobic surfaces than their chemical structure indicates: CH_2- and CH-groups face the surface; pyridine residues (C_5H_4N), the interior. Imide–carbonyl residues of polyimides, on the other hand, are preferentially found at the surface and aromatic rings in the interior. The surface is enriched by siloxane residues in polycarbonate–polydimethylsiloxane block copolymers but by styrene units in polystyrene–poly(ethylene oxide) block copolymers. Because the surface energy depends on the contact (air, water, metals, etc.) and also on kinetic effects (thermal history, solvents, etc.), one and the same polymer may possess various surface compositions and thus also surface properties.

5.5.2. Interfacial Tension

Interfacial tension is the force that acts at the interface between two phases; it is called surface tension for the interface condensed phase–gas phase.

Surface tensions γ_{lv} of liquid polymers against air decrease with the two-third power of the molar mass according to

$$\gamma_{lv} = \gamma_{lv}^{\infty} + K_e \times M^{-2/3}$$

They do not vary markedly with temperature. Typical values (at 150 °C) range from 13.6 mN/m (polydimethylsiloxane), 22.1 mN/m (it-polypropylene), 28.1 mN/m (polyethylene), and 33.0 mN/m poly(ethylene oxide). At present, no correlation of these surface tensions with chemical constitution is possible because the surface structures of liquid polymers are unknown.

Interfacial tensions between two liquid polymers are always lower than surface tensions. They are low for two apolar polymers but higher if one polymer or both of them are polar. For example, the interfacial tension of polyethylene–it-polypropylene is only 1.1 mN/m, but that of polyethylene–poly(ethylene oxide) is 9.5 mN/m and poly(ethylene oxide)—polydimethylsiloxane 9.8 mN/m.

The interfacial tensions between solid polymer and air are generally unknown. They do not differ markedly, however, from the critical surface tensions determined by the *Zisman method*. In this method, the liquid–air surface tensions of various liquids are plotted against the cosine of contact angles θ of these liquids against air and extrapolated to $\cos\theta \rightarrow 0$. The resulting "critical" surface tensions of polymers are always lower than the surface tension of water: Polytetrafluoroethylene, 18.5; polyethylene, 33; poly(vinyl alcohol), 37; polyamide 66, 46; and urea–formaldehyde resins, 61 mN/m. Fluorinated polymers have especially low critical surface tensions. They are not wetted by water (72 mN/m) or oils and fats (20–30 mN/m) and are therefore used as surface coatings to prevent sticking.

5.5.3. Adsorption

Macromolecules possess many adsorbable groups and segments. The type of adsorption depends on the adsorption energy per segment (group), the concentration of adsorbable

macromolecules, and the duration of the experiment.

"Adsorption equilibria" are established in minutes to hours at smooth surfaces but may take days to attain at rough surfaces or powders. The adsorption time increases with the concentration and molar mass of the polymer.

Polymer coils tend to overlap even in fairly dilute solutions: The adsorbed polymer layers are almost always multilayers, except for the adsorption of oligomers ($X < 10$–100) or from very dilute solutions (volume fractions $< 10^{-4}$–10^{-3}). At higher concentrations or molar masses, adsorbed amounts and structures of polymer layers are mainly kinetically controlled. Reorganization may occur with time; for example, the adsorption of polar polymers at polar surfaces can change from an initial loose loop structure to a more compact, flat covering. The layer of poly(ethylene oxide) adsorbed on chromium surfaces is only ca. 2 nm thick and so tightly packed that the refractive index of the adsorbed layer is identical with that of the crystalline polymer. The thickness of the surface layer of polystyrene of $M = 176\ 000$ g/mol adsorbed from a 5 mg/mL solution in the thermodynamically bad solvent cyclohexane is however about 27 nm (i.e., identical with the end-to-end distance in the unperturbed state). The physical structures of adsorbed polymers obviously play an important, yet widely unknown, role in many technological applications of polymers.

6. Thermal Properties [116]

6.1. Molecular Motion

6.1.1. Thermal Expansion

Isotropic bodies expand upon heating equally in all three spatial directions because of the increasing thermal motions of atoms, groups, and molecules. The expansion is characterized by the cubic expansion coefficient $\beta = V^{-1} (\partial V/\partial T)_p$, which is usually converted by $\beta = 3\ \alpha$ into the linear expansion coefficient $\alpha = L^{-1} (\vartheta L/\vartheta T)_p$. Such isotropic materials are, for example, diamond ($\alpha = 1.06 \times 10^{-6}\ K^{-1}$), iron ($12 \times 10^{-6}\ K^{-1}$), water ($70 \times 10^{-6}\ K^{-1}$), and carbon disulfide ($380 \times 10^{-6}\ K^{-1}$) (all data at 25°C). All of these materials exhibit the same types of bonds in the three directions: All covalent bonds between carbon atoms in diamond, all metallic bonds between iron atoms, all hydrogen bonds between water molecules, and all dispersion forces between CS_2 molecules.

Polymer chains are, however, anisotropic: The intramolecular bonds along the chain are chemical (almost always covalent); the intermolecular bonds perpendicular to the chain, physical (dispersion forces, dipole–dipole interactions). On thermal expansion of polymer crystals, chains contract because of the increasing amplitude of the lateral motions. The thermal expansion coefficient in the chain direction is thus zero to negative, whereas the overall expansion coefficient is positive. The linear thermal expansion coefficients of polymers are thus averages over the three spatial directions; they lie between those of metals and liquids. Typical values are $\alpha = 60 \times 10^{-6}\ K^{-1}$ (polyamide 6) and $80 \times 10^{-6}\ K^{-1}$ [poly(vinyl chloride)].

Significant problems may thus arise due to different expansion coefficients for polymer −metal composites upon thermal stress. Another problem is the low dimensional stability of polymers on temperature change. This problem may be aggravated by a concomitant change of the water content of polymers or by recrystallization phenomena, both of which can lead to warping.

6.1.2. Heat Capacity

The molar heat capacity can be 3 R per atom according to the law of equal distribution of energy. In reality, degrees of freedom are always frozen in and the molar heat capacity is lowered. Empirically, a value of ca. 1 R has been found for solid polymers at room temperature. Poly(2,6-dimethylphenylene oxide) $[(C_8H_8O)_n]$ at 25°C has a specific heat capacity of 1.22 J K^{-1} g^{-1} and a molar heat capacity (per monomeric unit) of 146.4 J $K^{-1}mol^{-1}$. The molar heat capacity (per mole of atoms) is thus 146.4 J $K^{-1}mol^{-1}/17 = 8.61$ J $K^{-1}mol^{-1}$ (i.e., approximately 1 $R = 8.314$ J K^{-1} mol^{-1}).

Below the glass transition temperature T_G, heat capacities are not influenced by the degree

of crystallinity of the polymer. At T_G, a stepwise increase is observed. The heat capacity passes through a maximum a few degrees below the macroscopic melting temperature; that is, the true melting temperature is given by the upper end of the melting range where the largest and most perfect crystals melt.

6.1.3. Heat Conductivity

Conventional polymers are electrical insulators. Heat is thus not transported by electrons but by elastic waves (phonones in the corpuscular model). The free path length of phonones is defined as the distance at which the intensity of elastic waves has decreased to 1/e. This free path length is about 0.7 nm for glasses, amorphous polymers, and liquids; it is practically independent of temperature. The slight decrease of heat conductivities (thermal conductivities) of amorphous plastics and elastomers below their glass transition temperatures must thus be caused by the decrease of heat capacities with decreasing temperature. For crystalline polymers, a strong decrease of heat capacities is observed at their melting points because packing densities decline drastically at these temperatures.

6.2. Thermal Transitions and Relaxations

6.2.1. Overview

Thermal transitions and relaxations are characterized by large changes of physical properties at the corresponding temperatures. In a true thermal transition, chemical compounds are in equilibrium on both sides of the transition temperature. An example is the melting transition.

Thermal relaxations, on the other hand, are kinetic effects. They depend on the frequency of the experimental method and thus on the time scale. Typical thermal relaxations are caused by the onset of translations and rotations of charges, dipoles, and chemical groups (i.e., by atomic motions).

Some experimental methods work at frequencies that such relaxations appear to be thermal transitions. The best-known example is the glass transition temperature at which hard, glassy polymers convert to soft, rubbery materials and vice versa. In many cases, a thermal effect cannot be unambiguously classified as either transition or relaxation.

Thermal transitions and relaxations can be detected and determined by many different experimental methods. The most commonly applied methods for the determination of *thermal transitions* are differential thermoanalysis (measures temperature differences between specimen and standard on heating or cooling with constant rate), differential scanning calorimetry (does the same for enthalpy differences), thermomechanical analysis (deformation of specimen under load), dynamical–mechanical analysis (either free or forced vibration of specimen), and torsional braid analysis (specimen on vibrating support). Figure 38 shows a typical thermogram.

Many methods are available for the study of molecular motions and thus *thermal relaxations*. These methods work with frequencies ν that correspond to correlation times t_c of 10^{-12} s $< 1/\nu < 10^6$ s (11.5 d). Typical methods include quasi-elastic neutron scattering ($10^{-12} < t_c/s < 10^{-8}$), NMR spin-lattice relaxation ($10^{-12} < t_c/s < 10^{-5}$), dielectric relaxation ($10^{-10} < t_c/s < 10^{-5}$), and photon correlation spectroscopy ($10^{-4} < t_c/s < 10^2$). Thermal relaxations furthermore manifest themselves in sudden changes of mechanical properties, such as rebound elasticity ($t_c/s \approx 10^{-5}$), penetrometry ($t_c/s \approx 10^2$), mechanical loss ($10^3 < t_c/s < 10^7$), and thermal expansion ($t_c/s \approx 10^4$). Slow methods (high t_c) are called "static" methods; fast ones, "dynamic." Transition–relaxation phenomena are also detected by several empirical, standardized methods that measure the resistance of specimens against flow under various loads (Vicat temperature, heat distortion temperature, Martens temperature, etc.).

Various characteristic signals are observed at a fixed temperature for a given frequency (see insert in Fig. 39). They often cannot be correlated with molecular processes and are commonly indicated with descending temperature by letters in the sequence of the Greek alphabet, starting with the melting temperature

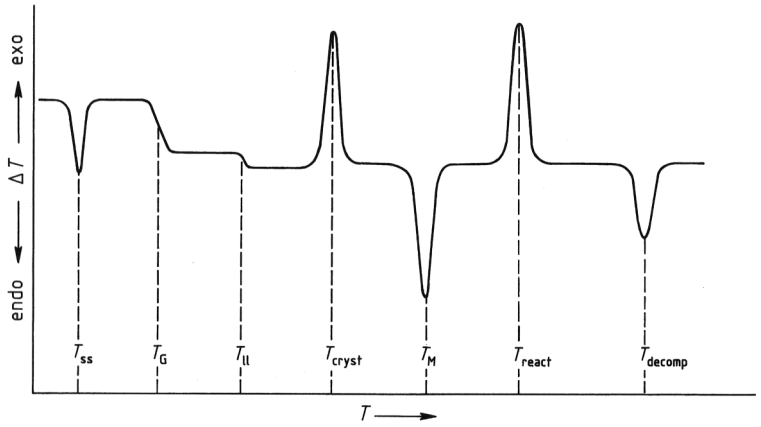


Figure 38. Idealized thermogram of a partially crystalline polymer with solid–solid transition T_{ss}, glass transition temperature T_G, liquid–liquid transition T_{ll}, maximum crystallization temperature T_{cryst}, melting temperature T_M, maximum temperature T_{react} of a chemical transformation, and maximum temperature T_{decomp} of chemical degradation
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(crystalline polymers, subscript c) or glass transition temperature (amorphous polymers, subscript a).

The various methods work at different frequencies and thus give different relaxation temperatures for the same molecular process. The frequency dependence of relaxation temperatures can be described by the Eyring equation for rate processes:

$$\nu = (k_B T/2\pi h) \exp(-\Delta H^{\neq}/RT) \exp(\Delta S^{\neq}/R) \quad (19)$$

where k_B is the Boltzmann constant, h the Planck constant, $\Delta H^{\neq}$ the activation enthalpy,

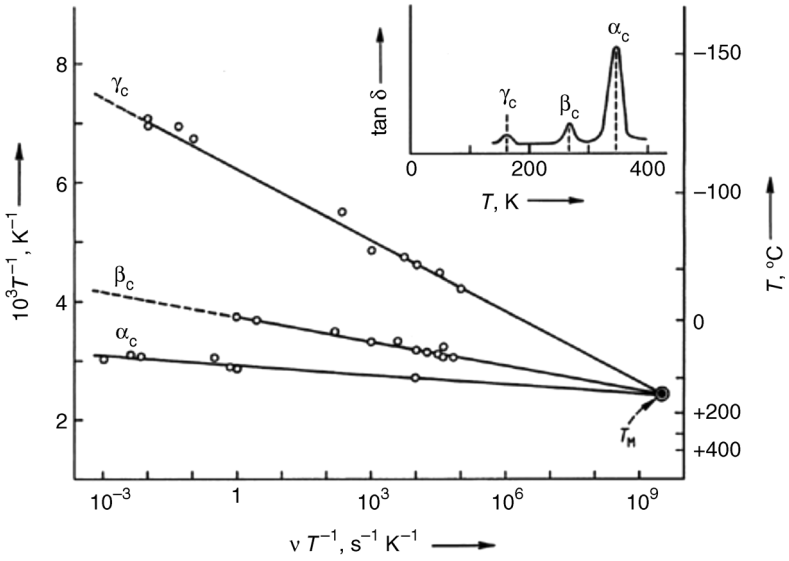


Figure 39. Dependence of inverse relaxation temperature $1/T$ on the logarithm of reduced frequency ν/T for various relaxation processes of a low-density polyethylene
Insert shows the mechanical relaxation spectrum at ν = 1 000 Hz.
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and $\Delta S^{\neq}$ the activation entropy. Transformation of Equation (19) leads to

$$\frac{1}{T} = \frac{R}{\Delta H^{\neq}} \cdot \left[\left(\frac{\Delta S^{\neq}}{R} + \ln \frac{k_B}{2\pi h} \right) - \ln \frac{\nu}{T} \right]$$

In a $(1/T) = f[\ln(\nu/T)]$ plot, lines for various processes intersect at the melting temperature ($T_M = 131$ °C in Fig. 39). Such common intersects seem to be general for nonhelical polymers.

6.2.2. Crystallization

The crystallization of coillike polymers from dilute solutions leads to platelets in which folded polymer chains are arranged with their stems perpendicular to the fold surface (Fig. 26). From concentrated solutions and melts at rest, lamellae are organized into spherulites (Fig. 28), which may be transformed to row structures by shearing or drawing (Fig. 40B).

Crystallization can be subdivided into two elementary processes: Primary nucleation and crystal growth (secondary nucleation). Both processes determine the crystallization rates, which depend strongly on both temperature and polymer structure. At 30 K below the melt temperature, the linear crystallization rate may, for example, range between 5000 μm/min for polyethylene and 0.01 μm/min for poly(vinyl chloride). Symmetrically structured polymers usually crystallize rapidly; polymers with bulky groups or low tacticities, only slowly. Quenching of poly(ethylene terephthalate) melts leads, for example, to amorphous polymers, whereas quenching of polyethylene melts never gives amorphous polymers, even if liquid nitrogen is used.

Primary nucleation may be homogeneous (spontaneous, sporadic, thermal) or heterogeneous (simultaneous, athermal). Homogeneous nuclei are formed from segments of the crystallizing polymer molecules; they are very rare. Heterogeneous nuclei result from extraneous materials such as additives, dust particles, container walls, or specially added nucleation agents. Such nuclei must have minimum sizes of 2–10 nm. Their concentrations can range from ca. 1 nucleus per cubic centimeter (polyoxyethylene) to ca. 10^{12} nuclei per cubic centimeter (polyethylene).

Above the melting temperature, fragments of crystallites may survive for certain time periods. These fragments act as athermal primary nucleation agents on subsequent cooling. They are responsible for the "memory effect" (i.e., the

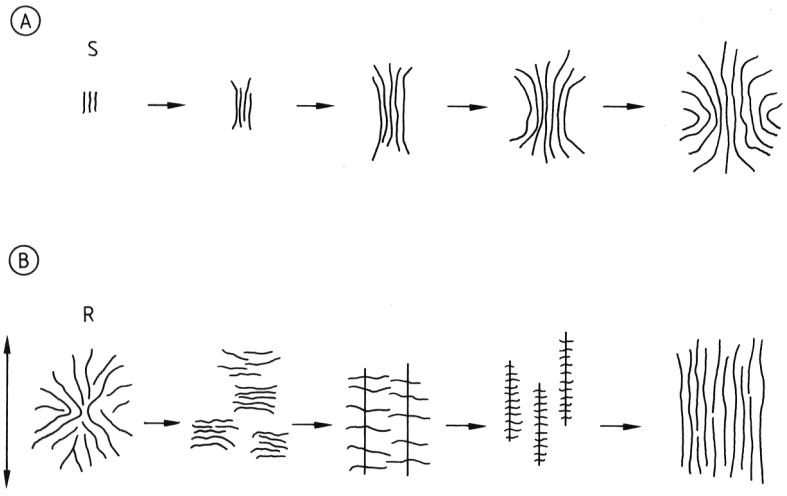


Figure 40. A) Formation of spherulites from lamellae on crystallization of melts at rest; B) Transformation of spherulites into row structures by shearing or drawing in ↕ direction.
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reappearance of spherulites at the same locations after and before the melting), which occurs because of low diffusion rates at very high melt viscosities.

Growth of primary nuclei occurs by a *secondary nucleation process*. The growth rate is low just below the melting temperature because secondary nuclei are formed and dissolved rapidly. About 50 K below the glass transition temperature, on the other hand, motions of molecule segments are practically zero and the crystal growth rate is therefore low as well. Crystallization rates must thus exhibit a maximum between the melting and glass transition temperatures; the maximum crystallization rates are usually at (0.80–0.87) T_M (in kelvin).

In addition, the entire crystallization process can be subdivided into a primary and a secondary phase. The *primary phase* comprise the conversion of the total volume to a solid. At the end of this phase, the volume may be filled (e.g., with spherulites), but not all polymer segments between spherulites or between the lamellae of the spherulites may have crystallized. The polymer has not attained its maximal crystallinity (the crystallizability). Crystallization may thus continue during the *second phase*. In this after-crystallization, lamellae may thicken, lattices become more perfect, etc.

Primary crystallization can be characterized by the Avrami equation:

$$\phi/\phi_\infty = 1 - \exp(-z \cdot t^n)$$

where ϕ = fraction of crystallized volume, ϕ_∞ = fraction of maximal attainable crystallinity for a given entity (e.g., spherulite), and z and n are constants that depend on both the nature of the nucleation process (homogeneous, heterogeneous) and the type of growing entity (rod, disk, sphere, sheaflet, etc.). The exponents n range between 1 and 7; empirically, they may assume fractional values.

6.2.3. Melting

Melting is defined as the thermal transition of a crystal to an isotropic melt. The melting temperature T_M (fusion temperature) is defined as the temperature at which crystallites are in equilibrium with the melt. Melting starts at the corners and edges of crystal surfaces; in contrast to crystallization, no nuclei are needed.

Segments of about 60–100 chain atoms participate in the melting process. During heating, segments are redistributed continuously between crystalline and noncrystalline regions; a melting range exists and no sharp melting point is observed. The melting temperature is defined as the upper end of the melting range because the biggest and most perfect crystals melt there. Published melting temperatures often refer to the maxima of $\Delta T = f(T)$ curves, however. Observed melting temperatures are in general lower than the thermodynamic melting temperatures of perfect crystals but may be occasionally higher because of overheating effects.

Melting temperatures increase with molar mass and become practically constant at molar masses of ca. 50 000–150 000 g/mol. The melt can be considered as a dilute solution of end groups in monomeric units, and the reduction of the melting temperature with decreasing molar mass (i.e., increasing concentration of end groups) can be described by the thermodynamic law for the lowering of freezing temperatures:

$$\frac{1}{T_M} = \frac{1}{T_M^0} + \left(\frac{2R}{\Delta H_{M,u}^m}\right) \cdot \frac{1}{\overline{X}_n}$$

where $\Delta H_{M,u}^m$ is the molar melt enthalpy per monomeric unit, $\overline{X}_n$ the number-average degree of polymerization, and T_M and T_M^o are the thermodynamic melting temperatures at finite and infinite molar masses. Similar depression of the melting point is caused by addition of low molar mass solvents and amorphous polymers or by statistical copolymerization; in all these cases, the term $2/\overline{X}_n$ must be replaced by

$$({}^*V_u^m / {}^*V_1^m)[(1-\phi_2) - \chi(1-\phi_2)^2] \text{ (solvent)}$$

$$({}^*V_u^m / {}^*V_A^m) - \chi(1-\phi_2)^2] \text{ (amorphous polymer)}$$

$$[-\ln x_u - \chi(1-\phi_2)^2] \text{ (statistical copolymer)}$$

where ${}^*V^m$ is the partial molar volume of solvent 1, amorphous polymer A, or monomeric units u of copolymer; x_u the mole fraction of units u; ϕ_2 the volume fraction of crystallizable polymer 2; and χ an interaction parameter.

Melting temperatures $T_M = \Delta H_M^m / \Delta S_M^m$ are determined by the changes in molar melting enthalpies ΔH_M^m and molar melting entropies ΔS_M^m. The *melting entropy* results from conformational changes and volume changes upon melting. The melting entropy theoretically adds $R \cdot \ln 3 = 9.12$ J K^{-1} mol^{-1} for the formation of three conformers with equal energy and 7.41 J $K^{-1}mol^{-1}$ for one *trans* and two *gauche* conformers in the case of polymethylene $\sim(CH_2)_n\sim$. The entropy change due to the volume change should add another 10.9 J $K^{-1}mol^{-1}$ so that the theoretical melt entropy of polymethylene should be ca. 18.3–20.0 J $K^{-1}mol^{-1}$. Experimentally, only 9.9 J $K^{-1}mol^{-1}$ is observed, which points toward either the existence of local order in melts or a high segment mobility below the melting temperature. The latter was found experimentally by broad-line NMR for *cis*-1,4-polyisoprene ($\Delta S_M^m = 4.8$ J K^{-1} mol^{-1}).

Melting enthalpies are usually between 1 and 5 kJ per mole of chain atom. Low values are to be expected for polymers with high chain mobilities below the melting temperature (*cis*-1,4-polyisoprene, aliphatic polyesters and polyethers). High values are found for polymers with strong interactions between chains and tight packing of chains in crystals (polyoxymethylene, it-polystyrene). Some of these strong interactions may survive the melting process; for example, most of the hydrogen bonds of polyamides are still detected by IR spectroscopy above the melting temperature.

Thus the primary factors for high melting temperatures are not intermolecular interactions (e.g., cohesive energies) but reduced flexibilities of chains. Low melting temperatures are found for polymers with low rotational barriers (ester, oxygen, sulfide groups in chains), high melting temperatures for tightly packed helices [polyoxymethylene, it-poly(3-methylbutene)] and for ladder and ladderlike polymers [poly(*p*-phenylene), polybenzimidazole, etc.]. Such factors are responsible for the variation of melting temperatures with the number of methylene units in aliphatic polymer chains of the type $\sim X-(CH_2)_n\sim$ (Fig. 41).

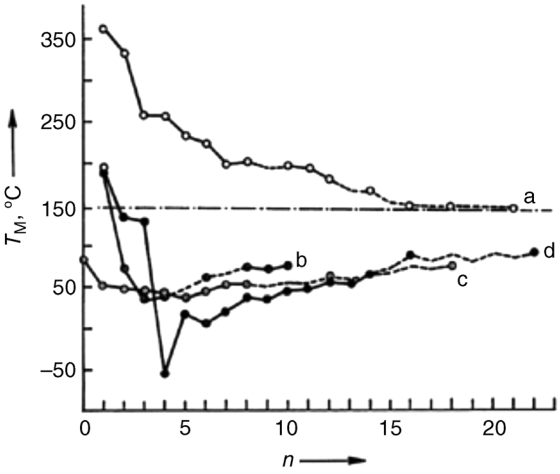


Figure 41. Melting temperatures of (○, ⊙, ⊕) aliphatic polymers $\sim[X\text{-}(CH_2)_n]\sim$ and (●) isotactic poly(α-olefins) $\sim\{CH_2-CH[(CH_2)_nH]\}\sim$ as function of the length n of methylene sequences
a) X = NHCO (polyamides); b) X = O (polyoxides);
c) X = $COO(CH_2)_3OOC$ (aliphatic polyesters of trimethylene glycol)
– ·–·– theoretical melting temperature of polyethylene

6.2.4. Liquid Crystal Transitions

Thermal transitions of thermotropic LC polymers from their crystals to smectic (T_{cs}) or nematic phases (T_{cn}), from smectic to nematic mesophases (T_{sn}), and from nematic phases to isotropic melts (T_{ni}, clearing temperature) are thermodynamic first-order transitions. They exhibit steplike changes in volume, enthalpy, and entropy, just like the melting of three-dimensional crystals to isotropic melts. Thermodynamically stable phases can exist only between melting and clearing temperatures (T_{cs}, $T_{cn} < T_{ni}$); they are called *enantiotropic phases*.

Mesophases form dispersions in supercooled isotropic melts if clearing temperatures are lower than melting temperatures (T_{cs}, $T_{cn} > T_{ni}$). Such phases are thermodynamically unstable compared to the crystalline; they are called *monotropic*.

Mesophases may be supercooled below $T_M = T_{cs}$ to smectic liquids sL* and below T_{sn} to nematic liquids nL* if crystallization can be suppressed. At even lower temperatures

T_{gn} and T_{gs}, these supercooled liquids may yield anisotropic glasses nG and sG, respectively. Some of these transition temperatures cannot be measured directly, but their existence can be deduced from extrapolations of transition temperatures of copolymers to 100% of the pure mesogenic compound (virtual transition temperatures).

The transition temperatures T_{trans} (i.e., T_{cs}, T_{gs}, T_{sn}, T_{cn}, T_{gn}, T_{ni}) depend on the degree of polymerization X in the same way the melting temperature does: $1/T_{trans} = f(1/X)$. The transition enthalpy ΔH_{ni} is always lower than the transition enthalpies ΔH_{gs} and ΔH_{sn} because the n → i transition is from order to disorder, whereas the g → s and s → n transitions are from order to less order. Transition entropies of mesophases are lower than melt entropies; they usually have values of ca. 0.5–1.5 J $K^{-1}mol^{-1}$, with $\Delta S_{sn} < \Delta S_{ni}$.

6.2.5. Glass Transitions

Glass transitions are phenomenologically characterized by a change from a "hard," noncrystalline, glasslike material to a rubbery to highly viscous "melt." The viscosities at glass transitions are ca. 10^{12} Pa · s, independent of chemical structures. Glass transitions were thus thought to be "isoviscous" phenomena. Today, glass transitions are considered to occur at that physical state where all materials exhibit the same "free volume."

Various free-volume fractions are discussed in the literature. The empirical Boyer–Simha rule relates a free-volume fraction f_{exp} to the cubic expansion coefficients β of liquid (L) and amorphous, glasslike (G) polymers and their glass transition temperatures T_G (see Table 16):

$$f_{exp} \approx (\beta_L - \beta_G) \cdot T_G \approx 0.11 \pm 0.02 \quad (20)$$

Table 16. Glass transition temperatures and free-volume fractions of polymers (for explanation of symbols, see text)

Polymer	T_G, °C	f_{exp}	f_{WLF}	f_{fluc}
Polyethylene	−80	0.098	0.025	
Polyisobutene	−73	0.079	0.026	0.0017
Poly(butyl methacrylate)	20	0.13	0.026	0.0010
Poly(vinyl acetate)	27	0.128	0.028	0.0023
Polystyrene	100	0.133	0.025	0.0035
Poly(methyl methacrylate)	105	0.118	0.025	0.0015

The Williams–Landel–Ferry (WLF) approach relates a free-volume fraction f_{WLF} to the probability of segment movements. Empirically, values of $f_{WLF} \approx 0.025 \pm 0.01$ were found; these values can be calculated, for example, from $K = f_{WLF}/(\beta_L - \beta_G)$ and $K' = \log e/f_{WLF}$ of the semiempirical WLF equation (Eq. 21) where $-\log a_t = \Delta(\log t)$ is a shift factor

$$T = T_G + \frac{K \cdot \log a_t}{K' - \log a_t} = T_G + \frac{51.6 \cdot \log a_t}{17.4 - \log a_t} \quad (21)$$

The Williams–Landel–Ferry equation applies to all relaxation processes; its use is restricted to temperatures in the range $T_G < T < (T_G + 100\ K)$.

The WLF equation allows calculation of the static glass transition from the various dynamic glass transition temperatures if the deformation times (inverse effective frequencies) of the methods are known. The glass transition temperatures of poly(methyl methacrylate) (PMMA) are given as 105 °C (thermal expansion, "static"), 120 °C (penetrometry), and 160 °C (rebound elasticity). The same polymer may thus exhibit very different mechanical properties if subjected to different stresses; at 140 °C, PMMA behaves as either a glass (rebound elasticity) or an elastomer (penetrometry).

The glass transition temperature indicates the onset of cooperative movements of chain segments of 25–50 chain atoms, which can be deduced from the ratio of molar activation energies and melt energies. These cooperative movements very probably involve *trans–gauche* transitions that proceed cooperatively along greater distances since only small changes of chain axes are involved according to deuterium NMR. The participation of segments of 25–50 chain atoms is also indicated by cross-linking experiments: As long as the average segment length N_{seg} between two cross-linking points is less than 25–50 chain atoms, no change of glass transition temperatures is observed. At $N_{seg} < 25$–50, T_G increases with the inverse molar mass of the segments.

Since both glass transition and melt temperatures depend on segmental motions, close relationship between these two temperatures can be expected. The empirical Beaman–Boyer rule

states that $T_G \approx (2/3)T_M$, which holds reasonably well for many polymers except for chains such as polyethylene and polyoxyethylene for which $T_G/T_m \approx 1/2$.

A vast literature exists about effects of constitution on T_G. Cyclic macromolecules possess no end groups, and thus no free-volume effects from these. Small rings are furthermore strained (less possible microconformations). The greater the molar mass, the more microconformations can be adopted, the greater is the chain flexibility and the lower is T_G. The same is true for segment flexibilities of star-branched polymers and long side chains in comblike molecules (side-chain "crystallization").

Linear relationships are found between the logarithms of glass transition temperatures T_G and the logarithms of cross-sectional areas A of carbon, carbon–oxygen, or carbon–nitrogen chains (another measure of segment flexibilities). The three lines intersect at $A = 0.17$ nm^2 and $T_G = 141$ K, which should be the lowest glass transition temperature possible. The lowest experimentally found glass transition temperature (150 K) is that of polydimethylsiloxane, $\sim[O-Si(CH_3)_2]_n\sim$.

Glass transitions can be decreased (or increased) by copolymerization with suitable monomers (internal plasticization) and by addition of external plasticizers (see Section 4.2.5).

6.2.6. Other Transitions and Relaxations

Experimentally, a number of other transition–relaxation temperatures are observed, mostly of unknown origin. Amorphous polymers exhibit weak "liquid–liquid" transitions at ca. $T_{ll} \approx 1.2\ T_G$. Below the critical molar mass for entanglements, transition temperatures T_{ll} equal flow temperatures T_F at which polymers start to flow under their own weight. At higher molar masses, $T_F > T_{ll}$.

Another transition temperature $T_U \approx 1.2\ T_M$ seems to exist for crystalline polymers. This transition has been interpreted as the dissolution of smectic structures.

Few β-relaxations have been correlated with molecular phenomena. An example is the frequency-dependent boat–chair transition of cyclohexane rings, which occurs at e.g., −125 °C (10^{-4} Hz) and + 80 °C (10^5 Hz).

6.2.7. Technical Methods

The technical testing on thermal transitions and relaxations of plastics is usually performed with simple methods under standardized conditions and always under load. *Martens numbers* measure temperatures at which the specimen has experienced a certain bend, *Vicat softening temperatures* give the temperatures for a certain penetration of a rod into the plastics, and the *heat distortion temperatures* (heat deflection temperatures) indicate the temperatures for a certain bending with a three-point method. The temperatures from these three methods do not only depend on transitions or relaxations but also on the elasticity of the specimen; Vicat and heat distortion temperatures are in addition affected by the surface hardness. The resulting softening temperatures are neither identical with glass transition nor with melting temperatures; they are often also not a good measure of the continuous service temperature of a plastic.

6.3. Transport

6.3.1. Self-Diffusion

Brownian movements cause molecules and their segments to interchange positions in fluid phases. If all entities are of the same type, such interchanges lead to a "self-diffusion", which involves no net transport of polymers. Self-diffusions can be measured by pulsed field-gradient spin-echo NMR (segments) and radioactive tracers (molecules).

Coiled molecules behave in their melts as unperturbed coils with low coil densities, which are filled with segments of other coils. Self-diffusion of a segment must therefore occur by interchanging position with a segment of another molecule.

Self-diffusion coefficients decrease with the squares of molar masses (Fig. 42). According to *reptation theory*, this functionality is caused by temporary (but fairly long-lived) entanglements of polymer chains. Such entanglements cause the sudden change of molar mass dependences

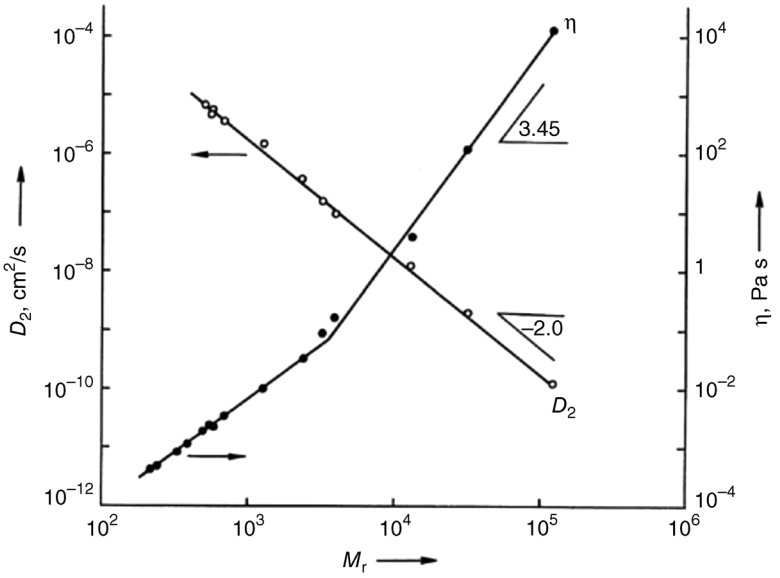


Figure 42. Segmental self-diffusion coefficients D_2 (○) and Newtonian melt viscosities η of alkanes and narrow-distribution polyethylenes (●) as function of the relative molecular mass M_r at 175°C
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of melt viscosities above a critical molar mass M_c (Fig. 42).

The resulting topological restraints make the polymer chain move through the maze of other segments like a reptile through brush. According to the Doi–Edwards theory, the test chain reptates in a tube of ca. 5 nm diameter, which is formed by other segments (Fig. 43). The theory predicts the experimentally found function $D_2 = f(M^{-2})$ albeit only for $M > M_c$. Experimentally, the same function is also observed for $M < M_c$, probably because end groups cause successively greater free-volume fractions, which are assumed by the reptation theory to be molar mass independent.

The same dependence of self-diffusion coefficients of test chains on the squares of their molar masses is theoretically predicted and experimentally found for test chains in higher molar mass matrices of the same constitution and configuration ($M_{test} \ll M_{matrix}$); the molar mass of the matrix exerts no influence. If however $M_{test} \gg M_{matrix}$, then a function $D_{test} = f[(M_{test})^{-1/2} \cdot (M_{matrix})^{-1}]$ is predicted and observed.

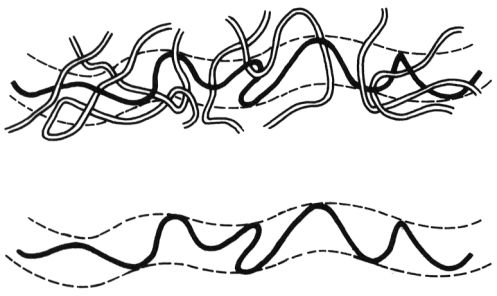


Figure 43. Reptation of a test chain (black) through the segments of a matrix (white). The "walls" of the tube are indicated by dotted lines.
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6.3.2. Permeation

The transport of extraneous material through polymers is called permeation. The resulting net flow of mass is caused by differences in chemical potentials, that is, concentration differences (at constant temperature) or thermal gradients (at constant concentration). Permeation may be desirable as in the dyeing of textiles or the controlled transdermal delivery

of pharmaceuticals, or undesirable as in the loss of carbon dioxide from plastic bottles for carbonated soft drinks or in migration of plasticizers.

Permeation of chemical compounds through amorphous polymers below their glass transition temperatures or through crystalline polymers below their melting temperatures can occur either by flow through pores or by molecular transport. Pores have diameters much greater than the diameters of permeating substances (diameter of spheres, cross section of coillike chains); the interactions of permeants and pore walls are negligible. Molecular transport, on the other hand, depends on such interactions between permeant and matrix (i.e., on the solubility of the former in the latter). Both types of transport can be distinguished by their temperature dependence: Permeation coefficients of gases decrease with temperature at pore membranes; they increase with temperature at solubility membranes.

The counteraction of the two types of permeation can be utilized in lamination. Oxygen permeates through pores in aluminum films but by molecular transport through polyethylene films. At 1 bar, permeation rates decrease from 5×10^{-5} cm^3/s for 0.025-mm-thick aluminum films to 5×10^{-13} cm^3/s for the same films laminated with 0.025-mm-thick PE films.

The permeation coefficient P is given by the product of the diffusion coefficient D and the solubility coefficient S of the permeant in the matrix and, in the steady state, by the expression to the right of the second equality sign:

$$P = D \cdot S = \frac{Q \cdot L}{A \cdot \Delta p \cdot t} \tag{22}$$

where Q = permeated amount, L = thickness of film (membrane, etc.), A = area, Δp = pressure difference, and t = time. The literature often uses different "practical units" for the various quantities of Equation (22), for example, Q in cm^3, L in mm, A in m^2, Δp in atm, and t in 24 h; P is then given in (cm^3 · mm)/(24 h m^2 atm). If like units are used, then the unit of P is of course length^2 · time^{-1} · pressure^{-1} and the unit of S is pressure^{-1}. Permeation coefficients P^* of liquids are usually measured without a pressure differential; their unit is cm^2/s and the unit of S is 1.

Table 17. Permeation coefficients of gases (P) and water vapor (P^*) through polymers at 30 °C [a]: $P = 1 \times 10^{-14}$ cm^2 s^{-1} Pa^{-1} corresponds to $P^* = 1 \times 10^{-9}$ cm^2/s at normal pressure ($p = 1 \times 10^5$ Pa)

Polymer	$\frac{10^{14} P}{\text{cm}^2\ \text{s}^{-1}\ \text{Pa}^{-1}}$		$\frac{10^9 P^*}{\text{cm}^2\ \text{s}^{-1}}$
	O_2	CO_2	H_2O
Polydimethylsiloxane	25 000	85 000	40
cis-1,4-Polyisoprene	2 000	10 000	0.3
Butyl rubber	100	500	0.1
Polystyrene			
regular	200	1 000	1
biaxially oriented	0.1	100	0.5
Poly(ethylene terephthalate)			
regular	4	20	0.2
biaxially oriented	0.2	1	0.2
Poly(vinylidene chloride)	0.05	0.15	0.02
Cellulose	0.03	0.1	10
Polyacrylonitrile, required for bottles	0.002	0.02	0.02
Cola	1	0.5	0.14
Beer	0.05	0.5	0.14

[a] Literature values vary widely because polymers are often not identical with respect to crystallinity, orientation, water absorption, etc.

Permeation coefficients of gases in polymers vary widely; for example, oxygen permeates 10 million times faster through polydimethylsiloxane than through polyacrylonitrile (Table 17). Gases in general, have lower permeation coefficients in thermoplastics than in elastomers because segmental movements of the former are frozen-in below the glass transition temperature. Bulky substituents, orientation of polymer segments, crystalline domains, and added fillers all increase the pathway for a gas molecule through a polymer matrix; these tortuosity factors decrease permeation coefficients.

The *permeation of nondissolving liquids* through a polymer is proportional to t^n. The exponent n depends on the ratio of the relaxation time of the polymer–solvent system to the diffusion time of the solvent (i.e., on the Deborah number DB).

Three different regimes are normally considered. In the regime denoted as *Case I*, the mobility of the permeant is much smaller than the relaxation of the polymer segments ($DB < 0.1$). The movement of the permeant causes "instantaneous" conformational changes of the polymer segments. Both permeant and polymer behave as viscous liquids: The system

can be described by Fickian diffusion laws (i.e., $n = 1/2$).

In the *Case II* regime, the mobility of the permeant is much higher than the relaxation of the polymer segments ($DB > 10$). The physical structure of the polymer does not change during the permeation; the polymer appears to the permeant as an elastic body. Case II is characterized by a sharp demarcation line between the glassy inner polymer core and the swollen zone advancing with constant speed. The permeating amount is directly proportional to time (i.e., n=1).

Relaxation and permeation become comparable for $0.1 < DB < 10$. This *third regime* is usually called anomalous diffusion or viscoelastic diffusion ($1/2 < n < 1$).

7. Rheological Properties [125, 126]

7.1. Introduction

Materials exhibit two limiting types of behavior against deformation. Typical liquids such as water flow under their own weight and are irreversibly deformed (viscous behavior). Typical solids such as iron resist deformation; they return from small deformations to their former states after removal of loads (elastic behavior). Polymers commonly combine both types of behavior: They are viscoelastic materials. Their melts exhibit viscous behavior at small deformations and elastic properties at larger ones. Polymer solids respond elastically at small deformations but begin to flow at larger ones.

Polymer melts and solutions have extremely high viscosities which may, in addition, be dependent on deformation rates and duration of the experiment. Air has, for example, a viscosity of 10^{-5} Pa · s; water, 10^{-3} Pa · s; and glycerol, 1 Pa · s, whereas polymer melts exhibit viscosities of ca. 10^2–10^8 Pa · s.

Three types of viscosity are usually distinguished:

1. Shear viscosity describes the rate of shear flow as function of the applied stress.
2. Extensional viscosity measures the rate of extensional (elongational) flow as function of tensile stress.
3. Bulk viscosity relates the rate of deformation of volume to the applied hydrostatic pressure.

Shear viscosities are the most often studied rheological properties of polymers; they are of great importance for the processing of plastics by extrusion or injection molding, for example. Much less is known about *extensional viscosities* (important for blow forming and fiber spinning) and practically nothing about the *bulk viscosities* of polymers.

7.2. Shear Viscosities at Rest

7.2.1. Fundamentals

Nine different shear stresses may be assigned to a three-dimensional body: One parallel to each of the three spatial directions (σ_{11}, σ_{22}, σ_{33}) and six perpendicular to these (σ_{12}, σ_{13}, etc.). A body is by definition sheared in the 2–1 direction. The ratio of shearing force K to contact area is called the shear(ing) stress $\sigma_{21} = K/A$; it produces a shear strain γ. The ratio $G = \sigma_{21}/\gamma$ is the shear modulus. Between layers of distance y moving parallel to each other with different rates v, a shear gradient $\dot{\gamma} = dv/dy$ thus exists. The ratio of shear stress to shear rate is the (dynamic) viscosity (Newton's law);

$$\eta = \sigma_{21}/\dot{\gamma}$$

its inverse $1/\eta$ is called fluidity.

Viscosities are independent of shear rates for Newtonian liquids ($\eta = \eta_o$); these viscosities are also called zero-shear viscosities, viscosities at rest, or stationary viscosities. For Newtonian liquids, the shear modulus G_o is independent of the extent of deformation. η_0 and G_o are true material constants, whereas η and G depend on shear rates and sometimes also on shearing time.

Shear stresses and shear gradients (and thus viscosities) can be measured with a variety of instruments that usually belong to one of three groups: Capillary, rotatory, and cone–plate viscometers. A number of industrially used instruments provide viscometric indicators (but neither shear stress, shear gradient,

nor viscosity); this group includes Höppler viscometers, Cochius tubes, Ford beakers, and instruments that measure melt flow indices or Mooney values (Mooney viscosities).

Thermoplastics are usually characterized by their *melt flow indices* $MFI_{T/F}$. The melt flow index measures the mass of polymer extruded in 10 min by a standard load F from a standard plastometer at temperature T. It is a measure of the (usually non-Newtonian) fluidity. The higher the melt flow indices, the lower are the molar masses of polymers of the same constitution.

The Mooney "viscosity" is really a measure of elasticity; it is used mainly for elastomers but also for polymer melts. A polymer is deformed in a standardized cone–plate viscometer at constant rotational speed and constant temperature T; after t minutes, the force to recover is read.

7.2.2. Molar Mass Dependence

Newtonian viscosities exhibit two different regimes for their (mass-average) molar mass dependencies $\eta_o = K \cdot M^a$: A weaker dependency ($a = 1/2$–1) for low molar masses and a stronger one ($a \approx 3.4$) at higher molar masses (Fig. 42). The transition from one to the other is thought to be caused by the onset of molecular entanglements that cause the molecules to behave as physically cross-linked networks.

The number of entanglements can be assumed to be constant at low shear rates. The elasticity of such a network is described by its shear modulus G (unit of pressure). Because shear viscosities have the unit pressure · time, $\eta_o = G_o \cdot t$. The reptation model identifies the time t as the time required for a chain to leave the tube. This time is proportional to the third power of the number of segments per molecule (i.e., the viscosity should be proportional to the third power of the molar mass). The deviation between the theoretically predicted $\alpha = 3$ and the experimental value of $\alpha = 3.4$ is thought to be due to "breathing" of the tube. Breathing pushes nonentangled chain loops back into the surrounding matrix; chain ends cause additional relaxations and the tube length decreases.

7.2.3. Concentrated Solutions

Newtonian viscosities of concentrated solutions increase with both solute concentrations c and molar masses M or, since $[\eta] = K \cdot M^a$, with intrinsic viscosity $[\eta]$ as well. The concentration c measures the mass of polymer per unit volume of solution; the intrinsic viscosity, the volume of polymer molecules per unit mass of polymer. The product $c \cdot [\eta]$ is thus a measure of the volume fraction of polymer molecules that would be occupied by isolated polymer coils. At higher concentrations, coils start to overlap and the total occupied volume is smaller than the one demanded by isolated coils (i.e. $c \cdot [\eta] > 1$).

At low values of $c \cdot [\eta]$, η_i (the "specific viscosity") and $c \cdot [\eta]$ are proportional (Fig. 44), where $\eta_i = (\eta/\eta_1) - 1$, η is the viscosity of the polymer solution at rest, and η_1 the viscosity of the solvent. At higher $c \cdot [\eta]$ values, $\eta_i \sim (c \cdot [\eta])^q$ or, because $[\eta] \sim M^a$, $\eta_i \sim c^q \cdot M^{aq}$. Because at very high concentrations $\eta_i \approx \eta/\eta_1$ and η approaches the Newtonian melt viscosity $\eta_o \sim M^{3.4}$ for high molar masses, $a \cdot q = 3.4$ is obtained. In theta solvents and melts, coils are unperturbed ($a = 1/2$) and $q = 6.8$ (Fig. 44). In good solvents, $a \rightarrow 0.764$ and $q = 4.55$. These relationships are

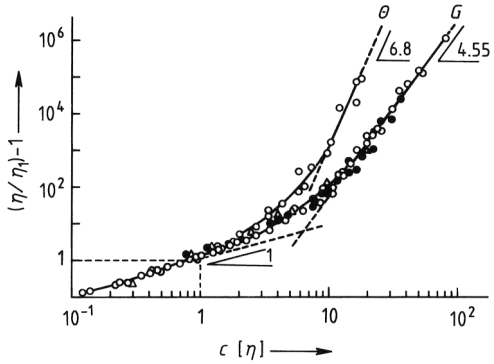


Figure 44. Relative viscosity increment ("specific viscosity") as function of $c \cdot [\eta]$ for (○) polystyrenes in *trans*-decalin (theta solvent) or toluene (good solvent G) at 25 °C; (●) *cis*-1,4-polyisoprene in toluene at 34°C; and (Δ) hyaluronates in water at 25°C
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independent of the chemical nature of polymers and solvents.

7.3. Non-Newtonian Shear Viscosities

7.3.1. Overview

The shear stress σ_{21} is directly proportional to the shear gradient γ for Newtonian liquids; these relationships and thus the viscosities η are moreover, independent of the duration of the experiments. Non-Newtonian viscosities (apparent viscosities), on the other hand, vary with shear rate and sometimes even with time.

Various dependencies of (apparent) viscosity on shear rate are found for time-independent non-Newtonian liquids (Fig. 45). *Plastic bodies* (Bingham bodies) exhibit a yield value *y*, i.e., shear stresses have finite values σ_o at $\dot{\gamma} \rightarrow 0$. Above σ_o, such bodies may behave in a Newtonian (ideal Bingham bodies) or non-Newtonian (pseudoplastic Bingham bodies) manner. This behavior seems to be due to the disappearance of aggregates. An example for a Bingham body is tomato ketchup.

In *dilatant liquids*, the shear stress increase is more than linearly proportional to shear rate; viscosities increase with shear rate (shear thickening). This behavior occurs frequently in polymer dispersions.

A decrease of apparent viscosity with shear rate is most common for polymer melts. Because such behavior resembles that of pseudoplastic Bingham bodies, it is called *pseudoplasticity* in the English literature ("structural viscosity" in German), although such "pseudoplastic" materials do not possess a yield value. Pseudoplastic behavior eases polymer processing from melts and reduces the energy required (e.g., lower pressures can be applied in injection molding). It is usually accompanied by an orientation of chain segments that is most pronounced in the processing of liquid crystalline polymers with rigid mesogens and the ultradrawing of flexible polymers.

Dilatant and pseudoplastic liquids are characterized by "instantaneous" adoption of shear rates on application of shear stresses (i.e., by time-independent apparent viscosities).

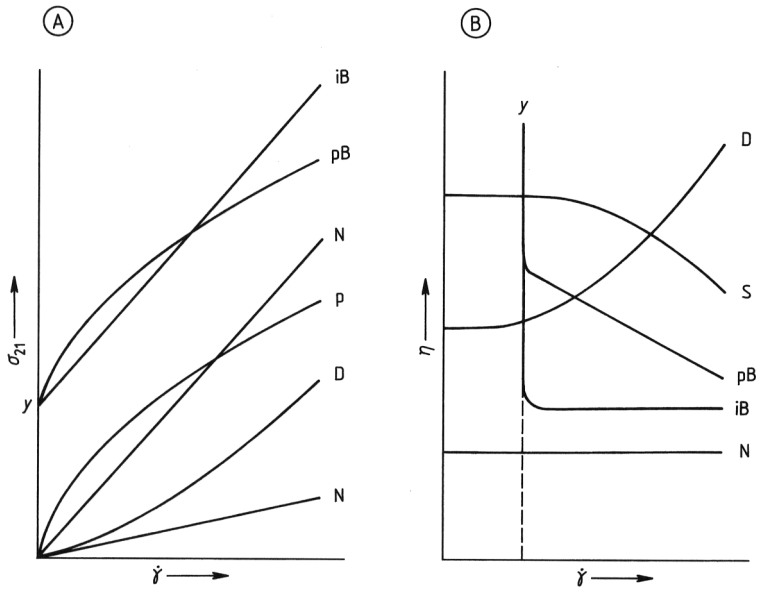


Figure 45. A) Shear stress σ_{21} and B) shear viscosity η as a function of shear rate $\dot{\gamma}$ for Newtonian (N), dilatant (D), and pseudoplastic (P) liquids and for ideal (iB) and pseudoplastic (pB) Bingham bodies (y = yield)
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Thixotropic materials exhibit a decrease of apparent viscosity with time at constant shear rate; examples are dispersions of bentonite and other platelet-like silicates. *Rheopectic* or *antithixotropic* materials show an increase of apparent viscosity with time at constant shear rate. The flow behavior may be further complicated by wall effects. Certain dispersions and gels exude liquid on application of a shear stress. The liquid acts as an external lubricant and a pluglike flow results (e.g., tooth pastes). An additional complication may result from the onset of turbulence, which usually occurs at much lower Reynolds numbers in non-Newtonian than in Newtonian liquids.

7.3.2. Flow Curves

A plot of $log\,\dot{\gamma} = f(\sigma_{21})$ or vice versa is usually called a flow curve. A generalized flow curve may contain an initial Newtonian region, followed by pseudoplasticity and a second Newtonian regime. Because experiments are difficult to conduct at high shear rates, many rheologists doubt the existence of true second Newtonian regions. Dilatancy may or may not be present. Finally, turbulence sets in and melt fracture occurs (Fig. 46).

Several empirical laws have been suggested for the description of flow curves, all of which usually apply only to limited ranges of shear rates. Examples include

$$\dot{\gamma} = a \cdot (\sigma_{21})^{m} \quad \text{Ostwald – de Waele}$$

$$\dot{\gamma} = b \cdot \sinh(\sigma_{21}/d) \quad \text{Prandtl – Eyring}$$

$$\dot{\gamma} = f \cdot \sigma_{21} + g \cdot (\sigma_{21})^{3} \quad \text{Rabinowitsch – Weissenberg}$$

where *a, b, d, f, g*, and *m* are empirical constants. The exponent *m* is known as the "flow exponent"; it takes a value of 1 (Newtonian liquid) and < 1 (pseudoplasticity). No constitutive equations are known that cover the entire range of rheological phenomena.

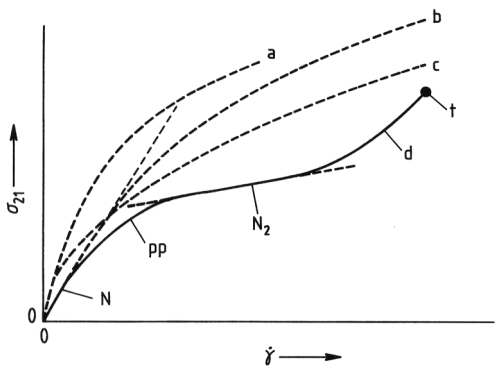


Figure 46. Generalized flow curve with first Newtonian region (N), pseudoplasticity (pp), second Newtonian region (N_2), dilatancy (d), and onset of turbulence (t)
- - - Schematic representations of various viscosity "laws": a) Prandtl–Eyring; b) Rabinowitsch–Weissenberg; c) Ostwald–de Waele
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7.3.3. Melt Viscosities

Polymers below the critical molar masses M_c for entanglements show extended Newtonian ranges. For $M > M_c$, non-Newtonian behavior appears at lower shear rates as molar mass increases (lower melt flow index) (Fig. 47). At high shear rates, a constant exponent q is approached for the function $\eta = f(\dot{\gamma}^{q})$. The non-Newtonian viscosities are no longer proportional to the mass-average molar masses; the broader the molar mass distribution, the more the number average seems to be the correct corresponding quantity.

Shear thinning, i.e., the decrease of apparent viscosity with shear rate, is very important for plastics processing. Viscosities describe a frictional behavior: The higher the viscosity, the higher is the internal friction of the melt and the greater is the proportion of energy provided that is converted into heat. Strong non-Newtonian behavior thus saves energy. Polymer melts are therefore processed at the highest possible shear rates. The upper range is given by the processing method (calendering, extrusion, etc.), and the polymer properties (thermal degradation, melt fracture, etc.).

Surface roughness of barrel walls, diameter changes, etc., create additional rate components in extrusion that are dampened by the viscosity of the liquid. These disturbances become stronger with increasing flow rate and can no longer be dampened at high shear rate. Finally, turbulence sets in. In entangled polymer melts, additional elastic vibrations occur due to the presence of physical cross-links. The resulting elastic turbulences lead to rough surfaces of the

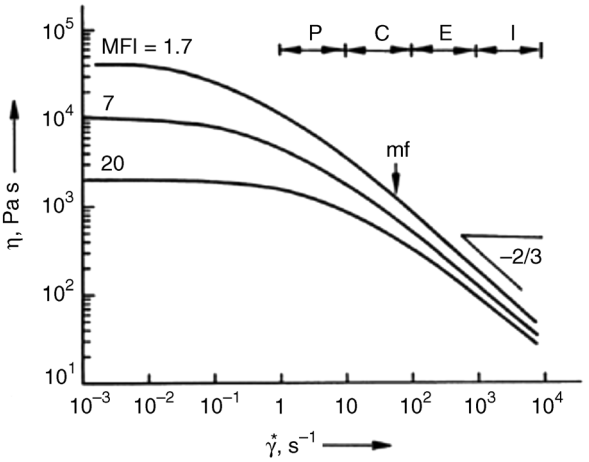


Figure 47. Dependence of melt viscosities of polyethylenes with different melt flow indices (MFI, inversely proportional to molar mass) on shear rates (mf = onset of melt fracture for the highest molar mass polyethylene)
The ranges of the various processing regimes overlap: P = compression molding, C = calendering, E = extrusion, I=injection molding. Shear rates refer to those at orifices and are much lower in the mold (tool, die).
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extrudate, which are subsequently frozen-in upon exit from the orifice. The polymer surface appears "fractured"; "melt fracture" thus does not refer to a breakage of the extrudate strand.

Molecular coils are deformed if their melt is pressed through an orifice (Fig. 48). For $M > M_c$, segments can no longer slip from each other at high stresses and short times because of entanglements; a "normal" stress builds up perpendicular to the stress direction. At the die exit, this stress is relieved and the coil returns to the thermodynamically more favorable shape of an unperturbed coil. The melt expands perpendicular to the flow direction. This phenomenon is known as Barus effect or memory effect (melts), the Weissenberg effect (solutions), parison swell (extrusion), swelling (blow molding), etc. It is especially pronounced for high molar mass tails in polymers with $M > M_c$ because of the 3.4 power dependence of η on $\overline{M}_w$.

Negative Barus effects are known for solutions of rodlike molecules or LCPs with rodlike mesogens (diameter of strand smaller than diameter of orifice). If such molecules crystallize after exiting from the die, the strand contracts perpendicular to the extrusion direction and the strand diameter becomes smaller than the diameter of the orifice.

The effect of normal stress can be determined by the Bagley equation. A force $F_f = \pi R^2 p$ is exerted on a liquid during the flow through a capillary with radius R and length L under a pressure p. It is counteracted by a frictional force $F_r = 2\pi RL\,\sigma_{21}$. In steady state, $F_f = F_r$; thus $p = 2\sigma_{21}(L/R) = 2\eta \cdot \dot{\gamma}(L/R)$ because $\sigma_{21} = \eta \cdot \dot{\gamma}$. In the Bagley diagram, pressure p is accordingly plotted at constant shear rate against die geometry L/R (Fig. 49). For non-Newtonian liquids, a relationship

$$p = p_o + K \cdot (L/R)$$

is found. The intercept p_o at $L/R \rightarrow 0$ is identified with the pressure loss caused by the elastically stored energy of the flowing melt and the formation of a steady-state flow

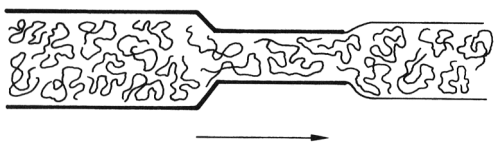


Figure 48. Parison swell upon extrusion (Barus effect)
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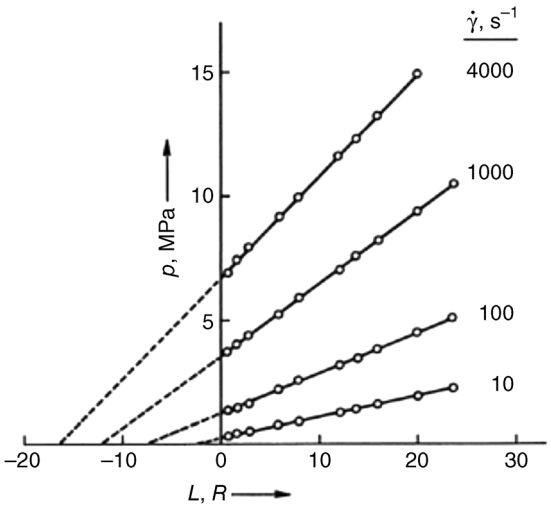


Figure 49. Bagley diagram for a high-impact polystyrene at 189°C and different shear rates
The intercept at $L/R \rightarrow 0$ is the pressure correction; the intercept at $p \rightarrow 0$, the Bagley correction a) $\dot{\gamma} = 4000\ s^{-1}$; b) $\dot{\gamma} = 1000\ s^{-1}$; c) $\dot{\gamma} = 100\ s^{-1}$; d) $\dot{\gamma} = 10\ s^{-1}$
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profile at both ends of the capillary (die). The higher *L/R* is, the higher must be the applied pressure. Die lengths should thus be as short as possible.

7.4. Extensional Viscosities

7.4.1. Fundamentals

Polymer liquids can be elongated considerably without being broken. This extensibility allows fiber spinning from melts and solutions, blow molding of hollow bodies, vacuum forming of parts, etc.

The extensional viscosity η_e (elongational viscosity) is given by the ratio of tensile stress σ_{11} in draw direction 11 to the elongational rate $\dot{\varepsilon}$

$$\eta_e = \sigma_{11}/\dot{\varepsilon} \tag{23}$$

The type of deformation must always be indicated for extensional viscosities, contrary to shear viscosities. The three principal deformation rates can be defined in such a way that $\dot{\varepsilon}_{11} \geq \dot{\varepsilon}_{22} \geq \dot{\varepsilon}_{33}$. The ratio $m = \dot{\varepsilon}_{22}/\dot{\varepsilon}_{11}$ characterizes the special type of elongational flow: Theory gives $m = -1/2$ for uniaxial elongation, $m = 1$ for equal-biaxial, and $m = 0$ for planar (pure shear). Uniaxial elongational viscosities are important for fiber spinning; they are the only ones used to characterize fluids. Biaxial elongational viscosities play an important role in blow and vacuum forming; very little is known about them.

The elongation in Equation (23) is the true strain $\varepsilon' = \ln(L/L_o)$ (Hencky strain) and not the nominal strain $\varepsilon = (L-L_0)/L_0$ (Cauchy strain, engineering strain). The rate of elongation is thus $\dot{\varepsilon} = d\varepsilon/dt = d \ln L/dt = L^{-1}\,(dL/dt)$.

Extensional viscosities are very difficult to measure. Elastomers and melts of entangled polymer coils can be stretched between rotating rollers. Extensional viscosities of solutions can be determined if two liquid jets streaming toward each other are redirected by rollers or siphoned off.

7.4.2. Melts

Extensional and shear viscosities depend very differently on deformation rates. At low rates, extensional viscosities are independent of the rate of extension (Fig. 50). The uniaxial extensional viscosity at rest (historically called "Trouton viscosity") is three times the Newton viscosity $[(\eta_e)_0 = 3\ (\eta_s)_0]$, whereas the biaxial

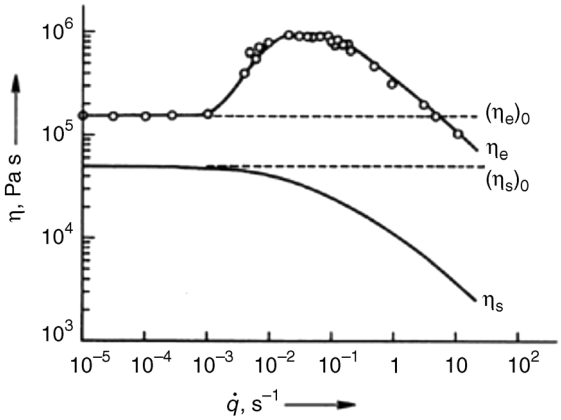


Figure 50. Shear viscosity η_s as function of shear rate $\dot{q} = \dot{\gamma}$, and extensional viscosity η_e as function of the uniaxial extensional rate $\dot{q} = \dot{\varepsilon}$ of a polyethylene at 150 °C
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extensional viscosity at rest is six times its shear counterpart.

Above a critical deformation rate, shear thinning is observed for the shearing and extension of melts of linear coil molecules. At the same rate, melts of branched coil molecules become dilatant on extension. The apparent extensional viscosities then pass through a maximum and decrease with further increase of extension rates. The maximum of the extensional viscosity increases with broader molar mass distribution and increased long chain branching, which indicates the strong influence of entanglements on extensional viscosities.

7.4.3. Solutions

Rodlike molecules and segments are increasingly oriented in the extensional direction with increasing elongational rates. The molecular axes are no longer distributed at random, and the solution becomes anisotropic and thus birefringent. A limiting value is asymptotically reached if all molecular axes are completely aligned in the flow direction.

Flexible molecules in solution are only slightly deformed and oriented at comparable extension rates because elastic (entropic) forces cause the chains to return to the thermodynamically favored coil shape. At high critical extension rates, these retraction forces can be overcome and the chain axes become oriented in the flow direction. Only an incremental increase of extension rates is needed to orient the chains completely. Molecules are stressed more and more above the critical extension rates until they finally break. This fracture occurs primarily in the middle of the molecule so that degradation products possess 1/2, 1/4, 1/8, etc., of the initial molar mass. Such degradation occurs under very low deformation rates for rigid macromolecules, for example, during pipetting of dilute solutions of high molar mass deoxyribonucleic acids.

These degradations by extensional flow are not caused by turbulence because they happen at lower Reynolds numbers than those of pure solvents. Chain degradations by turbulence do occur on shearing of very dilute solutions of flexible coil molecules (e.g., 10^{-4} g/mL aqueous solutions of polyoxyethylenes). The degradation reduces the frictional resistance of liquids up to 75%. This "Toms effect" by added small amounts of such polymers eases the flow of crude oil through pipelines and increases the distance and height to which water can be directed at fires.

8. Mechanical Properties [116, 129, 130]

8.1. Introduction

8.1.1. Deformation of Polymers

Mechanical properties of a polymer include the deformation of bulk polymers or their surfaces, the resistance to such deformation, and the fracture under static or dynamic loads. Deformations may be reversible or irreversible; they can be caused by drawing, shearing, compression, bending, and torsion, as well as by combinations of these.

Reversible deformations are due to the presence of elasticity. Irreversible deformations are also called inelastic; they are further subdivided into deformation by viscous flow, plasticity, phase transformations, craze formation, cracking, viscoelasticity, creep, etc. An inelastic deformation of metals by viscoelasticity is known as anelasticity; in polymer physics, anelasticity denotes a reversible elasticity with retardation, which does not lead to energy dissipation. Deformation of the upper layers of a polymer body is characterized by its "hardness," which influences friction and abrasion.

The term elasticity may refer to either energy or entropy elasticity. These elasticities differ in their molecular mechanisms and the resulting phenomenological behavior. In *energy-elastic bodies* (steel, plastics, and elastomers at low strains), torsion and bond angles are changed and bond distances are enlarged on deformation, whereas the macroconformations of chains, for example, remain basically the same. A deformation of *entropy-elastic bodies* (elastomers at high strains), on the other hand, leads to entropically unfavorable positions of chain segments which, however, cannot slip irreversibly from each other because of

their cross-linking ("rubber elasticity"). The deformation thus changes the macroconformation (molecular picture), decreases entropy (thermodynamics), and creates normal stresses (mechanics).

These molecular changes are reflected in the properties of energy- and entropy-elastic materials:

	Energy-elastic	Entropy-elastic
Elastic moduli	large	small
Reversible deformation	small	large
Temperature change on deformation	cooling	warming
Length change on heating	expansion	contraction

The deformation behavior of plastics depends on the molar mass of their constituting polymers and on the testing temperature: That is, whether the molar mass is greater than the one needed for the establishment of entanglements between chains ($M > M_{ent}$) and whether the testing temperature is lower than the glass transition temperature of the polymers ($T < T_G$). All mechanical deformations recover for $M > M_{ent}$ and $T < T_G$ because chain entanglements cannot reorganize below the glass transition temperature (memory effect). Yielded plastics and crazed plastics recover on (not too long) heating above the glass transition temperature. These plastics thus do not show true plastic flow.

8.1.2. Tensile Tests

Mechanical properties of polymers are most commonly evaluated by tensile tests in which a specimen is drawn with constant speed. The tensile stress σ_{11} is recorded as a function of time t, draw ratio (strain ratio) $\lambda = L/L_o$, or tensile strain (elongation) $\varepsilon = (L—L_o)/L_o = \lambda - 1$. If a specimen is extended to $L = 2.5\ L_o$ of the original length L_o, then it is said to have been drawn by 150%.

The tensile stress of *elastomers* increases continuously with increasing tensile strain until the polymer finally ruptures at σ_R and ε_R (Fig. 51). Typical *thermoplastics* (and most fibers) follow Hooke's law

$$\sigma_{11} = (F/A_o) \cdot \varepsilon = E \cdot \varepsilon$$

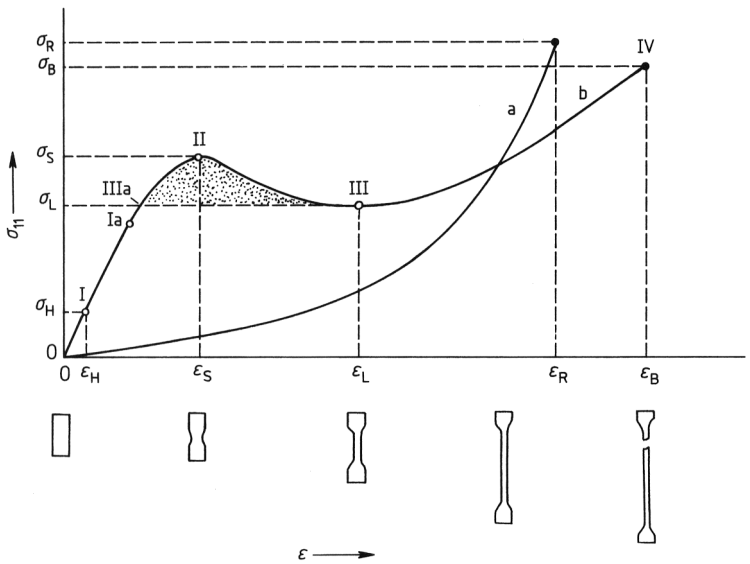


Figure 51. Stress–strain curves of an elastomer (a) and a partially crystalline thermoplastic (b) (schematic) (for further explanation, see text)
The necking effect shown below is characteristic for conventional thermoplastics; it is not found for elastomers and hard-elastic thermoplastics.
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for small strains (up to point I), where A_o is the original cross section of the specimen, F is the force, and E is the tensile modulus (Young's modulus). Point I is thus called the proportionality limit or elastic limit; it is defined for a remaining strain of 0.1% after removal of the stress.

The maximum of the stress–strain curve is called the upper yield (point II), and the subsequent minimum is the lower yield (point III). The ratio of upper yield stress σ_S to tensile modulus E is practically constant for all polymers; the numerical value of $\sigma_S/E \approx 0.025$ suggests that van der Waals bonds are broken and molecule segments begin to move more freely.

Brittle polymers break at the upper yield. Tough polymers continue to extend and the stress either remains constant (see below) or decreases. The latter phenomenon is called stress softening. It is typical for polymers with neck formation (telescope effect) and is nominal since it disappears if the stress is given relative to the actual cross section instead of the initial one.

The region between points IIIa−II−III is known as the ductile region; its area describes the absorbed energy and thus the toughness of the specimen. The subsequent increase of stress with strain is called stress hardening. At point IV, the ultimate strength (tensile strength, tenacity at break) σ_B and ultimate elongation (elongation at break) ε_B occur.

Stress–strain curves may differ considerably for plastics. Polymers with high Young's moduli (steep initial slopes) are called hard polymers; those with low moduli, soft; this hardness should not be confused with surface hardness. Typical hard polymers are phenolics [phenol–formaldehyde (PF)], polyacetals [polyoxymethylene (POM)], polycarbonates (PC), and poly(ethylene terephthalates) (Fig. 52). Polymers are further characterized by their stress–strain behavior between upper yield and failure. Polymers without yield cannot absorb energy and thus break easily; they are hard-brittle polymers (e.g., PF). Polycarbonates, on the other hand, show an extended ductile region and a fairly high fracture strain; they are called hard-tough. Polyethylene is similar with respect to ductile behavior and strain hardening; the modulus is however much lower, and PE is considered soft-tough.

The stress–strain behavior described above is typical for tensile experiments. Tensile stresses

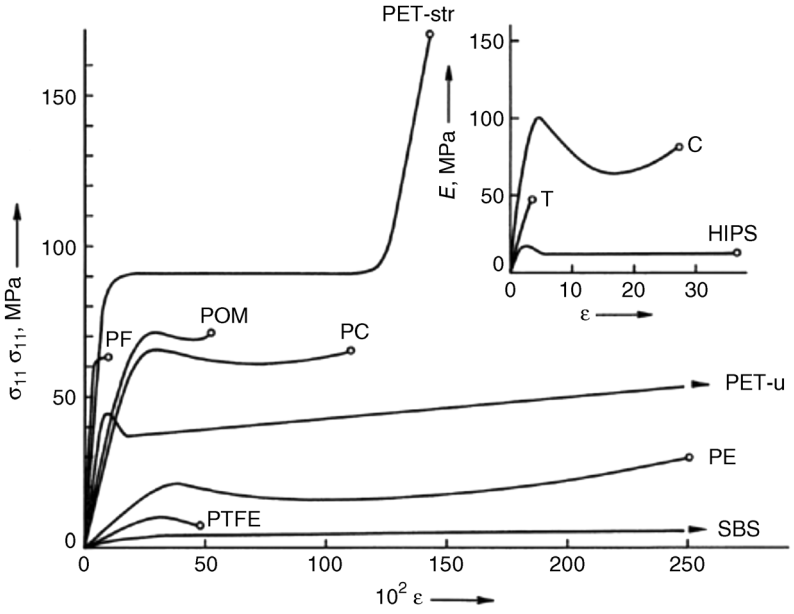


Figure 52. Stress–strain curves of polymers at room temperature (see text for explanation)

lead to strong deformations in neck zones and cause microscopic voids at which fracture originates. Atactic polystyrene (PS) is such a hard-brittle polymer under tension T. No voids can be formed, however, under compression C, and PS appears as a hard-tough material (Fig. 52, insert). Rubber modification of PS leads to high-impact polystyrene (HIPS), which behaves quite differently from PS under tension (see Section 8.6.4).

No yield value is found if drawn polymers are further subjected to tensile tests. In biaxially stretched poly(ethylene terephthalate) (PET-str) some chain segments are already oriented, whereas other remain in their original positions. Biaxially stretched films are thus under stress, which is utilized in shrink films. Such films are used for the packaging of goods. On heating semicrystalline polymers above the glass transition temperature and below the melting temperature, chain segments become more mobile. Molecules attempt to attain their unperturbed dimensions and the films shrink, covering the goods tightly.

8.1.3. Moduli and Poisson Ratios

Elasticities can be described by three elastic moduli: Tensile modulus or Young's modulus E, shear modulus G, and bulk modulus or compressive modulus K. Their values are inversely proportional to the corresponding compliances for static deformations (but not for dynamic ones):

Moduli	Compliances
$E = \sigma_{11}/\varepsilon$	$D = 1/E$
$G = \sigma_{21}/\gamma$	$J = 1/G$
$K = p/(-\Delta V/V_o)$	$B = 1/K$

The three simple moduli are related to each other for small deformations of simple isotropic bodies:

$$E = 2G \cdot (1 + \mu) = 3K \cdot (1 - 2\mu) \quad (24)$$

where $\mu = (\Delta d/d_o)/(\Delta L/L_o)$ is the Poisson ratio (Poisson number), d is the diameter, and L is the length of the specimen. Poisson ratios can only adopt values $0 < \mu < 1/2$ for isotropic bodies but may assume $\mu > 1/2$ for anisotropic ones. Equation (24) is invalid for anisotropic bodies and viscoelastic materials; $E/3 < G < E/2$ and $0 < K < E/3$, are however, still valid for these materials.

Table 18. Poisson ratios and elastic constants of various materials

Material	μ	E, GPa	G, GPa	K, GPa
Water	0.50	≈0	≈0	≈2
Gelatin (80% water)	0.50	0.002		
Natural rubber	0.495	0.0009	0.0003	≈ 2
Polyethylene, LD	0.49	0.20	0.070	3.3
Polystyrene	0.38	3.4	1.2	5.0
Granite	0.30	30	12	25
Steel	0.28	211	80	160
Glass	0.23	60	25	37
Quartz	0.07	101	47	39
Aluminum oxide Fibers	0	2 000	1 000	667

Common polymers behave with respect to μ, E, G, and K more like liquids than like metals (Table 18). Ultradrawn and self-reinforcing polymers may, however, exhibit tensile moduli that exceed those of steel (see below).

8.2. Energy Elasticity

8.2.1. Theoretical Moduli

The tensile moduli of common polymers are far lower than the theoretical moduli deduced from their chemical and physical structures (-Table 19). Such theoretical moduli can be calculated from bond lengths, valence angles, and force constants for the deformation of these quantities. The theoretical moduli agree well

Table 19. Modulus of elasticity

Polymer	$E_\parallel$, GPa			$E_\perp$, GPa
	Theory	Lattice	Tensile	Lattice
Polyethylene	340	325	< 1	3.4
Polypropylene, it	50	42	< 3	2.9
Polyoxymethylene				
orthorhombic	220	189	< 2	7.8
trigonal	48	54	2	
Poly(*p*-phenylene terephthalamide)	182	200	132	10
Poly(4-methylpentene)	6.7		1	2.9

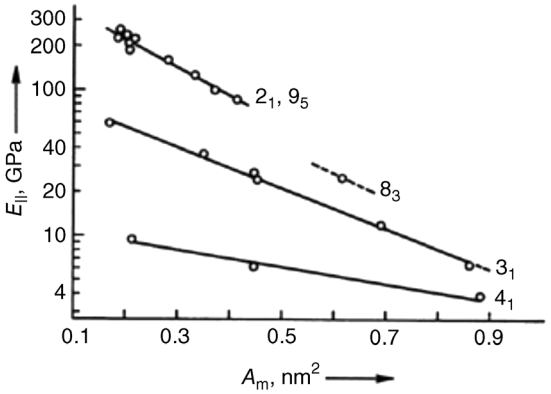


Figure 53. Longitudinal lattice moduli $E_{\|}$ as function of cross-sectional area A_m of polymer chains in all-*trans* (2_1) or helical conformations (9_5, 8_3, 3_1, 4_1) of their main chains Reprinted with permission by Hüthig and Wepf Publ., Basel [5]

with the microscopic lattice constants, which are determined experimentally by X-ray diffraction (change of Bragg reflexes), Raman spectroscopy, or inelastic neutron scattering under load. The longitudinal theoretical moduli $E_{\|}$ are far greater than the transverse moduli $E_{\perp}$; because the former are controlled by covalent bonds and the latter by van der Waals forces.

The larger the cross-section of the single polymer chain, the larger is the force distributed to fewer chains per unit area and the smaller are the moduli (Fig. 53). Chains in the all-*trans* conformation always exhibit higher theoretical moduli than do helical chains since the elongation of the former changes bond angles, whereas the extension of the latter involves only lower-energy torsion angles.

Polyethylene has the highest theoretical modulus of all one-dimensional chains ($E_{\|} = 340$ GPa), about one-third that of diamond ($E_{\|} = 1\ 160$ GPa) with its "naked" carbon chains. Polypropylene has the highest theoretical modulus of helical chains ($E_{\|} = 50$ GPa).

Moduli approaching these theoretical values have been realized by ultradrawing of mats of polyethylene single crystals, giving polymers with $E_{\|} = 240$ GPa. Industrially, high-modulus polyethylene fibers are manufactured by gel spinning of ultra-high molecular polyethylene ($E_{\|} = 97$ GPa 90 $\hat{=}$ N/tex, 1 tex = 1 g per 1 000 m).

8.2.2. Real Moduli

The much lower tensile moduli of conventionally processed polymers result from their disordered physical structures. In amorphous polymers, chain segments are oriented at random. Even in partially crystallized polymers, amorphous layers exist and chain axes (stems of lamellae) are distributed at random. The moduli of flexible polymers can be increased somewhat by processing under external force fields, for example, by partial orientation of chain segments during fiber spinning (Table 20, column L). Extrusion of solid polymers is a particularly effective method: The longitudinal modulus of polyoxymethylene increased to 24 GPa from 2 GPa on hydrostatic extrusion.

Rodlike mesogens of liquid semiflexible polymers align in mesophase domains. The domains orient themselves in shear fields; the orientations can be frozen-in to LCP glasses. Such self-orienting polymers possess much higher moduli in the longitudinal direction than conventionally processed flexible polymers (Table 19). Their transverse moduli are also higher because of intermolecular dipole–dipole interactions.

8.2.3. Temperature Dependence

Young's moduli change characteristically with temperature for the various classes of polymers

Table 20. Moduli and fracture strengths of conventional polymers as isotropic molding masses (I) or in draw direction of fibers (L) and of thermotropic (TT) and lyotropic (LT) glasses longitudinal (L) and transverse (T) to draw direction compared to isotropic polymers (I)

Polymer	E, GPa			σ_B, MPa		
	L	T	I	L	T	I
PE-LD	?	?	0.15	?	?	23
PA 6.6	13	?	2.5	1 000	?	74
PET	19	?	0.13	1 400	?	54
TT X 7 G[a]	54	1.4	2.2	151	10	63
TT Vectra[b]	11	2.6	5.0	144	54	97
LT Kevlar[c]	138	7	?	2 800	?	?
LT PPBT[d]	120	17	62	1 500	680	700

[a] X 7 G = poly(*p*-hydroxybenzoate-*co*-ethylene terephthalate).
[b] Vectra = poly(*p*-hydroxybenzoate-*co*-2-hydroxy-6-naphthalate).
[c] Kevlar 49 = poly(*p*-phenylene terephthalamide).
[d] PPBT = 30% poly(*p*-phenylene benzbisthiazole) in poly(2,5-benzimidazole).

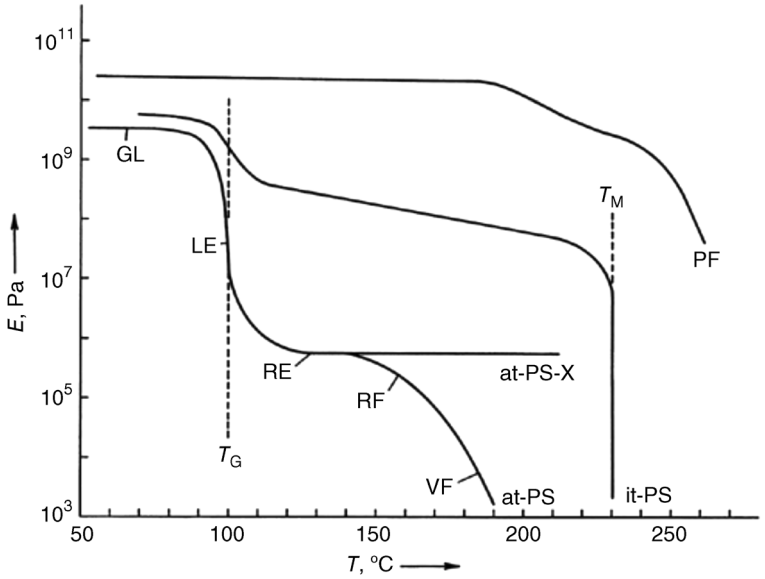


Figure 54. Temperature dependence of Young's moduli for conventional polymers
at-PS = amorphous (atactic) polystyrene ($M > M_c$); at-PS-X = its slightly cross-linked product; it-PS = partially crystalline (isotactic) polystyrene; PF = hardened phenol–formaldehyde resin; GL = glasslike; LE = leatherlike; RE = rubber (entangled); RF = viscoelastic; VF = viscous flow
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(Fig. 54). Five characteristic ranges can be distinguished: Glassy (GL), leatherlike (LE), rubbery (RE), viscoelastic (RF), and viscous (VF).

Amorphous Polymers. Moduli (0.1–1 GPa) are practically independent of temperature below the glass transition temperature T_G but drop to 10^5-10^6 Pa at $T = T_G$; the polymer appears leathery around T_G and rubbery above the glass transition temperature. The rubbery region is maintained for entangled (high molar mass) polymers but is nonexistent for low molar masses ($M < M_c$). Moduli decrease on further temperature increase until the polymers behave like viscous liquids ($E \approx 10^3$ Pa).

Elastomers. At use temperatures, these polymers are above their T_G and thus behave like cross-linked thermoplastics above the T_G of the latter. The decrease in modulus at T_G is limited by (and a measure of) the degree of cross-linking. At higher temperatures, elastomers decompose and the moduli decrease drastically.

Crystalline polymers have only a weak leathery region around T_G because their amorphicity is slight and their crystallites act as physical cross-linkers. The modulus at the beginning of the rubbery plateau is a measure of the degree of crystallinity. The moduli decrease slowly during the rubbery "plateau" because more and more crystallites are molten. The remaining crystallites practically disappear at the melt temperature: The moduli drop drastically and the polymers behave like viscous liquids.

Thermosets. Thermosets are highly cross-linked polymers. They have high Young's moduli below T_G, usually one decade higher than thermoplastics. A very weak glass transition is accompanied by a somewhat leathery behavior. The subsequent rubbery region is not very marked because the cross-linking density is high.

8.3. Entropy Elasticity

Elastomers show pronounced entropy elasticities. They exhibit simultaneously some

characteristics of solids, liquids, and gases. Like solids, they display Hookean behavior at not too high deformations (i.e., they show no permanent deformation after removal of the load). Moduli and expansion coefficients, on the other hand, resemble those of liquids. Like compressed gases, stresses increase with increasing temperature for elastomers at $T > T_G$.

The elastic behavior can be modeled with various theories. In the simplest case, dislocations of network junctions are assumed to be affine to the macroscopic deformation of the network. The tensile stress σ_{11} varies with the elongation $\lambda = L/L_o$ according to

$$\sigma_{11} = RT \cdot [M_c] \cdot (V_o/V)^{-1/3}(\lambda - \lambda^{-2})$$

It depends on the volumes before (V_o) and after (V) deformation and on the molar concentration $[M_c]$ of network junctions. True Young's moduli can be obtained from the limiting value of $\sigma_{11}/(\lambda - \lambda^{-2})$ at $\lambda \to 1$, for example, for volume-constant deformations ($V_o/V = 1$):

$$\begin{aligned} RT \cdot [M_c] &= lim_{\lambda \to 1}[\sigma_{11}/(\lambda - \lambda^{-2})] \\ &= \sigma_{11}/[3(\lambda - 1)] = \sigma_{11}/(3\varepsilon) = E_o \end{aligned} \quad (25)$$

The Young's modulus is thus directly proportional to the molar concentration of network junctions (cross-linking sites), independent of the nature of the latter. On shearing, elastomers behave like Hookean bodies because

$$RT \cdot [M_c] = \sigma_{21}/\gamma = G$$

They are, however, non-Hookean for elongations because $E_o \neq \sigma_{11}/\varepsilon$ (Eq. 25).

8.4. Viscoelasticity (→ Plastics, Properties and Testing)

8.4.1. Fundamentals

Most polymers do not revert "instantaneously" to their initial states after the removal of loads; they are neither ideal energy elastic (Section 8.2) nor ideal entropy elastic (Section 8.3). These processes take certain times, (i.e., time-independent elastic and time-dependent viscous properties work together to produce a viscoelastic behavior). If stress, strain, and strain rate can be combined linearly, then the process is said to be linear elastic. In addition, some polymers may be irreversibly deformed.

The two ideal cases of response to deformations can be well described by mechanical models: A spring for a Hookean body (instantaneous response) and a dashpot for a Newtonian liquid (linear time dependence of response) (Fig. 55). The Maxwell element combines spring and dashpot in a series; the Voigt−Kelvin element, in a parallel manner.

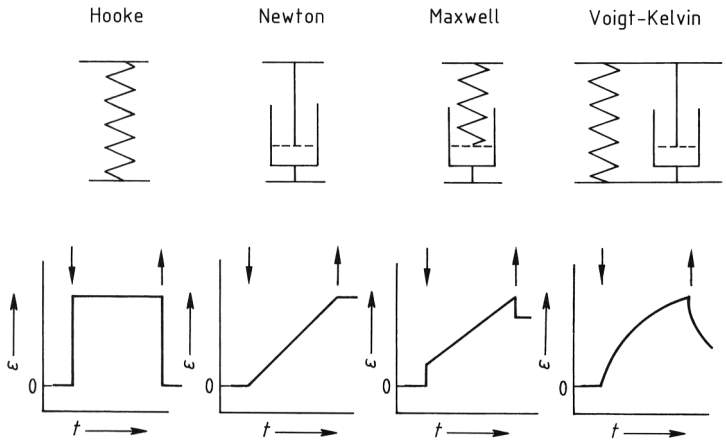


Figure 55. Time dependence of deformations according to various models. Loads are added at ↓ and removed at ↑
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Table 21. Simple mechanical models for the deformation of polymers

Model	Function	Behavior*	
		Initial	Final
Newtonian liquid	$\sigma = \eta \cdot \dot{\gamma}$	L	L
Voigt–Kelvin element	$\sigma = G \cdot \gamma + \eta \cdot \dot{\gamma}$	L	S
Maxwell element	$\sigma + (\eta/G) \cdot \dot{\sigma} = \eta \cdot \dot{\gamma}$	S	L
Hookean body	$\sigma = G \cdot \gamma$	S	S
Jeffrey's body	$\sigma + (\eta/G) \cdot \dot{\sigma} = G \cdot \gamma + \eta \cdot \dot{\gamma}$	S	S

* S = solid-like behavior; L = liquid-like.

The Maxwell element describes a *relaxation* (i.e., the decrease of stress at constant deformation; Table 21). Linear combination of elastic deformation rates $d\gamma_e/dt = (1/G)\ (d\sigma/dt)$ and viscous deformation rates $d\gamma_\eta/dt = \sigma/\eta$ yields, after integration of the resulting expression and indexing the time for this particular behavior for $d\gamma/dt = 0$,

$$\sigma = \sigma_o \cdot \exp(-G \cdot t_e/\eta) = \sigma_o \cdot \exp(-t_e/\tau)$$

The relaxation time $\tau = \eta/G$ indicates the time after which the stress has fallen to the e−1th fraction of its initial value. The ratio τ/t_e of the relaxation time τ to the time scale t_e of the experiment is called the Deborah number ($DB = \tau/t_e$); it is 0 for liquids, ∞ for ideal-elastic solids, and approximately 1 for polymers near their glass transition temperatures.

Retardation is defined as the increase of deformation with time at constant stress. It is characterized by a "creep" of the material. Since this phenomenon was first observed on seemingly solid polymers at room temperature, it is also called "cold flow." In principle, retardation phenomena can be described by a Maxwell element. Because of mathematical difficulties in the solution of the equations, a special model is prefered (Voigt−Kelvin element) (Fig. 55), which yields for the deformation γ_r at constant stress σ_o after indexation for retardations r

$$\gamma_r = (\sigma_o/G_r) \cdot [1 - \exp(-G_r \cdot t_r/\eta)] \quad (26)$$

where G_r is the retardation modulus, also often called the relaxation modulus. The retardation time t_r indicates the time at which the deformation has reached $(1 - 1/e) = 0.632$ of the final deformation σ_o/G_r. Retardation times and relaxation times are of the same magnitude, but not equal because they rely on different models.

The term "viscoelasticity" is sometimes used to describe the reversible deformation according to Equation (26). However, it is often applied to the total deformation, which is composed of the contributions by Equation (26), a Hookean body with $\gamma_e = \sigma_o/G_o$, and a Newtonian liquid [$\gamma_\eta = (\sigma_o/\eta_o) \cdot t$]:

$$\gamma_{tot} = \{(1 - G_o) + (t/\eta_o) + (1/G_r) \cdot [1 - \exp(-t/\tau)]\} \cdot \sigma_o$$
$$= \gamma_e + \gamma_\eta + \gamma_r$$

The three deformation terms γ_e (elastic), γ_η (viscous), and γ_r (viscoelastic) are often not explicitly evaluated. The time-dependent viscous and viscoelastic parts are rather combined into a new parameter $\gamma_c = \gamma \cdot t^n$ (Findlay law). The resulting function for the creep curve allows an extrapolation to long-time behavior from short-time experiments:

$$\gamma_{tot} = \gamma_e + \gamma_c = \gamma_e + \gamma \cdot t^n$$

8.4.2. Time−Temperature Superposition

Deformations, shear moduli, and shear compliances are time and temperature dependent (Fig. 56). The moduli vary about one decade for six decades in time at constant temperature, and up to one decade for each 10 K at constant frequency. Since no single experimental method can cover the 15–20 decades of frequency that are required for good characterization of a polymer, time–temperature data from various techniques are usually combined with the help of the Boltzmann superposition principle.

This principle states that the deformation (or recovery) caused by an additional load (or removal thereof) is independent of previous loads or their removal. The $G = f(t, T)$ curves can be combined if (1) the relaxation time spectrum is temperature independent and (2) the thermal activation is the same over the entire time and temperature range (no transition or relaxation temperatures). A reference temperature is chosen close to the static glass transition temperature (115 vs. 105 °C in

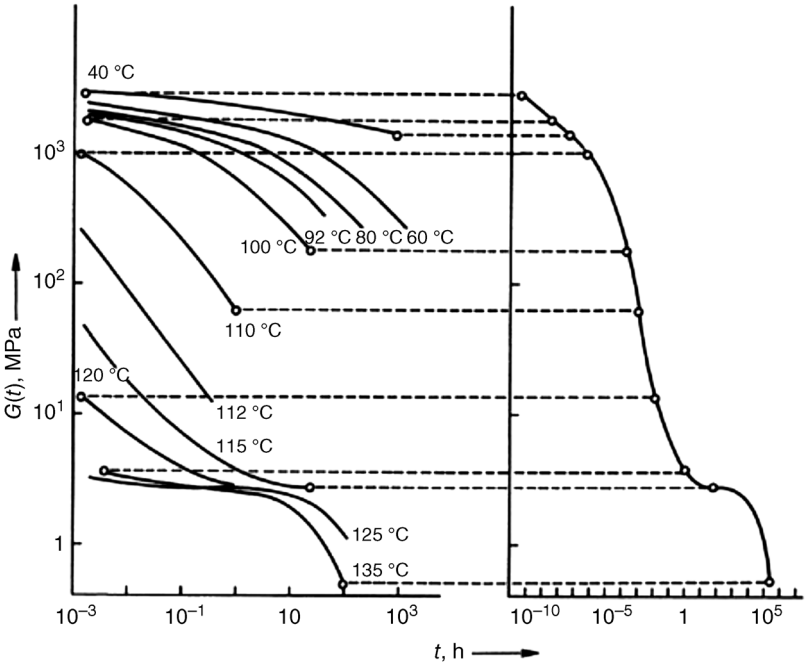


Figure 56. Time dependence of the shear modulus from measurements of the stress relaxation of a poly(methyl methacrylate) ($\overline{M}_n$ = 3 600 000 g/mol) at various temperatures (left) and the resulting time–temperature superpositions for a reference temperature of 115°C (right) (circles represent equivalent positions)
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Fig. 56) and the G values are shifted horizontally with the help of a shift factor from the WLF equation (Eq. 21).

8.5. Dynamic Behavior

8.5.1. Fundamentals

Dynamic–mechanical methods expose the specimen to periodic stresses. The polymer either is put under torsion once and then oscillates freely (torsion pendulum) or is subjected continuously to forced oscillations (e.g., Rheovibron). In addition, ultrasound, dielectric, and NMR methods can be used to study the dynamic properties of polymers.

In the simplest case, the applied stress is sinusoidal with a frequency ω ($\sigma_t = \sigma_o \cdot \sin \omega \cdot t$). The deformation of ideal-elastic bodies follows the stress instantaneously ($\gamma_t = \gamma_o \cdot \sin \omega \cdot t$) but that of viscoelastic polymers experiences a delay ($\gamma_t = \gamma_o \cdot \sin(\omega \cdot t - \vartheta)$. The stress vector is assumed to be a sum of two components: One component is in phase with the deformation ($\sigma' = \sigma_o \cdot \cos\theta$); the other is not ($\sigma'' = \sigma_o \cdot \sin\theta$).

Each of these two components possesses a modulus. The *real modulus* (*shear storage modulus*) G' measures the stiffness and shape stability of the specimen:

$$G' = \sigma'/\gamma_o = (\sigma_o/\gamma_o) \cdot \cos\theta = G^* \cdot \cos\theta$$

whereas the *imaginary modulus* (*shear loss modulus*) G'' describes the loss of usable mechanical energy by dissipation into heat:

$$G'' = \sigma''/\gamma_o = G^* \cdot \sin\theta$$

The same quantities can also be derived if complex variables are introduced

$$G^* = G' + i \cdot G'' = [(G')^2 + (G'')^2]^{-1/2}$$

The loss factor δ is the ratio of imaginary to real modulus. It is the same for shear and

Young's moduli but not for compression moduli

$$\Delta = \tan\theta = G''/G' = E''/E' < K''/K'$$

8.5.2. Molecular Interpretations

The *shear storage moduli* of low molar mass polymer melts with narrow molar mass distributions increase continually with increasing frequency (Fig. 57). At high normalized frequencies $\alpha_T\omega$, all storage moduli asymptotically approach a limiting line, regardless of molar mass. This part of the relaxation spectrum thus originates from the mobility of chain segments; it is called the transition range.

High molar mass polymers show a corresponding frequency dependence of *loss moduli* at very low frequencies (called end range), followed by a plateau at higher frequencies (plateau modulus G_N°), and finally the transition range. The end ranges of these spectra are molar mass dependent; this behavior must come from long-range conformational changes. Since the transition range characterizes viscous behavior, and the end range viscoelastic behavior, the plateau range must reflect rubbery behavior (see Fig. 54 for the temperature dependence).

The *rubbery behavior* of polymer melts can be described by the theories of entropy elasticity according to which the shear modulus of chemically cross-linked polymers depends on the molar concentration of network junctions. The plateau modulus G_N° of melts thus indicates the concentration of temporary junctions (entanglements). The molar mass M_e of segments between such junctions of polymers with volume fractions ϕ_p in solution ($\phi_p = 1$ for melts) and polymer melt densities ρ_p is given by

$$M_e = RT \cdot r_p \cdot \phi_p / G_N^\circ$$

These dynamic entanglement molar masses M_e are a factor 2.0 ± 0.2 lower than the corresponding molar masses M_c from rest viscosities (Table 22).

The plateau is not well developed or may even be absent for polymers with broad molar mass distributions; a complicated dependence of shear compliances on higher molar mass averages has been predicted by reptation theory.

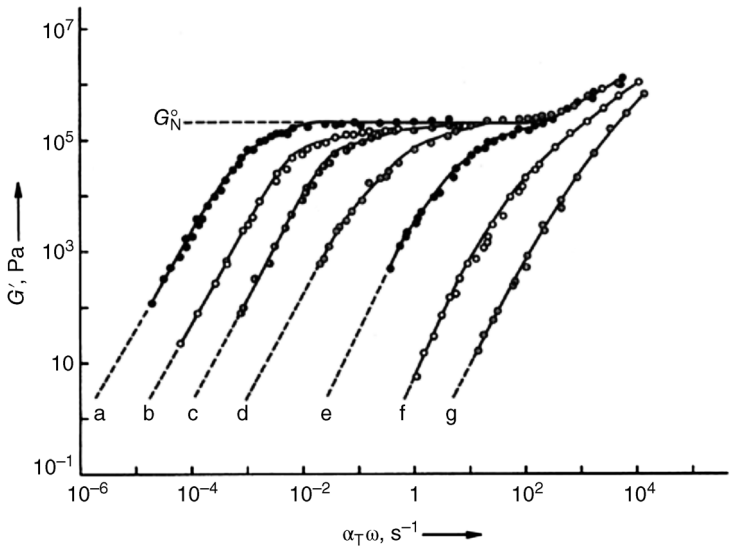


Figure 57. Frequency dependence of the shear storage modulus G' for narrow-distribution polystyrene melts of different molar masses M. A shift factor α_T was used to convert to 160°C data measured at various temperatures
a) M = 581 000 g/mol; b) M = 351 000 g/mol; c) M = 215 000 g/mol; d) M = 113 000 g/mol; e) M = 46 900 g/mol; f) M = 14 800 g/mol; g) M = 8 900 g/mol
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Table 22. Critical molar masses for entanglement from shear moduli (M_e) and rest viscosities (M_c)

Polymer	T, °C	M_c, g/mol	M_e, g/mol	M_c/M_e
Polyethylene	190	3 800	1 790	2.1
Polypropylene, it	190	7 000		
Polyisobutene	25	15 200	8 800	1.7
Polydimethylsiloxane	25	24 500	10 500	2.4
Poly(vinyl acetate), at	57	24 500	12 000	2.0
Poly(α-methylstyrene), at	100	28 000	13 500	2.1
Polystyrene, at	190	35 000	18 100	1.9

8.6. Fracture [129]

8.6.1. Overview

Polymers break very differently depending on their chemical and physical structure; environment (humidity, solvents, temperature); and the type, duration, and frequency of deformation. Some polymers break immediately; others are unchanged even after months. The fracture surface can be smooth or splintery; the elongation at fracture, less than 1% or greater than 1 000%.

Two fracture modes can be distinguished, brittle and tough (ductile). Brittle polymers fracture perpendicularly to the stress direction, tough polymers longitudinally (Fig. 58). A polymer is defined as brittle if its elongation at break is less than 20%.

Brittle fractures are rare for ideal solids since many bonds must be severed simultaneously. Real polymers however contain many small imperfect regions that act as "nuclei" for the formation of microcracks. Brittle polymers usually possess "natural" microvoids, which may also appear in drawn amorphous polymers or through separation of crystal lamellae in hard-tough polymers.

Tough failures (ductile fractures) are caused by viscous flow ("plastic flow"). This process may involve the slipping of chain segments past each other (amorphous polymers) or the movement of crystalline domains (partly crystalline polymers). Polymer chains may also de-entangle at long times and under small stresses. The same processes and additional ones may occur on failure of composites (Fig. 58).

Polymers are subjected to very different stress conditions in typical applications; they thus experience different failure modes. Test methods try to simulate complex real-life situations by standardized procedures. They include long-term experiments such as static deformations under constant load by tension, compression, or bending; short-term methods such as tensile tests under various speeds or impact tests with unnotched or notched specimens; dynamic testing with variation of the number of loadings–unloadings, impacts, vibrations, etc.

8.6.2. Theoretical Fracture Strength

The fracture of brittle polymers generates free radicals. Since the probabilities of such homolyses depend on bond strengths, which also determine tensile moduli, relationships must exist between the theoretical moduli and the theoretical fracture strengths of polymers.

Bonds are severed if atoms are separated from each other by certain distances L_b greater

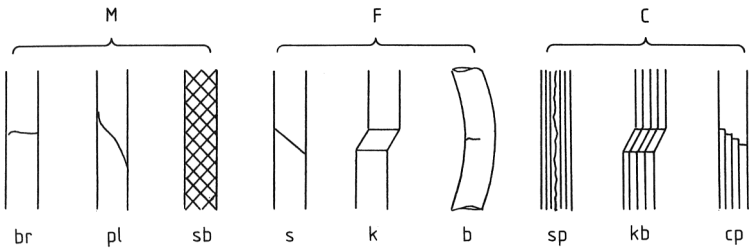


Figure 58. Failure modes of polymers (matrix M), fibers (F), and fiber-reinforced polymer composites (C) by brittle failure (br), plastic flow (pl), shear band formation (sb), shearing (s), kink formation (k), bending (b), longitudinal splicing (sp), formation of kink bands (kb), and step formation by compression (cp)
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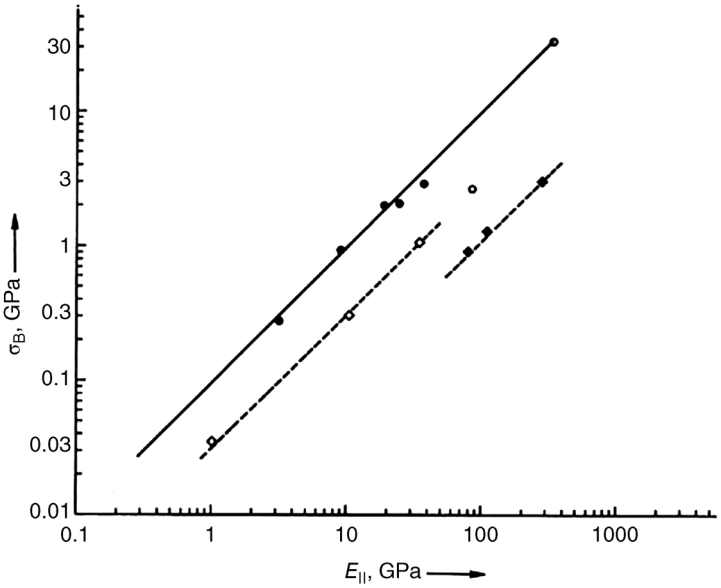


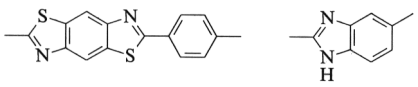
Figure 59. Tensile strength at break as function of tensile modulus: (●) Experimentally ultradrawn ultra-high-modulus polyethylenes; (○) Industrially manufactured ultradrawn polyethylene (Dyneema); (⊙) Theory for perfectly aligned polyethylene; (◆) Heterogeneous molecular composites of ABPBI fibers or PBT fibers or films in ABPBI matrix; (◆) Homogeneous molecular composites of PBT fibers or PBT fibers for films in ABPBI. Solid line corresponds to $\sigma_B = 0.095 \cdot E_\parallel$

than their equilibrium distances L_o. The necessary theoretical strength $\sigma_\parallel^o$ is given by [5].

$$\sigma_\parallel^o = \frac{E_\parallel^o \cdot (L_b - L_o)}{\pi L_o} = K \cdot E_\parallel^o \qquad (27)$$

Polymer main-chain bonds break at approximately the same relative distance ($L_b \approx 1.3\ L_o$) because bond lengths and strengths are not too different for bonds such as C−C, C−O, and C−N. Thus, $K \approx 0.095$ and the theoretical fracture strength $\sigma_\parallel^o$ should be ca. one-tenth of the theoretical tensile modulus $E_\parallel^o$ in the chain direction, regardless of the chemical nature of the polymer. Polyethylene with a theoretical modulus of 340 GPa (Table 19) should thus have a theoretical fracture strength of ca. 32 GPa [i.e., much higher than the theoretical strength of steel (ca. 20 GPa)]. Industrially manufactured ultradrawn polyethylene fibers have higher experimental fracture strengths than steel (2.9 GPa = 2.7 N/tex vs. 2.5 GPa).

The theoretical fracture strength–tensile modulus relationship of Equation (27) has been realized for certain ultradrawn poly- ethylenes in which both the predicted proportionality constant $K = 0.095$ and the first power of E were found (Fig. 59). The type of same relationship is also observed for molecular composites of poly (*p*-phenylene-2,6-bisbenzthiazole) (PPBT) with rodlike mesogens in coillike polybenzimide (ABPBI), albeit with a lower proportionality constant. In other ultradrawing experiments, a power dependence $\sigma = K' \cdot E^n$ was found, however.



PPBT ABPBI

8.6.3. Real Fracture Strength

The lower than theoretical fracture strengths of most polymers (see Tables 19 and 20) are caused by many factors. Theoretical fracture strengths relate to infinitely long, completely aligned, immobile polymer chains. End groups

and chain folds act as disturbances: Fracture strengths of conventional polymers increase with increasing molar mass and become practically constant above a "critical" molar mass.

At the latter molar mass range, chain segments of amorphous polymers are distributed at random. A brittle fracture across such polymers will create two new surfaces with a total surface energy of $2\,\gamma_{lv}$. The theoretical fracture strength for brittle, energy-elastic bodies

$$\sigma_a^o = (E \cdot \gamma_{lv}/L_o)^{1/2} \tag{28}$$

now depends on the product of modulus and surface energy (Ingles theory). The Ingles theory works well for silicate glasses.

The experimentally found fracture strengths σ_b of plastics are however much lower than the strengths predicted by Equation (28). The ratios σ_a^0/σ_{exp} of molded (unoriented) plastics decrease with increasing elongation ε_b at break (Fig. 60), whereas those of drawn fibers (partially oriented chain segments) increase.

The reason for the lower than expected fracture strengths of amorphous polymers is the presence of microvoids, which act on drawing as nuclei for cracks. According to the Griffith theory, a crack can grow only if the energy required for the fracture of chemical bonds is just surpassed by the stored elastic energy. This theory predicts a dependence of the fracture strength on crack length L:

$$\sigma_B = [(2E \cdot \gamma_{lv})/(\pi \cdot L)]^{1/2} \tag{29}$$

This functionality is indeed observed for artificially introduced long cracks. The predicted fracture strengths are however much lower than those found by experiment. Furthermore, deviations from Equation (29) occur at small crack lengths because the fracture behavior of plastics is not dominated by the cleavage of chemical bonds but by other types of energy absorption (crazing; shear flow).

On drawing, stresses are imposed on microvoids. The polymer reaches its upper yield stress at sufficiently high stress concentrations at the tip of such a void and relieves the stress by stress softening (Fig. 51). The induced cooperative movements of chain segments cause long-range changes of macroconformations. In partially crystalline polymers, these changes can occur

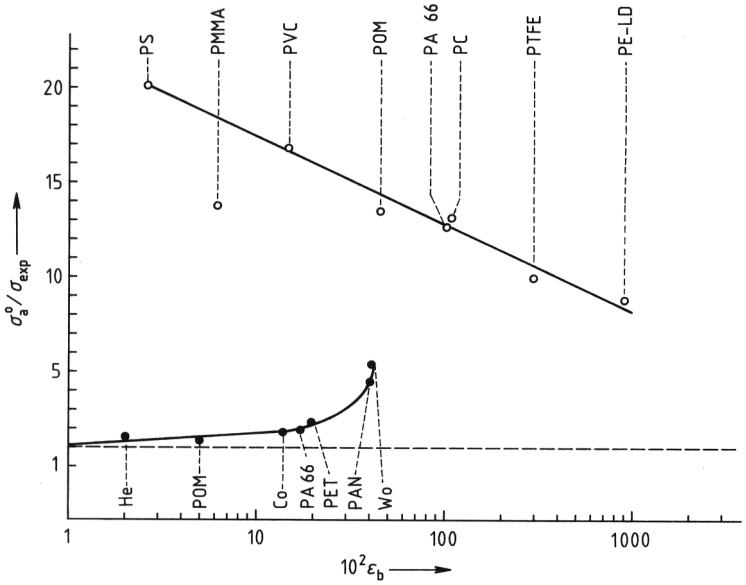


Figure 60. Ratio σ_a^0/σ_{exp} of theoretical [Eq. (28)] and experimental fracture strengths as function of elongation at break ε_b for (○) nonoriented (molded plastics) and (●) oriented (fibers) polymers
He = hemp, Co = cotton, Wo = wool (for other abbreviations see Tables 1–4)

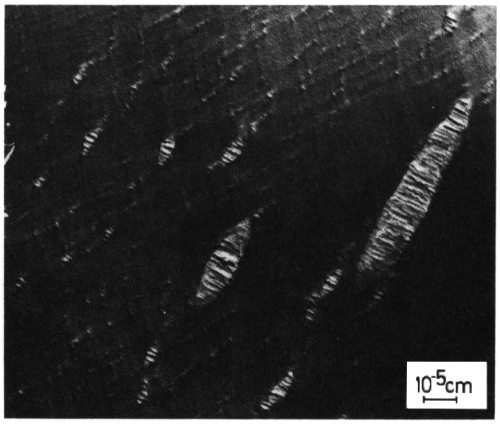


Figure 61. Crazes in a polystyrene drawn to 25% [132]

only in amorphous domains; spherulitic polymers break accordingly either between spherulites or in the radial spherulite direction.

The cooperative movements of segments lead to either shear or normal stress yielding. On shearing, the whole specimen yields either homogeneously or heterogeneously (localized). In the latter case, shear bands are formed at angles of 38–45° to the stress direction (Fig. 58). Chain segments are arranged at angles between shear bands and stress directions.

All polymers with upper yield values form crazes upon stress softening (Fig. 61), regardless of whether they are amorphous, crystalline, linear, or cross-linked. Crazes can be up to 100 μm long and 10 μm wide; their long axes are parallel to the stress direction. They are not voids since their interior is filled with amorphous microfibrils of 0.6–30 nm diameter; these microfibrils are oriented in the stress direction (i.e., perpendicular to the craze long axes). On further deformation, microvoids are formed.

The formation of crazes is the primary mechanism for the dissipation of stress energy. It is utilized in the rubber reinforcement of polystyrene. Rubber-modified polypropylene, on the other hand, deforms mainly by shear flow.

8.6.4. Impact Resistance

Impact strength is the resistance of a material to impact. It is one of the many quantities used to characterize the strength of a material under (the usually complex) use conditions; all test methods are thus standardized. Most test methods measure the energy required to break a notched or unnotched specimen (Izod, Charpy, high-speed tensile). Impact speeds range from $10^{-5}-10^{-1}$ m/s in conventional tensile tests to 20–240 m/s for high-speed tensiles; elongation speeds are usually from 10^{-3} to 10^{4} s^{-1}.

Impact strengths depend on experimental conditions. The smaller the radius of the notch, the higher is the stress concentration at the tip and the lower is the impact strength. At very low temperature, all polymers are brittle. The mobility of chain segments increases with increasing temperature, allowing stresses to be relieved by shear-band or craze formation. Impact strengths increase with temperature, especially near the glass transition temperature. Polymers with additional transition temperatures below the glass transition temperatures are for the same reason almost always more impact resistant than polymers without such transitions. Nonentangled polymers exhibit very low impact strengths because no crazes can be formed. The impact behavior of polymers can be improved considerably by modification with rubber (see Section 11.4.3).

8.6.5. Stress Cracking

Stress cracking (stress corrosion, stress crazing) is the formation of crazes under the physical action of chemicals, especially surfactants. Stress corrosion starts at polymer surfaces and proceeds into the interior until the polymer finally cracks. The appearance and the extent of stress cracking depend on the polymer–reagent interaction and the magnitude of the stress.

Effects are weak in nonwetting liquids but strong in polymer–liquid systems with solubility parameters of polymers and liquids matching each other and even more dramatic under tension in the presence of surfactants. Stress cracking decreases with increasing molar mass of the polymer since entanglements allow stresses to relax elastically. Cross-linked polymers are less prone to stress cracking for the same reason. Stress cracking

is also reduced if polymer plasticizers are present in plastics because these additives increase the mobility of chain segments and thus the ability to relieve stresses. The same action is responsible for the fact that no stress corrosions are observed above glass transition temperatures.

8.6.6. Fatigue

Materials may be damaged not only "instantaneously" (i.e., on impact) but also by static or periodic loads after certain times or number of loadings. This fatigue is characterized by the *fatigue limit* (endurance) at which the plastics are not damaged even after infinite time and the *fatigue strength*, which indicates the load at which damage sets in after a certain time.

Plastics may be subjected to static loads for certain times t, after which their fracture strengths σ_B are measured by tensile tests. The logarithms of strength of amorphous polymers usually decrease linearly with logarithms of time due to viscous flow (Fig. 62). Partially crystalline polymers show a bend in these lines after certain times, which indicates a change from tough fracture (short times) to brittle fracture (long times), probably caused by recrystallization phenomena.

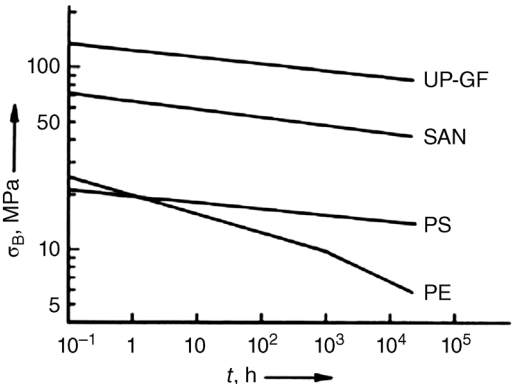


Figure 62. Time dependence of tensile fracture strengths after static loading during time t. UP-GF = glass-fiber-reinforced unsaturated polyester; SAN = styrene–acrylonitrile copolymer (impact polystyrene); PS = polystyrene; PE = polyethylene
Reprinted with permission by BASF AG, Ludwigshafen [127]

8.7. Surface Mechanics

8.7.1. Hardness

The hardness of a material is its resistance to penetration by another body. Hardness is a very complex quantity; it depends on Young's modulus, yield stress, and stress hardening. A general definition of hardness, applicable to all materials, does not exist; neither does a universally applicable testing method. The various technical test methods thus emphasize one or another factor that contributes to the hardness of a specific class of materials.

The hardness of *hard plastics* is normally characterized by various Rockwell (ISO, ASTM) or ball indentation hardnesses (DIN, ISO). These methods measure the indentation of a polymer by a steel sphere under load and thus the compression set and the recoverable deformation. The plastic deformations of polymers increase with time (creep), whereas those of metals are time independent. Because of the short duration of the hardness test polymers exhibit relatively high Rockwell hardnesses.

The hardness of *soft plastics* is characterized by their durometer (ASTM) or various Shore hardnesses (ISO, DIN). These methods measure the resistance to penetration by a truncated cone (static methods). Hardness properties of metals and hard plastics are evaluated by another Shore hardness that uses the rebound of a small steel sphere (dynamic method).

All methods measure the hardness of surfaces, not of the interior of the specimen. The surface may, for example, be plasticized by the humidity of the air. Crystallizable polymers may have lower surface hardnesses than interior hardnesses (if the plastic had been injected into a cold mold) or the reverse may be true (if transcrystallization occurred).

8.7.2. Friction

Friction, the resistance against the relative movement of two bodies contacting each other is measured by the friction coefficient $\mu = R/L$ (i.e., the ratio of friction R to total load L). Friction depends in a complex and not understood way

Table 23. Friction coefficients of various sliding bodies

Plastic	Friction coefficient of		
	Plastic on plastic	Plastic on steel	Steel on plastic
Poly(methyl methacrylate)	0.8	0.5	0.45
Polystyrene	0.5	0.3	0.35
Polyethylene, high density	0.1	0.15	0.20
Polyethylene, low density	0.3		0.80
Polytetrafluoroethylene	0.04	0.04	0.10

Table 24. Abrasion coefficients K for moving plastics against resting materials

Resting material	$10^{10}K$, MPa^{-1}	Moving polymer	$10^{10}K$, MPa^{-1}
Polycarbonate A	200 000	polyamide 66	11 000
Polyamide 66	250	polycarbonate A	9 800
Polyamide 66	220	polyamide 66	510
Polyamide 66	10	polyacetal	12
Polyacetal	11	polyamide 66	15
Steel		polyamide 66	8 600
Steel		polyamide 66 with 30% glass fibers	1

on both the surface roughness of the specimen and its mechanical properties.

The rolling of *hard bodies on soft materials* is determined almost exclusively by the deformation of the soft base (i.e., its viscoelastic properties). Elastomers thus have fairly high friction coefficients of $0.5 < \mu < 3.0$, depending on the contacting body and its type of movement (rolling, sliding).

The sliding of *hard bodies on other hard bodies* occurs on the tops of the microscopic surfaces: The true contact area is much smaller than the geometric one. The applied load thus acts on very small effective areas. Local stresses are high and the tops are leveled. Large adhesion forces exist between chemical groups of the resulting effective contact areas of both bodies, which must be overcome by breaking the bonds or by shearing one of the materials. The adhesive friction $R = A_w \cdot \sigma_b$ is given by the effective contact surface A_w and the shear strength σ_b. Soft materials possess high effective surfaces (large A_w) and are easily sheared (small σ_b), whereas the opposite is true for hard materials. Plastics, metals, and ceramics therefore often exhibit very similar friction coefficients (Table 23).

8.7.3. Abrasion and Wear

Abrasion is the loss of material from surfaces by friction. It is thus affected by both friction properties and hardnesses of the specimens. The abrasion coefficient K is given by the applied force F, the linear speed ν of the contacting body, the total time t, and the volume loss ΔV of the abraded material: $K = \Delta V/(F \cdot \nu \cdot t)$.

Abrasion coefficients vary widely with polymer type and state (resting, mobile) (Table 24).

The best resistance against abrasion is shown by polyureas, followed by polyamides and polyacetals. It can be enhanced greatly by addition of certain fillers (e.g., short fibers).

9. Electric Properties [116, 126, 133, 134]

Matter is subdivided according to its specific electrical conductivity σ into insulators ($\sigma = 10^{-14}$–10^{-22} S/cm), semiconductors (10^{2}–10^{-9} S/cm), conductors ($> 10^{3}$ S/cm), and superconductors ($\approx 10^{20}$ S/cm). Most plastics are insulators (Section 9.1), but certain polymers are intrinsic semiconductors and some may even be conductors after doping (Section 9.2).

9.1. Dielectric Properties

9.1.1. Relative Permittivity

Groups within a molecule and entire molecules of an insulator are polarized by applied electric fields. Polarization is usually measured by the ratio of capacitances of a condensor in vacuo and in the specimen (i.e., the relative

Table 25. Electrical properties of plastics

Polymer	Δw [a]		ρ_v [c]	ρ_s [d]	S [f]		
	%	ε_r [b]	Ω·cm	Ω	tan δ [e]	$kV^{-1}\,mm^{-1}$	U [g]/V
PTFE	0	2.15	10^{18}		0.0001	40	> 600
PE	0.05	2.3	10^{17}	10^{13}	0.0007	70	600
PS	0.1	2.5	10^{18}	10^{15}	0.0002	140	500
SAN		3			0.0070	100	
ABS		3.2	10^{15}	10^{13}	0.02	15	600
PVC	< 1.8[h]	< 3.7[h]	10^{15}	10^{13}	0.015	< 50	< 600
PA 6							
Dry	0	3.7	10^{15}		0.03	< 150	600
Conditioned	9.5	7	10^{12}		0.3	80	600
CA	4.7	5.8	10^{13}		0.03	35	
UP		3.4	10^{13}	10^{12}	0.01	50	500
PUR		4	10^{13}		0.05	30	
PF		8	10^{14}		0.05	12	
With inorganic fillers			10^{10}		< 0.5	14	< 150
Without inorganic fillers			10^{9}		< 0.5	10	125
UF		6	10^{11}		0.1	10	

[a] Δw = water absorption (at 50% relative humidity).
[b] ε_r = relative permittivity ("dielectric constant").
[c] ρ_v = volume resistivity (inverse specific electrical conductivity).
[d] ρ_S = surface resistivity (inverse surface conductivity).
[e] tan δ = dissipation factor (loss tangent, at 1 MHz).
[f] S = dielectric strength.
[g] U = tracking resistance (method KC).
[h] Depends on impurities from polymerization (e.g., emulsifier residues).

permittivity ε_r of the specimen; formerly called the dielectric constant). Relative permittivities are low for apolar polymers [polytetrafluoroethylene (PTFE); PE], higher for polymers with polarizable groups (PS, PC), and still higher for polar materials [dry polyamide (PA)] (Table 25).

The relative permittivity thus increases with increasing water content of plastics (ε_r = 81 for water). It also increases with increased segmental mobility (ε_r = 13.0 for *cis*-1,4-polyisoprene); rubber-modified plastics have higher relative permittivities than conventional plastics. Expanded plastics and elastomers are composites with air (ε_r = 1.00058) and subsequently have low relative permittivities of ca. 1–2. Fillers increase the relative permittivities to values up to 170 (filled thermoplastics) and up to 18 000 (filled elastomers).

9.1.2. Dielectric Loss

Dipoles try to follow the direction of an electric field if an alternating current is applied. The required adjustment times correspond to the orientation times of groups and molecules. The faster the alternation, the longer the orientation lags behind the field and the greater is the electrical energy consumed. Available output power is decreased because electric power is lost by conversion into thermal energy.

The ratio of power loss N_v to total power output N_b is called the dielectric dissipation factor or loss tangent tan δ, which can also be expressed as the ratio of imaginary relative permittivity (ε'') to real relative permittivity (ε'):

$$N_v/N_b = \tan\delta = \sin\delta/\cos\delta = \varepsilon''/\varepsilon'$$

Sometimes power factors sinδ are given instead of loss tangents tan δ.

Polymers with high loss factors $\varepsilon \cdot \tan\delta$ can be heated and thus welded by high-frequency fields; PVC is an example. Polymers with low loss factors [PE, PS, polyisobutene (PIB)], on the other hand, are excellent insulators for high-frequency conductors.

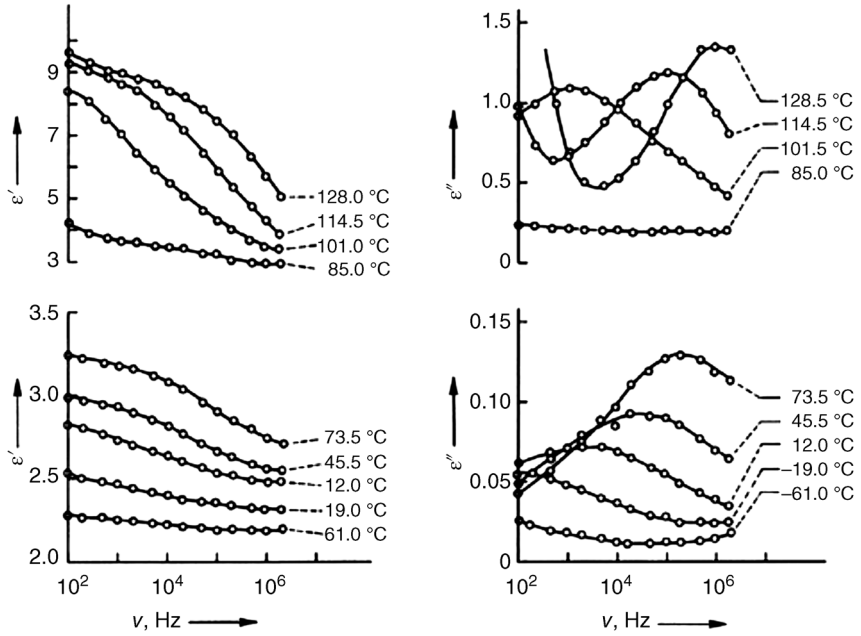


Figure 63. Frequency dependence of real (ε′) and imaginary relative permittivities (ε″) of a poly(vinyl chloride) at various temperatures
Upper: β-dispersion; lower: γ-dispersion.
Reprinted with permission by Hüthig and Wepf Publ., Basel [5]

Real and imaginary relative permittivities depend on the frequencies ν of the alternating current (Fig. 63). The function $\varepsilon' = f(\nu)$ corresponds to a dispersion and the function $\varepsilon'' = f(\nu)$ to an absorption of energy. Transitions and relaxations consume energy and therefore inflection points (ε′-curves) and maxima (ε″-curves) are found at appropriate temperatures and frequencies.

9.1.3. Dielectric Strength and Tracking Resistance

The imaginary part of the relative permittivity is caused by the dissociation of polar groups that may be either inherent to the polymer or introduced by extraneous impurities. These polar groups must be of ionic nature since the electrical conductivities of conventional plastics are strongly temperature dependent (electronic conductivities are far less temperature dependent).

Heat is caused to develop by the imaginary part of the relative permittivity. The low thermal conductivities of plastics do not allow this heat to dissipate, and the temperature increases. Ionic conductivities are thus increased until a breakdown (arcthrough) finally occurs. The resistance against such a breakdown is measured by the electric strengths S of a plastic ("dielectric strength") (Table 25).

A breakdown can also occur through tracking on the surface of a plastic. The tracking resistance is difficult to measure because surface resistivities are 2–3 decades lower than volume resistivities (Table 25). The tracking resistance is thus measured by standardized methods, such as the maximal voltage that does not cause tracking if 50 drops of an aqueous 0.1 wt% NH_4Cl solution are applied between two platinum electrodes that are under an alternating current and 4 mm apart

on the specimen surface. A polymer has a good tracking resistance if it forms volatile products and no carbon upon degradation (volatile monomer by depolymerization of PMMA, volatile oligomers by degradation of PE or PA). Poly(*N*-vinyl carbazole) does not form volatile products and thus has a poor tracking resistance although it is a good insulator.

9.1.4. Electrostatic Charging

Static electricity originates from an excess or a deficiency of electrons on isolated or ungrounded surfaces. It can be created by rubbing two surfaces against each other (triboelectric charging) or by contact of a surface with ionized air. Matter is charged electrostatically if specific conductivities are lower than ca. 10^{-8} S/cm and relative humidities lower than ca. 70%. All conventional plastics can thus be electrostatically charged (Table 25). Charge densities may vary between, e. g., 8.2 C/g for polychlorotrifluoroethylene (PCTFE) and − 13.9 C/g for phenolic resins, and charges may vary between 3 000 V/cm (POM vs. PA 6) and – 1 700 V/cm (ABS vs. PA 6).

Static charging can be reduced by incorporation of conducting fillers into the plastics, such as carbon black or metal powders (internal antistatics). External antistatics reduce surface resistivities by increasing the polarity of the surface via application of humidity-absorbing additives or by reducing friction through lubricants or coating with PTFE.

9.2. Electrical Conductivity (→ Polymers, Electrically Conducting) [126, 133–137]

Electrical conductivities in metals are caused by $N/V = 10^{21}$–10^{22} (quasi) free electrons per cubic centimeter with electric charges $e \equiv 1.6 \times 10^{-19}$ C and mobilities $\mu = 10$–10^6 cm^2 V^{-1} s^{-1}. According to

$$\sigma = (N/V) \cdot \mu \cdot e$$

specific electrical conductivities of metals are therefore between ca. 630 000 (Ag) and 10 400 (Hg) S/cm. Graphite exhibits $\sigma = 10^4$ S/cm in plane direction and 1 S/cm perpendicular to it. Semiconductors possess carrier mobilities similar to metals but at far lower carrier concentrations.

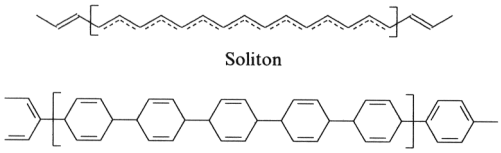
Charge transfer occurs fairly easily in metals and semimetals because atoms are tightly packed. Chain atoms of polymer molecules are also close in the chain direction because of covalent bonds. Only van der Waals and/or dipole forces act between chains, however, resulting in large intermolecular atomic distances and very difficult charge transfers. All electrons are furthermore localized in covalent polymer chains. Conventional polymers are thus insulators.

Polymers with conjugated chains [e.g., *trans*-polyacetylene $\sim(CH{=}CH)_n\sim$] are, for these reasons, merely semiconductors and insulators even if the chains are planar. These low conductivities can be increased substantially, however, if the polymers are doped with substances such as I_2, AsF_5, BF_3, etc.: Doping with AsF_5 increases the specific electrical conductivity of *trans*-polyacetylene from 10^{-9} to 1 200 S/cm and of poly(*p*-phenylene) from 10^{-15} to 500 S/cm. Such doped polymers can be processed like thermoplastics to any shape desired, which together with their light weight makes them attractive for many applications.

The action of these dopants is quite different from those of small amounts of dopants in inorganic semiconductors. The doping of inorganic semiconductors such as GaP, InSb, or Ge generates quasi-free electrons (*n*-carriers) or defect electrons (*p*-carriers), whereas the doping of suitable organic polymers leads to oxidation (*p*-doping) or reduction (*n*-doping) reactions. Sizable effects in organics are thus achieved only if large amounts of dopants are used, often up to 1 : 1 molar ratios of dopants to repeating units.

Doped polymers exhibit neither Curie paramagnetism (localized charge carriers) nor Pauli paramagnetism (electrons delocalized over the entire system). Thus the electrical conductivity of such systems is assumed to be due to *solitons* or *polarons*.

Double and single bonds alternate in *trans*-polyacetylene. Since these bonds are exchangeable, two low-energy states A and B with equal energy must exist. A soliton is a kind of topological kink that separates the A state from the B state with opposite bond alternation. Polarons are similar kinks between aromatic and quinoid structures:



The kink is small (about 14 chain atoms in *trans*-polyacetylene) and thus very mobile. Two types of solitons and polarons exist. Neutral solitons and polarons possess radicals that are produced as defects during isomerization of the polymers. Charged solitons and polarons are created by doping, either as carbonium ions or as carbanions.

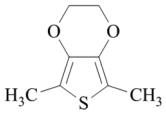
Solitons can move only along the chain; there is no tunnel effect between chains. Because of this anisotropic behavior, doped polymers (and conducting low molar mass organic molecules) are called low-dimensional conductors, synthetic metals, or organic metals.

The most important condition for the existence of electrical conductivity in organic polymers seems to be the ability to form overlapping orbitals. The planar structure of *trans*-polyacetylene promotes the overlapping of its π and *p* orbitals. In poly(*p*-phenylene sulfide) (PPS) $\sim[S-(p\text{-}C_6H_4)]_n\sim$, *p* and *d* orbitals of sulfur atoms probably overlap with the π systems of phenylene groups; $PPS-AsF_5$ shows an electrical conductivity of 10 S/cm, although the chain is not planar and the phenylene residues are arranged at angles of 45 °C to the planar zigzag chain of the sulfur atoms.

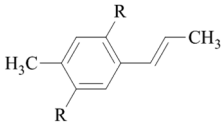
Electrically conducting polymers are presently used in small batteries, for example, a complex of poly(2-vinylpyridine)/I_2 as cathode in Li/I_2 batteries for pacemakers ($\sigma = 10^{-3}$ S/cm). Other possible applications of electrically conducting polymers are in solar cells, electrolysis membranes, microwave shielding, and integrated circuits.

One prime example of an electrically conducting polymer is poly-3,4-ethylendioxythiophene (PEDOT), which consists of 2,5-coupled 3,4-ethylendioxythiophene repeat units and is made by oxidative coupling. In its oxidized form, PEDOT is an almost transparent, light-blue conductor, and, depending on the application, several counterions can be employed. The most common form of PEDOT is the commercially available blend with polystyrene sulfonate (PSS) in aqueous suspension (PEDOT:PSS, Baytron P). High conductivities up to 1 000 S/cm allow to apply this material as thin film for electrode coatings in solar cells or sensor devices to replace the traditionally used indium tin oxide.

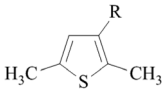
Although high electrical conductivities of conjugated polymers obtained by chemical doping are important for e.g., electrode applications, conjugated absorber materials in organic photovoltaics are required to exhibit semiconducting behavior. An appropriate design of conjugated polymers for organic photovoltaics is of critical importance, as several parameters, such as absorption, energy levels, charge carrier mobility, molar mass, or solubility have to be considered simultaneously and are mutually dependent. Consequently, numerous new conjugated polymer structures have been prepared by transition metal-catalyzed cross coupling since the 1990s, whereby the most successful materials have moved from the class of polyphenylene–vinylenes (PPV) and poly(3-alkylthiophene)s (P3ATs) to donor–acceptor polymers with alternating electron-rich and electron-deficient repeat units. The photovoltaic performance of the best donor–acceptor copolymers are now approaching 10%, which is considered an important threshold value to commercialization. Two successful copolymers DPPTT and PTB7 are shown below:



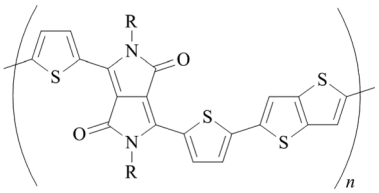
PEDOT



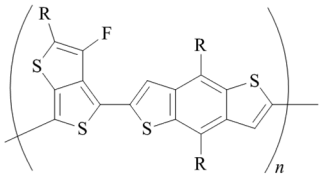
PPV



P3AT



DPPTT



PTB7

9.3. Photoconductivity

Light generates radical ions and thus photoconductivities in certain systems. This effect is used in xerography to generate pictures of objects (e.g., copies of documents). The early photoconducting material As_2Se_3 has since been replaced by poly(*N*-vinylcarbazole), which absorbs UV light and forms an exciton, which is ionized by an electric field. The polymer is nonconducting in visible light; upon sensibilization by certain electron donors, charge-transfer complexes are formed, however. Another photoconducting system consists of polycarbonate A and triphenylamine.

10. Optical Properties [116]

Many optical properties of plastics depend on their *refractive index n*, for example, reflection, gloss, transparency, and hiding power. Refractive indices are in turn determined by the polarizabilities *Q* according to the Lorenz–Lorentz relationship

$$(n^2 - 1)/(n^2 - 2) = (4/3)\pi Q = (4/3)\pi(N/V) \cdot \alpha$$

where *N/V* is the number concentration of molecules with polarization α. The polarization is a function of the dipole moments of all groups in a molecule (i.e., the mobility and the number of electrons per molecule). Contributions to the refractive index are thus much higher for carbon atoms than for hydrogen atoms. Because the contributions of the latter can be neglected and because carbon atoms dominate the structures of polymers, all polymers possess approximately the same refractive index of 1.5 (e.g., PMMA 1.492, PP-it 1.53, PS 1.59). Deviations from this rule exist for strongly polarizable polymers (PTFE 1.37), polymers with bulky conjugated substituents (PVK 1.69), or polymers with a high content of noncarbon atoms (PDMS 1.40). According to the molecular structure of all known polymers, their refractive indices should be between ca. 1.33 and 1.73.

Molecules are more tightly packed in crystalline polymers than in amorphous ones. Refractive indices thus increase with increasing crystallinity. Because crystalline polymers are always anisotropic, different polarizabilities and

refractive indices are exhibited in the chain direction and perpendicular to it.

A part of the light falling on a homogeneous, transparent body is reflected. *Reflectivity* is defined as the ratio of the intensities of reflected and incident light $R = I_r/I_o$, which according to Fresnel's law depends on the angles of incidence α and refraction β:

$$R = \frac{I_r}{I_0} = \frac{1}{2}\left[\frac{\sin^2(\alpha-\beta)}{\sin^2(\alpha+\beta)} + \frac{\tan^2(\alpha-\beta)}{\tan^2(\alpha+\beta)}\right] \quad (30)$$

The reflectivity is low at small incident angles ($R = 0.040$ for $n = 1.5$ at 10°) and rises sharply at higher ones ($R = 0.388$ for $n = 1.5$ at 80°).

Gloss is the ratio of the reflection of the specimen to that of a standard, for example, a body with $n_D = 1.567$ in the paint industry. The maximum theoretical gloss R_o is given by Equation (30). It increases with increasing refractive index of the specimen and with increasing angle of incidence (Fig. 64). The maximum theoretical gloss is almost never achieved because of surface roughness.

The maximum *transparencies* $\tau_i = 1 - R_o$ can be calculated from $R_o = (n-1)^2/(n+1)^2$ by Fresnel's law for $\alpha \to 0$ and $\beta \to 0$. They can have values between 98.0% ($n = 1.33$) and 92.8% ($n = 1.73$) for polymers, (i.e., between 2 and 7.2% of the incident light is maximally reflected at the polymer–air interface). These ideal transparencies are rarely achieved for polymers because a small portion of the light is always absorbed and/or scattered. Poly(methyl methacrylate), one of the most transparent plastics, never exceeds a transparency of ca. 93% between wavelengths of 430 and 1 100 nm (theory 96.1%). Transparencies decrease above wavelengths of ca. 1 150 nm and (rapidly) below 380 nm. All polymers except halogenated polyethylenes absorb infrared radiation.

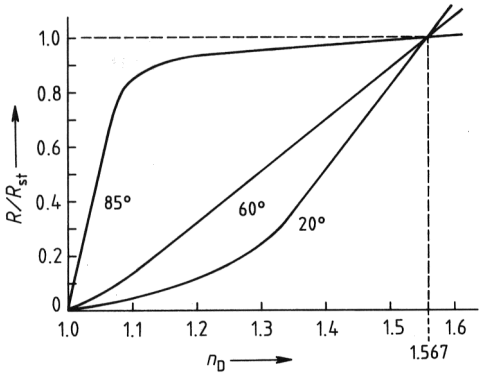


Figure 64. Maximum theoretical gloss as a function of the refractive index of specimen for various angles of incidence α and a standard with $n_D = 1.567$
Reprinted with permission by Hüthig and Wepf Publ., Basel [5]

A distinction is usually made between transparent and translucent polymers. *Transparent* polymers have transparencies > 90%; they look clear even at greater thicknesses. *Translucent* polymers ($\tau_i < 0.90$) appear clear only as thin films. They are also called contact clear because films look clear in contact with packaged goods but turbid when viewed alone.

An additional loss of clarity is caused by light scattering. Electromagnetic waves lose part of their energy by scattering in inhomogeneous systems. The loss of contrast by forward scattering is called *haze*. The combined loss by forward and backward scattering makes a specimen milky. A body appears opaque if local fluctuations of refractive indices or orientations of anisotropic volume elements are present. The different volume elements must also be larger than the wavelength of incident light. The clarity of a material can thus be increased considerably if the size of the different volume elements (e.g., microdomains) is decreased. Diminished differences in refractive indices improve the clarity to only a small extent. Lamellar structures are optically less heterogeneous than spherulites of approximately the same diameter. Under certain conditions, clear polyethylene films can be produced by quenching and orientation, although crystalline lamellae with dimensions greater than the wavelength of light are present in these films.

11. Polymer Composites (→ Composite Materials) [138]

11.1. Introduction

11.1.1. Overview

The term composite has various meanings. In general, it denotes a complex material in which

two or more distinct substances combine to produce some properties not present in any individual component. In biomaterials, it means any two joined materials (e.g., polymer-coated titanium parts). In engineering, composites are more narrowly defined as physical admixtures of various materials that are present as distinct phases. The term "phase" is used here in the descriptive sense, not in the thermodynamic one. The engineering term "composite" thus includes only heterogeneous composites. Heterocomposites can be further subdivided into nanocomposites (dispersed phase has at least one dimension smaller than 100 nm), microcomposites (dispersed phase in the micrometer to millimeter range), and macrocomposites. Polymer composites are defined as composites in which at least one component is of a polymeric nature. In accordance with the general definition of a composite and in contrast to the engineering use of the word, the term "polymer composite" is often used to cover not only heterogeneous mixtures of a polymer and another material (minerals, fibers, other plastics, elastomers, etc.), but also homogeneous (single-phase) materials of two polymers (homogeneous polymer blends). Such polymer composites are a subgroup of "multicomponent polymer systems", which also include copolymers (two or more types of monomeric units chemically bound together).

Polymer composites occur naturally (wood, bamboo, lobster shells, bone, muscle tissue, etc.) or are manufactured synthetically. Synthetic polymer composites can also be subdivided into single-phase (homogeneous) and multiphase (heterogeneous) composites. Further subdivisions may be according to the second component's size (microcomposites, macrocomposites), chemical nature (air, low molar mass plasticizer, elastomer, plastic, mineral), geometry (particulate, fiber, platelet, fabric), and macroconformation (if polymeric: coil, rod), etc. (see Fig. 65). Most of these subclasses have different technical names depending on whether the glass transition temperature of the continuous phase is above (plastics) or below (rubbers) the use temperature. The same name is often given to various subtypes.

A mixture of two (or more) different polymers is often called a *blend* when both polymers are either above (rubber) or below (plastics) their glass transition temperatures. Blends are distinguished from composites of two polymers such as polymer–fiber-reinforced or rubber-toughened plastics. The term blend is sometimes restricted to mean only "incompatible polymer mixtures", whereas compatible polymer mixtures are called polymer alloys. The latter term is, however, occasionally more narrowly used for mixtures of two crystallizable polymers.

The term *miscibility* refers to admixtures on the molecular level (nanometer range), that is true thermodynamic solubility. It is sometimes used more loosely for any polymer mixture that exhibits only one glass transition temperature. *Compatibility* denotes the ability of admixtures to be blended to heterogeneous microcomposites that do not separate into macroscopic phases.

11.1.2. Mixture Rules

The composition dependence of properties Q of composites can often be described by mixture rules. The *generalized simple mixing law* relates Q to the fractions $f_A = 1 - f_B$ of components A and B with properties Q_A and Q_B:

$$Q^n = Q_A^n \cdot f_A + Q_B^n \cdot f_B \tag{31}$$

The generalized simple mixing law is usually applicable to single-phase composites without specific interactions of its components and to two-phase systems with regularly dispersed discrete phases of "infinite" dimensions. It includes three special cases that are known by different names in different fields (Table 26) and are illustrated in Figure 66.

The *rule of mixtures* ($n = 1$) applies, for example, to various moduli if both components behave elastically. An example is Young's modulus parallel to the fiber direction for epoxide resins reinforced with long glass fibers (see below). The same composites follow the *inverse rule of mixtures* ($n = -1$) if the modulus is measured perpendicular to the fiber direction and no slippage occurs. The *logarithmic mixture rule*

$$\log Q = f_A \cdot \log Q_A + f_B \cdot \log Q_B \tag{32}$$

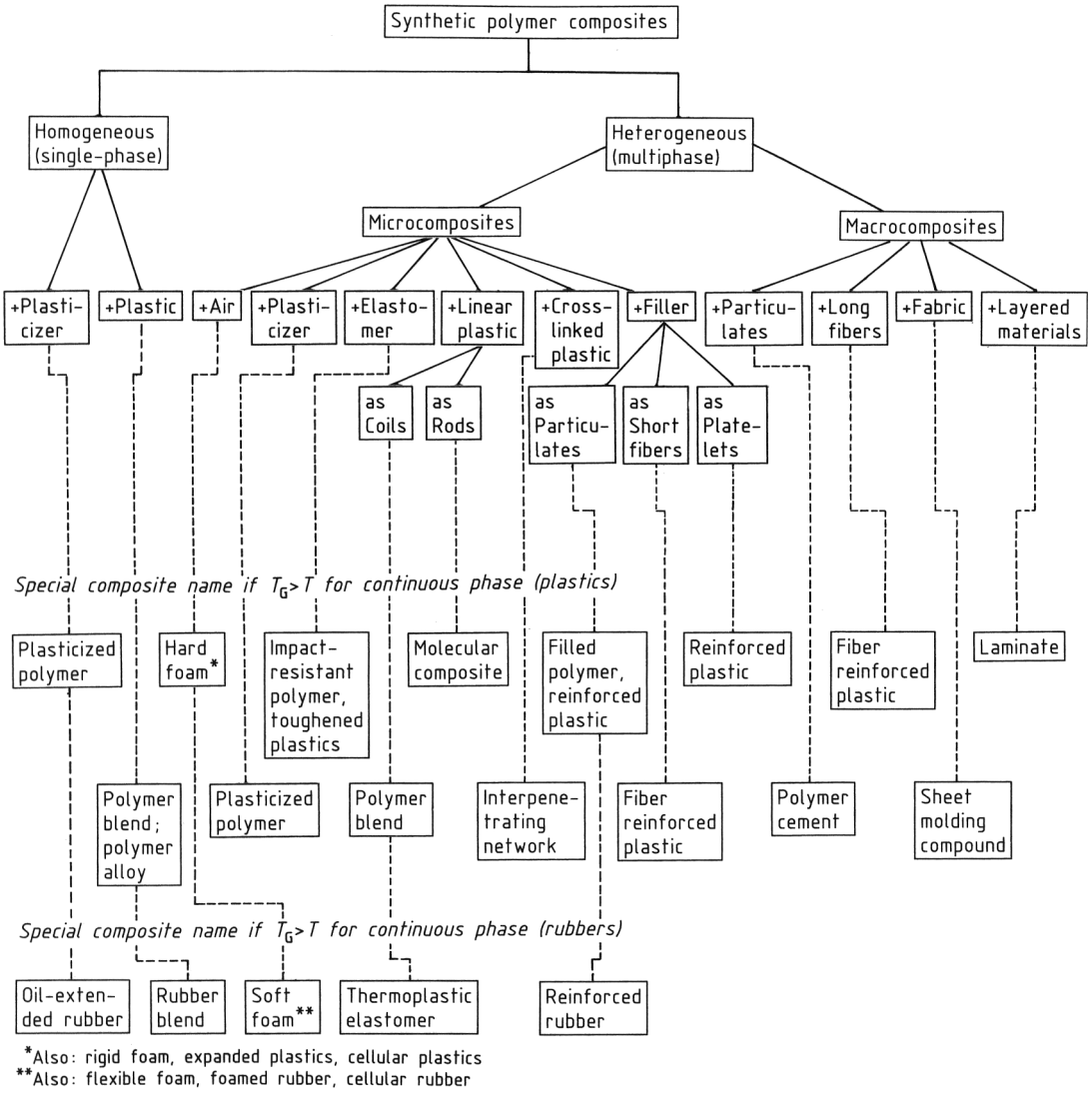


Figure 65. Classification of polymer composites of a base polymer (matrix polymer) with other materials (plasticizer, plastic, air, long fiber, layered materials). Some of these materials have their molecules in different shapes (coils, rods) or have various outer shapes (particulates, short fibers, platelets). Adopted from [1]

Table 26. Names of simple mixing rules

Field	Property exponent in generalized mixing law		
	$n = 1$	$n = 0$	$n = -1$
Mathematics	arithmetic mean	harmonic mean	geometric mean
Chemical engineering	rule of mixtures	logarithmic mixture rule	inverse rule of mixtures
Mechanical engineering	Voigt model		Reuss model
Electrical engineering	parallel		series
Materials science	upper bound		lower bound

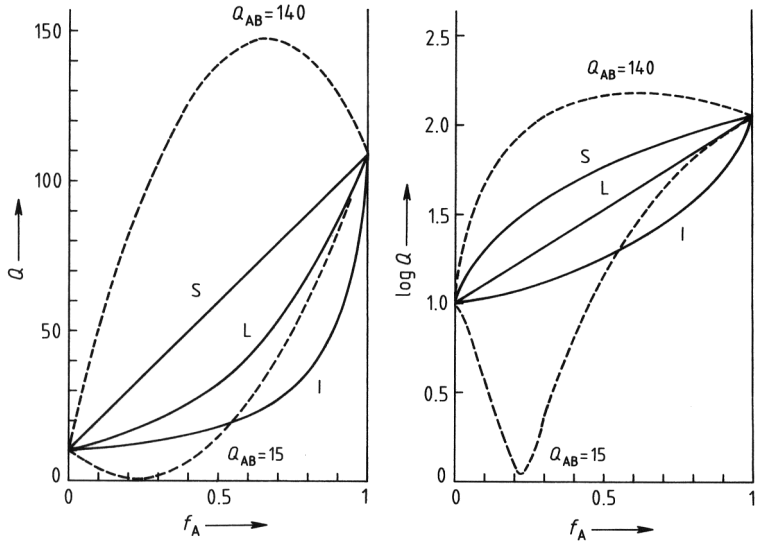


Figure 66. Mixing laws for composites with $Q_A = 110$ and $Q_B = 10$: left: $Q = f(f_A)$; right: log $Q = f(f_A)$
Simple mixing laws with interaction parameter
$Q_{AB} = 0$ (S = simple mixing law; L = logarithmic mixing law; I = inverse mixing law
- - - Composites with interaction parameters $Q_{AB} = 140$ and 15, as indicated

is obtained from Equation (31) for $n = 0$ after some mathematical manipulation. The only known case concerns the permeation of oxygen through ABS resins. The proper fraction f_i in Equations (31) and (32) is always the volume fraction. If mass fractions are used instead, deviations from the curves shown in Figure 66 occur, which may be confused with either deviations from additivity or specific interactions.

True deviations from the upper bound S and lower bound I (Fig. 66) may be caused by irregularities in phase distributions (discrete phases) or phase continuities (continuous phases), phase alignments (anisotropic phases), bonding (adhesion), or nonuniform stresses. The resulting functions always lie between the upper and the lower bound if specific interactions are absent. Many empirical, semiempirical, and theoretical expressions have been proposed for such composites. A widely used function is the Halpin–Tsai equation

$$Q = Q_B \cdot \frac{1 + K_1 K_2 f_A}{1 - K_2 f_A}; K_2 = \frac{Q_A - Q_B}{Q_A + K_1 Q_B}$$

where K_1 is an adjustable constant. The Halpin−Tsai equation gives the lower bound for $K_1 \to 0$ and the upper bound for $K_1 \to \infty$. Particulate fillers often have $K_1 \approx 0$, and fiber-reinforced plastics $K_1 \approx 2\,L/d$, where $2\,L/d$ is the aspect ratio of the fiber.

Specific interactions between components can be considered by an additional interaction term. This term is differently defined, for example:

$$Q = Q_A f_A + Q_B f_B + K_i f_A f_B;$$

$$K_i = 2(2Q_{AB} - Q_A - Q_B)$$

where the property term Q_{AB} is taken at $f_A = f_B = 1/2$. The value Q_{AB} may be an interaction parameter between components A and B in homogeneous mixtures or the property of the interphase between A and B phases in heterogeneous mixtures. The upper bound for absent interactions or interphases is retrieved for the condition $Q_{AB} = (Q_A + Q_B)/2$. The functions for $Q_{AB} \neq (Q_A + Q_B)/2$ may lie fully or partially outside the range between upper and lower bounds (Fig. 66); that is synergistic effects (above the upper bound) or antagonistic effects (below the lower bound) may be present. They may also show maxima and minima, depending on the relative magnitudes of Q_{AB}, Q_A, and Q_B.

Maxima or minima that exceed the highest property value (either Q_A or Q_B) are sometimes considered the true criteria for synergistic and antagonistic effects, respectively.

11.2. Filled Polymers

11.2.1. Microcomposites

The addition of fillers (low thermal expansion) to polymers (high thermal expansion) reduces the proportion of the latter and thus the shrinkage of plastics on processing (Table 27). The melt flow is also lower. Heat deflection temperatures (HDT) of amorphous polymers are either the same as those of unfilled plastics or no more than ca. 10 K higher (Fig. 67), group a), probably because of the increased viscosity of the filled plastic. The HDTs of amorphous thermoplastics are almost identical with glass transition temperatures.

The HDTs of crystalline polymers depend on a number of factors. Unfilled or particulate-filled crystalline polymers show HDTs that are often considerably lower than their melting temperature. Upon fiber-filling, HDTs of crystalline polymers increase strongly; they may reach values near the melting temperatures. This behavior is thought to be due to additional polymer crystallization near, or polymer adsorption on, the fiber surface, epitaxial

Table 27. Effect of fillers on some properties of amorphous (A) and crystalline (C) thermoplastics [(↑) weak increase, ↑ increase, ↑↑ strong increase, (↓) weak decrease, ↓ decrease, ↓↓ strong decrease]

Property	Extenders		Reinforcing agents	
	A	C	A	C
Shrinkage	↓	↓	↓	↓
Heat deflection temperature		(↑ ↓)		↑
Melt flow	↓	↓	↓	↓
Young's modulus	(↑)	(↑)	↑	↑
Flexural modulus	↑	↑	↑	↑↑
Fracture strength	↓	↓	↑	↑
Brittleness	↑	↑	↑↓*	↑↓*

*Tough plastics become more brittle, and brittle plastics become tough.

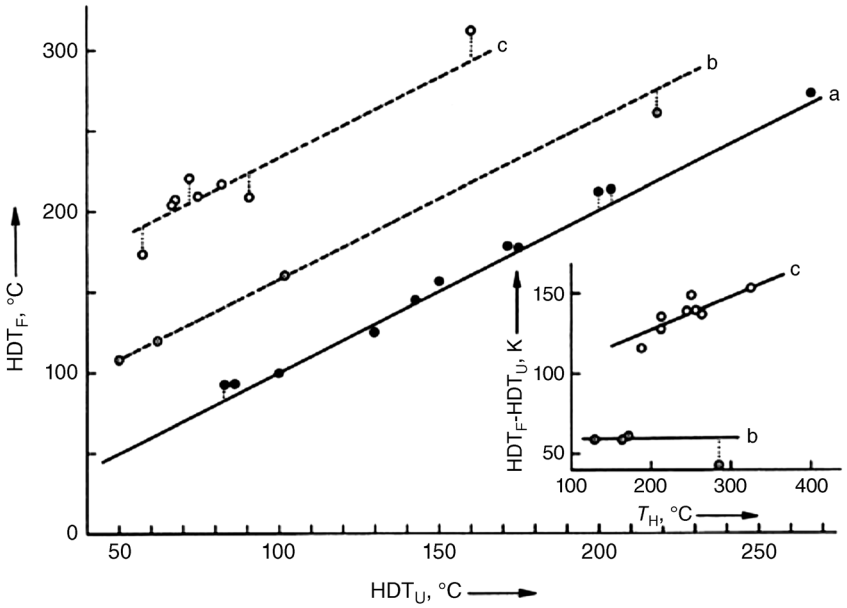


Figure 67. Heat deflection temperatures HDT_F of thermoplastics filled with 30 wt % short glass fibers as a function of heat deflection temperatures HDT_u of the corresponding unfilled polymers, both at 1.85 N/mm^2 (ISO/R 75 A)
(●) Amorphous polymers; (⊙, ○) crystalline polymers; solid line: $HDT_F = HDT_u$; broken lines: empirical
a) Amorphous polymers; b) Apolar crystalline polymers; c) Polar crystalline polymers
Insert: Difference $HDT_F - HDT_u$ as function of melting temperatures T_M of unfilled crystalline polymers

layers have been found to extend from the filler up to 150 nm into the matrix. The surface layers overlap; the resulting physical network reduces creep.

Two groups of HDTs of glass-fiber-filled crystalline polymers can be distinguished (Fig. 67). The HDTs of group b are about 50–60 K above those of their unfilled counterparts. This group comprises apolar polymers such as polyethylene, polypropylene, and poly (phenylene sulfide); polyoxymethylene also belongs to group b because its oxygen groups are buried deep inside compact helical structures, which are thus apolar on their surfaces. The difference in HDTs of filled and unfilled group b polymers does not vary with melting temperature. Group c includes polar crystalline polymers (polyesters, polyamides, etc.). For this group, the difference in HDTs of filled and unfilled polymers increases with the melting temperature of the unfilled polymer.

Young's moduli of thermoplastics increase with filler content (Fig. 68). The increase is small for spheroidal fillers (glass spheres, chalk), stronger for platelets (kaolin, talc), and strongest for fibers (glass). Short fibers are usually added in amounts of ca. 30 wt %, which corresponds to ca. 17 vol % for glass fibers (ρ = 2.55 g/cm^3) in an average polymer ($\rho \approx$ 1.2 g/cm^3). Higher fiber content often leads to packing problems since the maximum volume fraction of three-dimensional randomly packed rods with L/d = 20 is already ca. 25% (glass fibers typically have diameters d = 10–20 μm and lengths of ca. 0.2 mm after injection molding). Particulate fillers can be added in far greater amounts without sacrificing properties (see Table 14) because maximum packing densities of spheres are, for example, 0.745 for the hexagonally most dense and 0.637 for the randomly most dense packing.

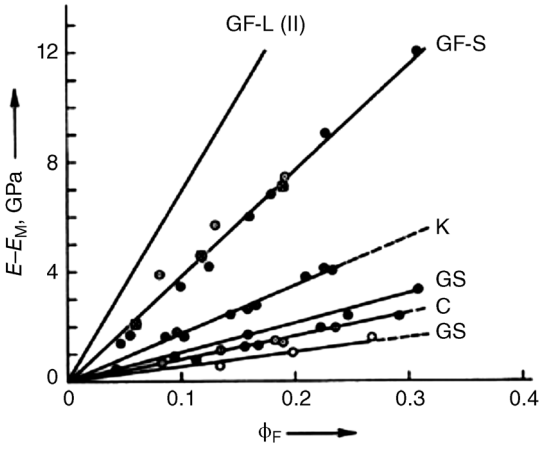


Figure 68. Influence of the volume fraction ϕ_F of fillers on the difference in Young's moduli of filled thermoplastics (E) and their polymer matrices (E_M)
GS = glass spheres; C = chalk; K = kaolin; GF = glass fibers; (S = short; L = long)
○ = polyethylene; (⊙) = polypropylene; ⊗ = polyoxymethylene; ⊕ = poly(butylene terephthalate); • = polyamide 6
The solid line for GF-L (‖) corresponds to the simple mixing law. From data of [140]

Young's moduli E of filled materials can be described by a modified mixing law

$$E = E_M\phi_M + f\,E_F\phi_F = E_M + (f\,E_F - E_M)\cdot\phi_F \quad (33)$$

where f is an adjustable parameter. The data in Figure 68 can be described with f = 0.39 ± 0.03 (chalk), 0.66 ± 0.04 (kaolin), and 1.61 (talc). The effect of 30 wt % of short glass fiber was tested in 14 thermoplastics, and f was found to be 0.57 ± 0.04. These numbers increase with the specific area of the fillers, which are given as 0.3–2.2 (ground limestone), 0.5–1 (glass fibers), 6–22 (kaolin), and 6–17 m^2/g (talc) [139]. Composites obviously increase in stiffness as the contact between filler and polymer segments increases. Good adhesion is not necessary, since E is measured for strains approaching zero.

The adjustable parameter f of Equation (33) adopts a physical meaning for short fiber reinforced plastics. In such composites, forces are transferred to the hard fiber from the soft matrix if (i) the Young's modulus of the fiber is greater than the Young's modulus of the matrix ($E_F > E_M$), (ii) the fiber length L_F exceeds a certain critical value $L_{F,\,crit}$, and (iii) the shear strength in the matrix is smaller than the shear strength between fiber and matrix (the fiber would be otherwise pulled out of the matrix unless the fiber breaks). In this case, $f = 1 - [L_{F,crit}/(2\,L_F)]$.

Fracture strengths are, however, measured for maximum strains. The failure mode of filled thermoplastics is matrix dominated. Electron micrographs show that at low fiber contents, planar cracks spread through the matrices and

debonded fibers are pulled out of either surface; the matrix must thus adhere well to the filler.

The tensile strength σ_B at break is given by the rule of mixtures ($\sigma_B = \sigma_F \phi_F + \sigma'_{M'} \phi_M$) where $\sigma'_{M'}$ is the tensile stress of the matrix upon application of a load σ_B to the composite. This relationship applies if (i) the tensile strength σ_B is greater than the contribution $\sigma_M \phi_M$ of the matrix component to the total tensile strength σ_B (that is $\sigma_B > \sigma_M \phi_M$), and (ii) the volume fraction ϕ_F of the fiber exceeds a certain minimum value ($\phi_F > \phi_{F,\,min}$).

Particulate fillers usually strongly reduce the fracture strengths of composites of amorphous thermoplastics, whereas those of crystalline polymers are reduced less or not at all. *Short fibers* generally increase the fracture strengths by factors of 1.5–2 for amorphous and crystalline polymers alike. Rigid PVC is an exception because its fracture strength is reduced on fiber-filling. The moduli and strengths can be further enhanced if coupling agents are used, which improves the bonding between fiber and matrix (e.g., silanes for glass-fiber-filled polymers).

11.2.2. Molecular Composites

The problem of insufficient bonding between fiber and matrix can be dramatically reduced if so-called molecular composites are used. These materials are dispersions of semiflexible (rodlike) polymer molecules with mesogenic units in chemically similar polymer matrices, e.g., poly(*p*-phenylenebenzobisthiazoles) in polybenzimides (see Fig. 59). The mesogens are not truly molecularly dissolved; rather, they form microdomains in the matrix. The segment axes are randomly distributed in these domains if the molecular composites are formed from polymer solutions with total polymer concentrations c below the critical isotrope phase–mesophase concentration $c_{i/n}$. Microdomains show mesophase behavior if films or fiber are formed at $c > c_i/_n$. Such microcomposites have excellent moduli and fracture strengths (Fig. 59).

11.2.3. Macrocomposites

Polymer macrocomposites are heterogeneous composites of polymers and "macro"-sized additives. Examples are polymer concrete, composition board, long fiber-reinforced polymers, and plywood.

Polymer concrete is composed of polymer [usually polyester or poly(methyl methacrylate)], aggregate (sand, ground limestone, etc.), and other additives (dyes, etc.); it does not contain cement. *Polymer–concrete hybrids* include polymer–cement hybrids (cement is partially replaced by polymers) and polymer-impregnated concrete (conventional concrete saturated with a monomer that is polymerized in place). Polymer concretes have higher moduli and higher tensile and compressive strengths than ordinary concretes. They are not vulnerable to damage by freeze-thaw cycles.

Composition boards are panel products. They include particleboard, fiberboard, hard board from flakes or shearings, etc. The fillers are mainly wood products; the resins, urea–formaldehyde (interior applications), and polyurethanes or phenolic resins (exterior).

Long-fiber-filled polymer macrocomposites range in structure from polymers filled with "long" fibers 6–12 mm in length to fiber strands and mats filled with polymers. The filler content can often reach 65 wt%. Upon application of tensile stress, local stress concentrations are transferred by shear forces onto the plastic–fiber interface and distributed over the much greater fiber surface area. The fibers must therefore bond well to the plastic (use of coupling agents) and must have a certain length to avoid slipping.

Young's moduli of long glass-fiber-reinforced epoxide resins follow the simple mixing law if the tensile stress is in the fiber direction (Fig. 69). The inverse mixing law is not observed as well for stresses perpendicular to the fiber direction since some fibers bend under stress.

The simple mixing law corresponds to $f = 1$ in Equation (33). For long fibers, f has the meaning of an orientation factor. It becomes 1/6 for fibers distributed three-dimensionally at random, 1/2 for 90° cross-plies measured in either fiber direction, and 3/8 for a uniform, planar distribution of fibers.

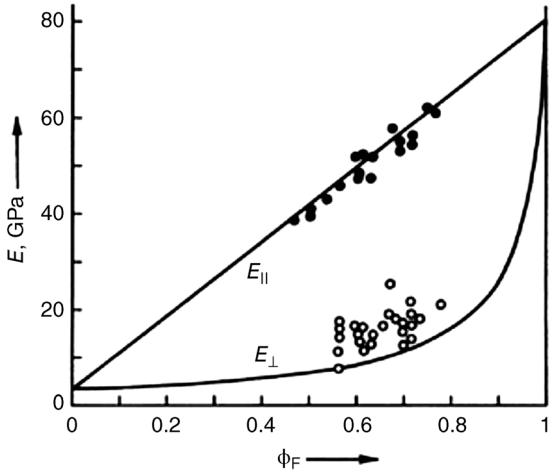


Figure 69. Young's moduli of epoxy–glass-fiber composites parallel (∥) and perpendicular (⊥) to the fiber direction

This group of macrocomposites also includes prepregs (fiber mats soaked with unsaturated polyester resins) and the composites generated by filament winding (wound filaments saturated with epoxies or unsaturated polyesters), both of which are subsequently polymerized.

11.2.4. Nanocomposites [108, 141, 142]

Polymeric nanocomposites are defined as multiphase materials in which at least one dimension of the dispersed or continuous phase is smaller than 100 nm. This includes organic–inorganic hybrid materials as well as "all-polymer" nanocomposites in which matrix and reinforcing phase consist of the same polymer. In contrast to micro- and macrocomposites, most polymers are allocated due to the presence of nanostructures at interfaces that affect the chain mobility and entanglement (see Fig. 20). Hence, the properties of interfacial polymers substantially differ from those of bulk polymers, especially regarding their thermal, mechanical, electrical, optical, and biological properties. For instance, polymeric nanocomposites can be optically transparent, exhibit improved stiffness, high surface gloss, high scratch resistance, and even electrical conductivity. Three different strategies lead to polymeric nanocomposites: (i) Dispersion of functional nanofillers in a polymer matrix, (ii) formation of organic–inorganic hybrid polymers, and (iii) oriented polymer crystallization.

Nanofiller Dispersion [108, 141–144]. Since the 1990s, significant progress in nanotechnology has made a large variety of nanometer-scaled inorganic and organic fillers as well as nanofibers commercially available for nanocomposite preparation (see Section 4.2.4) and Fig. 21). When the size of inorganic fillers is reduced, a transition from the inorganic solids to the molecules takes place. Molecular nanofillers include nanosilica, such as POSS; 2D carbon polymers, such as graphene; and multifunctional hyperbranched polymers with nanometer dimensions.

Nanometer-scaled silica spheres, prepared by a flame process, are known as pyrogenic silica of around 5 nm diameter, which is widely applied as thixotropic agents in coatings, adhesives, and sealants. Due to the shear-sensitive formation of hydrogen bridges between silanol groups at the silica particle surface, silica percolation networks are destroyed upon shearing, thus accounting for shear thinning. This thixotropic effect, caused by less than 0.5 wt% silica nanoparticles, prevents sedimentation of fillers in formulated thermoset systems. Moreover, functionalized silica fillers play an important role in improving scratch resistance in coatings. Nano silica together with disulfide-functional silane coupling agents are used for the preparation of silica–rubber nanocomposites.

For many years, carbon black nanoparticles have been commercially employed to improve electrical conductivity of plastics and coatings. This is important for antistatics and electromagnetic interference shielding. Compared to micron-sized carbon black, the percolation threshold of nanocarbon black is much lower, which drastically reduces the amount of carbon black required for achieving electrical conductivity. Highly anisotropic carbon nanofillers, such as carbon nanotubes and graphene, further reduce the percolation threshold. Moreover, both carbon nanotubes and ultrathin but micron-sized graphene enable combining

electrical conductivity with improved matrix reinforcement. Alignment of graphene in a polymer matrix improves barrier resistance to permeation of gas and liquids ("labyrinth effect") together with improved electrical conductivity and matrix reinforcement. Another approach to improved barrier resistance combined with halogen-free flame retardency and matrix reinforcement employs organophilic layered silicates. When layered silicates are made organophilic by cation exchange of sodium cations for alkyl ammonium cations (see Fig. 21), they can be intercalated and exfoliated during polymer melt compounding. The family of organophilic nanofillers is rapidly expanding.

Inorganic—Organic Hybrids [108, 145, 146]. Polymer hybrids combine the properties typical for ceramics with facile processing typical for polymers. Sol–gel chemistry is employed to equip inorganic particles and resins with reactive groups that enable efficient covalent coupling with various polymers. For example, functionalized alkoxysilanes are cocondensed with tetraethoxysilane and other metal alkoxides, such as zirconates and aluminates to produce reactive liquid oligomers or reactive nanoparticles. They are mixed and cured together with thermoset resins to form nanostructured polymer–ceramic hybrids. Sol–gel coatings are well known for their extraordinary scratch resistance. Moreover, sol–gel chemistry is used to functionalize inorganic nanoparticles by incorporating initiator and transfer agents, which enables covalent attachment of polymer chains by "grafting-from" and "grafting-to" processes. Polymer grafting of nanoparticles greatly facilitates nanoparticle dispersion and prevents undesirable agglomeration.

Self-Reinforcing Plastics and All-Polymer Nanocomposites [147, 148]. Going well beyond the scope of liquid crystalline polymers and conventional nanocomposites, the self-reinforcement of polymers does not require mesogens as comonomers and eliminates the special handling and safety precautions related to the use of potentially hazardous alien nanoparticles and nanofibers. Moreover, such all-polymer nanocomposites, in which both the matrix and the reinforcing phase consist of the same polymer, have much lower mass and are much easier to recycle than conventional polymer composites. This is highly advantageous for applications in sustainable lightweight engineering. Key concept for achieving self-reinforcement is the oriented polymer crystallization during processing. Whereas one-dimensional crystallization affords in situ aligned polymer nanofibers, the two-dimensional crystallization produces nanosheets and all-polymer multilayer composites. Because this nanostructure formation of polymers does not require nanofibers and nanoparticles, nanometer-scaled particles will not be emitted. In contrast to many other nanocomposites, all-polymer nanocomposites are environmentally benign. In one strategy, oriented films are laminated or coextruded to produce multilayer all-polymer nanocomposites. In another strategy, multilayer all-polymer nanocomposites are produced by pressure- and flow-induced crystallization near the melting temperature of thermoplastics. Extrusion of polyethylene containing ultrahigh molecular mass polyethylene (UHMWPE) close to the PE melting temperature can afford shish-kebab-like aligned UHMWPE nanofibers. However, because UHMWPE has very high viscosity, the incorporation of UHMWPE in PE reactor blends has been restricted to a few percent. Exploiting advanced multisite ethylene polymerization catalysis, it became possible to incorporate much larger amounts of UHMWPE into reactor blends without impairing processing. Because no entanglement with HDPE takes place, the nanometer-scaled UHMWPE forms a low viscosity phase separated melt and elongates during processing. Because the lower HDPE fraction crystallizes much faster, it crystallizes onto UHMWPE nanofibers to produce shish-kebab-like UHMWPE fibers in conventional melt processing without narrowing the processing window. The development of self-reinforcing plastics and all-polymer nanocomposites, which do not require the addition of (nano)fillers and fibers, holds great promise for the sustainable development of lightweight engineering plastics.

11.3. Homogeneous Blends [149, 150]

Mixtures of polymers with other polymers are called polymer blends (→ Polymer Blends). Such blends may be composed of two thermoplastics (plastic blends), two elastomers (rubber blends), a plastic filled with an elastomer as the dispersed phase (rubber-modified plastics), an elastomer with a plastic as the dispersed phase (polymer-filled elastomer), or a plastic filled with a polymer melt or a low molar mass liquid (plasticized polymers). Whether or not these blends are truly miscible on a molecular level depends on the thermodynamics of the systems.

11.3.1. Thermodynamics

If two components 1 and 2 are mixed, entropy S, enthalpy H, and volume V change. In many cases, volume changes can be neglected and the Gibbs energy of mixing is given by the changes in enthalpy and entropy: $\Delta G_{mix} = \Delta H_{mix} = T \cdot \Delta S_{mix}$. These changes can be calculated by the Flory–Huggins theory, which assumes that the mixture can be modeled by a three-dimensional lattice on which the monomeric units (or solvent molecules) can be placed. Each monomeric unit experiences the same force field; the theory is thus a mean-field theory. The assumption of a constant force field is fairly well fulfilled for polymer blends and concentrated polymer solutions but not for dilute solutions.

The entropy and enthalpy of mixing are calculated separately. Entropies are calculated for ideal solutions (zero mixing enthalpy); all environment-dependent entropy changes are thus zero (translational, vibrational, and inner rotational entropies do not change). Units can however be arranged relative to each other in many ways; however, there is a combinatorial entropy that is also called "configurational entropy" in statistical mechanics.

The mixing of two components is modeled as a quasi-chemical reaction. The mixing enthalpy is thus determined by the change in interaction energies and the number and type of nearest neighbors. Enthalpy and entropy terms are added to give the molar Gibbs energy of mixing:

$$(\Delta G_{mix})^m/RT = \chi \cdot \phi_1\phi_2 + \phi_1 \cdot \ln\phi_1 + (X_1/X_2) \cdot \phi_2 \cdot \ln\phi_2$$

which, on differentiation with respect to the molar amounts of the components, yields the chemical potentials, for example, of component 1

$$\Delta\mu_1 = RT\{\chi \cdot \phi_2^2 + \ln(1-\phi_2) + [1-(X_1/X_2)] \cdot \phi_2^2\}$$

where χ is the parameter for the interaction between component 1 and component 2 (usually with numerical values between 0 and 2), also called the Flory–Huggins parameter. All three terms in braces must be considered if a polymer 2 is mixed with a solvent 1, for example, a plasticizer ($X_1 \ll X_2$). If both components are polymers however, then $X_1 \approx X_2$ and the entire entropy contribution comes from the relatively small logarithmic term. Thus little combinatorial entropy is gained on mixing two polymers, and the miscibility is determined mainly by the mixing enthalpy, that is, by the term $\chi\,\phi_2^2$.

Phase separation occurs if the curve $(\Delta G_{mix})^m = f(\phi_2)$ (at T = const.) has a shape that can be touched at two points by a tangent. The compositions at these points are ϕ_2' and ϕ_2'' (with $\phi_2' < \phi_2''$). Two phases exist for the unstable range $\phi_2' < \phi_2 < \phi_2''$, which is separated from the stable ranges $\phi_2 < \phi_2'$ and $\phi_2'' > \phi_2$ by the so-called binodal. The unstable range itself is subdivided by the spinodal into two metastable ranges and one unstable one. Spinodals are characterized by inflection points in the Gibbs energy–composition functions and extremal values in the chemical potential–composition functions. Maximum, minimum, and inflection point become identical at the critical point, which is defined by a zero value of the second derivative of the chemical potential

$$\partial^2\Delta\mu_1/\partial\phi_2^2 = RT \cdot [2\chi - (1-\phi_2)^{-2}] = 0 \qquad (34)$$

This critical point is characterized by a critical volume fraction $\phi_{2,crit} = 1/(1 + X_2^{1/2})$ and a critical interaction parameter $\chi_{crit} \approx (1/2) + (1/X_2)^{1/2}$.

The temperature dependence of χ is approximately

$$\chi \approx A + (B/T) \tag{35}$$

where A and B are system-dependent constants; B is positive for endothermal mixtures [i.e., χ increases with increasing temperature and a homogeneous solution exists above an "upper critical solution temperature" (UCST)]. Other systems are homogeneous only below a "lower critical solution temperature" (LCST). The demixing is correspondingly either enthalpy (UCST) or entropy (LCST) induced.

The terms UCST and LCST do not indicate the absolute position of demixing temperatures since some systems show LCST > UCST (Fig. 70). Depending on the system, either an hourglass-type diagram or a closed miscibility gap is shown.

11.3.2. Plastification

Plastification of a plastic is the flexibilization of the material either by added plasticizers (external plastification) or by incorporated flexibilizing comonomer units (internal plastification).

The molecular action of plasticizers consists of a flexibilization of chain segments, which can have various causes. *Polar plasticizers* increase the proportion of *gauche* conformations in polar chains, thus decreasing rotational barriers. *Primary plasticizers* can dissolve helical structures and crystalline regions if they are thermodynamically good solvents. Furthermore both *primary and secondary plasticizers* are diluents; their addition increases the distance between polymer segments and thus decreases the activation energy needed for cooperative movement of segments. Solvation does not per se increase chain flexibility, however, because solvent shells act as substituents and increase the rotational barriers.

The molecular effect of an increase in chain flexibility by plasticization is measured as a decrease of glass transition temperatures (Fig. 71). Small molecules are better plasticizers than bigger ones of similar chemical

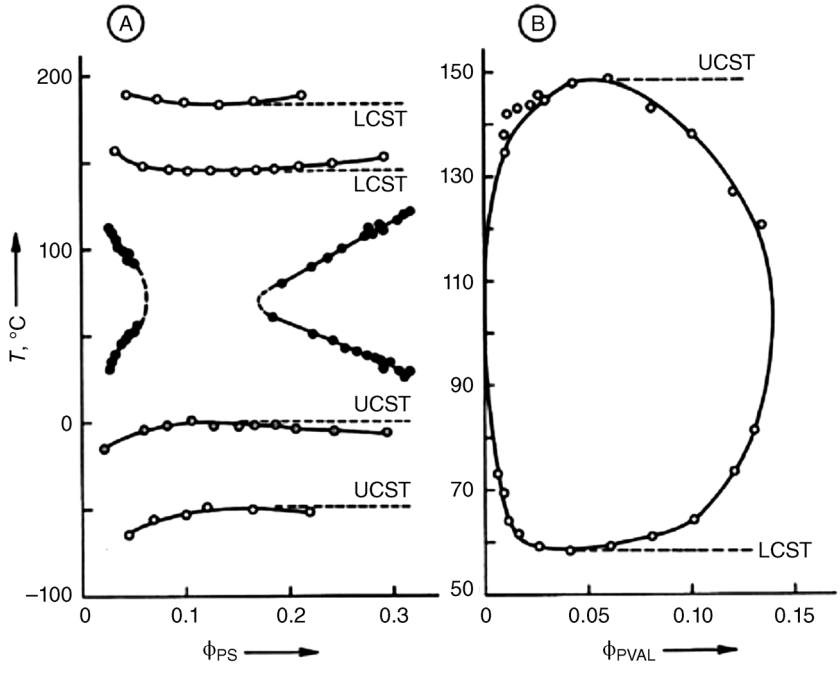


Figure 70. Phase separation temperature as function of polymer–solvent composition
A) Polystyrenes with various molar masses in acetone; B) Poly(vinyl alcohol-*co*-vinyl acetate) (93 : 7) in water
Reprinted with permission by Hüthig and Wepf Publ., Basel [5]

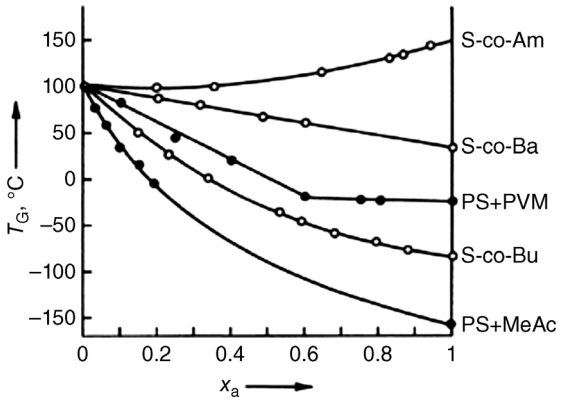


Figure 71. Glass transition temperatures of (•) polystyrene plasticized with methyl acetate (MeAc) or poly(vinyl methyl ether) (PVM) and (○) copolymers of styrene with butadiene (Bu), butyl acrylate (Ba), or acryl amide (Am)

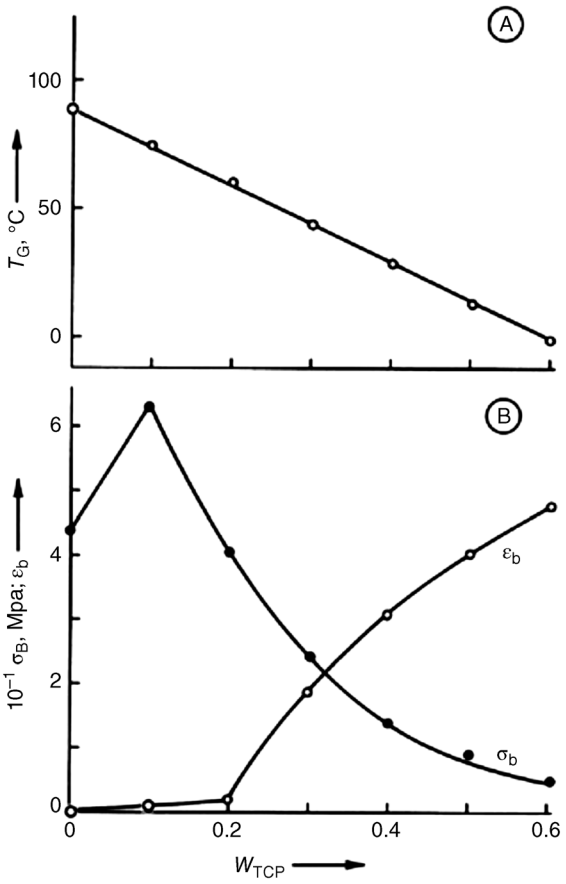


Figure 72. A) Glass transition temperature T_G and B) fracture strength σ_B and elongations ε_B at break of a poly(vinyl chloride) plasticized with tricresyl phosphate (TCP) Reprinted with permission by Hüthig and Wepf Publ., Basel [151]

constitution. The plasticizer efficiency decreases with increasing thermodynamic "goodness" of the plasticizer for the polymer (greater interaction, i.e., bigger solvation). Good plasticizers with respect to lowering glass transition temperatures are thus small molecules that act as theta solvents. These plasticizers are however bad for technological applications because they bleed (transport of plasticizer to the surface of the plastic), migrate (transport of plasticizer into another contacting material), or are extractable (e.g., transport into packaged foods). These transport phenomena can be reduced if polymer plasticizers are used. Increasing molar masses lead to decreasing thermodynamic compatibility, however (see below). Technical plasticizers are therefore in most cases a compromise between thermodynamic plasticizer efficiency and kinetically hindered plasticizer transport.

Plastification can also be followed by the changes of certain mechanical properties such as lowering of fracture strength, increase of elongation, and decrease of tensile moduli. Such methods sometimes show "anti-plasticizations" at low plasticizer concentrations (Fig. 72) (e.g., increases of moduli). Glass transition temperatures are not increased, however. The effect thus cannot be the result of increased segment mobility. It may be due to a healing of microvoids in amorphous polymers such as polystyrene or to additional crystallization of slightly crystalline polymers, such as poly(vinyl chloride).

11.3.3. Rubber Blends [149, 150, 152, 153]

About 75% of all elastomers are employed as blends. Heterogeneous blends of natural (rubber–styrene)–butadiene rubber or (*cis*-butadiene rubber–styrene)–butadiene rubber are used mainly for tire treads since they reduce abrasion. Homogeneous blends are more rare. They possess only one glass transition temperature which, for 50 : 50 blends, is

an average of the glass transition temperatures of the two parent polymers. Heterogeneous blends exhibit two glass transition temperatures, both practically identical to those of the parent polymers. Homogeneous blends are usually formed if the difference in solubility parameters is smaller than 0.7 $cal^{1/2}$ $cm^{-3/2}$ (1.44 $J^{1/2}$ $cm^{-3/2}$).

11.3.4. Plastic Blends

Plastic blends are usually immiscible because the combinatorial entropy of mixing is too small (high molar masses) and the enthalpy changes on mixing are often positive. Miscibility is observed for three types of systems:

1. Chemically similar polymers, for example, polystyrene–poly(*o*-chlorostyrene), showing both LCST and UCST
2. Systems having specific interactions between different components, for example, polystyrene–poly(vinyl methyl ether); these systems show only LCSTs
3. Systems consisting of oligomers, for example, oligo(ethylene oxide)–oligo(propylene oxide); these systems possess only UCSTs

Homogeneous polymer blends show only single glass transition temperatures; the composition dependence of these T_G's can be described by the simple rule of mixtures. Two-phase systems always show two glass transition temperatures if the phase diameters are greater than ca. 3 nm. Transparency, on the other hand, is no indication of a single-phase blend since opacity can be observed only if the refractive indices of the two phases are sufficiently different and if the phase diameters are greater than ca. one-half the wavelength of incident light. The presence of two phases in clear specimens can often be detected with electron microscopy by special staining techniques.

Modified PPO, a blend of poly(2,6-dimethylphenylene oxide) and polystyrene, is the industrially leading *homogeneous blend*. Blends of poly(vinyl chloride) with poly(methyl methacrylate), poly(ethylene-co-vinyl acetate) or chlorinated polyethylene are also said to be one-phase systems.

11.4. Heterogeneous Blends [149, 150, 152, 153]

11.4.1. Compatible Polymers

Two polymers may be thermodynamically immiscible but still mechanically compatible. These compatible blends are two- or multiphase systems that show multiple glass transition temperatures, which do not change with composition. The components do not separate, however, under mechanical stress during the expected life of the product. Such mechanical compatibilities can be improved or introduced by the addition of diblock polymers. One block of these diblock polymers is compatible with one phase type of the heterogeneous blend and the other one with the other type (see Section 5.3.6). The two blocks need not necessarily be chemically identical with the two parent polymers, that is, a compatibility of poly (A) and poly (B) can be achieved not only by addition of poly (A)−*block*-poly (B) but also by poly (A)−*block*-poly (C) if the C block is either miscible with poly (B) or can form mixed crystals with poly (B).

11.4.2. Blend Formation

Heterogeneous polymer blends can be produced by mixing together two polymers (as melts, lattices, or in solution) or by in situ polymerization of a monomer in the presence of a dissolved polymer.

The energy taken up during *melt mixing* is used for flow processes and for the generation of surfaces of new microdomains. After some time, a steady state is established and the domain size becomes constant. No macroscopic demixing occurs because of the low diffusion coefficients resulting from the high viscosities.

Latex blending consists of the mixing of aqueous dispersions of two polymers. Far lower temperatures and lower shear fields can be employed compared to melt blending. The good mixing of the latex particles remains after coagulation. The domain size is, however, restricted to the size of the latex particles themselves; it is not altered by subsequent melting of the coagulate.

Solution blending involves the mixing of two polymer solutions. Miscible polymers can be blended to domains of molecular size. Solutions of immiscible polymers demix, however, at very low concentrations, sometimes under fractionation with respect to molar masses. Domains grow further on solvent removal by distillation or freeze drying.

In situ polymerization involves solutions or gels of polymers in monomers, which are subsequently polymerized. The in situ polymerization of styrene in a styrenic polydiene solution, which leads to rubber-toughened polystyrene (HIPS) is most important industrially. The polymerization of a cross-linkable monomer in a gel of a cross-linked rubber in the very same monomer results in interpenetrating networks.

Various blending processes produce blends with very different properties (Fig. 73). The high notched impact strengths of the polymerization-blended materials (line P) are caused by a strong anchoring of phases due to the formation of graft copolymers of styrene on polybutadiene and cross-linking within the rubber domains, both caused by free-radical initiators. Such processes are less prevalent during melt blending (radical formation by high shearing at elevated temperature) (line M) and latex blending (low shearing at ambient temperature) (line L). In situ polymerization is thus the method of choice for unsaturated rubber (easy cross-linking and grafting by chain transfer) and monomer–rubber pairs with favorable Q, e-values for copolymerizations. In all other cases, blends are formed by melt mixing.

11.4.3. Toughened Plastics

Rubber-modified plastics (toughened plastics, high-impact plastics) consist of rubber domains dispersed in plastic matrices. The domain size varies with the blending process. Typical values are ca. 0.1 μm for melt-blended poly(vinyl chloride)–acryl rubber and 1 μm for polystyrene–polybutadiene. The domains are often multiphased; small plastic domains are imbedded in the rubber domains (Fig. 74). The morphologies depend strongly on the blending process. During stirred in situ polymerizations, phase inversions often occur if the amount of newly formed plastic approaches that of the incipient rubber. During phase inversion, already present plastic particles may be embedded in the newly formed rubber domains.

Rubber-toughened plastics are valued because of their improved impact strength. On impact, very many crazes are formed near the equators of the rubber particles. The crazes propagate until they encounter an obstacle (e.g., rubber particle or shear band) or until

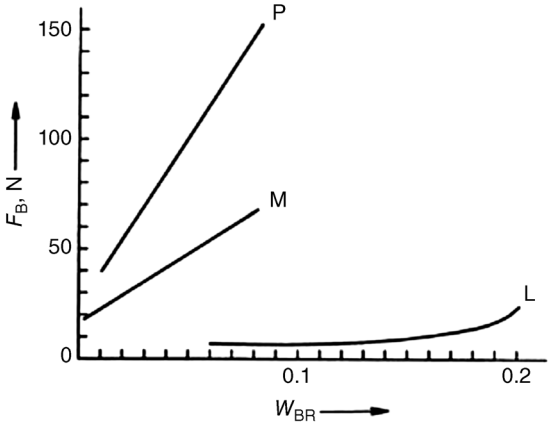


Figure 73. Impact strength with notch F_B as function of the mass concentration w_{BR} of *cis*-1,4-polybutadiene in its blends with polystyrene. P = in situ polymerization of styrene; M = melt blending; L = latex blending
Reprinted with permission by Plenum, New York [154]

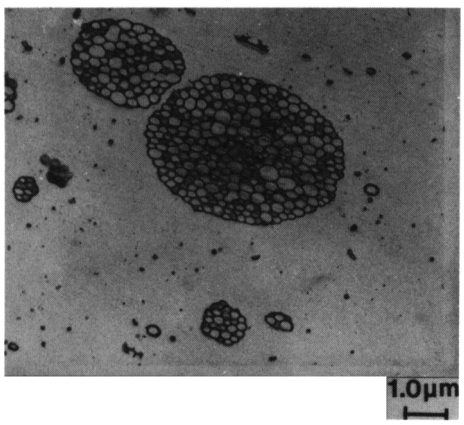


Figure 74. Rubber domains in high-impact polystyrene by in situ free-radical polymerization of styrenic polybutadiene solutions
Reprinted with permission by Society of Plastics Engineers [155]

the stress concentration at the tip of the craze becomes very low. Many small crazes result, and the stress is evenly distributed if the rubber phase is cross-linked and binds well to the thermoplast phase [e.g., by in situ formed graft copolymers (HIPS)]. In contrast, stress peaks concentrate at a few defect points in normal thermoplasts.

11.4.4. Thermoplastic Elastomers (→ Thermoplastic Elastomers)

Thermoplastic elastomers (elastoplastics, thermoplastics, plastomers) are processed like thermoplastics but applied like elastomers. Their unique properties follow from their molecular structures; their chains consist of "soft" and "hard" segments in block, graft, or segmented copolymers composed of monomeric units A and B. The A and B segments are mutually incompatible and form locally separated regions. With a well-designed molecular architecture, domains of the "hard" A segments (transition temperature > service temperature) act as physical cross-links in the continuous matrix of the "soft" B segments (transition temperature < service temperature) (Section 5.3.6). Such transition temperatures may be glass transition temperatures in amorphous polymers or melting temperatures in partially crystalline polymers. The A segments attain mobility above these transition temperatures and the elastoplasts become processible.

Thermoplastic elastomers comprise linear triblock polymers of the polystyrene–*block*-polydiene–*block*-polystyrene type; radial, star, or "teleblock" polymers of the same monomeric units; urethane segment or block copolymers with polyester or polyether soft segments; polyesteramides and polyesteretheramides; graft copolymers of butyl rubber on polyethylene, vinyl chloride on poly(ethylene-co-vinyl acetate), styrene–acrylonitrile on saturated acryl rubbers, and various ionomers.

Thermoplastic elastomers can also be produced by "dynamic vulcanization." The mastication of blends of conventional rubbers and crystalline poly(α-olefins) leads to chain scissions. The resulting macroradicals cross-link the rubber domains.

The mechanical properties of thermoplastic elastomers are determined mainly by their morphologies. In styrene–butadiene–styrene triblock polymers, for example, morphologies are governed by the spatial requirements of the various blocks (Section 5.3.6). With a low content of hard styrene segments, small spherical polystyrene microdomains are formed in the soft polybutadiene matrix. These microdomains act as physical cross-linkers. The distances between the domains are large, and the polymer behaves as a weakly linked elastomer with correspondingly high extension (Fig. 75). The domains are larger and their distances are shorter at 28% styrene units and the polymer strengthens (stiffens). The stiffening becomes stronger for rodlike styrene domains (39% S). Lamellar morphologies (53% S) show an "unruly" behavior initially because of reorientation of lamellae. At even higher styrene content, the polymer behaves as a plasticized tough thermoplast (65% S) or almost like polystyrene itself (80% S).

11.5. Expanded Plastics (→ Foamed Plastics) [156, 157]

Expanded plastics (foams, foamed plastics, cellular plastics) are blends of plastics with air. They are subdivided according to their rigidity, their cell structure, and the nature of the parent plastics. Rigid expanded plastics are used mainly for thermal insulation, and flexible foams for damping and cushioning materials.

The rigidity ("hardness") of expanded plastics follows the properties of the parent polymers. Phenolic and urea resins thus yield brittle-rigid plastics; polystyrene and hard poly(vinyl chloride), tough-rigid; and polyethylenes, polyurethanes, and plasticized PVC, semirigid to flexible foams. The elastic moduli of expanded plastics decrease approximately proportional to their polymer content (simple mixing law). Because the stiffness of an article increases with the third power of the wall thickness, the gases in expanded plastics work as enhancers that reduce material costs and weights.

Tensile strengths of foamed plastics also follow the simple mixing law. Because the tensile strengths of gases are diminishingly

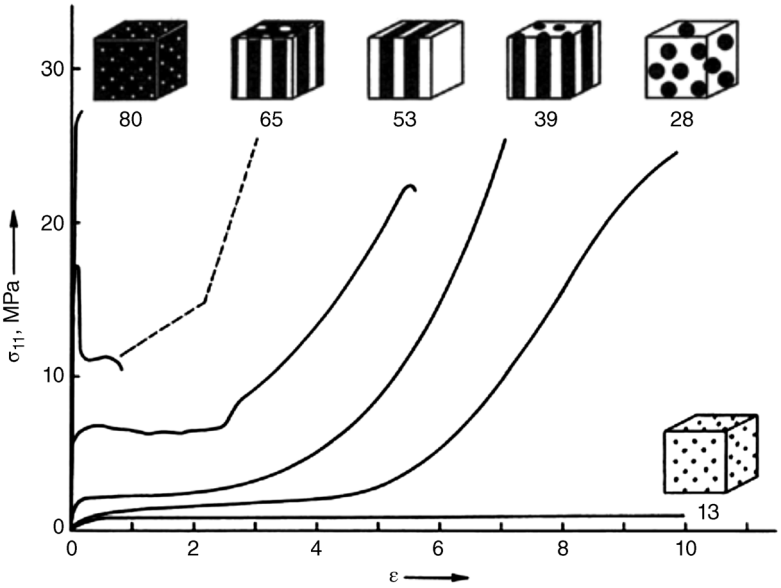


Figure 75. Stress–strain curves and morphologies of styrene–butadiene–styrene triblock polymers with various styrene contents
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small, tensile strengths σ_B of foamed plastics are determined by the volume fraction ϕ_p and strengths $\sigma_{B,p}$ of the plastics themselves [i.e., $\sigma_B \approx \sigma_{B,p} \cdot \phi_p = \sigma_{B,p} \cdot (\rho/\rho_p)$] (Fig. 76). Compression strengths follow a similar simple mixing law.

The cell structure can be open, closed, or mixed. Open-celled foams are always air filled, regardless of the blowing or expanding gases used for foam manufacture. The trapped gases in closed-cell structures can be exchanged with the surrounding air only by slow diffusion through the polymer matrix. Because thermal conductivities of low-density foams ($\rho_p < 0.3$) obey, to a first approximation, a logarithmic mixing law, they are considerably affected by the thermal conductivities of trapped gases [(λ = 93 J m^{-1} h^{-1} K^{-1} (nitrogen), 56 J m^{-1} h^{-1} K^{-1} (CO_2), 26.4 J m^{-1} h^{-1} K^{-1} (CCl_3F)]. The gas exchange is considerably reduced in integral skin foams (dense skin, low-density core) and in syntactic foams (plastics filled with hollow spheres; spheres may be made of glass, ceramics, or plastics and contain either gases or a vacuum).

12. Plastics and Sustainability (→ Plastics, Recycling)

12.1. Plastics and Environment [158–162]

During the first decade of the 21st century, more plastics were produced than during the entire 20th century. The plastics production rapidly increases and follows the growth of the world population (see Fig. 1). Originally introduced as rather poor imitation of natural materials, such as silk, natural rubber, and ivory, modern plastics have emerged as advanced materials with tailored property profiles, which is unparalleled in nature. Synthetic polymers are engineered to meet the demands of diversified technologies ranging from food packaging to textiles, shelter, communication, mobility, and health care. Plastics play an important role in daily life. Without plastics, the high quality of modern life with secure supply of food, water, and energy would not be feasible. Highly cost-efficient and versatile polymeric materials have made hightech

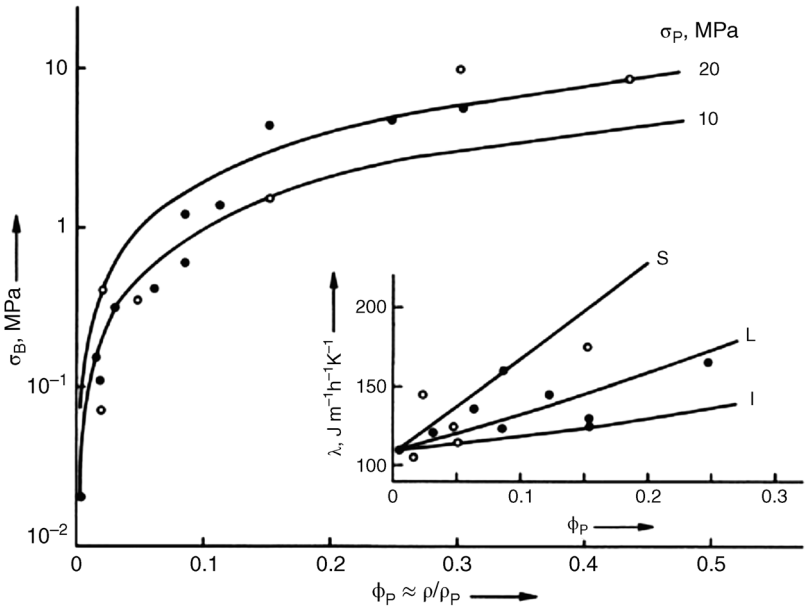


Figure 76. Tensile strengths of expanded plastics as a function of the volume fraction of the rigid (●) or flexible (○) parent polymers P
Solid lines indicate a) Simple mixing law for σ_p = 20 MPa; b) Simple mixing law for σ_p = 10 MPa;
Insert: Thermal conductivities (for λ_p=700 and λ_{air} = 110 J (m^{-1} h^{-1} K^{-1}) of rigid (●) and flexible (○) plastic foams
S: Simple mixing law; L: Logarithmic mixing law; I: Inverse mixing law

affordable for people of all income groups. At present, plastics production consumes around 5% of the world's fossil resources, which is equivalent to about 60% of the petrochemical production. At present around 90% of the world's fossil resources are burned in energy production accompanied by severe emission of carbon dioxide, which contributes to global warming and climate change. The emission of green house gases, i.e., carbon dioxide and methane, is also being referred to as carbon footprint. More than 30% of durable plastics are used in packaging, such as bags, wraps, and bottles, all of which possess short product life of a few months. According to the statistics of the Environmental Protection Agency (EPA), around 251 $\times 10^6$ t of municipal trash composed of paper (27.4%), food wastes (14.5%), yard trimmings (13.5%), plastics (12.7%), metals (8.9%), rubber, leather, and textiles (8.7%), wood (6.3%), and glass (4.6%) were created in the United States in 2012. Archaeological studies of landfills have revealed that the biodegradation processes of synthetic polymers and biopolymers are very slow in landfills, especially in the absence of light, air, and water. Some buried news papers could be read after residing for 25 years in a landfill. Clearly, recycling and incineration are the only possible ways for disposing of plastics. Because most plastics have an oillike, high energy content, plastic wastes are valuable raw materials that need to be reused. While in 2012 the plastics recycling and energy recovery reached 61.9% in Europe, it was around 9% in the United States (for comparison: paper recycling reaches 50% in the United States). When plastic recycling fails, the consequences of littering are clearly visible in nature. Driven by marine and wind currents, nontoxic plastics debris together with hazardous chemical sludge accumulate in the ocean, in particular in a region known as the northern pacific garbage vortex. Addressing high

sustainability is an important issue in plastics development. As stated in 1987 by the Brundtland Commission of the UN General Assembly, sustainability means meeting the needs of the present without compromising the ability of future generations to meet their own needs. High resource-, eco-, and energy efficiency of plastics together with their low carbon footprint and high energy content, typical for the large-scale commodity plastics, holds great promise for achieving high sustainability. Efficient plastics recycling, exploiting renewable feedstocks, and especially tailoring advanced polymeric materials for sustainable development are important tasks in the plastics industry.

12.2. Green Polymer Chemistry [163, 164] and Life Cycle Assessment [165]

According to the definition by ANASTAS, important elements of green chemistry include high resource effectiveness by maximizing the content of raw materials in the product; clean and lean production processes; catalytic reactions at ambient temperature and pressure; preventing wastes and reducing greenhouse gas emissions; high safety standards; no use of auxiliary substances, such as organic solvents, blocking groups etc.; low energy demand of production and processing; no health and environmental hazards by substituting toxic chemicals; using renewable resources; low carbon footprint,; and controlled product life cycles with effective waste recycling. This definition of "green" is not at all synonymous with biomaterials and biotechnology.

An important tool for assessing the environmental impact of materials is the life cycle analysis, which is also referred to as ecobalance, cradle-to-grave analysis, and life cycle assessment (LCA). LCA addresses the environmental aspects of all stages of a product's life time from feedstock recovery to monomer and polymer manufacturing, processing, distribution, use, maintenance, disposal, and recycling. Taking into account all relevant materials and energy inputs and output together with environmental aspects, the following LCA ranking of plastics was determined in 2010:

1. Polypropylene (PP),
2. High density polyethylene (HDPE),
3. Low density polyethylene (LLDPE).

The LCA ranking of bio-based polylactic acid (rank 9) was similar to that of PVC (rank 7). According to LCA, converting petrochemical plastics into green plastics by using renewable feedstocks lowers the LCA ranking. The success of polyolefins, such as PP, HDPE, and LLDPE is clearly associated with significant progress made in polyolefin production since the 1950s. The polyethylene life cycle is displayed in Figure 77. Produced in solvent-free catalytic polymerization processes with low energy demand using a highly active stereospecific catalysts, polyolefins are readily tailored to meet the demands of diversified applications ranging from food packaging to baby diapers, carpets, and automotive bumpers. Modern reactor granule technology produces pellet-sized polyolefin particles, which eliminates pelletizing extrusion. The heat of polymerization can be used as power generator. No water and no purification are required. This is in contrast to biotechnology processes and to pulping. The latter has very high water demand and produces byproducts, such as organic compounds and salts. Compared with paper, LLDPE packaging has much lower mass and is easy to process by blow molding. After completing their product life, polyolefins are readily recycled by mechanical, feedstock, and energy recycling. As hydrocarbon resins, they have oillike energy content. On heating above 300 °C, they are converted into oil and gas, which are valuable sources for feedstocks and energy. The raw materials of polyolefins are highly flexible. Virtually any carbon source, ranging from oil, gas, and coal to biomass and bioethanol, can be employed in polyolefin production.

From the LCA it is apparent that the substitution of plastics packaging by paper and other materials would substantially increase mass, energy demand, and greenhouse gas emission. Contrary to the public opinion, increased use of

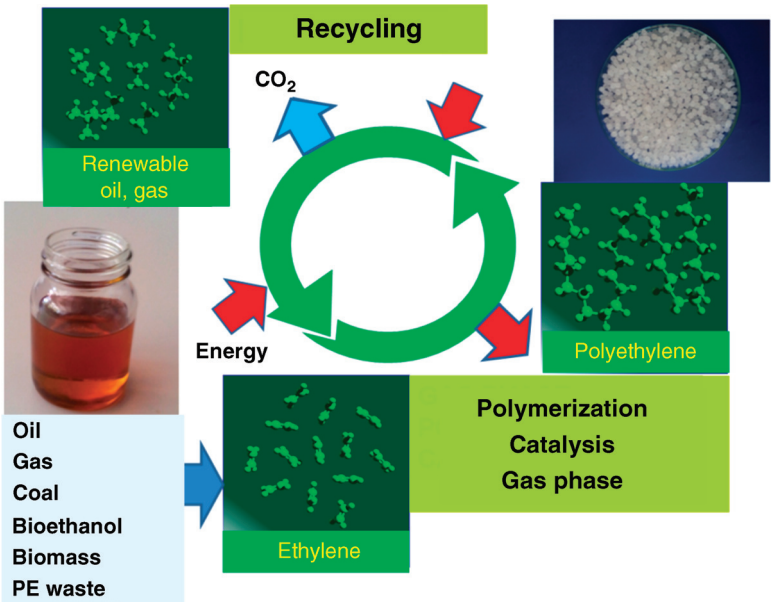


Figure 77. Life cycle of polyethylene

plastics reduces the greenhouse gas emission, whereas the substitution of plastics by other materials would have a stringent detrimental environmental impact and drastically enhance greenhouse gas emissions. At the end of their service life, plastics wastes are too valuable to be thrown away.

12.3. Plastics Waste Recycling

12.3.1. Mechanical Recycling [166, 167]

For identification and for facilitating their recycling, plastic products bear special codes consisting of label with three broken arrows, arranged in a triangle, and a number, sometimes also combined with letters and/or bar code. The numbers and letter combinations indicate the type of plastics. The letter combinations are not always identical with the acronyms and abbreviations recommended by ISO, ASTM, DIN, IUPAC, etc., for the same polymers. The following number and letter codes are used:

- 1 = PET [poly(ethylene terephthalate)]
- 2 = HDPE (high-density polyethylene)
- 3 = PVC (polyvinylchloride)
- 4 = LDPE (low-density polyethylene)
- 5 = PP (polypropylene)
- 6 = PS (polystyrene)
- 7 = for all other plastics, including multilayered materials

Different waste management systems have been established to collect and sort wastes from different applications, such as packaging, automotive, electronics, and construction. A large variety of waste-pretreatment and sorting technologies are in place including shredding, magnetic separation, flotation, and air separation assisted by plastics identification by spectroscopy, such as near infrared sensing.

Especially when plastics wastes are clean and composed of as single type of plastics, mechanical recycling is attractive. In thermoplastics mechanical recycling, wastes are sorted, purified, and extruded to produce granulates. For example, mechanical recycling converts PET bottle waste into new PET bottles or PET textile fleeces for jackets. Due to polymer ageing by degradation and autoxidation during product life and recycling, most recycled plastics are

somewhat inferior with respect to the corresponding virgin plastics. Therefore, most recycled plastics are blended together with virgin polymers in mechanical recycling. Because most polymers are highly immiscible, mechanical recycling of mixed plastics wastes produces blends, which require the addition of compatibilizers. Because cross-linked plastics do not melt, they can be recycled by grinding. Recycled thermoset resin powders or ground rubber are used as organic fillers for thermoset or rubber formulations.

12.3.2. Feedstock Recycling [167, 168]

During pyrolysis plastics are broken down at elevated temperatures in the absence of air to produce liquid and gaseous fragments. Thermolysis is of particular interest for recycling highly polluted complex plastic mixtures. In the case of PVC, HCl is formed and removed by washing the thermolysis gases with water. Hydrocarbons, such as polyolefins, are readily thermolyzed to produce oil and gas in essentially quantitative yields. Plastics, such as polyoxymethylene and poly(methyl methacrylate) are thermally depolymerized to recover the corresponding monomers. On thermolysis, carbohydrates decompose to form a considerable amount of water and ashes. Whereas pyrolysis requires rather high temperatures, typically above 500 °C, catalytic liquefaction converts biomass and plastics wastes into diesel fuel at temperature well below 500 °C. In this process, water is catalytically converted into hydrogen, which improves the yield of low molecular mass hydrocarbons by hydrogenation. In sharp contrast, hydrogenation of plastics wastes and distillation residues in oil refinery require much higher hydrogen pressure and temperature. The presence of hydrogen increases the amount of liquid hydrocarbon. In the case of biomass and biopolymers, anaerobic digestion can be employed to convert biowastes into methane or bioethanol. Lignocellulose from forestry and agricultural wastes is an attractive source of sugar that serves as raw material for biorefineries without competing with food production.

When small amounts of oxygen are present, gasification by incomplete combustion converts plastics into a mixture of carbon monoxide and hydrogen (syngas), which can be used as feedstock for producing a variety of chemicals and monomers in refineries. Similar to the Fischer–Tropsch process for coal-to-liquid conversion, this process can also be applied to biomass (biomass-to-liquid conversion) and plastics wastes. Moreover, syngas is of interest as reducing gas for metal oxide ores in steel mills, thus substituting oil and gas. Polycondensates, such as polyesters and polyurethanes are readily cleaved by hydrolysis and glycolysis, thus recovering monomers useful in polycondensation reactions.

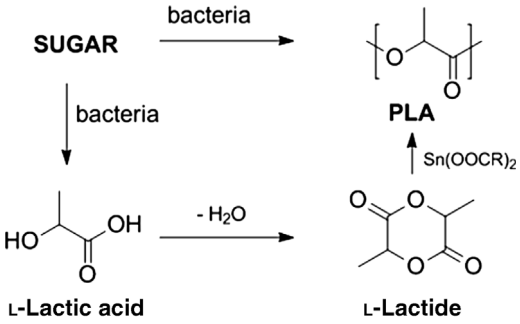
12.3.3. Energy Recycling [166–168]

Taking into account the high energy content and hydrocarbon nature of commodity plastics, in many countries incineration is the preferred method for municipal waste recycling, which does not need extensive sorting and purification of the plastics wastes. In fact, the plastics wastes represent an attractive source of energy for the combustion of municipal wastes, which contain components with much less energy content. In contrast to inorganic wastes and biomass, commodity plastics do not form large amounts of ashes but completely decompose to produce gas and heat. For many years, public fears concern the formation of dioxin by waste incineration. Today, the incineration off-gases are carefully purified to remove gaseous and dustlike particulate pollutants. This includes the catalytic conversion of dioxin and furan traces. Incineration is the preferred process for disposing of hazardous wastes containing microorganisms, toxins, or chemicals.

12.3.4. Biodegradation and Bio-based Plastics [79–83, 164, 169] (→ Polymers, Biodegradable)

In the early 1900s, all plastics were bio-based because carbohydrates and proteins were the only industrially available feedstocks for plastics production. Because abundant biopolymers, such as cellulose, are infusible and insoluble, extensive chemical modifications are required to enable melt and solution processing of cellulosics. Within very short time during the first half of the 20th century, the emerging highly

versatile and low-cost synthetic plastics, based on fossil feedstocks and petrochemistry, have outperformed biopolymers and conventional bio-based plastics. In spite of the ongoing commercial significance of natural rubber, claiming 40% of the rubber market, and the successful development of wood plastics compounds and natural fiber reinforced composites, the total biopolymer share of the annual world's plastics production is still below 5%. However, there is a renaissance of the use of renewable and natural resources as well as the development of biopolymers. In view of the dwindling fossil resources, which are rapidly being depleted in energy production, the shift from fossil to renewable resources is thought to safeguard plastics production against an expected future oil crisis. Moreover, the growing consumers' concerns regarding global warming and the fear that a collapse of the biosphere is imminent, stimulate the surging demand for renewable and bio-based products. Because most natural polymers still fail to match the performance of synthetic polymers, synthetic plastics are rendered "green" and bio-based by using renewable raw materials for the production of monomers. For example, bioethanol is converted into ethylene and propene, which are polymerized in highly efficient gas phase processes to afford "green" polyolefins, which have properties equivalent to petrochemical polyolefins. In contrast to bacterial poly-L-lactic acid (PLA), which requires separation of PLA from cell proteins and water recovery, the solvent-free ring-opening polymerization of bio-based dilactide affords much better control of polymer properties, such as crystallization rate and shear thinning.



In life cycle assessment, most bio-based products have lower performance with respect to the corresponding petrochemical products due to the additional process steps. Moreover, in many industrialized countries the biomass supply is insufficient to substitute oil in energy and plastics production. PLA, polyolefins, or paper are not completely biodegradable in landfill, especially when air and water are absent. In contrast to the public opinion, biodegradation and bioerosion, which are highly dependent on the climate, do not instantaneously degrade biopolymers to produce carbon dioxide and water. Instead, biodegradation makes polymers brittle. They disintegrate to form tiny particles, invisible for human eyes, which are carried away by wind or rain and serve as breeding ground for spores and bacteria. Because the label "biodegradable" stimulates consumers to carelessly dump wastes and ignore recycling efforts, biodegradable plastics are contra productive to recycling. Moreover, the high energy content of polymers is wasted during biodegradation in landfill. Hence, biodegradable polymers do not seem to be the universal solution to the plastics waste problem. Yet, they offer prospects for special applications like bioresorbable implants, surgical sutures, drug release, as well as agricultural films and packaging. Today, it is well recognized that the surging biomass demand in bioenergy production, accompanied by extensive farming of energy crops, endangers both the biosphere and the food supply of the rapidly growing world population. Many industrialized countries do not have enough biomass to serve the need of both energy and plastic production.

12.3.5. Plastics from Carbon Dioxide [164, 170] (→ Carbon Dioxide 12.4.10. Polymers from Carbon Dioxide)

In order to prevent a conflict with food production, several successful attempts have been made to exploit the direct chemical fixation of carbon dioxide in plastics production. Because carbon dioxide is the energy sink in the combustion process, it must be activated in order to be useful in polymer production. In copolymerization this is achieved by reacting carbon dioxide with energy-rich highly strained

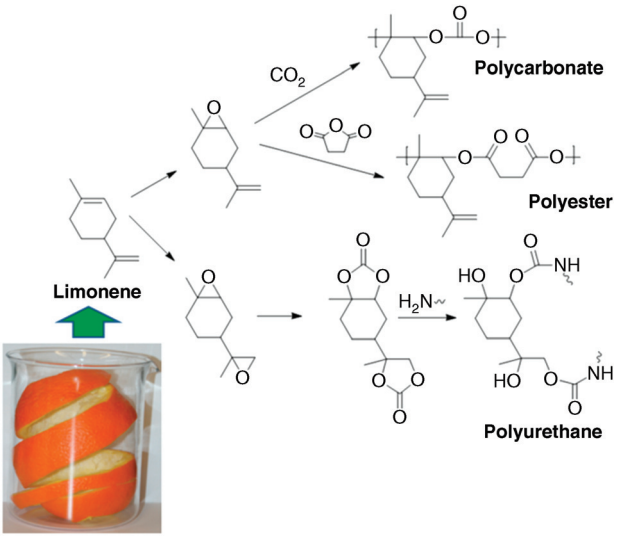


Figure 78. Bio-based polyesters, polycarbonates, and nonisocyanate polyurethanes from orange peels
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oxirane and oxetane rings, thus producing polyfunctional cyclic carbonates and linear polycarbonates. Dihydroxy-terminated poly(propylene ether carbonates) are of special interest as polyols in polyurethane synthesis. Polyfunctional cyclic carbonates, prepared by reacting epoxy resins with carbon dioxide, are attractive intermediates for the isocyanate- and phosgene-free production of hydroxyl-functional polyurethanes (NIPU for nonisocyanate polyurethane). Biowastes, such as orange peels can be used as a source of limonene, which upon oxidation and carbonation affords mono- and difunctional cyclic carbonates as intermediates for bio-based polyesters and NIPU (Fig. 78). Electrochemical processes are developed to exploit excess renewable energy supplied by wind mills and solar power plants to convert carbon dioxide into methane, which is useful as chemical storage of renewable energy, as fuel, and as intermediate for the production of chemicals and plastics.

12.4. Polymers for Sustainable Development [164]

In many ways plastics serve the needs of sustainable development. Produced in highly energy- and resource-efficient polymerization processes, plastics have low carbon footprint and preserve high oillike energy content. After completing their product life, they are mechanically recycled or serve as valuable source of energy and feedstocks. This attractive balance of low energy demand during production and processing combined with low carbon footprint and high energy content is typical for all large-volume commodity and most engineering plastics and rubbers, amounting to more than 90% of the world's plastics production. Among them, hydrocarbon plastics, such as polypropylene and polyethylene, produced by solvent-free catalytic polymerizations processes, meet the demands of green chemistry and achieve top rankings in life cycle assessment. Moreover, plastics have a low mass and are corrosion resistant. In lightweight engineering and packaging, polymeric materials contribute to considerable weight savings, thus reducing fuel consumption and dioxide emission in transportation. Moreover, unparalleled by other materials, plastics are highly versatile with respect to tailoring property profiles, processing, and applications. Owing to their low mass together with thermal and electrical insulation, plastics contribute to high energy efficiency and secure the supply of food, water, and energy.

Although plastics consume around 5% of fossil fuels, they help to preserve close to 20% oil by thermal insulation and mass reduction in transportation. As advanced functional materials and integrated into systems, polymers bring high resource efficiency to a variety of applications ranging from lightweight engineering to health care. For example, as filters and membranes, functional plastics enable water and air purification, water desalination, and recovery of precious metals from wastes. This unique combination of high cost-, eco-, resource-, and energy efficiency with high versatility typical for most plastics holds great promise for sustainable development.

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Plastics, General Survey, 2. Production of Polymers and Plastics

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ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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1. Polymer Manufacture

1.1. Raw Materials [1]

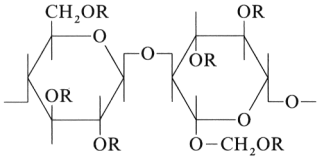
The raw materials for most industrially used plastics are synthetic polymers and prepolymers; only a few are derived from naturally occurring polymers or monomers. The overwhelming majority of polymers for plastics are organic materials; very few are semiorganics (i.e., inorganic polymer chains with organic substituents). Raw materials for polymers include biomass, such as wood and fossil resources, such as coal, petroleum, natural gas, and gases supplied by fracking. In view of the increasing energy demand and the limited fossil resources, an important objective is to substitute fossil resources by renewable ones. Another important strategy aims at direct chemical fixation of carbon dioxide to produce monomers and polymers directly from carbon dioxide without endangering food supply.

1.1.1. Wood

Wood (→ Wood) is a naturally occurring composite of oriented cellulose fibers in a continuous matrix of cross-linked lignin; it is plasticized by water and "foamed" by air (vacuoles). The water content varies from 40–60% for green wood to 10–20% for air-dried wood. Solids include cellulose (42%); hemicelluloses (28–38%); lignin (19–28%); and proteins, resins, and waxes (2–3%), depending on the type

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and age of the plant. Most of the wood is used directly as fuel or for construction purposes, but one-sixth is converted into wood pulp or cellulose pulp for the manufacture of paper, cardboard, or rayon. A very small amount of wood is filled with monomers that are subsequently polymerized to give polymer wood.



Repeating unit (cellobiose) of cellulose (R=H) and cellulose derivatives

Cellulose pulp is chemically transformed into cellulose derivatives (→ Cellulose; → Cellulose Esters; → Cellulose Ethers):

- 2,5-Acetate with 2,5 acetate groups, R = $OOC-CH_3$, per glucose residue (fibers, cigarette filters)
- Cellulose triacetate with three acetate groups per glucose residue (fibers)
- Cellulose acetobutyrate with R=29–6 mol% acetyl and 17–48 mol% butyryl groups (a thermoplastic for tubes, packaging)
- Cellulose nitrate ($R-NO_2$; various degrees of substitution; gun cotton, films, lacquers, celluloid)
- Cellulose ethers with $R-CH_3$, C_2H_5, $CH_2CH_2OR^1$, or $CH_2-CHOR^2-CH_3$, where R^1 may be $CH_2CH_2OR^1$ or CH_2CH_2OH and $R^2-CH_2-CHOR^2-CH_3$ or $CH_2-CHOH-CH_3$ (thickeners, binders, suspension agents, injection molding materials, etc.)

Huge amounts of *lignin sulfonates* (→ Lignin) are generated during wood pulp production, most of which are burned. Small amounts are used for street pavement, as binders for foundry sand, or as drilling agents, and even smaller amounts as raw materials for organic intermediates (→ Lignin). Degradation products of lignin have been utilized for the synthesis of ion-exchange resins and other polymers. Lignocellulose of forestry and agricultural wastes represents an attractive source of glucose as a renewable feedstock for biorefineries without competing with food production. In biorefineries glucose is converted into a variety of monomers including lactic acid, butadiene, acrylic acid, and even ethylene and propene.

1.1.2. Coal

Coals (→ Coal) are polymerized and partly cross-linked hydrocarbons with average compositions between $C_{75}H_{140}O_{56}N_2S$ (peat) and $C_{240}H_{90}O_4NS$ (anthracite). They were the primary raw materials for acetylene-based monomers during the first half of the 20th century but have since been replaced in most countries by oil and natural gas as monomer sources.

Coals deliver coke and coal tar. A number of aliphatic monomers are produced from coke via acetylene, such as chloroprene, various vinyl monomers, acrylonitrile, and hexamethylenediamine. Coal tar delivers aromatics, such as benzene, xylene, phenol, and phthalic anhydride, which lead subsequently to polystyrene, phenolic resins, and glyptal resins, to name a few.

1.1.3. Natural Gas and Fracking

Natural gas (→ Natural Gas) is a gas with a high proportion of aliphatic hydrocarbons. European gas is rich in methane, whereas American and Saudi Arabian gases are relatively rich in higher hydrocarbons. Natural gas is processed to synthesis gas, ethylene, and acetylene. These gases are used to produce a variety of monomers for polymers. The increasing exploitation of fracking enables the production of hydrocarbons which offer great potential as cost-effective alternative to crude oil.

1.1.4. Petroleum

Petroleum (crude oil) (→ Oil Refining) is the main feedstock for monomers. It consists of 95–98% hydrocarbons and 2–5% oxygen, nitrogen, and sulfur compounds. The hydrocarbons are largely aliphatic, partly naphthenic, and to a small extent aromatic, depending on the source. Petroleum distillation leads to saturated hydrocarbons (gas, naphtha, gasoline, kerosene,

diesel fuel, heating oil, etc.). For monomer production, these hydrocarbons are subsequently cracked to mixtures of olefins that are fractionated by distillation. The resulting compounds are used as such or are converted further into the desired monomers.

The polymer industry is a major petrochemical customer: About 60% of the cracking and subsequent products of naphtha are used to produce polymers (ca. 50% for plastics–elastomers, ca. 10% for fibers).

1.1.5. Other Renewable Resources and Biorefineries [2–6]

Vegetable oils are a relatively large source of raw materials. They have high hydrocarbon content and consist of mixtures of fatty acid triglycerides and are usually subdivided into drying oils with high linolenic and linoleic acid content, semidrying oils with high linoleic and oleic acid content, and nondrying oils with high oleic acid content (→ Fats and Fatty Oils). Some oils are used directly for paints; others are chemically converted into monomers.

Castor oil is converted into methyl ricinoleate, which is thermally cracked into methyl undecenate and heptanal. Methyl undecenate is the raw material for 11-aminoundecanoic acid, which is subsequently polycondensed to form polyamide 11. Alkali scission of castor oil or ricinoleic acid produces sebacic acid, a monomer used to prepare polyamide PA6,10. Moreover, castor is propoxylated and end-tipped with ethylene oxide in order to produce polyols, thus enabling the formation of polyurethanes containing up to 30 wt % renewable resources.

Soybean oil is converted by a series of chemical reactions into the methyl ester of the C_{10} amino acid $H_2N(CH_2)_9COOCH_3$, which is the monomer for PA 10. The plant *Crambe abyssinica* contains about 55% of erucic acid, which leads to the C_{13} amino acid and subsequently to PA 13 ($\sim[NH(CH_2)_{12}CO]_n\sim$).

Corn husks and other agricultural waste are rich in *pentosans*, which can be converted into tetrahydrofuran and further into polytetrahydrofuran $[HO(CH_2CH_2CH_2CH_2O)_nH]$, which serves as a soft block in certain polyurethanes. Moreover, epoxidized soybean oil is produced in large scale and employed as plasticizers for PVC.

Other Natural Oils. Although the production of polymers based upon soybean oil feedstocks may compete with food production, other nonfood oils, such as linseed and tung oil are attractive intermediates for plant-oil based polymers.

Bio-Based Monomers from Biorefineries. Progress made in biotechnology and in the production of biofuels is stimulating the development of new processes for exploiting biomass conversion in biorefineries as intermediates for bio-based plastics. In principle, there are three different strategies for biomass conversion (i) biomass-to-liquid conversion, (ii) biorefining exploiting glucose, bioethanol, glycerol, and plant oils as raw materials, and (iii) direct catalytic liquefaction and hydrothermal carbonization of biomass. Figure 1 gives an overview on the different strategies to produce bio-based monomers. Similar to the Fischer–Tropsch chemistry in coal-to-liquid conversion, biomass is converted by partial oxidation into syngas consisting of a mixture of carbon monoxide and hydrogen, which serves as feedstock for monomer production. This is a rather energy intensive process that is sensitive to catalyst poisoning by biomass components. A more energy-efficient process is the biotechnological conversion of glucose, preferably gained from nonfood sources, such as lignocellulose from agricultural and forestry wastes, into ethanol and a variety of other monomers, such as glycols and lactic acid. Bioethanol is readily converted into ethylene by splitting off water. In addition, butadiene and propene can be produced from bioethanol. In biodiesel production, vegetable oils are converted in their methyl ester by transesterification of oils with methanol. The byproduct glycerol can be converted into a variety of monomers including epichlorhydrin, acrylic acid, and polyols (see Fig. 1).

Whereas biomass-to-liquid conversion is energy intensive, the catalytic direct conversion

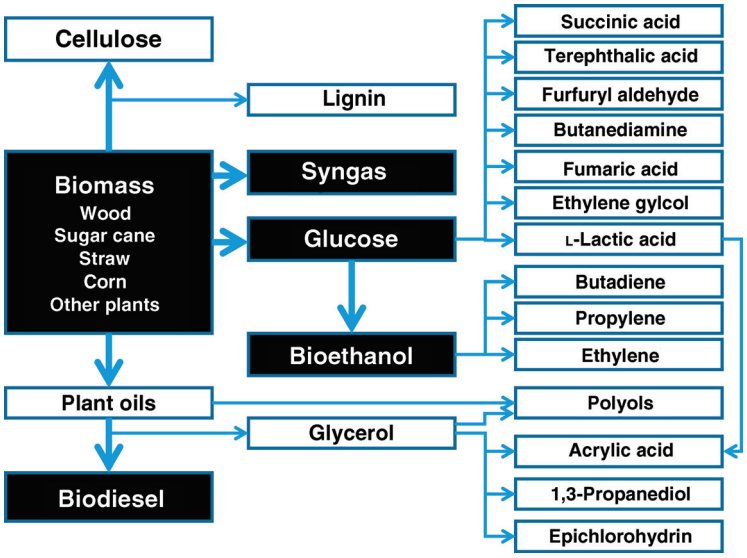


Figure 1. Biorefineries and biobased monomers

of biomass into diesel represents another attractive green route to renewable oil. In this process, plastics wastes as well as biomass can be employed as carbon source. In the third approach, entire plants can be converted into coal by hydrothermal carbonization. This is an exothermic process that operates at much lower temperature than the Fischer–Tropsch process. This renewable coal obtained by hydrothermal biomass carbonization is an attractive feedstock for catalytic liquefaction and production of renewable oil.

Carbon dioxide that is emitted by power plants, is the energy sink in combustion processes. Activation and chemical fixation of carbon dioxide requires energy, which can be supplied from renewable resources, thus enabling chemical energy storage of excess energy from wind and solar power plants. In contrast to traditional conversion of carbon dioxide into carbon monoxide and hydrogen by reduction with coal at very high temperatures, oil and gas are produced by electrochemical reduction of carbon dioxide in water. However, this process is not yet feasible for the production of monomers on industrial scale. Another more viable approach exploits the direct conversion of carbon dioxide with reactants, such as epoxides with a high energy content. Thus cyclic carbonates as well as linear aliphatic polycarbonates are available. Polyfunctional cyclic carbonates serve as intermediates for the formation of green polyurethanes without requiring phosgene or isocyanates.

1.2. Polymer Syntheses: Overview [7]

1.2.1. Classifications

Polymers may be synthesized from monomers by polymerization or from other polymers by chemical transformations. The nomenclature and classification of these reactions have grown and changed with the times; they are not very systematic and are sometimes confusing.

All reactions of small monomer molecules to macromolecules are called *polymerizations*. Polymerizations are classified according to the:

- Origin of polymers (bio and chemical polymer synthesis)
- Chemical structure of monomers (vinyl polymerizations, diene polymerizations, ring-opening polymerizations, etc.)

- Chemical structure of resulting polymers (linear, branching, cross-linking, isomerizing, cyclopolymerization, etc.)
- Relative composition of monomers and monomer units (addition, condensation, etc.)
- Formation of low molar mass byproducts (polycondensation)
- Type of polymerization initiation (thermal, catalytic, photochemical, enzymatic, etc.)
- Type of propagating species (free radical, anionic, cationic, polyinsertion, etc.)
- Type of mechanism (chain growth, step growth, living, controlled, catalytic, etc.)
- Reaction media (bulk, solution, emulsion, suspension, mesophase, etc.)
- State of matter (gaseous, homogeneous, heterogeneous, super critical, etc.)

The resulting four types of polymerization can be depicted schematically as

$$P_n + P_m \rightarrow P_{n+m}$$ Polyaddition

$$P_n + M \rightarrow P_{n+1}$$ Chain polymerization

$$P_n + P_m \rightarrow P_{n+m} + L$$ Polycondensation

$$P_n + M \rightarrow P_{n+1} + L$$ Polyelimination

where M denotes monomer; P_n, P_m, P_{n+m}, P_{n+}, denote polymers and L leaving molecules (e. g., water in polyesterifications of diacids and diols).

The names of three of these four types have been used with different meanings by different researchers since the 1930s. The following discussion thus centers on the present nomenclature recommendations by IUPAC.

Chain-Growth Polymerization. Polymer chains grow by repeated addition of monomer molecules M to polymer molecules P_i, consisting of i monomeric units m, an initiator end group R, and an "active center ∗," without the formation of leaving molecules:

$$R(m_n)m^* + M \rightarrow R(m_{n+1})m^*$$

An example is the polymerization of vinyl monomers (CH_2=CHR) by chain carriers Y∗, which may be free radicals $Y^{\cdot}$, anions Y^-, or cations Y^+:

$$Y-CH_2-CHR^* + CH_2=CHR \rightarrow Y-CH_2-CHR-CH_2-CHR^*$$

A *living polymerization* is a chain polymerization consisting only of fast initiating reactions (Y∗ + CH_2=CHR → Y−CH_2−CHR∗) and propagation reactions [Y−$(CH_2-CHR)_n$∗ + CH_2=CHR → Y−$(CH_2-CHR)_{n+1}$∗] without termination of the growing chains and without side reactions. In such reactions, the degree of polymerization is directly proportional to the conversion u of monomer molecules or p of functional groups, respectively (Fig. 2, curve CP−L). An example is the polymerization of styrene CH_2=CH(C_6H_5) by the butyl anion $C_4H_9^-$ from butyllithium, LiC_4H_9.

The variation of the degree of polymerization with monomer conversion is quite different for *radical polymerizations*, such as the polymerization of styrene by benzoyloxy radicals $C_6H_5COO^*$ from the thermal decomposition of dibenzoyl peroxide, $C_6H_5COO-OOCC_6H_5$. Radicals are here formed successively and not "at once" as are the butyl anions in living

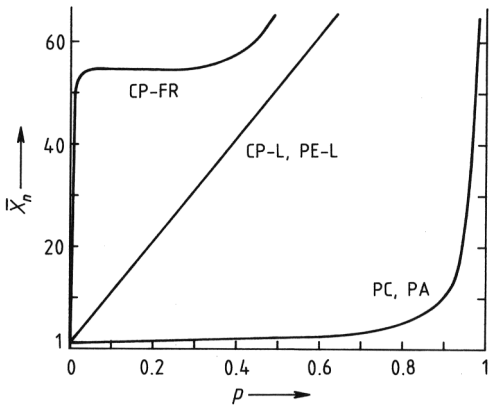


Figure 2. Change of number-average degree of polymerization $\overline{X}_n X^-$ with the extent of reaction of functional monomer groups p for living chain polymerizations CP−L and living polyeliminations PE−L (with initial monomer−−initiator ratio 100 : 1 mol/mol), free-radical chain polymerizations CP−FR with gel effect (schematic for high initiator concentrations), and equilibrium polycondensations PC and polyadditions PA (numerically exact)

polymerizations. Growing polymer chains are terminated by reaction with other radicals (recombination, disproportionation). Many side reactions may occur because of the high and fairly indiscriminate reactivity of radicals. Depending on reaction conditions, the degree of polymerization may remain constant (primarily at low conversions) or increase with monomer conversion (so-called gel effect, also referred to as autoacceleration or Trommsdorff effect) (Fig. 2, curve CP–FR). Whereas in living chain-growth polymerizations all chain ends are active during polymerization, in controlled polymerization reactions there is a rapid equilibrium between temporarily inactive ("dormant") chain ends and active chain ends. Similar to living polymerization, controlled chain-growth polymerizations afford narrow molar mass distribution, first order polymerization kinetics, and a degree of polymerization which is proportional to conversion.

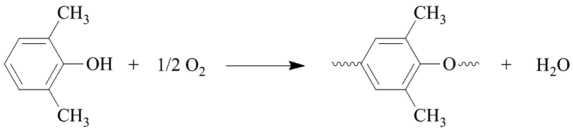
Chain-growth polymerizations have generally been called *addition polymerizations* in the literature. Addition polymerization is not to be confused with polyaddition (see below).

Condensative Chain-Growth Polymerization is the name recommended by IUPAC for a polymerization by repeated addition of monomer molecules with elimination of low molar mass molecules L; this polymerization has thus also been called *polyelimination* [8]:

$$R(m_n)m^* + M \rightarrow R(m_{n+1})m^* + L \quad (1)$$

Biological polymerizations to polysaccharides seem to proceed exclusively through polyeliminations. Cellulose of cotton, for example, is formed by polymerization of guanosine diphosphate D-glucose attached to a lipid matrix. The reaction proceeds via insertion of the glucose moiety into the chain with elimination of guanosine diphosphate.

Synthetic polymers are rarely formed by polyelimination. Examples are the polymerizations of α-amino acid *N*-carboxyanhydrides Leuchs anhydrides) and the "oxidative polymerization" of 2,6-dimethylphenol to polyphenylene oxide (PPO, PPE):



Polycondensation [9]. The step-growth polymerization, known as polycondensation, proceeds by reaction between molecules of all degrees of polymerization (not just between a polymer molecule and a monomer molecule as in chain polymerization and polyelimination) resulting in the formation of low molar mass molecules as byproducts. Many polymers with hetero atoms in the chains are generated by polycondensation. An example is the polycondensation of 11-aminoundecanoic acid to polyamide 11:

$$n\,H_2N(CH_2)_{10}COOH \rightarrow H[NH(CH_2)_{10}CO]_nOH + (n-1)H_2O \quad (2)$$

In these reactions, dimers ($n = 2$) are formed first, which then react to form tetramers ($n = 4$), etc. The reaction is thus statistical with respect to the size of the molecules to which the functional groups are attached. The degree of polymerization of the polymer is a number average $\overline{X}_n$ over all degrees of polymerizations of the polymer molecules.

All amino groups have the same chance to react if their reactivity is independent of molecule size. The reaction of amino groups attached to molecules with higher molar mass adds, however, considerably more to the increase of the degree of polymerization than the reaction of lower molar mass molecules: The degree of polymerization snowballs with increasing extent of reaction of functional groups (Fig. 2, PC). High conversion of functional groups and no side reactions are prime requirements for achieving high molar mass in step-growth polymerization. Molar mass is controlled either by adjusting the conversion of functional groups or by adding monofunctional chain terminating agents. The term polycondensation was used in the past as a synonym for condensation polymerization. The latter term included both the current concepts of polycondensation and polyelimination (condensative chain polymerization).

Polyaddition. This is a polymerization by reaction among molecules of all degrees of polymerization but without the formation of low molar mass byproducts. The number-average degree of polymerization of the resulting polymers varies with the extent of reaction of functional groups in the same way as it does in polycondensation. An example of polyaddition is the polymerization of diisocyanate with diol to form polyurethane:

$$n\,\mathrm{OCN{-}R{-}NCO} + n\,\mathrm{HO{-}R' - OH} \rightarrow \mathrm{OCN(R{-}NH - CO - O - R'O)}_n\mathrm{H} \quad (3)$$

These polymerizations have also been called "polyadduct formations." Polyaddition is not to be confused with addition polymerization, the term used in the literature for chain-growth polymerization.

1.2.2. Functionality

The functionality of monomers is essential for controlling polymer constitution. (e.g., see Eq. 1). When difunctional monomers, such as divinylbenzenes $CH_2{=}CH{-}C_6H_4{-}CH{=}CH_2$, are added to the chain-growth polymerization of styrene, first branching and later cross-linking takes place. The second vinyl group of a divinylbenzene possesses, however, a different reactivity after polymerization of the first one. The two reactivities may differ so strongly in certain ionic polymerizations of divinylbenzenes that linear polymers, and not cross-linked ones, result (e.g., in the cationic polymerization of 1,4-divinylbenzene by acetyl perchlorate in dichloromethane).

The isocyanate group $-N{=}C{=}O$ of diisocyanates can react with hydroxy groups of diols to produce linear polyurethanes by step-growth polyaddition (Eq. 3). It may, however, undergo a chain-growth polymerization to form polyisocyanates via the polymerization of the N=C double bond

$$n\,\mathrm{R{-}N = C = O} \rightarrow \mathrm{(NR - CO)}_n$$

It should be noted that isocyanates react with urethane to afford branching via allophanate groups (Eq. 4)

$$\sim\mathrm{NH{-}CO{-}O}\sim + \mathrm{O{=}C{=}N}\sim \longrightarrow \sim\mathrm{NH{-}CO{-}\underset{?}{N}{-}CO{-}O}\sim \quad (4)$$

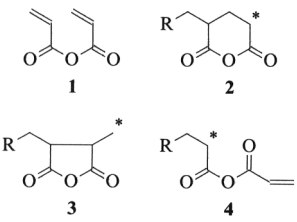
The functionality f of polymer molecules is given by the functionality f_o of the monomer molecules and the number X of mers if no intramolecular rings are formed between functional groups.

$$f = 2(f_o - 1) + (X - 2)(f_o - 2) = 2 + X(f_o - 2)$$

A monomer with functionality $f_o = 3$ thus gives a dimer ($X = 2$) with a functionality $f = 4$ and a 100-mer ($X = 100$) with a functionality $f = 102$. Because the molecule needs to be bifunctional only for the formation of linear molecules, the "extra" functionalities lead to interconnections between various molecules (branching) and thus finally to cross-linked, "infinitely large" molecules.

1.2.3. Cyclopolymerizations

Polymerizations of multifunctional molecules may proceed not only intermolecularly to produce branched and cross-linked molecules but also intra/intermolecularly with the formation of rings in chains. These polymerizations are called cyclopolymerizations. They occur especially with monomers having carbon–carbon double bonds in the 1,5- or 1,6-position. An example is acrylic anhydride (**1**), $CH_2{=}CH{-}CO{-}O{-}OC{-}CH{=}CH_2$, which polymerizes free-radically even at high monomer concentrations to soluble polymers with 90–100% six-membered (**2**) and five-membered (**3**) ring structures, and only 0–10% "linear" monomeric units **4** (R symbolizes a polymer chain and $*$ an active chain end):



1.3. Chain-Growth Polymerization

Chain-growth polymerization and polyelimination (condensative chain polymerization) agree in their polymerization kinetics, molar mass distributions, etc., if similar polymerization mechanisms are compared. They differ in the formation of low molar mass byproducts and thus in the design of industrial polymerization reactors.

1.3.1. Thermodynamics

Polymerizations occur only if their molar standard Gibbs energies ΔG_p^o are negative. Because the Gibbs energy

$$\Delta G_p^o = \Delta H_p^o - T \cdot \Delta S_p^o = -RT \cdot \ln K \quad (5)$$

is determined by both the polymerization enthalpy ΔH_p^o and the polymerization entropy ΔS_p^o, four different cases are possible:

Case 1. Both enthalpy and entropy are negative; the entropy term $-T \cdot \Delta S_p^o$ becomes more positive with increasing temperature. At a certain temperature, the enthalpy and entropy terms balance each other; no polymerization to high molar mass molecules is possible above this *ceiling temperature*. Oligomers, however, may be formed at the ceiling temperature, because polymerization equilibria consist of a series of consecutive equilibria between monomer and growing chains of different degrees of polymerization.

Case 1 is the most common case. It is found for monomers with polymerizable double and triple bonds, such as C=C, C=O, C=S, or C=N. The polymerization entropies of such monomers are practically determined only by the loss of translational entropy; they are thus almost independent of the chemical structure of the monomers. The polymerization enthalpy of α-olefins CH_2=CHR is influenced little by resonance stabilization and is practically independent of the size of the substituent R. Steric hindrance, however, strongly decreases the polymerization enthalpy of 1,1-disubstituted compounds CH_2=CRR′. Styrene and α-methylstyrene, have practically the same polymerization entropies (-105 J K^{-1} mol^{-1}) but very different polymerization enthalpies (-71 vs. -35 kJ/mol, respectively) for the polymerization of liquid monomers to condensed polymers. The ceiling temperatures in bulk are 303°C (styrene) and 60°C (α-methylstyrene), (i.e., the latter cannot be homopolymerized to high molar mass compounds above 60°C).

σ-Bonds are opened and formed again in ring-opening polymerization of cyclic monomers. Differences of bond energies in monomers and polymers are thus practically zero, and the polymerization enthalpy is determined by delocalization and strain energies. Polymerization enthalpies are very negative for ring-opening polymerization of three-membered rings, increase to about zero for five- or six-membered rings, drop again to negative values, and return almost to zero for very large rings. The polymerization entropies of very small rings are very negative due to the release of rotational entropy upon polymerization. They become less negative with increasing ring size.

Case 2. The polymerization enthalpy is negative (or zero) and the polymerization entropy positive. Polymerization is possible at all temperatures in this rare case, the polymerization of cyclooctamethyltetrasiloxane being an example.

Case 3. The polymerization enthalpy is positive (or zero) and the polymerization entropy is negative. No polymerization is possible at any temperature. This case seems to apply to the polymerization of acetone.

Case 4. Both polymerization enthalpy and polymerization entropy are positive. A *floor temperature* exists below which no polymerization is possible. This rare case is fulfilled for the polymerization of tightly packed cyclic monomers, such as cyclooctasulfur or oxacycloheptane (oxepane) since the number of rotatory degrees of freedom increases strongly upon polymerization to open chains.

Polymerization enthalpies and entropies are influenced by the state of monomers and polymers (gaseous, liquid, crystalline, etc.), the physical interaction between reactants themselves or reactants and solvents, and pressure. Especially important for industrial polymerizations is the fact that most (but not all, see above) chain polymerizations are exothermic. The heat

of polymerization can be considerable: Adiabatic polymerization of gaseous ethylene to crystalline polyethylene would result in a temperature increase of 1 800 K for complete monomer conversion. Polymerization reactors must be designed in such a way that the heat of polymerization can be removed rapidly because, otherwise, inhomogeneous charges may result or the reactor may even explode.

1.3.2. Free-Radical Polymerizations [10]

Free-radical polymerizations are initiated and propagated by free radicals. Such polymerizations are relatively insensitive to impurities in the reaction mixture and fairly easy to control. They are thus the methods of choice for the industrial production of plastics if the monomers can be subjected to free-radical polymerizations. This is true for ethylene and many ethylene derivatives: Most commodity plastics are thus obtained from free-radical polymerizations (Table 1).

Other industrial polymers formed by free-radical homopolymerizations include poly (vinyl acetate) (for coatings and adhesives), poly(acryl ester) (for adhesives), polyacrylamide (for thickeners), polyacrylonitrile (for fibers), polychloroprene (for elastomers), poly(acryl acid) (for thickeners), and poly(*N*-vinylpyrrolidone) (for various applications).

Polymerizations may be carried out in the gas phase, bulk, suspension, emulsion, solution, or under precipitation. Most monomers are bifunctional; they lead to linear or slightly branched polymers and thus to thermoplastics. Thermosets obtained from free-radical homopolymerizations include bis- and trimethacrylates as well as diallyl and triallyl compounds that cross-link under polymerization conditions:

$$CH_2{=}CH{-}CH_2{-}R{-}CH_2{-}CH{=}CH_2 \longrightarrow \begin{array}{l} \sim CH_2 \qquad\qquad\qquad CH_2\sim \\ \sim CH{-}CH_2{-}R{-}CH_2{-}CH\sim \end{array}$$

where R may be $COO(CH_2)_2O(CH_2)_2OOC$ [diethylene glycol bis(allyl carbonate], *o*-$C_6H_4(COO)_2$ (diallyl phthalate), or *m*-$C_6H_4(COO)_2$ (diallyl isophthalate). Other allyl compounds are used as cross-linking comonomers (diallyl fumarate, diallyl maleate, triallyl cyanurate).

Most free-radical polymerizations follow the kinetics of true chain reactions. In initiating (start) reactions (Eq. 7), radicals $R^{\bullet}$ are formed by the decomposition (Eq. 6) of initiator

Table 1. Plastics by free-radical chain-growth polymerizations*

Monomers	Polymerization in						Monomeric units
	Gas phase	Bulk	Suspension	Emulsion	Solution	Precipitation	
Living polymerization							
p-Xylylene	+						$-CH_2-(p\text{-}C_6H_4)-CH_2-$
Irreversible polymerization to linear or slightly branched polymers							
Ethylene		+	+	(+)	(+)	(+)	$-CH_2-CH_2-$
Styrene		+	+	(+)	(+)		$-CH_2-CH(C_6H_5)-$
p-Methylstyrene			+	+			$-CH_2-CH(p\text{-}CH_3C_6H_4)-$
Vinyl acetate		(+)	(+)	+	(+)		$-CH_2-CH(OOCCH_3)-$
Vinyl chloride	+	(+)	(+)	+	(+)		$-CH_2-CHCl-$
Vinyl fluoride		+					$-CH_2-CHF-$
Vinylidene fluoride			+	+			$-CH_2-CF_2-$
Trifluorochloroethylene			+				$-CF_2-CFCl-$
Tetrafluoroethylene			+				$-CF_2-CF_2-$
Methyl methacrylate		+	+	+	+		$-CH_2-C(CH_3)(COOCH_3)-$
Cross-linking polymerization							
Diallyl phthalate		+					see Equation (5)

* + = major processes; (+) = minor processes.

Other industrial polymers by free radical homopolymerizations include poly(vinyl acetate) (for coatings and adhesives), poly(acryl ester) (for adhesives), polyacrylamide (for thickeners), polyacrylonitrile (for fibers), polychloroprene (for elastomers), poly(acrylic acid) (for thickeners), and poly(*N*-vinyl pyrrolidone) (for various applications).

molecules I, that react with monomer molecules M. The resulting polymeric free radicals add further monomer molecules in the propagation reaction (Eq. 8) until the growing polymer radicals are terminated by recombination (Eq. 9) or disproportionation (Eq. 10) with other polymer radicals or by addition of initiator radicals (Eq. 11):

$$I \rightarrow 2\,R^{\bullet} \tag{6}$$

$$R^{\bullet} + M \rightarrow R - M^{\bullet} \tag{7}$$

$$R - M^{\bullet} + M \rightarrow R - M - M^{\bullet}, \text{etc.} \rightarrow R - M_{n-1} - M^{\bullet} \tag{8}$$

$$R - M_{n-1} - M^{\bullet} + {}^{\bullet}M - M_{m-1} - R \rightarrow R - M_{n+m} - R \tag{9}$$

$$R - M_{n-1} - M^{\bullet} + {}^{\bullet}M - M_{m-1} - R \rightarrow R - M_{n-2} - M = M + X - M_m - R \tag{10}$$

$$R - M_{n-1} - M^{\bullet} + R^{\bullet} \rightarrow R - M_n - R \tag{11}$$

In Equation (10), X is an atom or a group that is transferred from the ultimate monomeric unit of one polymer radical to another polymer radical, for example, the H atom in the reaction

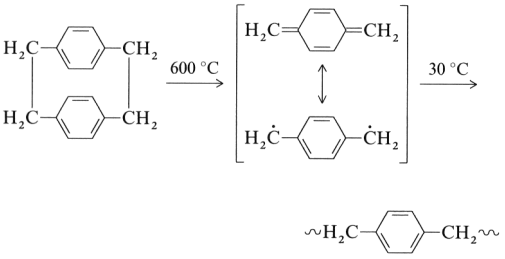
$$CH_2 - C^{\bullet}HR + {}^{\bullet}CHR - CH_2 \rightarrow CH_2 - CH_2R + CHR = CH_2$$

These reactions are kinetically classified as termination reactions and not as transfers because they lead to dead chains. The term "transfer" is rather reserved for chemical transfers that generate new propagating radicals, such as

$$CH_2 - C^{\bullet}HR + AX \rightarrow CH_2 - CH_2\,RX + A^{\bullet} \tag{12}$$

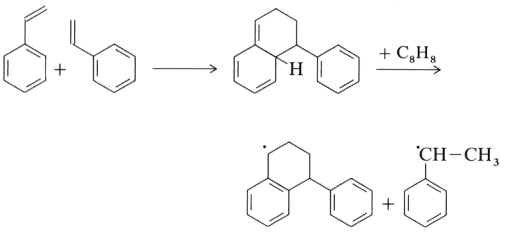
Initiation. Free-radical polymerizations can be initiated thermally by thermal initiators, by redox initiators, by photoinitiators, or electrolytically.

Thermal initiation is utilized in the polymerization of *p*-cyclophane to poly(*p*-xylylene):



Propagation proceeds by addition of biradicals of various sizes i.e., by polyaddition and not by chain polymerization. The resulting polymer is cross-linked because radicals also attack methylene groups, which generates more than two radical sites per reactant and thus cross-linking sites. The reaction is utilized for the formation of thin coatings.

Styrene is the only monomer that is polymerized commercially by thermal initiation through monoradicals. The primary Diels–Alder adduct of two styrene molecules reacts with another styrene molecule to give two different starter radicals:



Only relatively small amounts of styrene are, however, polymerized commercially by this method. Most styrene polymerizations, like many other commercial free-radical polymerizations, are started by radicals from *thermal initiators*. These thermal initiators dissociate homolytically into two radicals at elevated temperature, usually 60–80°C. For the bulk polymerization of styrene, high-temperature initiators, such as 1,2-dimethyl-1,2-diethyl-1,1-diphenyl-ethane or vinylsilane triacetate are preferred. For styrene polymerization in suspension, dibenzoyl peroxide (BPO) ($C_6H_5CO-O-O-OCC_6H_5$) and *tert*-butyl perbenzoate [$C_6H_5CO-O-O-C(CH_3)_3$] are used.

Many other bulk polymerizations employ diisopropyl peroxydicarbonate (IPP), which

decomposes according to

$$(CH_3)_2CHO - COO - OOC - OCH(CH_3)_2 \rightarrow 2(CH_3)_2CHO - COO^{\bullet}$$

Water-soluble initiators, such as dipotassium persulfate ($K_2S_2O_8$) and certain redox initiators are used in emulsion polymerizations. *Redox initiators* generate radicals by reaction of a reducing agent with an oxidizing agent (e.g., $Fe^{2+} + H_2O_2$). These systems need far less activation energy for the formation of radicals, and polymerization can thus be initiated at low temperature.

Photochemical initiations are utilized for the production of lithographic plates (→ Imaging Technology, 3. Imaging in Graphics Art) and for hardening lacquers but not in the manufacture of plastics. *Electrolytic polymerizations* find applications in the coating of metal sheets by plastics.

Only initiator radicals are formed at the early stages of free-radical polymerizations. These radicals are successively converted into monomer radicals by addition of initiator radicals to monomer molecules and into polymer radicals by further addition of monomers. At the same time, some polymer radicals are removed by termination reactions. Finally, a steady state is established in which as many radicals are formed as are removed by termination. This state of constant total radical concentration (ca. 10^{-8} mol/L) is in general observed within seconds at monomer conversions of 10^{-2}–10^{-4}%.

Propagation. Monomer molecules are usually added head-to-tail to growing polymer radicals:

$$CH_2 - CHR^{\bullet} + CH_2 = CHR \rightarrow CH_2 - CHR - CH_2 - CHR^{\bullet}$$

Tail-to-tail additions also occur (see → Plastics, General Survey).

Free-radical polymerizations lead in general to atactic or predominantly syndiotactic polymers. The syndiotacticity increases with decreasing polymerization temperature.

Termination. Termination reactions by recombination, disproportionation, and (at higher initiator concentrations) addition of initiator radicals, cannot be avoided. Because initiator radicals and thus also polymer radicals are formed successively and are deactivated at random by different termination reactions, distributions of molar masses are formed. The width of these distributions is given by the relative proportion of the different types of termination reactions.

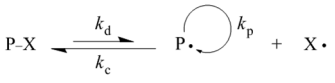
Chain Transfer. The transfers of radicals to monomers, solvents, and initiators terminate polymer chains and generate others (Eq. 12). The ratios of rate constants k_{tr} of transfer to rate constants k_p of propagation are called transfer constants, $C_{tr} = k_{tr}/k_p$; at 60°C they possess values between ca. 2×10^{-6} for the transfer of polystyryl radicals to benzene and 5 700 for the transfer of poly(vinyl acetate) radicals to carbon tetrabromide.

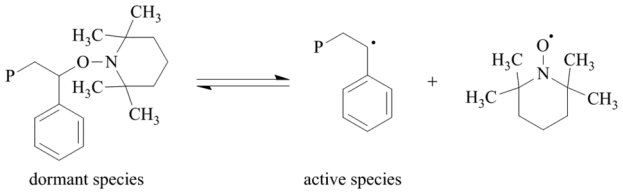
Chain transfers often lead to new radicals that have approximately the same reactivity as the disappearing ones. In this case, the rate of polymerization is not decreased by chain transfer, but the degree of polymerization is lowered. Certain transfer agents with high transfer constants (such as thiols) are thus often employed to regulate molar mass.

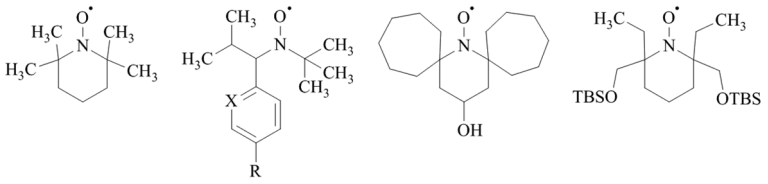
Inhibition and retardation occur if the new radical is more sluggish in adding monomers than the transferring polymer radical. In the case of *inhibition*, stable radicals are formed by chain transfer reactions. Typically, inhibitors, such as methylhydroquinone, are added. Moreover, retardation is observed when chain transfer to nonionic allyl monomers generates resonance-stabilized allyl radicals. The addition of monomer molecules to these radicals produces radicals that are more stabilized by resonance than their precursors and thus do not start a polymer chain. The polymerization of noncharged monoallyl monomers thus leads to oligomers with degrees of polymerization of ca. 10–20.

Controlled Radical Polymerization [11, 12]. Reversible deactivation is the key feature of controlled radical polymerization. Unlike living polymerization, the free radicals at the chain end are rendered temporarily inactive ("dormant"). Because there is a rapid equilibrium between free radical and dormant sites, controlled radical polymerization exhibits all features typical for living polymerization, i.e.,

the degree of polymerization is proportional to conversion and the rate of polymerization follows first order kinetics. The reversible trapping of free radicals prevents undesirable chain termination by recombination and disproportionation.

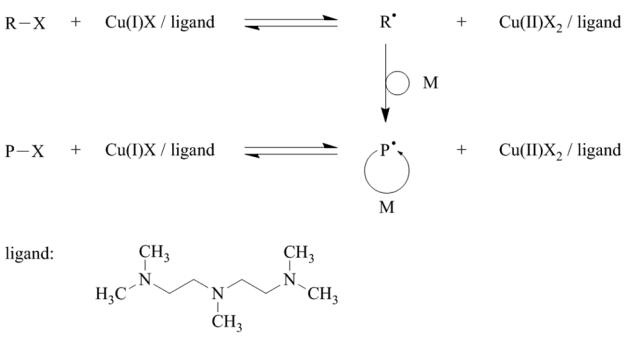




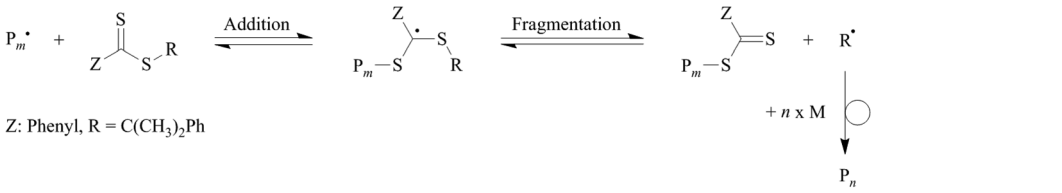


By using controlled radical polymerization techniques, it is possible to synthesize block-, graft-, and star copolymers as well as polymers with narrow molar mass distribution and well-defined end group functionalities. In *nitroxide-mediated controlled radical polymerization* (NMRP), stable nitroxide free radicals, such as (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) radicals are added to a free radical polymerization. Immediately after the nitroxide radical traps the free radial at the polymer chain end, thermal bond cleavage reinitiates chain growth by free radical polymerization. Because free radicals are temporarily trapped, the polymerization rate and monomer conversions are lower than in a living anionic polymerization.

In *atom transfer radical polymerization* (ATRP) organic halides react with redox metals, such as Cu^+, to produce organic free radicals via transfer of the halogen atom. This free radical at the chain end is temporarily terminated by transfer of the halogen, accompanied by changing of the oxidation state resulting from electron transfer of the redox metal. Although copper is preferred for ATRP, various other redox transition metals can be employed. The addition of ligands is required to prevent precipitation of the metal complex.



In *reversible addition chain tranfer polymerization* (RAFT) the polymer free radical adds to a thiocarbonyl group of dithioesters, dithiocarbamate or dithiocarbonates, forming a free radical that undergoes fragmentation to form a polymer radical and thiocarbonyl group.



Polymerization Kinetics of Free Radical Polymerization. Initiator radicals are generated by initiator decomposition (Eq. 13) with a rate of $2f \cdot k_d \cdot [I]$ where f is the radical yield (i.e., the fraction of radicals that start the polymerization). Initiator radicals disappear in the start reaction with a rate of $k_{st}[P]\,[M]$. In the steady state, as recognized by BODENSTEIN, the polymer radical concentration is constant. Hence, the rate of the start reaction equals the rate of the termination reaction(s), thus $R_{st} = R_t$, and for terminations through deactivation by other polymer radicals,

$$d[P]/dt = R_{st} - R_t = 2f \cdot k_d \cdot [I] - k_t[P]^2 = 0 \quad (13)$$

Because monomer is practically consumed only by the propagation reaction with a rate of $R_p = -d[M]/dt = k_p[P]\,[M]$, the propagation rate at diminishing initiator consumption is obtained from Equation (14)

$$R_p = -d[M]/dt = k_p(2f \cdot k_d/k_t)^{1/2} \cdot [I]_o^{1/2}[M] \quad (14)$$

The polymerization rate is directly proportional to the monomer concentration; bulk polymerization is thus always faster than solution polymerization. Because the kinetic chain length is equivalent to R_p/R_t, the degree of polymerization increases with increasing monomer concentration. Because ethylene has rather low reactivity, as reflected by its low k_p value, high pressure (i.e., high monomer concentration) and high temperature are required for achieving free radical ethylene polymerization. Due to inter- and intramolecular chain transfer reactions, the resulting polyethylene chains contain long- and chain alkyl branches. Whereas small amounts of long chain branches account for shear thinning during melt processing, the incorporation of short chain propyl- and butyl-branches impairs crystallization and lowers the polyethylene density. Therefore, high pressure free radical polymerization produces low density polyethylene (LDPE).

A "self-acceleration" of the polymerization and a concomitant increase of both the polymerization rate and degree of polymerization are observed at higher monomer conversion, especially in bulk and in concentrated solutions. This so-called gel-effect, also known as the Trommsdorff effect, is caused by a changing diffusion control of the termination by mutual reaction of two polymer radicals (i.e., a decrease of termination reactions), which in turn comes from an increasing entanglement of polymer chains. Because neither the rate of the initiator decomposition nor the rate of monomer addition is affected by increasing entanglements, and only the termination is slowed down, the Bodenstein steady-state principle does not apply anymore. Hence, both overall polymerization rates and molar masses simultaneously increase. This autoacceleration broadens molar mass distributions. Owing to the drastically reduced heat transfer at high viscosity, the autoacceleration can cause severe increase of temperature and even explosions, resulting from pyrolysis of polymers and gas evolution at temperatures above 400°C. The addition of chain transfer

agents, such as alkylthiols reduces molecular masses, thus preventing viscosity buildup and autoacceleration.

Cross-Linking Polymerization. Free-radical chain polymerizations are employed commercially in the manufacture of diallyl thermosets and in styrene–divinylbenzene copolymerizations for polymer beads. Primary macromolecules produced at very low monomer conversions are almost linear and carry pendant polymerizable groups. The likelihood of an attack at these groups increases with increasing mass average molar mass. Branched molecules are formed that convert to cross-linked polymers at the gel point. Monomer conversion at the gel point cannot at present be predicted theoretically for such free-radical polymerizations.

Process Engineering. Free-radical polymerizations may be performed in the gas phase, in bulk, solution, emulsion, suspension, or under precipitation (Table 1). Each method has advantages and disadvantages.

Bulk Polymerizations. Industrial bulk polymerizations are performed in *liquid monomers*, occasionally with the addition of 5–15 vol% solvent as a polymerization aid. The process leads to very pure products. However, much heat is generated per unit volume and, in addition, by the Trommsdorff effect. Local overheating may cause multimodal molar mass distributions, branching, polymer degradation, discoloring, or explosion. Bulk polymerizations are thus often terminated at 40–60% monomer conversion. The remaining monomer is distilled and recovered. Alternatively, polymerizations may be performed in two steps: First in large batch reactors, then in thin layers. Residual monomer is usually removed by steam.

Suspension polymerization is a "water-cooled" bulk polymerization. Water-insoluble monomers are suspended as small droplets of 0.001–1 cm diameter with the help of suspending agents, such as water-soluble polymers. The polymerization is initiated by oil-soluble initiators. The droplets are converted by polymerization into pearls; thus the process is also called *pearl polymerization*. The addition of protective colloids, such as water-soluble polymers, affords steric stabilization of the formed polymer particles and prevents their agglomeration. Suspension polymerization allows easy control of the reaction and delivers the polymer as easy-to-handle beads. A disadvantage is the cost of water removal and cleaning, along with the sometimes deleterious effects of incorporated suspension agents. The average size of spherical polymer particles decreases with increasing stirring speed. Prominent applications of styrene pearl polymerization include the formation of polystyrene pellets containing pentane as foaming agent and the production of cross-linked polystyrene beads that are sulfonated to produce polymeric cation exchange resins for water deionization.

Emulsion Polymerization. In emulsion polymerizations, water-insoluble monomers are solubilized in water by micelles of surfactant molecules (4–10 nm diameter); the monomers are also suspended in a few droplets (ca. 1 000 nm diameter). Water-soluble initiators decompose into radicals that travel through the water to the micelles where polymerization begins. Polymerization takes place in this micellar reaction compartment, referred to as polymer *latex*. Diffusion of monomer from the droplets to the latex replenishes the monomer that has been used up by reaction in the micelles. The average diameter of these latex particles is 500–5 000 nm. Each latex particle contains just one free radical, which is terminated when another initiator radical enters the latex particle; this remains dormant until a new initiator radical initiates the growth of a new chain. Because the reaction volume is very small in micelles (and in growing latex particles), termination reactions are rare, and polymerization proceeds in a quasi-living manner, leading to much higher molar masses than bulk polymerization. In terms of reaction control, emulsion polymerizations have advantages similar to suspension polymerizations. In addition, they offer higher polymerization rates by redox initiators and higher molar masses (which can be regulated by transfer agents). Emulsion polymerization is applied to produce homo- and copolymers based upon styrene, butadiene, vinyl chloride, vinyl acetate, acrylates as well as tetrafluoroethylene. The resulting latex can furthermore be used directly for producing

water-borne paints, adhesives, and coatings forming corrosion resistant polymer films when water vaporizes and the polymers entangle.

Gas-phase polymerizations can be initiated photochemically. Each growing particle contains only one radical and the polymerization is thus quasi-living. The polymerization rate is determined by the rate of monomer adsorption in the precipitating particles and later by monomer diffusion to the occluded polymer radicals. The resulting polymers are very clean.

Solution polymerizations decrease polymerization rates by monomer dilution and allow easy removal of the heat of polymerization. Solvents are, however, costly to remove, and the process is used only if the resulting polymer solutions can be used directly or if monomers and polymers decompose in melts.

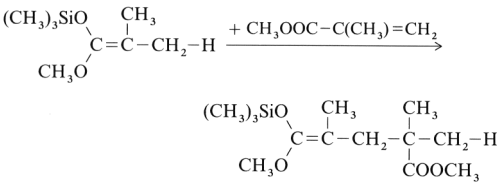
1.3.3. Anionic Polymerizations [13]

Anionic polymerizations are initiated by bases, such as alkali metals, alkoxides, amines, phosphines, Grignard compounds, and sodium naphthalene, very often in solution. The initiators dissociate "instantaneously" into the initiating species. These dissociations and the subsequent start reactions need little activation energy; anionic polymerizations thus often proceed with high speed even at −100 °C.

The initiating species and the growing macroions are rarely completely dissociated into anions and counterions. They are rather in equilibrium with various types of ion pairs (nondissociated species, contact ion pair, solvent-separated ion pair, free ions plus associates of these species). The type and amount of initiating species strongly affect the polymerization rates and the tacticity of polymers.

The initiating species are present in their effective concentrations at the beginning of polymerization; they are not formed one after another as in free-radical polymerization. Termination reactions are fairly rare if protons are absent. Hence, anionic polymerizations are often "living." Very low initiator concentrations are required for living polymerizations to high molar masses (see Section 1.2.1); however, high monomer−initiator ratios are difficult to control and may lead to low polymerization rates. In general, polymers from living polymerizations have very narrow molar mass distributions of the Poisson type if diffusion effects are avoided during the mixing of monomer and initiator solutions.

Contrary to traditional living polymerizations, a variety of controlled anionic polymerizations have been developed. Key feature is a rapid equilibrium between active and dormant endgroups. For example, in *group transfer polymerization (GTP)* there is a rapid equilibrium between inactive silyl ketene acetals and enolate anions, catalyzed by nucleophilic catalysts ($[(CH_3)_3SiF_2]^-$, $[HF_2]^-$, CN^-, etc.):



Very few anionic polymerizations are employed for the production of thermoplastics, most notably those of formaldehyde, ε-caprolactam (also used in reaction injection molding), and laurolactam (Table 2). Anionic polymerizations are, however, the method of choice for the syntheses of block copolymers, such as thermoplastic elastomers, e.g., polystyrene −block−polybutadiene− block−polystyrene (SBS).

1.3.4. Cationic Polymerizations [14]

Three groups of monomers can be polymerized cationically: (i) Olefin derivatives CH_2=CHR with electron-rich double bonds, (ii) monomers with double bonds containing heteroatoms or heterogroups Z (e.g., CH_2=Z), and (iii) rings with heteroatoms. Initiators are Brønsted acids (perchloric acid, trichloroacetic acid, trifluoromethanesulfonic acid, etc.); Lewis acids ($AlCl_3$, $TiCl_4$, $SnCl_4$, etc.) with "coinitiators", such as water; and carbenium salts (acetyl perchlorate, tropylium hexachloroantimonate, etc.). The propagating macrocations are thermodynamically and kinetically unstable. They attempt to stabilize themselves by addition

Table 2. Industrial anionic homopolymerizations

Monomer	Repeating unit	Application
Butadiene	$\sim CH_2-CH=CH-CH_2\sim$	elastomer (1,4-*cis*)
Isoprene	$\sim CH_2-C(CH_3)=CH-CH_2\sim$	elastomer (1,4-*cis*)
Methyl cyanoacrylate	$\sim CH_2C(CN)\,(COOCH_3)\sim$	adhesive
Formaldehyde	$\sim O-CH_2\sim$	engineering plastics
Ethylene oxide	$\sim O-CH_2-CH_2\sim$	thickener
Glycolide	$\sim O-CO-CH_2\sim$	surgical threads
ε-Caprolactone	$\sim O-CO-(CH_2)_5\sim$	polymer plasticizer
ε-Caprolactam	$\sim NH-CO-(CH_2)_5\sim$	fiber, thermoplastic
Lauryllactam	$\sim NH-CO-(CH_2)_{11}\sim$	fiber, film
Hexamethylcyclotrisiloxane	$\sim O-Si(CH_3)_2\sim$	elastomer

of nucleophilic species, which leads to very fast polymerization on one hand and to a host of transfer and termination reactions on the other. Very few monomers are thus polymerized cationically on an industrial scale (Table 3). Prominent examples include polyisobutene and poly(isobutene-co-isoprene) rubber.

1.3.5. Ziegler–Natta [15–19], ROMP [20] and ADMET [21] Catalysis

Ziegler–Natta polymerization catalysis involves a chain-growth polymerization on Ziegler catalysts, comprising a vast group of transition-metal compounds activated with main group metal alkyls, preferably aluminum alkyls. Today, in line with pioneering advances at Phillips using activator-free silica supported Cr(III) catalysts, a variety of cationic transition metal alkyls containing weakly coordinating counterions are available that do not require the addition of main group metal activators. Because monomers are inserted into the transition metal alkyl bonds, this catalytic polymerization is named polyinsertion. In older literature, polyinsertions are also referred to as coordination polymerizations or anionic–coordination polymerizations, although coordination of a monomer to an initiator need not lead to a Ziegler–Natta type of polymerization catalysis. Whereas free-radical polymerization of ethylene requires temperatures above 150°C and pressures well above 1 000 bar and produces branched low-density polyethylenes, catalytic ethylene polymerization takes place at ambient temperature and pressure below 10 bar, thus producing linear high density polyethylene. Short chain branches are introduced by copolymerization of ethylene with α-olefins. Stereospecific catalytic diene polymerization produces highly stereoregular poly(*cis*-1,4-isoprene) and poly(*cis*-1,4-butadiene) as synthetic alternative to natural rubber. Both KARL ZIEGLER and GIULIO NATTA were awarded the Nobel Prize for Chemistry in 1963, honoring their groundbreaking research, which paved the way for the

Table 3. Industrial cationic polymerizations

Monomer		Application**
Name	Structure*	
Isobutene	$CH_2=C(CH_3)_2$	elastomers, adhesives, VI improvers
Vinyl ethers	$CH_2=CHOR$	adhesives, textile aids, plasticizers
Formaldehyde	$CH_2=O$	engineering plastic
Ethyleneimine	c-$(NHCH_2CH_2)$	paper additive, flocculant
Tetrahydrofuran	c-$[O(CH_2)_4]$	soft segment for polyurethanes or polyether–ester elastomers

* c = cyclo.
** VI = viscosity index.

Table 4. Important industrial polymerizations with transition-metal catalysts

Monomer	Initiator	Application
Ethylene	$MgX_2/TiY_4/AlR_3$ (X = Cl, R, OR; Y = Cl, R, OR); (post)metallocene (Ti, Zr, Hf, Fe, Co), halfsandwich (Ti) and Cr(III) catalysts supported on silica	thermoplastic (HDPE, LLDPE)
Propene	$MgCl_2$/1,3-diether/$TiCl_4/AlR_3$; (post)metallocene (Ti, Zr, Hf) supported on silica	thermoplastic (PP)
Ethylene+propene+nonconjugated diene	Metallocene and halfsandwich catalysts, $VOCl_3/R_2AlCl$	elastomer (EPDM)
Butadiene	Co-, Ni-, Nd-, Sm-, Ln-catalysts, (post)metallocene and halfsandwich catalysts,	elastomer
Isoprene	Ti-, Co-, Ni-, Nd-, Sm-, Ln-catalysts, (post)metallocene and halfsandwich catalysts	elastomer
Butene-1	$MgCl_2$/1,3-diether/$TiCl_4/AlR_3$; (post)metallocene (Ti, Zr, Hf) supported on silica$TiCl_3$–Et_2AlCl	thermoplastic

industrial production of polyolefins. Half of the annual world production of polymers is based on this process.

Typical Ziegler catalysts for industrial polymerizations of olefins, such as ethylene, propene are shown in Table 4. Metallocenes and post-metallocene complexes have been developed since the early 1980s to produce tailor-made polyolefins in which the molecular architectures of polyolefins are tuned as a function of the molecular architectures of the catalytically active transition metal complexes. Traditionally, Ziegler catalysts are multi-site catalysts that contain different catalytically active sites and produce polymer chains with different molecular masses and molar-mass dependent comonomer sequence distribution. In contrast, modern single-site catalysts, which are based on metallocene and post-metallocene complexes, contain a single type of catalytically active site and give much more uniform polymers; molecular mass and molar-mass independent comonomer incorporation can be controlled easily.

Homogeneous catalysts are used in solution polymerization forming elastomers, such as ethylene−propene copolymers, which can contain a small amount of nonconjugated dienes, such as ethylidene norbornene as cross-linking sites. Slurry polymerizations, in which polymers precipitate during polymerization, require heterogeneous catalysts in order to prevent reactor fouling. Incorporating active transition metal alkyl sites on high surface area supports boosts catalyst activity and enables control of both polyolefin molecular architectures and polyolefin particle morphologies. In slurry polymerizations, most soluble catalysts produce small submicron dustlike polyolefin particles, thus causing severe reactor fouling and handling problems. Owing to fragmentation of supported catalysts during slurry polymerization (see Fig. 3), much larger micron-sized polyolefin particles are formed, which prevent reactor fouling. Moreover, spherical supported catalysts produce spherical pellet-sized polyolefin particles, thus eliminating the need for pelletizing extrusion.

The development of highly active and stereoselective supported catalysts was essential for enabling solvent-free gas phase and liquid pool olefin polymerization. The choice of the support materials and the selection of supporting strategies depend on the selected transition metal component. Because $MgCl_2$ has the same crystal structure as $TiCl_3$, it can substitute inactive bulk $TiCl_3$ that does not have vacant coordination sites. Hence, $MgCl_2$ supported titanium catalysts, activated with aluminum alkyls, afford orders of magnitude higher catalyst activities. In propene polymerization, the addition of small amounts of Lewis bases, such as 1,3-diethers promotes high stereospecifity, leading to the formation of highly isotactic polypropylene. Most (post) metallocene and chromium catalysts are preferably immobilized on high surface area silica supports.

Breakthroughs in catalyst and process technologies have greatly simplified olefin

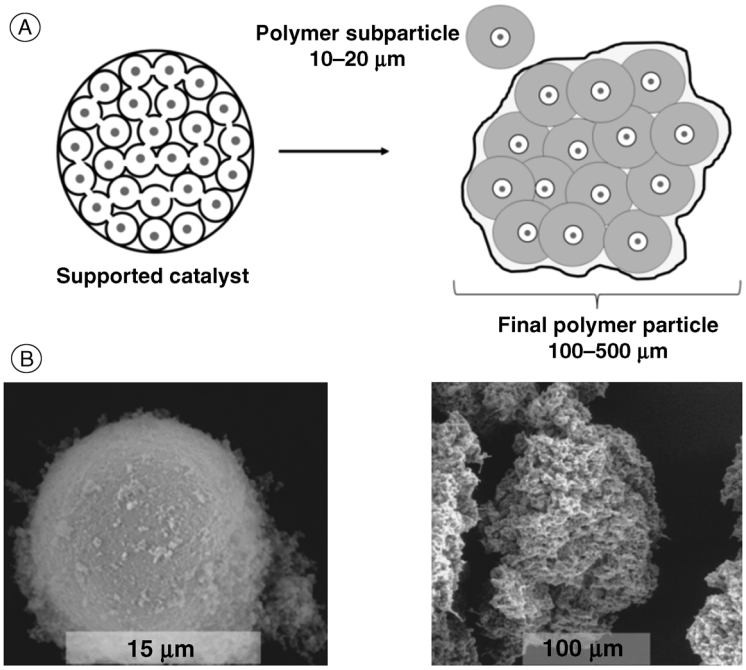


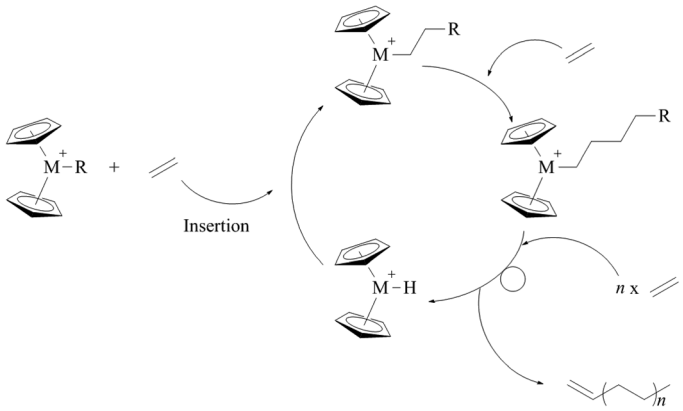
Figure 3. Morphology control in catalytic olefin polymerization by fragmentation of catalyst particles during polymerization A) Fragmentation of catalyst particle; B) Scanning Electron Microscope image of a catalyst particle (left) and a polyethylene particle (right)

polymerization. With catalyst activities exceeding 1 000 kg polyolefin/g Ti, the titanium content in the polyolefin is below 1 ppm. Hence, catalyst residues can be left in the polymers, i.e., the catalyst does not need to be removed by extraction or by adsorber beds typical for early catalysts generations. Furthermore, highly energy- and resource-efficient polymerization in gas phase and bulk eliminates the need for organic solvents as polymerization media and for their recycling. Because of the excellent control of molecular mass and stereoregularity, polyolefin purification by solvent extraction of low molecular mass polyolefin waxes and atactic polypropylene is no longer required. Employing fossil and renewable feedstocks, such as oil, gas and even bioethanol in environmentally friendly and highly energy-efficient catalytic polymerization processes meets the demands of green chemistry. As hydrocarbon resins, polyolefins preserve oillike energy content. They are readily recycled by remolding and serve as valuable source of energy and "renewable oil", produced by thermal degradation of polyolefins.

The basic reaction mechanisms and the correlations between the architectures of catalytically active transition metal complexes and polyolefin architectures are quite well understood. As illustrated below for olefin polymerization on a cationic metallocene alkyl catalyst, the olefin forms a π-complex with the transition metal prior to insertion into the transition metal carbon bond. After repeated insertion β-hydride elimination terminates the polymer chain, thus forming vinyl-terminated polyethylene. The resulting transition metal hydride is the catalytically active intermediate, which adds to an olefin and starts the growth of a new polyethylene chain. Additionally, hydrogen can be added to control molecular mass by chain transfer that involves hydrogenation of the transition metal alkyls and formation of a

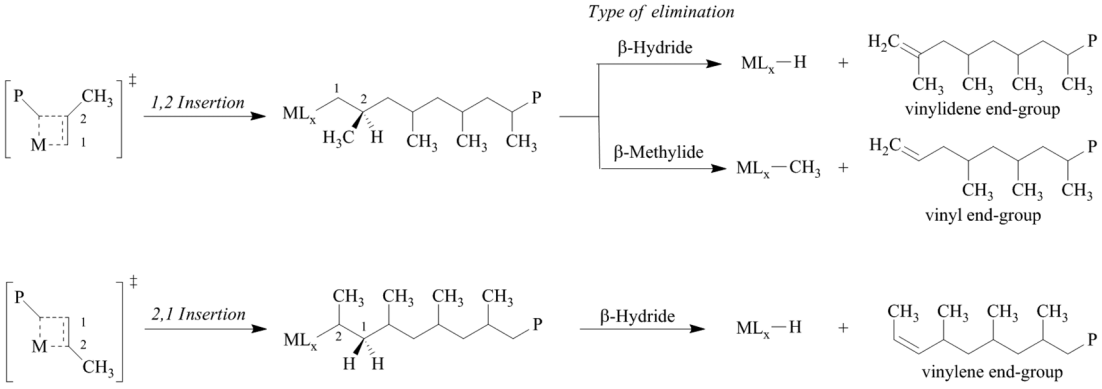
transition metal hydride, which subsequently adds to the ethylene.

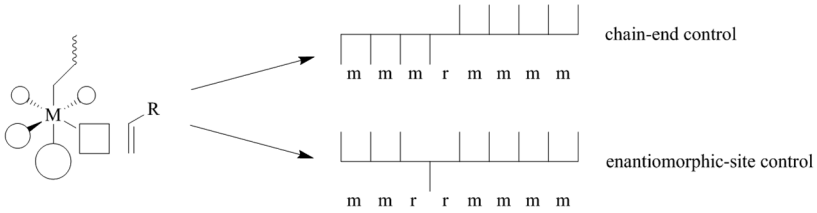
The stereospecificty of α-olefin polymerization is governed either by the configuration



The regioselectivity in α-olefin and the polyolefin constitution is governed by the insertion type. Whereas 100% of 1,2- or 2,1-insertion exclusively afford head-to-chain polyolefins, lower regioselectivity accounts for head-to-head enchainment in the polyolefin backbone. Most α-olefins are polymerized by 1,2-insertion in highly regioselective catalytic polymerization. The insertion type is identified by end group analysis of poly(α-olefins), taking into account chain termination by β-hydride as well as β-methylide transfer.

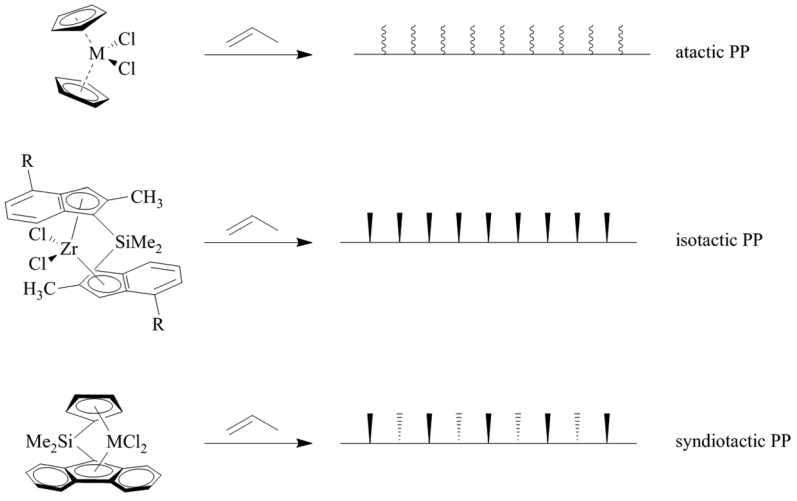
of transition metal complex (enantiomorphic site control) or by that of the asymmetric carbon atom of the monomeric unit at the chain end (chain end control). When a false insertion occurs, the resulting change of configuration is isolated in the case of enantiomorphic site control but is perpetuated in the case of chain end control (see below, m denotes meso, r denotes racemic). The analysis of polyolefin microstructures reveals that for most catalysts the chirality of the transition metal accounts for the control of the stereoregularity.





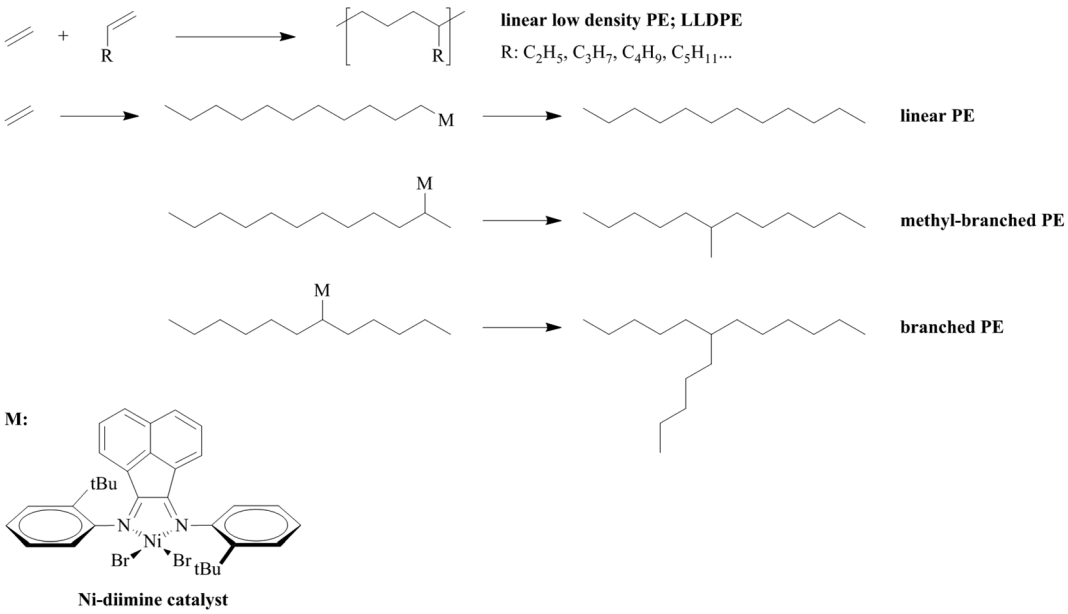
The ability of catalysts to control the stereochemistry of poly(α-olefins) and polydienes makes Ziegler–Natta polymerization catalysis industrially extremely useful. Propene, for example, polymerizes cationically to highly branched, atactic, low molar mass polymers that do not crystallize and have low glass transition temperatures. They can be used only as hotmelt adhesives and lubricants. Ziegler–Natta polymerization catalysis (Table 4) leads, however, to stereoregular polymers with high melting temperatures. Isotactic polypropylenes find extensive use as thermoplastics. Stereoblock polypropylenes can be engineered to produce thermoplastic elastomers containing highly flexible amorphous and rigid crystalline segments. The structure of single-site metallocene catalysts can be varied to produce virtually any kind of poly(α-olefin) microstructure industrially:

Similar to free radical polymerization, short and long chain branches are readily introduced by catalytic olefin polymerization. With increasing α-olefin comonomer incorporation, both crystallinity and density of polyethylene decrease. Whereas high density linear polyethylene (HDPE) is attractive for producing pipes, linear low density polyethylene (LLDPE) is highly flexible and has lower density, thus meeting the demands of packaging applications. A small amount of long chain branching promotes shear thinning and melt strengthening, which is beneficial to blow molding of films. At a high degree of branching, polyethylene is rendered amorphous and elastomeric. In principle, there are two synthetic strategies for branching of polyolefins: (i) Copolymerization of ethylene with various α-olefins, and (ii) branching homopolymerization of ethylene according to the "chain



walking" mechanism. In chain walking, the catalytically active transition metal alkyl travels up and down the polymer chain via repeated β-hydride elimination followed by addition of the transition metal hydride to the resulting double bond. Whereas titanium catalysts form linear polyethylene chains, branching ethylene homopolymerization takes place on postmetallocene complexes, such as cationic alkyl Ni diimine. Alkyl Pd diimine complexes produce high molecular mass highly branched amorphous polyethylenes. Because Pd metal alkyl travels up and down the main chain and side chains, branches are formed.

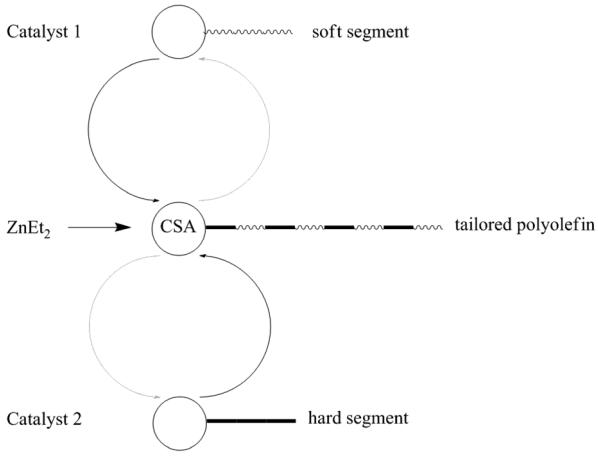
developed for producing HDPE, LLDPE, and EP(D)M rubbers. Since the 1980s, the development of single-site catalysts based upon metallocene, post-metallocene, and constrained geometry half-sandwich complexes has revolutionized the industrial synthesis of branched polyethylenes. As a function of the ligand framework, it is possible to control molecular mass independent incorporation of α-olefins into polyethylene backbone to produce LLDPE as well as very low density polyethylenes and elastomers by the same catalyst. Moreover, improved reactivity enables the efficient copolymerization of polyethylene vinyl endgroups, thus producing long chain branched polyethylene.



Ni-diimine catalyst

In the early days of catalyst development, the multisite nature of catalysts accounted for the formation of rather complex copolymer compositions in slurry polymerizations. Frequently, the α-olefin comonomer was predominantly incorporated in low molar mass waxlike fractions. More uniform copolymer compositions are obtained in high temperature solution polymerization operating at temperatures above 130°C. In the past, very different catalyst systems were

In a chain shuttling solution process, zinc alkyls transfer polymer chains between catalytically active sites producing exclusively linear polyethylene or ethylene–1-octene copolymers. As a consequence, block copolymers are obtained that contain alternating rigid HDPE segments and elastomeric poly(ethylene-co-1-octene) segments. Such block copolymers are attractive as thermoplastic elastomers.



CSA: chain shuttling agent Et_2Zn-P

Although single-site catalysts afford uniform polyolefins, it is highly desirable to tailor polyolefins with broad molecular mass distributions and preferred incorporation of branches exclusively into the ultrahigh molar mass fraction. This greatly improves shear thinning during melt processing. Moreover, small amounts of slightly branched ultrahigh molar mass poylolefins function as "tie molecules" bonding together polyethylene crystallites and significantly improve the fatigue resistance and durability of polyethylene pipes. Two strategies are exploited: (i) Ethylene polymerization in cascade reactors, and (ii) ethylene polymerization in a single reactor using multi-site catalysts, prepared by incorporating different single-site catalysts on the same support (see Fig. 4). In cascade reactors, ethylene is polymerized in the

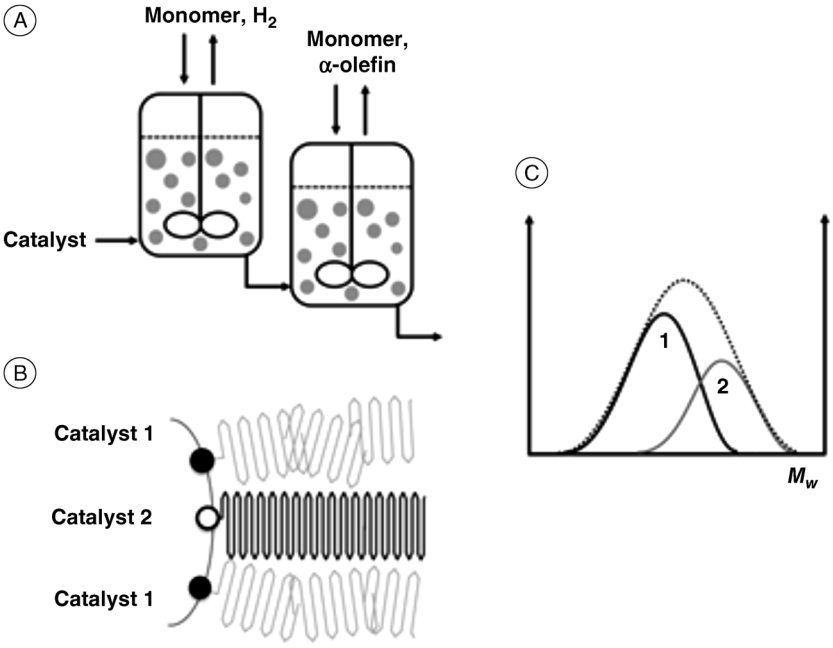


Figure 4. A) Reactor cascades; B) Multi-site catalysts producing reactor blends of HDPE with ultrahigh molecular mass polyethylene (UHMWPE); C) Polyolefin with bimodal molar mass distribution containing UHMWPE (2)

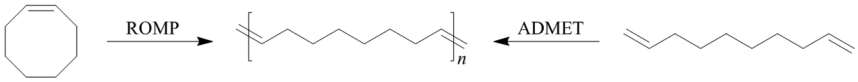
absence and the presence of hydrogen to control molar mass dstribution. The addition of α-olefin as comonomer selectively branches UHMWPE without affecting HDPE.

In multi-site catalysis, different catalytically active complexes that produce high and low molecular mass polyethylenes are incorporated on the same support, thus enabling simultaneous production and blending of both polyolefins. Reactor blend formation is advantageous compared to blends prepared by conventional melt compounding, especially with respect to dispersion problems due to the high viscosity of ultrahigh molecular mass polyolefins and rubbers. The reactor blend formation of HDPE with UHMWPE (see Fig. 4) is the key to self-reinforcing polyethylene (see Plastics, General Survey, 4. Polymer Composites). The reactor granule technology, which combines liquid pool propene homopolymerization with subsequent propene–ethylene copolymerization in a gas phase reactor, incorporates EPM rubber phases directly into the matrix of the PP granules (Catalloy technology). Most conventional Ziegler and related catalyst systems polymerize cyclic olefin, such as cyclopentene via 1,2 polymerization, thus linking together cyclic hydrocarbons by covalent bonds to form rigid polymers. In contrast, transition carbene complexes enable ring-opening polymerization of cyclic olefins to produce flexible polyalkenamers. Catalytic intermediate of this ring-opening metathesis polymerizations (ROMP) are metallcylobutanes formed by cycloaddition of carbene complexes to cycloolefins.

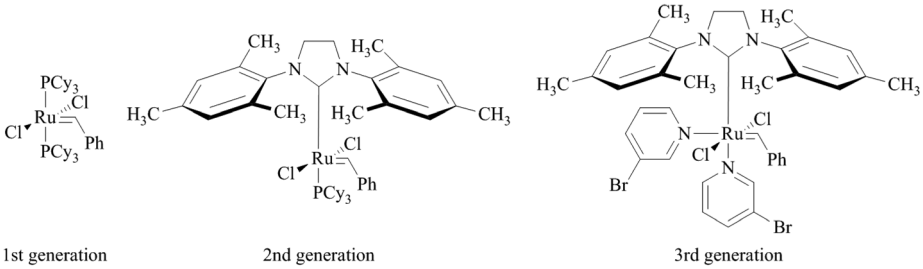
Metatheses reactions are exchange and disproportionation reactions of double bonds, mainly carbon–carbon double bonds in olefins and cycloolefins. A low molar mass example is the metathesis of pentene-2 to butene-2, pentene-2, and hexene-3 (in the ratio 1 : 2 : 1) by the catalyst system $WCl_6-C_2H_5AlCl_2-C_2H_5OH$. Stable carbene complexes are at hand for metathesis reaction and ROMP. Industrially, cyclooctene, norbornene, and dicyclopentadiene are polymerized by ROMP. Cyclooctene gives polyoctenamer $\sim CH{=}CH-(CH_2)_6\sim$; both the *cis* and the *trans* isomers are elastomers (→ Rubber, 6. Sythesis by Radical and Other Mechanisms). Norbornene polymerizes to a thermoplastic polymer that is plasticized with mineral oil to give an elastomer (→ Rubber, 6. Sythesis by Radical and Other Mechanisms). Dicyclopentadiene is polymerized by reaction injection molding (RIM) processes to produce rigid engineering materials.



In *acyclic diene metathesis polymerization* (ADMET), the polycondensation of a variety of nonconjugated linear dienes, such as 1,5-headiene, affords polyenes. Using functional nonconjugated diene monomers, ADMET enables precise control of the spacer length between two branches, whereas conventional copolymerization process affords broad distributions. Unlike industrial Ziegler catalysts, Ru carbene complexes are tolerant to polar



Grubbs catalyst



1st generation 2nd generation 3rd generation

groups, thus enabling the formation of polyolefins with polar groups attached as side chains.

1.3.6. Copolymerizations [22]

Copolymerizations are joint polymerizations of two or more monomers; they were also called interpolymerizations in the older literature. In the simplest case, both active chain ends ∼a∗ and ∼b∗ react irreversibly with the two monomers A and B:

$$\sim a^* + A \rightarrow \sim a - a^*; R_{aA} = k_{aA}[a^*][A]$$

$$\sim a^* + B \rightarrow \sim a - b^*; R_{aB} = k_{aB}[a^*][B]$$

$$\sim b^* + A \rightarrow \sim b - a^*; R_{bA} = k_{bA}[b^*][A]$$

$$\sim b^* + B \rightarrow \sim b - b^*; R_{bB} = k_{bB}[b^*][B]$$

Four rates R_{ij} and four rate constants k_{ij} are to be considered in this terminal model, which corresponds to Markov first-order statistics. At high molar masses, monomers are consumed only by the four propagation reactions. The relative monomer conversion is given by

$$\frac{-d[A]/dt}{-d[B]/dt} = \frac{R_{aA} + R_{bA}}{R_{bB} + R_{aB}} = \left(\frac{k_{bA} + k_{aA}([a^*]/[b^*])}{k_{bB} + k_{aB}([a^*]/[b^*])}\right) \cdot \frac{[A]}{[B]} = \frac{d[A]}{d[B]}$$

The ratios of rate constants of homopropagations and cross-propagations are called copolymerization parameters

$$r_A \equiv k_{aA}/k_{aB};\ r_B \equiv k_{bB}/k_{bA}$$

Five different cases can be distinguished for each copolymerization parameter:

- $r = 0$ The rate constant of homopropagation is zero; the active center adds only the other monomer.
- $r<1$ The other monomer is added preferentially.
- $r = 1$ Both monomers are added in the same amounts.
- $r > 1$ The own monomer is added preferentially but not exclusively.
- $r = \infty$ No copolymerization, only homopolymerization.

Table 5. Types of copolymerization of monomers A and B

Types	Copolymerization parameters				
	Azeotropic		Nonazeotropic		
	r_A	r_B	r_A	r_B	$r_A r_B$
Alternating	0	0	0	> 0	0
Statistical	< 1	< 1	$< 1/r_B$	> 1	< 1
Ideal	1	1	$1/r_B$	$1/r_A$	1
Block forming	> 1	> 1	$> 1/r_B$	< 1	> 1
Blend forming	∞	∞	∞	< ∞	∞

Depending on the relative numerical value of the two copolymerization parameters, five different types of copolymerization can be distinguished (Table 5).

In general, one of the monomers is consumed preferentially during copolymerization ($r_A \neq r_B$). This drift of copolymer composition can be avoided if the more reactive monomer is fed into the reactor according to its consumption. A conversion-independent polymer composition also results if copolymerization is performed under azeotropic conditions, which are defined by

$$d[A]/d[B] \equiv [A]/[B]$$

i.e., the relative rate of monomer consumption equals the ratio of monomer concentrations at any time: The monomer and the polymer compositions do not drift with the progress of polymerization.

This equation is a special case of the Lewis–Mayo equation, which describes the instantaneous composition of the copolymer as a function of the ratio of instantaneous monomer concentrations:

$$\frac{d[A]}{d[B]} = \frac{1 + r_A([A]/[B])}{1 + r_B([B]/[A])} = \frac{x_a}{x_b}$$

All types of copolymerization can in principle occur with the same monomer pair if various initiators are used. All copolymerizations of styrene and methyl methacrylate shown in Figure 5 are, for example, statistical. The free-radical-initiated copolymerization is, however, azeotropic, and the cationic and anionic ones are nonazeotropic. Initiation by $Et_3Al_2Cl_3$ and traces of oxygen leads to almost alternating

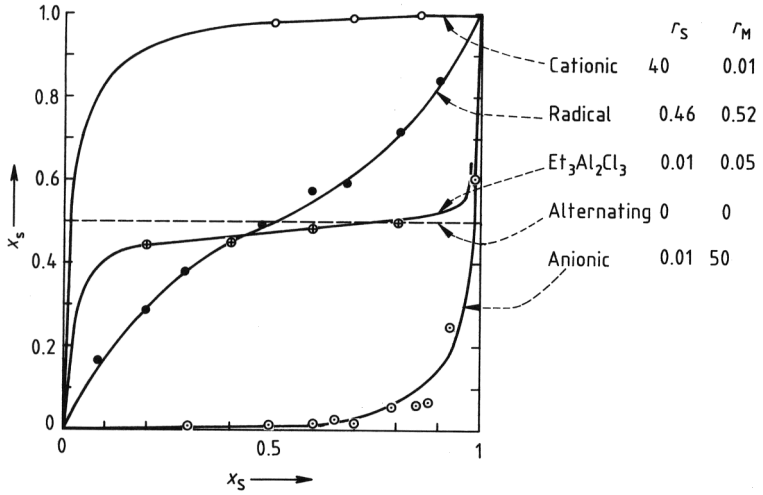


Figure 5. Instantaneous mole fraction x_s of styrene units in the polymer formed as a function of the instantaneous mole fraction x_s of styrene in the copolymerization of styrene with methyl methacrylate initiated by (○) cations; (●) free radicals; (⊕) $Et_3Al_2Cl_3$; (⊙) Anions
Solid lines: calculated with copolymerization parameters shown to the right; dotted line: theory for alternating copolymerizations.

copolymers, whereas cationic polymerization generates long styrene sequences and anionic polymerization produces long methyl methacrylate ones. The sequence length determines many polymer properties, most notably glass and melting temperatures.

Ionic copolymerizations very often lead to long block sequences, whereas free-radical copolymerizations tend in general to produce more random copolymers. Free-radical copolymerizations are thus the method of choice for industrial purposes if allowed by monomer structures (Table 6).

1.4. Polycondensations and Polyadditions [9]

1.4.1. Bifunctional Polycondensations

Polycondensations and polyadditions are generally divided into bifunctional reactions (two functional groups per reactant) and multifunctional ones (three or more functional groups per monomer molecule). Bifunctional reactions lead to linear macromolecules; multifunctional ones, to branched and finally cross-linked polymers. Bifunctional reactions are further subdivided into AB reactions (e.g., that of $H_2N-R-COOH$) and AA/BB reactions (e.g., $H_2N-R-NH_2$ + $HOOC-R'-COOH$).

All reactants, from monomer to high polymer, may react to form macromolecules in bifunctional polycondensations and polyadditions. Only monomers are present at the beginning of the reaction; later, oligomers are present. If the reactivity of the functional groups is independent of molecule size, then the greater number of smaller molecules leads first to low molar mass polymers and only at high conversions to chemical compounds with high molar masses (see Fig. 2). In equilibrium, the number-average degree of polymerization of polymers from AB and stoichiometric AA−BB reactions is dictated by the extent of functional group reaction p:

$$\overline{X}_n = 1/(1-p)$$

At 50% conversion ($p = 0.5$), the number-average degree of polymerization of reactants is only 2 (this includes monomer molecules), and the number-average degree of polymerization of polymers ($2 < X_i < \infty$) is only 3.

Table 6. Industrial copolymerizations

Monomers	Polymerization	Application
Free radical, linear (or slightly branched)		
Ethylene + 10% vinyl acetate	bulk	shrink films
Ethylene + 10–35% vinyl acetate	bulk	thermoplastics
Ethylene + 35–40% vinyl acetate	under precipitation[a]	films
Ethylene + > 60% vinyl acetate	emulsion	elastomers
Ethylene + < 10% methacrylic acid	bulk	extrusion coating
Ethylene + trifluorochloroethylene		thermoplastics
Butadiene + styrene	emulsion	multipurpose elastomers
Butadiene + 37% acrylonitrile	emulsion	oil-resistant elastomers
Vinyl chloride + 3–20% vinyl acetate	solution[b]	Paints
Vinyl chloride + 15% vinyl acetate	solution[b]	Hi-fi records
Vinyl chloride + 3–10% propene	bulk	thermoplastics
Acryl esters + 5–15% acrylonitrile		oil-resistant elastomers
Acrylonitrile + 4% different monomers	under precipitation[c]	fibers with improved dyeability
Acrylonitrile + styrene		thermoplastics
Acrylonitrile + butadiene + styrene		thermoplastics
Tetrafluoroethylene + propene	emulsion	thermoplastics
Methacrylic acid + methacrylonitrile		hard foams (after cyclization)
Free radical, cross-linking		
Glycol methacrylate + 2–4% glycol dimethacrylate		contact lenses
Unsaturated polyesters + styrene or methyl methacrylate	bulk	glass-fiber-reinforced thermosets
Anionic		
Styrene + butadiene	solution	elastomers
Cationic		
Isobutene + 2% isoprene	solution	butyl rubber
Trioxane + ethylene oxide	solution	thermoplastics
Ethylene oxide + propylene oxide	solution	thickener, detergents
Ziegler–Natta polymerization		
Propylene oxide + nonconjugated dienes	solution	elastomers
Ethylene + propene + nonconjugated dienes		elastomers

[a] In *tert*-butanol.
[b] In acetone, 1,4-dioxane or hexane.
[c] In water.

Industrial polycondensations rarely deliver number-average degrees of polymerization greater than 100–200 (i.e., $p = 0.99$–0.995 in equilibrium). The endgroups of these equilibrium polymers may condense further during processing by, e.g., extrusion or injection molding. The accompanying strong increase in viscosity is undesirable and these endgroups are therefore blocked against further polycondensation by "sealing" them with monofunctional reagents.

Equilibria are established not only by retroreactions (reversal of polycondensations and polyadditions) but also by catalyzed exchange reactions between chain segments. In these trans reactions, number-average molar masses remain constant, but mass-average molar masses increase if the initial ratio of mass to number-average molar mass was smaller than dictated by equilibrium conditions. An example is the transesterification of poly(ethylene terephthalate):

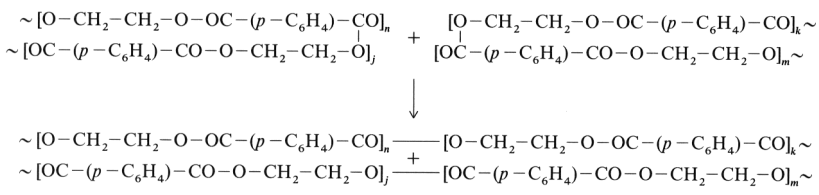


Table 7. Industrially important linear AA–BB polycondensations following Equation (15)

Polymer	Chemical structure				Remarks
	A	V	W	B	
Poly(ethylene terephthalate)	H	$O(CH_2)_iO$	CO–*p*-Ph–CO	OH	$i = 2$ (ethylene) or
	H	$O(CH_2)_iO$	CO–*p*-Ph–CO	OCH_3	4 (butene)
Unsaturated polyesters	H	$O(CH_2)_2O$	CO–CH=CH–CO	$O_{1/2}$	from maleic anhydride (isomerizes mainly to fumaric acid residues)
Polycarbonate	H	O–*p*-Ph–$C(CH_3)_2$–*p*-Ph–O	CO	OC_6H_5	
	Na	O–*p*-Ph–$C(CH_3)_2$–*p*-Ph–O	CO	Cl	
Polyarylates	Na	O–Ar–O	CO–Ar–CO	Cl	different Ar
Poly(phenylene sulfide)	Na	S	*p*-Ph	Cl	
Polysulfides	Na	S	R	Cl	different R
Polysulfones	K	O–*p*-Ph–O	SO_2–*p*-Ph–O–*p*-Ph–SO_2	Cl	different V and W units
Polyamides	H	$NH(CH_2)_iNH$	$CO(CH_2)_jCO$	OH	PA 66 ($i = 6$; $j = 4$) PA 610 ($i = 6$; $j = 8$) PA 46 ($i = 4$; $j = 4$)
Polyetheretherketone	K	O–*p*-Ph–CO–*p*-Ph–O	*p*-Ph–CO–*p*-Ph	F	

Ar = aromatic residue; *p*-Ph = *para*-substituted phenylene group; R = organic residue.

Higher degrees of polymerization at lower extents of reaction can be obtained by irreversible "activated reactions" and especially by heterogeneous reactions of fast reacting monomers. An example is the Schotten–Baumann reaction of diamines in water with diacid dichlorides in chloroform, for example. A polyamide film is formed at the interface of the two solutions. Functional groups of this polymer are buried in the interior of the film; they cannot react with each other. Exchange reactions and retroreactions are also absent. Only surface groups can react; the resulting irreversible reaction leads to high molar masses. Industrially, this reaction is utilized for one of the two industrial syntheses of polycarbonates, i.e., from the sodium salt of bisphenol A and phosgene (Table 7).

Most industrial polycondensations are of the AA–BB type (Table 7); they can be described by

$$n\,A-V-A + n\,B-W-B \rightarrow A-(V-W)_n-B + (2n-1)AB \quad (15)$$

where A– and B– are leaving groups, AB represents leaving molecules, –V– and –W– are monomeric units, and –V–W– are repeating units.

Industrial AB polycondensations are fairly rare. Examples are the formation of polyamide 11 (nylon 11) (Eq. 2), the polycondensation of carbodiimides

$$O=C=N-R-N=C=O \rightarrow R-N=C=N + CO_2$$

and the synthesis of certain polysulfones

$$C_6H_5O(p\text{–}C_6H_4)SO_2Cl \rightarrow$$
$$(p\text{–}C_6H_4)-O-(p-C_6H_4)-SO_2 + HCl$$

1.4.2. Multifunctional Polycondensations and Hyperbranched Polymers [23]

Multifunctional polycondensations are condensation reactions with the participation of monomers having higher functionality ($f_o > 2$). At low conversions, branched molecules are formed with increasingly higher number of functional end groups per molecule (i.e., increased functionality *f*):

$$f = 2(f_o - 1) + (X - 2)(f_o - 2) = 2 + X(f_o - 2)$$

Only one such group is, however, needed to link two molecules; the probability of such a linkage thus increases dramatically with increasing degree of polymerization X. At a certain degree of conversion of functional groups, molecules are linked throughout the volume of the reactor. The viscosity increases strongly, and the mass-average molar mass of the cross-linked polymer approaches infinity at this "gel point." Not all reactants are linked at the gel point; some are still soluble up to high conversions. The number-average degrees of polymerization of reactants are thus fairly low at the gel point, usually in the range $10<\overline{X}_n<50$.

Knowledge of the gel point is technically very important. Polymers cannot, or can only with difficulty, be processed beyond the gel point and must thus be shaped before or during the cross-linking reaction. The gel point can be calculated from the functionality and relative amounts of reactive groups if intramolecular cyclizations are assumed absent. In practice, such cyclizations are often present and cross-linking occurs at higher extents of reaction than calculated. The theoretical calculations thus provide a safety margin.

Chemical cross-linking reactions are utilized for thermosets, certain leathers, and the preparation of elastomers from rubber. Thermosetting polycondensation reactions allow the hardening of phenol, amino, and alkyd resins. In the reaction of phenol(s) with formaldehyde, methylene, formal, and ether bridges are formed between the *ortho* and *para* positions of the phenols; the hardening of novolacs with hexamethylenetetramine (urotropin) also leads to imine structures (→ Phenolic Resins). Amino plastics result from the reaction of urea or melamine with formaldehyde (→ Amino Resins), and alkyd resins from multifunctional alcohols with bifunctional organic acids or their anhydrides (→ Alkyd Resins).

Homopolymerization of AB_n monomers and copolymerization of AB with B_n monomers, respectively, affords hyperbranched polymers. Due to their low entanglement, hyperbranched polymers have reduced viscosity compared to linear polymer. Moreover, they have very high end-group functionality and can be tailored for applications in thermoset resin formulations and drug carriers. Amphiphilic hyperbranched polymers are effective dispersing agents for pigments and various other particles.

1.4.3. Polyaddition

No leaving molecules have to be removed during polyadditions, an important advantage for process engineering. Practically all industrially important polyadditions are thus performed with thermosetting resins. Polyurethanes are formed from diisocyanates (or triisocyanates) and polyols (see Eq. 3 for diols). Polyurethane formation may be so rapid that cross-linking and shaping can be performed in one step through reaction injection molding with short cycle times. Epoxides (epoxy resins) contain two or more epoxy groups per prepolymer molecule and are cured with either difunctional or multifunctional amines or with anhydrides of organic acids.

1.5. Polymer Reactions [24, 25]

1.5.1. Polymer Transformations

Several polymers are chemically transformed into industrially useful polymers by polymer-analogous reactions of their substituents (Table 8).

These reactions per group are chemically identical to their low molar mass analogues. They differ in the effect of side reactions, which do not lead to removable byproducts as in micromolecules but to "wrong" structures in the polymer chain. In most cases, such structures decrease the desired polymer properties. Polymer transformations that are prone to side reactions are thus generally avoided. This is one reason why only five types of polymer-analogous reactions are utilized commercially: Transesterification−saponification, chlorination
−sulfochlorination, etherification, hydrogenation, and cyclization.

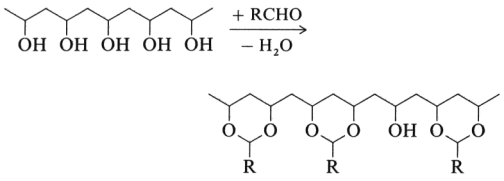
The reaction of poly(vinyl alcohol) with butyraldehyde leads to acetals. For statistical

Table 8. Industrial polymer transformations (for ring formations see text)

Base units in primary polymer	Reagent	Conversion, %	Base units in final polymer	Application
$CH_2CH(OOCCH_3)$	ROH	98	CH_2-CHOH	thickener
$CH_2CH_2CH_2CH(OOCCH_3)$	CH_3OH	99	CH_2-CHOH/CH_2-CH_2	engineering plastics
Cellulose$-NHCOCH_3$	H_2O	?	Cellulose NH_2	paper additive
Cellulose OH	CH_3COOH	83–100	Cellulose $OOCCH_3$	fibers, films
Cellulose OH	HNO_3	67–97	Cellulose$-ONO_2$	plastics, fibers
Cellulose ONa	oxirane	53–87	Cellulose$-OCH_2CHRCH_3$	thickener
Cellulose OH	oxirane	100–400[a]	Cellulose$-OCH_2CH(OR')CH_3$	thickener
CH_2-CH_2	Cl_2	25–40[b]	CH_2-CHCl	elastomer
		>40[b]	$CH_2-CHCl/CHCl-CHCl$	impact improver for PVC
CH_2-CHCl	Cl_2	64[b]	$CH_2-CHCl/CHCl-CHCl$	adhesives, paints
CH_2-CH_2	Cl_2/SO_2	<42[b]; <2[c]		coatings
$CH_2CH=CHCH_2/CH_2-CHCN$	H_2	?	$(CH_2)_4/CH_2-CHCN$	elastomer
$CH_2-CH(C_6H_5)$	SO_3	low	$CH_2-CH(C_6H_4SO_3H)$	ion exchangers
$N=PCl_2$	RONa	?	$N=P(OR)_2$	elastomer

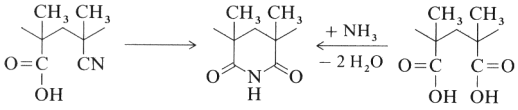
[a] Further reaction of primary reaction products may lead to more than one monomeric unit of reagent per hydroxyl group of cellulose.
[b] Chlorine content in %.
[c] Ether groups per glucose unit.

reasons, however, not all hydroxyl groups can be transformed:



The resulting poly(vinyl butyral) is used as an intermediate layer in safety glass and for wash primers.

Heating of methacrylic acid–methacrylonitrile copolymers with ammonia produces polymethacrylimide structures that are hard foams:



The thermal treatment and carbonization of polyacrylonitrile fibers represents the key to the industrial production of carbon fibers, which are highly attractive for reinforcement of thermosets and the formation of carbon-fiber reinforced polymers in lightweight engineering.

1.5.2. Block and Graft Formations [26]

Reactive chain ends can either initiate the polymerization of other monomers or couple with other preformed macromolecules to give block polymers:

$$A_n^* + mB \rightarrow A_nB_m^*$$

$$A_n^* + B_m^* \rightarrow A_nB_m$$

Both methods are used industrially with a variety of strategies for the synthesis of diblock polymers A_nB_m as compatibilizing agents for polymer blends, triblock polymers $A_nB_mA_n$ as thermoplastic elastomers, and various multiblock polymers for different purposes, especially for thermoplastic elastomers. Anionic living polymerizations are used for the syntheses of poly(styrene–block-butadiene–block-styrene) and poly(styrene–block-isoprene–block-styrene). Polycondensations serve for the preparation of multi[{poly(butylene terephthalate)}–block-poly{(polytetrahydrofuran)–terephthalate}], and various polyesteramide and polyetheramide segmented block polymers.

Graft copolymers result from the grafting of monomers on chemically different polymer chains. Grafts of isobutene–isoprene on polyethylenes, vinyl chloride on poly

(ethylene-stat-vinyl acetate), ethylene–propene on poly(vinyl chloride), or styrene–acrylonitrile on saturated acryl rubber also yield thermoplastic elastomers.

1.5.3. Cross-Linking Reactions

Cross-linking of preformed polymers is used for vulcanizing unsaturated rubbers with sulfur, vulcanizing saturated rubbers with peroxides, hardening unsaturated polyester chains with styrene or methyl methacrylate via copolymerization, or tanning collagen with certain reagents to leather.

1.5.4. Degradation Reactions

Degradation of polymers is undesirable for their application and often desirable for their disposal after use. The term degradation includes the decrease in degree of polymerization with preservation of the chemical structure of monomeric units (depolymerization), the unwanted chemical transformation of some monomeric units with preservation of the degree of polymerization (decomposition), and a combination of both. The terms degradation, depolymerization, and decomposition are sometimes used with the same meaning as in this article, but other times with broader or more restricted meanings; no accepted usage exists.

Depolymerizations involve chain scissions. They are retroreactions (i.e., the reverse of chain polymerizations, polyeliminations, polycondensations, or polyadditions). Chain scissions may be at random as in retropolycondensations and retropolyadditions or may be unzipping reactions as in retro-chain polymerizations and retropolyeliminations.

Unzipping can occur only with activated chains above their ceiling temperatures, that is, with living polymers, chain ends comprising certain functional groups, or radical ends generated by a prior chain scission. Unzipping at higher temperature results in gaseous monomers that lead to voids in molded parts. This can be prevented or reduced by shorter sequence lengths of the unzippable polymer blocks. This strategy is utilized, for example, in the formation of acetal copolymers by copolymerization of trioxane (gives unzippable oxymethylene sequences $\sim OCH_2\sim$) with ethylene oxide (oxyethylene sequences $\sim OCH_2CH_2\sim$ do not unzip).

Decomposition can be caused by heat, light, oxygen, water, or other environmental agents as well as mechanical forces such as extensional flow, ultrasound, or a combination of these. It may lead to undesirable changes of mechanical, electrical, or optical properties. Unstabilized poly(vinyl chloride) $\sim(CH_2CHCl)_n\sim$ discolors on decomposition because HCl is eliminated and colored polyene sequences $\sim(CH{=}CH)_i\sim$ are formed. The polymer ultimately becomes brittle.

Decomposition is the primary degradation process in the pyrolysis of polymers, which may be desirable (rocket fuels, waste disposal) or not (fires), and often produces toxic fumes or smoke at lower flame temperatures. The risk of pyrolysis is enhanced for polymers with branching points, electron-accepting groups, long methylene sequences, and all groups capable of forming five- or six-membered rings. Thermostability is enhanced by aromatic rings, ladder structures, fluorine as a substituent, and low hydrogen content. On heating above 400°C, polyolefins degrade to form small molar mass hydrocarbons, which are equivalent to those obtained from fossil resources. This route to "renewable oil" from polyolefin wastes is attractive with respect to recycling and sustainability.

2. Plastics Manufacture [27]

2.1. Homogenization and Compounding

Polymerization reactors do not deliver polymers that can be used directly as raw materials for plastics. Polymer melts must be filtered; melts, powders, beads, pellets, and granulates must be degassed; and all particulates must be dried or conditioned to environmental surroundings. Beads from suspension polymerization are washed and polymer solutions concentrated.

Batchwise polymerizations often lead to slightly different products, which are mixed

(blended) to guarantee customers polymer grades according to specifications (microhomogenization). Granulates and pellets are sometimes similarly blended by macrohomogenization.

Compounding is the mixing of polymers and additives. This process can be performed by adding single additives one at a time, by using additive systems, or by employing master batches. Additive systems are carefully adjusted mixtures of additives that are formulated to avoid mutually synergistic or antagonistic effects. Master batches are concentrates of additives in polymers; they facilitate the dosage of small amounts of additives.

The properties of compounds depend very much on the compounding process. Only heterogeneous compounds result when poly(vinyl chloride) is mixed with additives in regular mixers; these compounds cannot be processed directly to end-use products. High-performance mixers deliver free-flowing powders; these "dry blends" can be extruded and injection molded. Compounding is often carried out by specialized companies (compounders).

2.2. Additives [8, 28, 29] (→ Plastics, Additives)

2.2.1. Overview

Polymers are rarely used directly as materials. They do not fulfill per se all technological requirements and become commercially useful only after they have been mixed with certain additives. These additives average ca. 23% of the total mass of plastics but may range for individual plastics from 0.01% (packaging films for food) to 90% (barium ferrite-filled ethylene–vinyl acetate copolymers for magnetizable sealing strips). Polymer additives are to be distinguished from *polymer auxiliaries*; the former are added to polymers after the polymerization process, whereas the latter are used for the manufacture of polymers (e.g., polymerization catalysts, emulsifiers, initiators). The free-radical initiators used for the hardening of unsaturated polyesters are sometimes considered additives (added to the solution of unsaturated polyester molecules in monomers such as styrene) and sometimes auxiliaries (promoting the thermosetting reaction).

Additives are usually subdivided according to their application into process additives and functional additives. Process additives aid the processing of plastics by either stabilizing the chemical composition of polymers (processing stabilizers) or facilitating the processing itself (processing aids). Functional additives stabilize the chemical composition against attacks by environmental agents (stabilizing additives) or improve certain end-use properties (modifiers). Additives may also be classified according to their primary mode of action (chemical or physical). Some additives act in more than one way: A filler or colorant may also be a nucleating agent for crystallization; a pigment may enhance discoloration, etc.

2.2.2. Chemofunctional Additives

Polymers can be attacked by oxygen and ozone during processing and use. The attack generates radicals that cause chain reactions to produce even more radicals. Ultimately, changed chemical compositions, degradation, or cross-linking occur. Oxidation is reduced if the accessibility of the oxidizable groups is limited or if radical formation is prevented. Oxygen diffusion into the polymer is slowed by certain coatings that act as mechanical barriers or by additives that diffuse into surface layers and are preferentially oxidized there.

Antioxidants (→ Antioxidants) prevent radical formation, at least during processing and for the targeted lifetime of the plastic. They are subdivided into deinitiators and chain terminators.

Deinitiators prevent the formation of radicals (i.e., preventive antioxidants) and are always used in combination with chain terminators (also called secondary antioxidants). They are further subdivided into peroxide deactivators, metal deactivators, and UV absorbers. Peroxide deactivators (tertiary amines, tertiary phosphines, sulfides) convert hydroperoxides into harmless compounds before they can form radicals. Metal deactivators are chelating agents that

form inactive complexes with catalytically active metal species (mainly from Ziegler–Natta polymerizations).

Chain terminators, such as hindered phenols, amines, and anellated hydrocarbons, react with already formed radicals and terminate the kinetic chain (chain-breaking or primary antioxidants). A combination of deinitiators and chain terminators often leads to synergistic effects. Antagonistic effects are also known (e.g., with carbon black as filler).

Light-induced degradation reactions can be prevented by the reduction of light absorption or by the addition of *UV absorbers* and quenchers. Less light is absorbed by the plastic if the surfaces are reflective or if certain pigments are added (e.g., carbon black). Ultraviolet absorbers either convert the incident light into harmless infrared radiation or are transformed into other chemical compounds. Quenchers deactivate excited states and become excited themselves.

Heat stabilizers prevent chemical transformations of plastics at higher temperature; their main application is for the stabilization of poly(vinyl chloride) against HCl elimination during processing. PVC additives include HCl scavangers, such as metal stearates, metal oxides, and epoxidized soybean oil. PVC additives, such as dibutyltin dithiolate react with thermally labile allylic chloride and double bonds in the PVC backbone.

Flame retardants either prevent oxygen access to burning plastics by formation of nonburning gases or by "poisoning" radicals generated by the burning. Some plastics are self-extinguishing because either CO_2 (polycarbonates) or water vapor and a protecting carbon layer are formed (vulcanized fiber: a $ZnCl_2$-treated cellulose) during burning. Chlorine and bromine compounds generate radicals during burning; these radicals combine with radicals from the degradation of plastics and stop the kinetic chain. Phosphorus compounds are oxidized during the burning to nonvolatile phosphor oxides, which either form a protective layer or are converted by water into phosphorus acids that catalyze the elimination of water. Intumescent additives, such as ammonium polyphosphate, form a carbon form that serves as a thermal insulator.

The flammability of plastics is often characterized by the limiting oxygen index (LOI). The LOI value indicates the limiting value of the volume fraction of oxygen in an oxygen–nitrogen mixture that just allows the polymer to burn after ignition with a flame. Materials with LOI > 0.225 are called flame retardant; those with LOI > 0.27, self-extinguishing. Low LOI values (high flammabilities) are exhibited by polyoxymethylenes (0.14), polyolefins (0.17–0.18), saturated polyesters (0.20), and cellulose (0.20). High LOI values are exhibited by poly(vinyl chloride) (0.32), polybenzimidazole (0.48), and polytetrafluoroethylene (0.95). However, LOI values are not absolute measures of the flammability or combustibility of plastics because these properties also depend on flame temperatures, heat capacities, heat conductivities, melting temperatures, and melt viscosities. The hazard of burning plastics is also determined by smoke formation and the toxicity of the evolving gases. In view of growing environmental and health concerns, halogenated flame retardants are gradually substituted by halogen-free flame retardants, such as $Al(OH)_3$ hydrate, $Mg(OH)_2$, and ammonium polyphosphate.

2.2.3. Processing Aids

Processing aids facilitate the processing of plastics by enhancing either transport rates to the processing machines, flow behavior in these machines, achievement of final properties during processing, or removal of shaped articles from the machines or from each other.

Easy-flow grades of powdered polystyrenes, for example, often contain 3–4% mineral oil, which forms a low-viscosity film on the surface of the particles and thus reduces friction in polar polymers; amphiphilic compounds such as metal stearates or fatty acid amides are used for this purpose. Such *external lubricants* also reduce the friction between polymer particles and the walls of the processing machine and the friction of polymer melts at such walls; they also prevent the cleavage of particles to smaller flow units. External lubricants are always incompatible with polymers and are thus found predominantly at polymer surfaces. They are

related to *release agents*, which facilitate the separation of shaped articles from the tools (molds), and *slip agents*, which prevent the sticking together of shaped articles. Slip agents are thus sometimes also called lubricants.

Internal lubricants improve the flow behavior and homogeneity of polymer melts; they also reduce the Barus effect and the melt fracture. Internal lubricants probably act by desegregating larger units (aggregates), which were probably formed during polymerization and are still present shortly after the melting of the polymer to a macroscopically homogeneous material. Typical internal lubricants are amphipolar compounds, e.g., modified esters of long-chain fatty acids.

Nucleating agents promote the crystallization of crystallizable polymers by generating many nuclei for crystallites. They prevent the formation of larger spherulites and thus improve the mechanical properties of plastics.

2.2.4. Extending and Functional Fillers [30–32]

Fillers are solid inorganic or organic materials. Some fillers are added mainly to improve the economics of expensive polymers; they are *extenders*. Extenders are usually particulate materials of corpuscular nature, such as chalk and glass spheres (aspect ratio ca. 1). Functional fillers improve certain properties, such as stiffness, strength, scratch resistance, electrical conductivity, crystallization rate, etc. Reinforcing fillers possess aspect ratios higher than 1; they may be short fibers, platelets (e.g., kaolin, talc, mica) (→ Reinforced Plastics), or long fibers (continuous filaments). Active fillers are sometimes subdivided into property enhancers (aspect ratio < 100) and true reinforcing fillers (aspect ratio > 100). No sharp dividing line exists between fillers and reinforcing agents, nor can the term "reinforcement" be unambiguously defined (e.g., it may denote an increase in breaking or impact strength or a decrease of brittleness).

A variety of fillers are used for plastics (-Table 9). Glass-fiber-reinforced polymers often carry the abbreviation GRP (or FRP); those reinforced by carbon fibers, CRP. Syntactic plastics are polymers reinforced with hollow glass spheres. The amounts of fillers added vary widely: In general, industry standards are about 30 wt % for thermoplastics and 60 wt % for thermosets. Fillers act very differently in polymers. Some fillers form chemical bonds with polymers; an example is carbon black, which acts as a chemical cross-linker in elastomers. Other fillers can adsorb polymers on their surfaces, i.e., physical bonds are

Table 9. Fillers for thermoplastics (T), thermosets (D), and elastomers (E). For definition of other acronyms see Tables [1–4]

Filler	Application in	Concentration in %	Improved property
Inorganic fillers			
Chalk	PE, PVC, PPS, PB, UP	< 33 in PVC	price, gloss
Potassium titanate	PA	40	dimensional stability
Heavy spar	PVC, PUR	< 25	density
Talc	PUR, UP, PVC, EP, PE, PS, PP		white pigment, impact strength, plasticizer uptake
Mica	PUR, UP	< 25	dimensional stability, stiffness, hardness
Kaolin	UP, vinyls	< 60	demolding
Glass spheres	T, D	< 40	modulus of elasticity, shrinkage, compressive strength, surface properties
Glass fibers	T, D	< 40	fracture strength, impact strength
Fumed silica	T, D	< 3	tear strength, viscosity (increase)
Quartz	PE, PMMA, EP	< 45	heat stability, fracture
Sand	EP, UP, PF	< 60	shrinkage (decrease)
Al, Zn, Cu, Ni, etc.	PA, POM, PP	< 100	conductivity (heat and electricity)
MgO	UP	< 70	stiffness, hardness
ZnO	PP, PUR, UP, EP	< 70	UV stability, heat conductivity
Organic fillers			
Carbon black	PVC, HDPE, PUR, PI, PE, E	< 60	UV stability, pigmentation, cross-linking
Graphite	EP, MF, PB, PI, PPS, UP, PMMA, PTFE	< 50	stiffness, creep
Wood flour	PF, MF, UF, UP	< 5	shrinkage (decrease), impact strength
Starch	PVAL, PE	< 7	biological degradation

introduced between fillers and polymers. On impact, adsorbed chain segments may take up energy and slip from the surface, which increases impact strength. Still other fillers act as nucleating agents in crystallizable polymers. Fillers furthermore constitute impenetrable walls to polymer coils. They restrict the number of conformational positions of chain segments near the filler surface; chains become less flexible, and tensile strengths and moduli of elasticity increase.

Due to the significant progress made in nanotechnology, a large variety of nanofillers have emerged since the mid-1990s. As compared to conventional filled polymers that contain micron-sized filler particles nanocomposites have nine orders of magnitude larger number of nanometer-scaled particles at the same volume fraction (Fig. 6). As a consequence, most polymers are allocated in nanocomposites at the nanofiller interface. Converting bulk polymers into interfacial polymers account for novel property profiles. The high surface area lowers considerably the percolation threshold required for particle network formation. This improves the electrical conductivity at much lower filler content. However, in view of the nanoparticle interactions, dispersion of nanoparticles is more difficult than micron-sized particles. Therefore, special processing technology and nanofiller surface modification are required. As illustrated in Figure 7, the nanofiller family includes inorganic nanoparticles as well as organic–inorganic hybrid particles, among them dispersions of metal oxides and silicate nanoparticles with shapes varying from spheres to platelets and sheets. The smallest silica nanoparticles are polyhedral oligomeric silsesquioxanes (POSS), which are readily functionalized. The exfoliation of graphite affords graphene that consists of a honeycomb-like planar arrangement of sp^2 hybridized carbon atoms equivalent to a single layer of the graphite lattice. Other carbon allotropes, such as nanometer-scaled carbon particles ("conducting carbon black"), fullerenes, nano diamonds, and single- and multi-walled carbon nanotubes (CNT) are employed as nanofillers. Nanometer-sized carbon particles and especially carbon macromolecules render polymer nanocomposites electrically conductive without sacrificing optical clarity. Organophilic layered silicates ("organoclay") are obtained by cation exchange of the intergallery sodium cations of bentonite for alkyl ammonium. Alternatively, layered silicates with cationic layers, such as hydrotalcites are rendered organophilic by modification with long chain aliphatic carboxylates. As a function of the layered silicate modification and polymer processing conditions, either individual silicate layers are dispersed within the polymer matrix or the polymer is intercalated between silicates layers. The dispersion of sheetlike nanoparticles improves the barrier resistance of polymers. Going beyond wood flour, bio-based nanofillers (cellulose whiskers, nanocellulose) are derived from cellulose by etching of the amorphous regions.

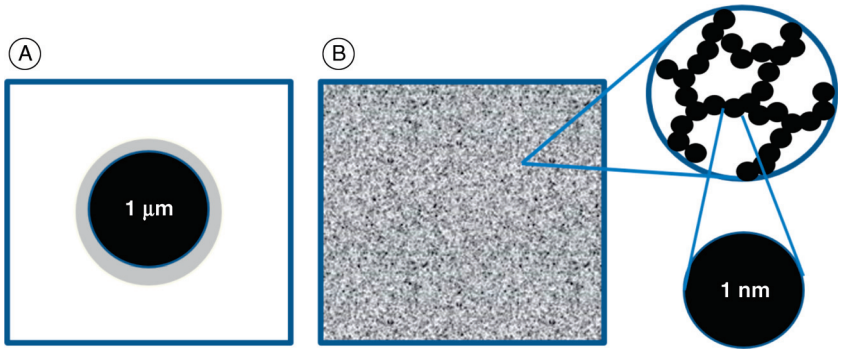


Figure 6. Different sized polymer composites containing the same volume fraction
A) One particle (1 μm) microfiller-sized fillers; B) 10^9 particles (1 nm) nanofiller with the same volume fraction like microfiller

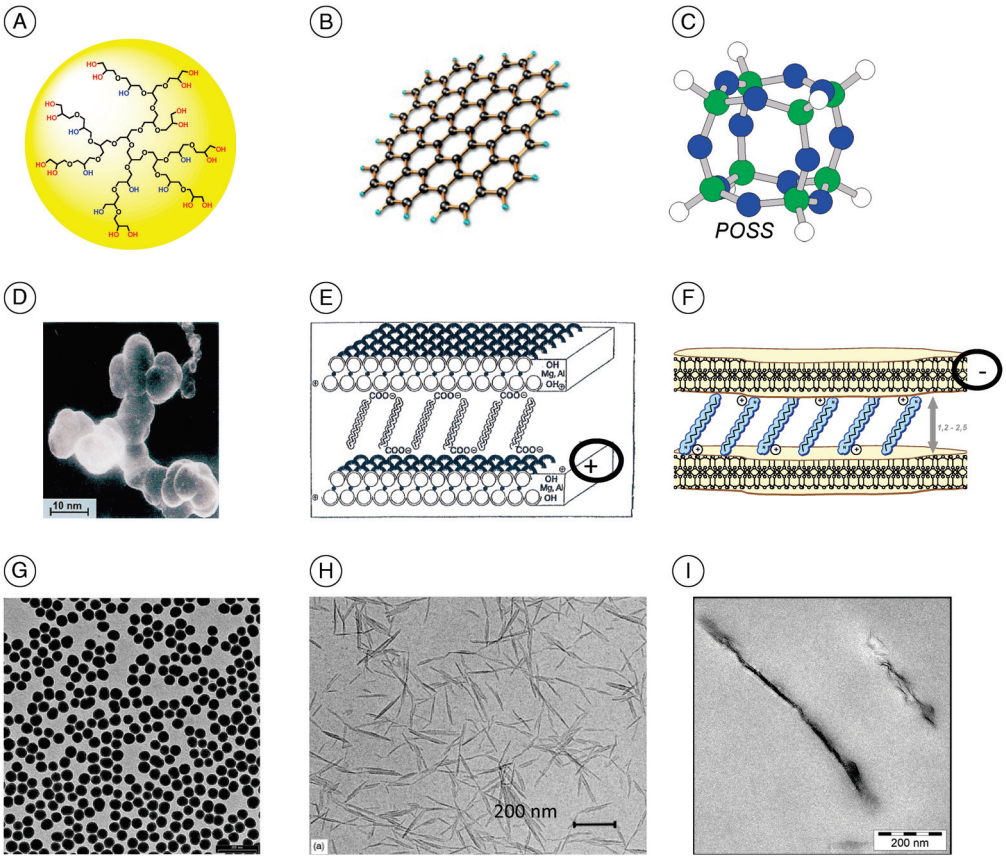


Figure 7. Different types of nanofillers
A) Nanomolecules; B) Molecular carbon; C) Molecular silica (POSS); D) Pyrogenic silica nanoparticles; E) Hydrotalcite; F) Organoclay; G) SiO_2 dispersion; H) Cellulose nanowhiskers; I) Graphene embedded in polypropylene

2.2.5. Plasticizers (→ Plasticizers) [33]

Plasticizers are added to polymers to improve their flexibility, processibility, or foamability. About 500 different types of plasticizers are marketed. They are generally low molar mass liquids; polymer plasticizers are used in much smaller amounts. Of all plasticizers for thermoplastics, 80–85% are used for poly(vinyl chloride); the most important plasticizers are di-2-ethylhexyl phthalate ("dioctyl phthalate," DOP) and dinonyl phthalate. The main plasticizer for elastomers is mineral oil; tires contain up to 40%. Polymer plasticizers are mainly aliphatic polyesters and polyethers. The former are prepared by polycondensation; they thus possess fairly broad molar mass distributions and also contain monomeric and oligomeric molecules. Because their number-average molar mass is low (ca. 4 000 g/mol), they are called oligomer plasticizers. Plasticization can also be achieved by copolymerization of the parent monomer with certain other monomers; this effect is called internal plasticization, in analogy to external plasticization by added high and low molar mass plasticizers.

External plasticizers are subdivided into primary and secondary ones. Primary plasticizers interact directly with chains by way of solvation. Secondary plasticizers are merely extenders; they can be used only in combination with a primary plasticizer. A certain plasticizer may thus be a primary or a secondary one, depending on the chemical constitution of the polymer. Mineral oils are, for example, primary plasticizers for polydienes but extenders for poly(vinyl chloride).

2.2.6. Colorants

Colorants are subdivided into dyes (soluble in polymer matrix) and pigments (insoluble). Textile fibers are dyed mainly with dyes. Pigments are preferred for plastics because they have a higher light-fastness and are more stable against migration than dyes. Colorants for plastics are dominated by titanium dioxide (60–65%) and carbon black (20%); only 2% are dyes.

Pigment particles generally possess diameters of 0.3–0.8 μm, which allows the pigmentation of films and fibers of > 20 μm thickness. Very thin films and fibers are colored exclusively by organic pigments because these can be ground to much smaller diameters than inorganic ones. The hiding power of pigments increases with increasing difference between refractive indices of pigment and polymer.

Pigments need not have a special affinity for polymers. They must be wettable by the polymer melt, however, which can be achieved by treating them with surfactants. The aggregation of pigments is mainly the result of air inclusions; it can be removed by the application of vacuum. Pigments can be metered into plastics via master batches (in plastics), color concentrates (in plasticizers), or electric charging of the surface of polymer particles in granulate mixers. Up to 1 wt % of pigment can be mixed in by the last method.

2.2.7. Blowing Agents

Foamed plastics (plastic foams, cellular plastics, expanded plastics) are blends of polymers with gases (→ Foamed Plastics). They may be rigid (glass transition or melting temperature higher than use temperature) or flexible; their cell structure can be open or closed. The gases may be air, nitrogen, carbon dioxide, fluorinated hydrocarbons, etc.

Plastic foams can be produced by mechanical means (whipping, stirring), physical methods (shock volatilization of liquids, washing-out of solids), or chemical foaming either by internal foaming during the polymerization or by external foaming with chemical blowing agents. Chemical blowing agents are chemical compounds that decompose at elevated temperature with release of gases. The most widely used agent for natural rubber is *N,N′*-azobisisobutyronitrile $(CH_3)_2C(CN)-N=N-C(CN)(CH_3)_2$ (AIBN); for plasticized PVC, *N,N′*-dinitroso dimethyl terephthalamide $CH_3-N(NO)-CO-(p\text{-}C_6H_4)-CO-N(NO)-CH_3$ (NTA); and for other plastics, 1,1′-azobisformamide $H_2N-CO-N=N-CO-NH_2$ (ABFA). Blowing agents are used in amounts of ca. 0.1% to eliminate sinks in injection molding; 0.2–0.8% for injection-molded structural foams; 0.3% for extended profiles; 1–15% for vinyl plastisol foaming; and 5–15% for compression-molded foam products. Because of the depletion of the ozone layer, some fluorine-containing blowing agents were banned.

2.3. Processing [34–37]

There are many different types of processes to convert monomers, prepolymers, or polymers into plastics. In general, four procedures can be distinguished for processing raw materials into shaped plastics:

1. From monomers to polymers by direct polymerization with simultaneous shaping
2. From monomers by oligomerization to prepolymers, followed by simultaneous polymerization and shaping
3. From monomers by polymerization to polymers, followed by separate shaping
4. From monomers by polymerization to polymers, shaping to semifinished product, and finally to the end product

In all four cases, end products must sometimes be after-treated (degated, polished, etc.).

Procedure 1 has only one process step and should be the most economical. It is widely used for wire coatings and casting. However, technological problems are often encountered for shaped articles because the process involves the conversion of a low-viscosity liquid into a high-viscosity body. Because very high polymerization rates are required for this process to achieve high cycle times (phase sequences) in molding (i.e., number of articles produced per unit time), very few monomers, types of polymerization, and shaping methods are suitable. The method is utilized industrially

in the RIM (reaction injection molding) process, mainly for the polyaddition of diisocyanates with polyols. The anionic polymerization of lactams and the Diels–Alder polymerization of dicyclopentadienes and related compounds are also suitable for RIM. In resin transfer molding (RTM), thermoset resins and curing agents are mixed together, injected, and cured in the mold.

Procedure 2 is typical for thermosets. Oligomerizations are conducted to conversions shortly before the gel point. Additives are added, and the final processing step consists of a simultaneous cross-linking polymerization and shaping. Typical processing methods include molding, compression molding, cavity compression molding (hot pressing), injection–compression molding, and resin transfer molding.

Procedure 3 is generally chosen for thermoplastics. Polymers from the polymerization process are isolated before shaping and stored (e.g., as granulate) for a shorter or longer period of time. The stored polymers must be dried before further processing; otherwise, steam produced at higher processing temperatures may lead to voids and cavities in shaped articles. After compounding, the plastic raw material must be weighed out accurately for each cycle in discontinuous processing procedures. The filling factor (= raw material density/bulk density) must be known.

The choice of a processing technique is influenced technically by the rheological properties of the material and the form or shape of the desired article. The cost of processing machines and the cycle time are economically important. Commodity articles are produced by casting, centrifugal casting, hot pressing, compression molding, coating, spraying, roll milling, extrusion, injection molding, blow molding, cold forming, press forming, calendering, stretch forming, blowing, extrusion blowing, sintering, fluidized-bed sintering, flame spraying, or hot blast sprinkling, and specialty articles by molding.

Procedure 4 is the method of choice for difficult-to-manufacture articles. Procedures, such as welding, stamping, cutting, forging, sawing, boring, turning, milling (in the metalworking sense), sintering, and baking are employed for both thermoplastics and thermosets. The surfaces of plastics are sometimes treated further for technical (surface hardness, friction) or aesthetic reasons (gloss, color) by polishing, painting, metallizing, coating, etc.

Whereas conventional processing requires molds or machining, in additive processing, also referred to as additives processing and solid freeform fabrication, complex 3D objects are built by computer-assisted layer-by-layer assembly. Typically, 3D scanner or computer-assisted design are used to create virtual 3D objects, which are sliced and used to construct the real 3D objects layer by layer. Originally designed to serve the special needs of model making, tooling, and rapid prototyping, this mold-free fabrication is emerging as highly versatile processing technology for rapid manufacturing and digital 3D printing. Typical 3D printing technologies include stereolithography with laser-induced photopolymerization of acrylic monomers, selective laser sintering of metal, ceramic and polymer powders, fused deposition molding using 3D extrusion of thermoplastic filaments, and 3D printing by ink-jet printing of binders to bind together powder layers.

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Plastics, General Survey, 3. Supermolecular Structures

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ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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1. Supermolecular Structures (→ Plastics, Properties and Testing) [1–3]

Polymer properties are influenced not only by the chemical structure (constitution, molar mass, configuration, microconformation) but also by the physical structure of polymers. These structures may range from totally irregular arrangements of chain segments over shorter or longer parallelizations of chains, to voids and other defects in otherwise highly organized assemblies of polymer molecules. Two possible ideal structures exist in the solid state: Perfect crystals and totally amorphous polymers. Polymer molecules are perfectly ordered in ideal crystals. They convert at the thermodynamic melting temperature into melts, which ideally are totally disordered. Amorphous polymers can be viewed as frozen-in polymer melts. They are polymer glasses that convert to melts at the glass transition temperature.

1.1. Noncrystalline States

1.1.1. Structure

Isolated polymer coils possess approximately a Gaussian distribution of chain segments; their segment density decreases with increasing chain length. However, the macroscopic densities of polymer melts do not change with chain lengths if end group effects on small molar mass molecules are neglected. Coils must therefore overlap considerably in polymer melts. At the glass transition temperature, cooperative segmental movements freeze in, and the physical structure of the melt is conserved. Small-angle neutron scattering studies have shown that the radii of gyration of amorphous polymers are indeed essentially identical for their melts, glasses, and solutions in theta solvents.

The absence of long-range order in melts and amorphous polymers does not exclude the presence of short-range order in these states.

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Because of the persistence of polymer chains, a parallelization of short segments seems probable, as is found, for example, for alkanes according to X-ray investigation. This local order does not exceed 1 nm in each direction.

The packing of chain segments cannot be perfect. Amorphous polymers thus possess "free volumes", which are regions of approximately atomic diameters. The volume fraction of this free volume is ca. 2.5% at the glass transition temperature and is independent of polymer constitution. Polymer segments in melts can move more freely than in the glassy state; the densities of melts are thus higher than the densities of glasses at the same temperature.

1.1.2. Orientation

Polymer segments, polymer molecules, and crystalline domains may be oriented along the machine direction by drawing or other mechanical processes. The orientation of chain segments need not necessarily lead to crystallization, however. An example is injection-molded polystyrene, which shows optical birefringence due to the orientation of segments but no X-ray crystallinity.

The degree of orientation of segments or crystallites can be measured by wide-angle X-ray or small-angle light scattering, infrared dichroism, optical birefringence, polarized fluorescence, and ultrasound velocity. The orientation is usually characterized for each of the three directions *a*, *b*, and *c* by a *Hermans orientation factor* f_i, where β is the angle between the draw direction and the principal axis of the segments:

$$f_i = (1/2)(3\cos^2\beta - 1)$$

The orientation factor becomes 1 for a complete orientation of that axis in the draw direction ($\beta = 0°$), −1/2 for a complete orientation perpendicular to the draw direction ($\beta = 90°$), and 0 for a random orientation.

Since methods to determine orientation factors are often expensive, time consuming, or difficult to perform, the easy-to-calculate *draw ratio* (length after drawing/length before drawing) is often used to characterize orientation. The draw ratio is, however, not a good measure of the degree of orientation because it depends on the history of the specimen. Drawing may also lead to viscous flow of the polymer without any orientation of segments and crystallites.

1.2. Polymer Crystals [4, 5]

1.2.1. Introduction

Spheres and other geometrically simple entities can be arranged in crystal lattices irrespective of whether they are atoms, small molecules, large molecules such as enzyme, or latex particles. The centers of gravity of these entities occupy lattice sites that are regularly spaced in three dimensions. Lattices are called *superlattices* if the distances between lattice points significantly exceed atomic dimensions. The existence of three-dimensional order on the atomic level is called crystallinity.

Chain molecules can also be arranged in crystal lattices. The whole chain may be completely parallel to other chains as in the case of truly extended chain crystals; the microconformation of the chain can be all *trans* or helical (Fig. 1), and the chains may have a directional sense as in polyamide 6 or an inversion center as in polyamide 66 (Fig. 2). In other cases, only sections of the chains may be parallel to each other, either sections of a single chain as in folded chain crystals or those of neighboring chains as in fringed micelles. These ordered segments form crystalline regions in otherwise less ordered (though not necessarily completely disordered) polymers.

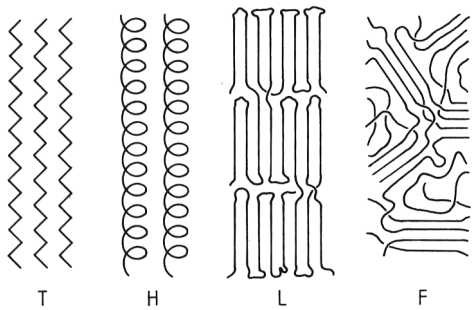
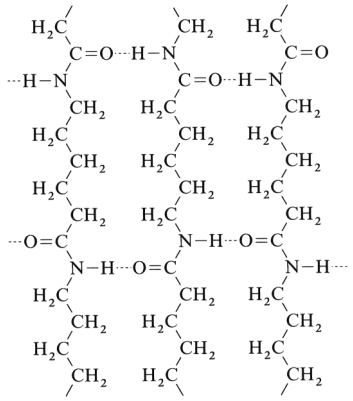
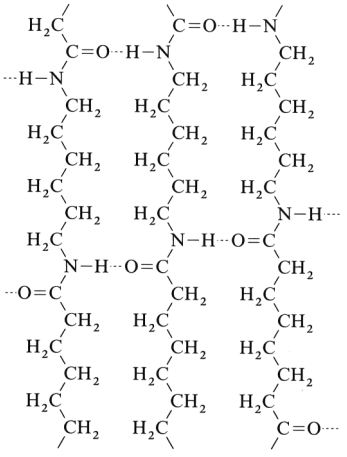


Figure 1. Schematic representation of crystalline polymers as extended chain crystals with chains in all-*trans* (T) or helical conformation (H), (L) lamellae of chains interconnected by tie molecules, and (F) fringed micelles. No bond angles are shown for H, L, and F.



PA 6



PA 66

Figure 2. Pleated-sheet structures of polyamides PA 6 (anticlinal) and PA 66 (isoclinal)

Crystalline regions may be assembled into greater entities, which themselves may be more or less ordered. The types and degrees of order−disorder depend on external conditions such as temperature, pressure, cooling and heating rates, and presence of solvents. A variety of morphologies may thus exist for any crystallizable polymer [6], for example, spherical, platelet-like, fibrillar, and sheaflike structures of a polyamide 6 (Fig. 3).

1.2.2. Crystal Structures

The unit cell describes the smallest, regularly repeating structure of a parallelepiped that generates a crystal by parallel displacements in three directions. The parallelepipeds are characterized by three lattice constants (distances between lattice points in three directions) and three lattice angles (Table 1).

Lattice constants reflect the microconformations of chains in crystal lattices. The *c*-direction is normally assigned to the chain direction; a value of $c = 0.254$ nm thus gives the distance between repeating units $-CH_2-CH_2-$ in all-*trans* conformation (bond distance 0.154 nm, bond angle 112°). The *c*-values in carbon chains that are non-multiples of 0.254 indicate the presence of non-all-*trans* conformations (e.g., helical structures in it-polypropylene and it-polybutene-1). The *a* and *b* values reflect physical bonds (such as van der Waals or hydrogen bonds) that are longer than the chemical bonds in the *c*-direction. The anisotropy of bond lengths in the three spatial directions prevents the existence of cubic lattices for chain molecules. The other six lattice types are however found [hexagonal, tetragonal, trigonal, (ortho) rhombic, monoclinic, triclinic].

Most polymers form polymorphs (i.e., polymers of the same constitution and configuration can possess various energetically different crystal modifications). *Polymorphism* may be caused by different microconformations of polymer chains (e.g., polybutene-1) or by different packing of chains with identical chain conformations (e.g., it-polypropylene). Such differences can be generated by small changes in processing conditions (e.g., different crystallization temperatures) or by stretching.

Copolymers can furthermore show *isomorphism* if different monomeric units can replace each other without change of lattice structure. Isomorphism of chains is also possible if the two corresponding homopolymers have analogous crystal modifications, similar lattice constants, and the same helix types. An example is a mixture of the γ-modification of it-polypropylene and the modification I of it-polybutene-1 (Table 1). This phenomenon is sometimes also called allomerism. One company calls its crystalline copolymers from two or more olefinic monomers *polyallomers*, because the monomeric units are isomorphic.

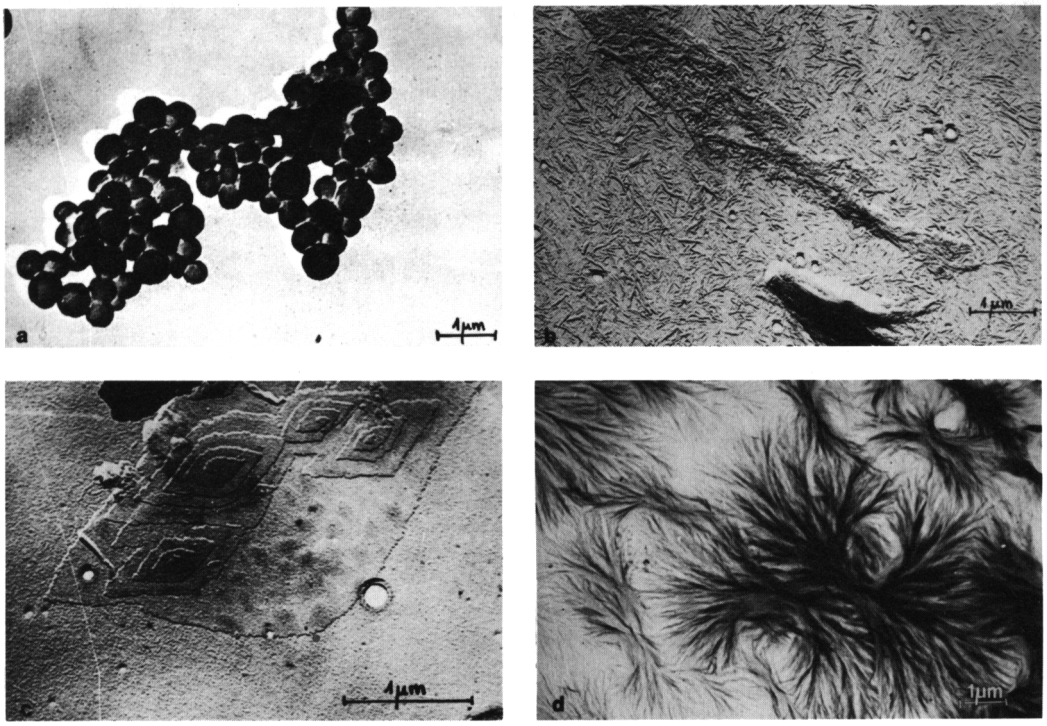


Figure 3. Electron micrographs of different morphologies of a polyamide 6
a) From a 260°C solution in glycerol quenched into 20°C glycerol; b) Same solution fast cooled (40 K/min); c) Same solution slowly cooled (1–2 K/min); d) Slow evaporation of formic acid solution at room temperature [7]

1.2.3. Crystallinity

Perfect crystal lattices should give sharp X-ray reflections and sharp melting points. Polymers do not exhibit these features, even if they show a crystallike appearance in electron micrographs. In addition, X-ray patterns of polymers frequently exhibit continuous, diffuse scattering. These findings can be interpreted by either a one-phase model (voids in crystals) or a two-phase model (coexistence of completely crystalline and completely amorphous regions).

Table 1. Crystal structure of some polymers

Polymer				Lattice constants			Angles of unit cell			Helix type	Crystal system
			N_u	nm[a]	nm[b]	nm[c]	α°	β°	γ°		
PE		I[b]	2	0.742	0.495	0.254	90	90	90	2_1	R
		II[a b]	2	0.809	0.479	0.253	90	90	107.9	2_1	M
PP	st	8	1.450	0.560	0.74	90	90	90	2_1	R	
	it	α[b]	12	0.665	2.09	0.495	90	99.6	90	3_1	M
	it	β[b]	3	0.638	0.638	0.633	90	90	120	3_1	VI
	it	γ[b]	12	0.647	2.140	6.50	89	100	99	3_1	T
PB	it	I[b]	18	1.769	1.769	0.650	90	90	90	3_1	VI
		II[b]	44	1.485	1.485	2.060	90	90	90	11_3	IV
		III[b]	8	1.238	0.892	0.745	90	90	90	4_1	R

[a] N_u = Number of monomeric units per unit cell.
[b] Crystal modification.
[c] R = (ortho)rhombic; M = monoclinic; VI = hexagonal; T = triclinic; IV = tetragonal.

Crystallinity is defined as the presence of three-dimensional order on the level of atomic dimensions.

In reality, segments are ordered to various degrees. Because most experimental methods are sensitive to different types and degrees of order, various "degrees of crystallinities" are found depending on the experiment. The degree of crystallinity is the fractional amount of crystallinity. Stretched poly(ethylene terephthalate) has, for example, a degree of crystallinity of 59% by IR spectroscopy, 20% by density determination, and 2% by X-ray diffraction.

1.2.4. Morphology

Earlier experimental findings were interpreted in terms of the two-phase model of partially crystalline polymers: The coexistence of crystalline reflexes and amorphous halos in X-ray diagrams, the independence of X-ray short periodicities on molar masses, the disappearance of X-ray long periodicities with increasing molar masses, lower macroscopic densities than predicted by X-ray densities of unit cells, broad melting ranges, optical birefringence of oriented polymers, and heterogeneity of partially crystalline polymers against chemical reactions.

In 1957, however, three different groups found that rhombic platelets are obtained if very dilute solutions of polyethylene are cooled. Similar platelets of 5–20 nm thickness are now known from many other crystallizable polymers (e.g., see Fig. 3). Electron diffraction showed sharp reflections typical of single crystals and chain directions perpendicular to the surface of the platelets. Since the contour lengths of the chains are greater than the thicknesses of the platelets, chains must be folded back as shown in Figure 1, L.

Crystallization from polyethylene melts similarly shows stacked single crystals. These lamellae are 75–80% X-ray crystalline. After oxidation of the surface, a 100% crystalline material remains. The folds or the interface between lamellae must thus be "amorphous." Various models have been suggested for the surface layers: Loose folds with adjacent reentry of the chains, a switchboard-like structure, adsorbed chains not involved in chain folding, loose or entangled cilia (tangling chain ends), and crystal bridges composed of tie molecules (Fig. 4). Electron microscopy has shown that crystal bridges exist in crystallized mixtures of high and low molar mass polyethylenes. Such interlamellar connections are responsible for some remarkable properties of partially crystalline polymers (see below). Highly crystalline polymers result if tie molecules and surface layers are removed (e.g., by grinding); these fairly low molar mass materials are called microcrystalline polymers.

Crystallization of melts sometimes delivers spherical, polycrystalline entities (Fig. 5). These spherulites exhibit radial symmetry. They consist of lamellae with tangential chain axes (Fig. 6A); radial chain axes seem to be unknown (Fig. 6B). The formation of spherulites can be controlled by the crystallization temperature, the cooling rate, and the addition of nucleating agents.

Spherulites lead to opaque plastics if their diameters are greater than one-half the wavelength of incident light and their densities and refractive indices are different for crystalline and noncrystalline regions. The numbers and sizes of such spherulites are important for the fracture behavior of polymers.

Spherulites develop in a viscous environment if crystallization nuclei are present and if equal crystallization rates prevail in all three directions. Different crystallization rates exist in strongly stirred dilute solutions. Polymer chains then try to orient themselves along the flow gradients and crystallize in an extended (nonfolded) conformation. The resulting fibrils are organized in bundles with chains parallel to the fibril axes. These bundles act as nuclei–substrate for the epitaxial growth of the remaining chains. Since the shear rate is strongly reduced between bundles, crystallization leads to lamellae with folded chains whose axes are parallel to the fibril axes (Fig. 7). The resulting extended-chain structures are responsible for the remarkable properties of some ultraoriented polymers.

1.3. Mesophases and Liquid-Crystalline Polymers [8]

1.3.1. Introduction

Mesomorphic chemical compounds exhibit microscopic structures (mesophases) that are

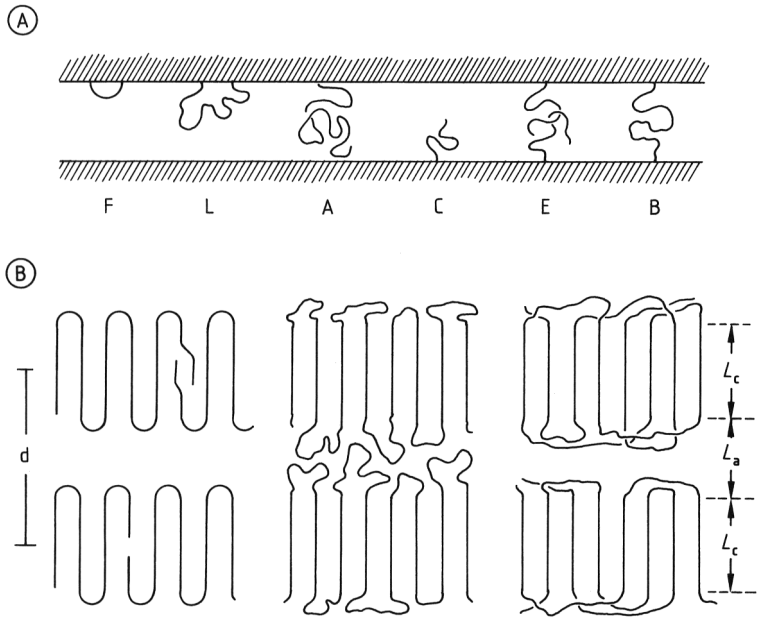


Figure 4. Models for the fine structure of lamellae of single crystals
A) Chains between two adjacent lamellae: F = sharp folds, L = loose loops, A = adsorbed chain, C = cilium, E = entangled cilium, B = crystal bridge or tie segment; B) Structures of lamellae: R=Regular lamellae with sharp folds, adjacent chain reentry, void from chain ends (below) and dislocation (above); L = lamellae with loose loops and adjacent reentry; S = switchboard model; d = crystallographic long period; L_c = thickness of lamella; L_a = thickness of "amorphous" surface layer ($d = L_c + L_a$)
Reprinted with permission by Hüthig and Wepf Publ., Basel [9]

intermediate between crystals with long-range three-dimensional order and liquids without long-range order (Greek: *mesos* = middle, *morphe* = shape, form). Three types of mesophases are distinguished: Liquid crystals, plastic crystals, and condis crystals. Since liquid crystals were discovered first and are furthermore the most common of the three classes, the term mesophase is often used as a synonym for liquid crystal.

Liquid crystals (LCs) (→ Liquid Crystals for Display Application) possess a certain ordered structure like crystals, but they flow like liquids. *Thermotropic liquid crystals* exhibit this phenomenon in the pure state above a certain solid−mesophase transition temperature, where the solid may be a crystal or a glass. *Lyotropic liquid crystals* exhibit mesophase behavior in certain solvents above critical concentrations. Liquid crystalline behavior is present in both cases if the molecules contain "mesogens", that are short rodlike sections that comprise the whole molecule as in low molar mass LCs, or segments thereof as in polymer liquid crystals (LCPs). Mesogens are anisotropic; they are oriented with respect to their mesogen axes but not with respect to their positions.

Plastic crystals exhibit order of positions but disorder of orientations of molecules. They are found for certain spherical low molar mass molecules packed in cubic lattices (i.e., they are isotropic). The absence of strong attractive forces between molecules and the presence of slip planes lead to easy deformabilities of plastic crystals, sometimes even under their own weight. No polymers are known that form plastic crystals.

Condis crystals are *con*formationally *dis*ordered crystals containing several conformational isomers in more or less ideal

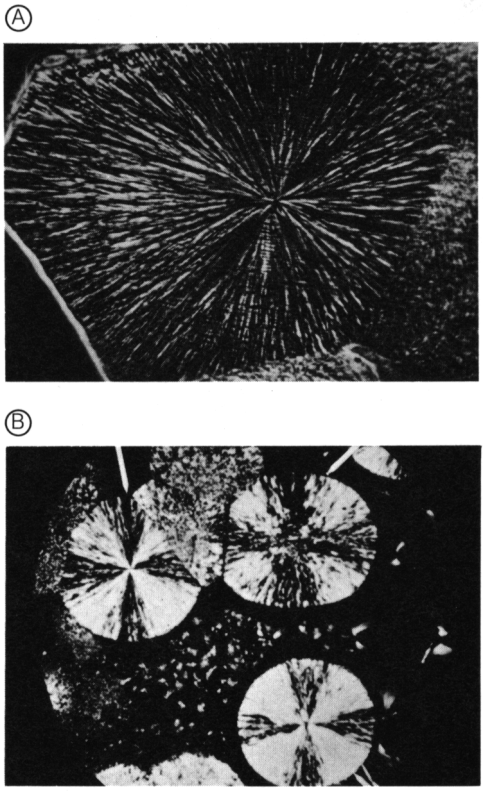


Figure 5. Spherulites of it-polypropylene under the phase contrast microscope (A) and the polarization microscope (B) [10]

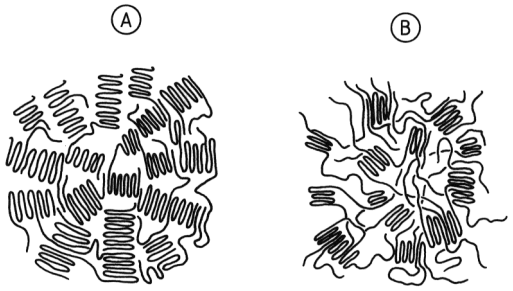


Figure 6. Schematic representation of spherulite structures A) Tangential chain axes; B) Radial chain axes (hypothetical) Reprinted with permission by Hüthig and Wepf Publ., Basel [9]

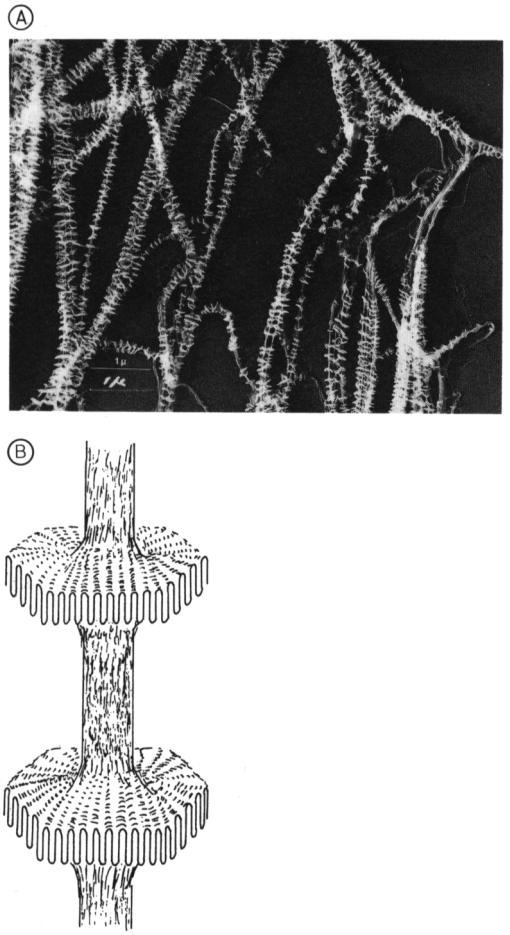


Figure 7. Shish kebab structures of linear polyethylene crystallized from rapidly stirred 5% solutions in toluene [11] A) Electron micrograph; B) Schematic drawing of chain arrangements

crystalline positions with respect to position and orientation of segments (conformational isomorphs). An example is the hexagonal high-pressure phase of polyethylene extended-chain crystals. It is often difficult to determine whether polymer crystals are normal or condis crystals.

On cooling, thermotropic liquid crystals either crystallize or solidify to "mesomorphic glasses" with retention of their liquid crystal structures. These glasses do not carry special names, but since "liquid crystalline glass" and similar names are oxymorons, the terms "LC glass," "PC glass," and "CD glass" have been suggested for the three classes of mesomorphic materials. The LCPs are used mainly as LC glasses not as liquid crystals per se, except in processing.

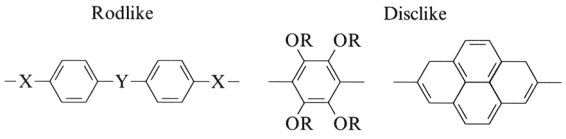
Condensed matter can thus exist in several of the five possible classes of pure phases:

Completely ordered crystal oC, mesomorphic glass mG, amorphous glass aG, ordered mesophase oM, and isotropic melt (liquid) iL. Seven types of biphasic materials exist: oC + mG, oC + aG, oC + oM, oC + iL, mG + aG, mG + iL, oM + iL, and three types of triphasic materials: oC + mG + aG, oC + mG + iL, oC + oM + iL. Because each class can be subdivided further, many physical structures (and thus properties) are possible for the same polymer.

Mesophasic polymers are characterized by domains of microscopic size (see below). "Microdomains" of similar size are also exhibited by certain block copolymers and, in much smaller sizes, by ionomers.

1.3.2. Types of Liquid Crystals

Liquid crystals and LC glasses are generated by rod- or disclike mesogens, which either comprise the whole molecule (as in low molar mass LCs) or sections of it (LCPs). Examples are



where X = O, OOC, COO, etc.; Y = COO, *p*-C_6H_4, CH=CH, N=N, etc.; R = CO $(CH_2)_nCH_3$, etc.; and phenylene residues may be replaced by 1,4-cyclohexane rings. The lengths of polymer mesogens are often comparable to those of repeating units; they seem to be identical with respect to persistence lengths.

Rodlike mesogens are also called calamitic (Greek: *calamos* = reed) and disclike ones discotic. Calamitic liquid crystals are further subdivided into smectic, nematic, and cholesteric mesophases. Smectic LCs show fan-shaped structures under the polarization microscope; they feel like soaps (Greek: *smegma* = soap). Nematic LCs form threadlike schlieren (Greek: *nema* = thread). Cholesteric LCs exhibit beautiful reflective colors, which were first discovered with cholesterol.

The birefringence of LCs originates from the anisotropy of mesogens, which are more or less aligned in microscopic domains with diameters in the micrometer range. These alignments lead to different refractive indices parallel and perpendicular to the direction of polarization of incident light. The domains themselves are arranged randomly. The presence of birefringence however is not proof for the existence of mesogens; it may also result from higher-melting crystallites in partially molten polymers or from crystallites in partially molten polymers or from crystallites in gels or concentrated solutions.

Liquid crystals are turbid because their domains are anisotropic structures whose dimensions are greater than the wavelength of incident light. At a certain "clearing temperature," these domains melt to a transparent (isotropic) liquid.

The soaplike character of *smectic LCs* is due to two-dimensional, layerlike arrangements of mesogens (Fig. 8). At present, twelve different smectic types are known: Four with the average direction of the long axes perpendicular to layer planes and seven with tilted axes. Examples are type S-A with mesogens perpendicular to the layer planes; type S-B, the same but with perfect hexagonal packing of mesogens; type S-C, with mesogen axes at an angle to the planes, etc.

Nematic mesophases (Fig. 8, N) are one-dimensionally ordered. The principal axes of

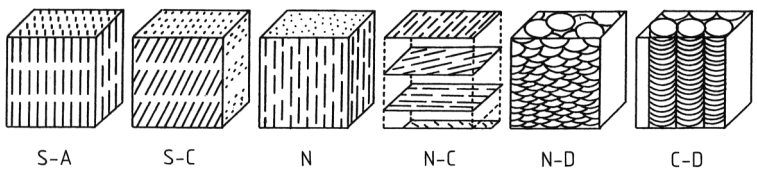


Figure 8. Schematic representation of mesogens in different types of mesophases
S = smectic (types A and C); N = nematic; N−C = nematic cholesteric; C−D = columnar discotic; N−D = nematic discotic
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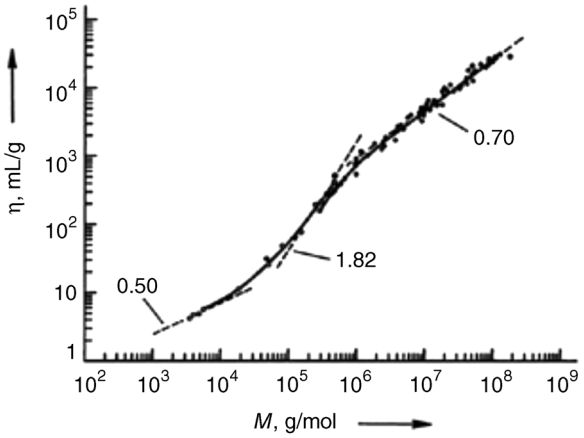


Figure 9. Molar mass dependence of intrinsic viscosities of wormlike chains
(○) Helices of poly(γ-benzyl-L-glutamate) (PLBG) in *N,N*-dimethylformamide at 25°C; (●) double helices of deoxyribonucleic acids in dilute aqueous NaCl solutions at 20°C. The two polymers are comparable because the helix diameters are similar (1.5 nm for PLBG, 2.0 nm for DNA). Numbers indicate exponents *a* in Equation (1)
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mesogens are more or less parallel to each other; the centers of mass are however distributed at random.

Cholesteric mesophases (Fig. 8, N−C) are observed only with chiral mesogens. They consist of layers of nematically ordered mesogens. These layers have a sense of rotation relative to each other due to the presence of chirality centers in mesogens. Cholesteric mesophases are thus screwlike nematics.

Discotic mesophases may exist in many different structures. The disclike mesogens are randomly arranged in nematic-discotic types (Fig. 8, N−D) but stacked like coins in columnar-discotic ones (Fig. 8, C−D).

1.3.3. Mesogens

Mesogens of polymers can be contained in main chains (MC-LCPs) or in side chains (SC-LCPs). Thermotropic MC-LCP glasses are used as engineering plastics; lyotropic MC-LCP glasses, for fibers. Thermotropic SC-LCPs are not used commercially at present but may find use in optical recording devices.

Mesogens usually constitute the whole molecule in low molar mass LC molecules. In macromolecules, this is true only for dissolved helices up to certain molar masses. Such helicogenic macromolecules are rigid rods at small molar masses but become coillike at very high degrees of polymerization (cf. the behavior of short and very long garden hoses). This behavior is demonstrated by the molar mass dependence of their intrinsic viscosities, which are measures of the molecule volume per unit mass (Fig. 9). Rodlike molecules are characterized by their axial ratio (aspect ratio) Λ (length/diameter).

All other polymer chains form either flexible or semiflexible coils in dilute solution or in their isotropic melts (see examples in Fig. 10). Semiflexible (wormlike) chains SF allow rotations around some of their chain bonds. The rodlike character of their segments is however preserved in melts or concentrated solutions if the chain axes remain linear or if the segment linearity can be restored by a crankshaft motion. Conjugated bond structures are helpful but not necessarily required for mesogens since, for example, 1,4-phenylene rings may be replaced by 1,4-cyclohexylene units.

Linear chain axes are present in poly(*p*-phenylene) (PPP) or poly(*p*-phenylene benzoxazole) (PBO). Crankshaft motions around the chain axes are possible in the conjugated chains of poly(*p*-phenylene vinylene) (PPV), the partially conjugated chains of poly(*p*-hydroxybenzoic

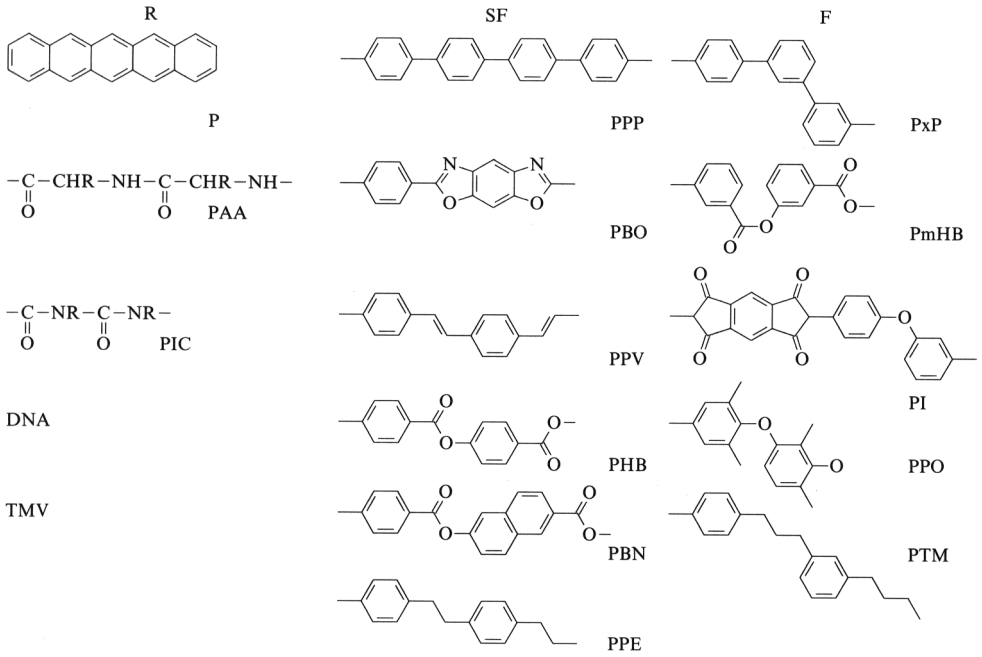


Figure 10. Examples of rodlike (R), wormlike or semiflexible (SF), and flexible (F) molecules and segments. See text for further explanation.
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acid) (PHB), and even in the nonconjugated poly(*p*-phenylene alkylenes) as long as even numbers of methylene groups are present between phenylene rings as in poly(*p*-phenylene ethylene). Semiflexible molecules are characterized by their persistence lengths a or their Kuhn lengths $L_K = 2\ a$.

Rodlike molecules and semiflexible molecules with long persistence lengths form many physical bonds between parallel chains. The total energy of such assemblies is so high that individual intramolecular chemical bonds rather than all of the physical bonds are broken upon heating: These molecules decompose instead of producing thermotropic mesophases. They may however form lyotropic mesophases in suitable solvents. An example is poly (*p*-phenylene bisbenzoxazole).

The "stiffness" of the chain segments can be removed or reduced by several means (Fig. 11). Bulky substituents prevent the parallelization of chains; they "frustrate" crystallization. Nonlinear chain elements (such as *ortho* and *meta* substituents) work in the same way. Flexible chain segments reduce the persistence lengths of the chains.

1.3.4. Lyotropic Liquid-Crystalline Polymers

Molecule axes of low molar mass rodlike molecules are disordered in isotropic melts, whereas mesogen axes are more or less parallel to each other in nematic and smectic mesophases. Very short rods resemble spheroids. They can arrange themselves in various stable ways, but the parallel ordering need not be much more stable than other arrangements. Therefore, a critical axial ratio exists above which the simple geometric anisotropy is sufficient to stabilize a mesophase.

This critical axial ratio has been calculated with the lattice theory of polymer solutions as $\Lambda_{crit} \approx 6.42$. A geometric stabilization by repulsion is insufficient for $\Lambda < \Lambda_{crit}$ and the mesogens must exert additional orientation-dependent attractive forces.

In solution, repulsive forces between mesogens can act only at sufficiently high mesogen

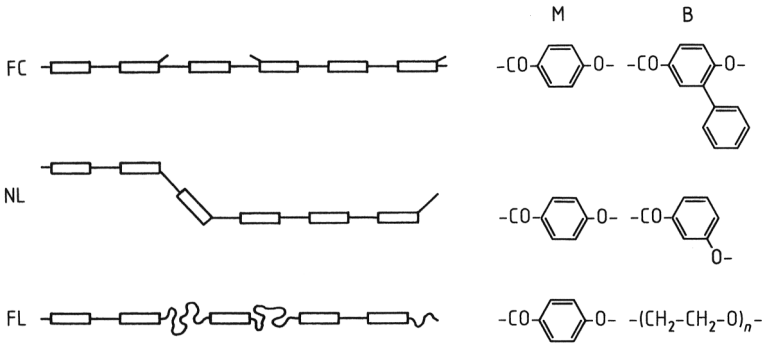


Figure 11. Flexibilization of rigid chain segments by frustrated crystallization (FC), nonlinear chains (NL), or flexible chain elements (FL); M = mesogen-forming monomeric units; B = stiffness-breaking units
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concentrations. At a critical volume fraction, Φ_p^* phase separation occurs into a polymer-rich mesophase and a dilute isotropic phase. The dependence of Φ_p^* on Λ can be described to a first approximation by [12]

$$\Phi_p^* \approx 8(1 - 2L^{-1})/L \quad (1)$$

The axial ratio Λ is the molar mass-dependent true axial ratio of rodlike molecules (i.e., helices) and the molar mass-independent Kuhn length of semiflexible molecules. Equation 1 is remarkably well fulfilled for both helical and semiflexible molecules (Fig. 12). An exception is the tobacco mosaic virus, probably because of additional charge effects that are not considered by the theory.

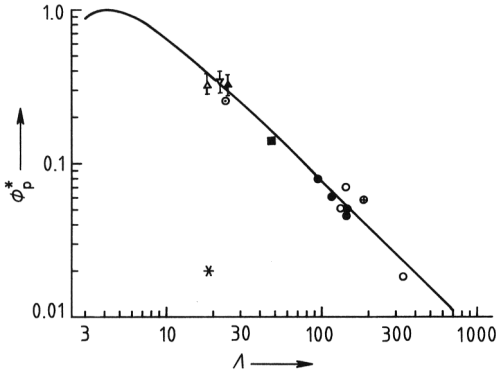


Figure 12. Critical volume fractions ϕ_p^* for phase separations of isotropic solution → nematic mesophase as function of Λ [i.e., the axial ratio of helical (rigid) molecules (circles) and the Kuhn length of semiflexible molecules (triangles, square)]
∗ Tobacco mosaic virus; solid line: prediction of Equation (1)
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Lyotropic mesophases are formed by the helices of tobacco mosaic virus ($c > 2\%$) and deoxyribonucleic acids ($c > 6\%$) in dilute aqueous salt solutions as well as by poly (α-amino acids) in helicogenic solvents, e.g., poly(γ-methyl L-glutamate) in dichloromethane–ethyl acetate (12 : 5) ($c > 15\%$). Hydroxypropyl cellulose (HPC) forms a cholesteric mesophase at room temperature in water at $w_{HPC} > 0.41$.

On shearing, mesophase domains become oriented with respect to the mesogen axes (Fig. 13). This alignment becomes frozen-in on rapid quenching of thermotropic LCs or by precipitation of lyotropic ones into baths (half-lifes of orientation between a few seconds and a few hundredths seconds). The resulting

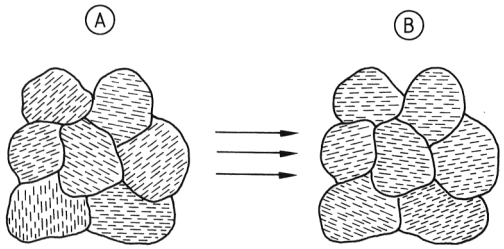
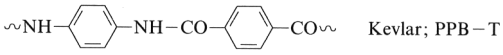


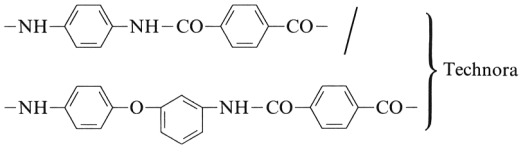
Figure 13. Alignment of mesogen axes upon shearing
A) Mesophase domains in liquid crystalline state at rest; B) During shearing or as LC glass with "frozen in sheared state"

LC glasses possess good orientations of mesogen axes in the shear direction (e.g., fiber direction), high tensile strengths, and low extensibilities.

A number of LC fibers are produced commercially. Poly(*p*-phenylene terephthalamide) (PPB−T) was originally spun from concentrated sulfuric acid solutions, whereas chlorinated *N*-methyl pyrrolidine is now used:



A similar copolyamide is also on the market



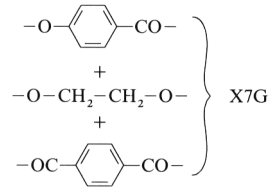
Even better LC fibers are produced from poly(*p*-phenylene-2,6-benzoxazoles) and poly(*p*-phenylene-2,6-benzthiazoles) (PBT), which are spun from poly(phosphoric acid) solutions, at present on a bench scale. Both "*cis*" (shown) and "*trans*" (X and N exchanged at one ring) structures are known:

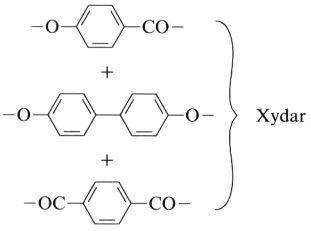


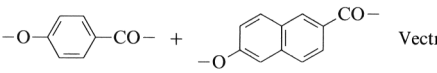
1.3.5. Thermotropic Liquid Crystal Polymers

Non-Newtonian shear viscosities of liquid crystal polymers drop drastically with increasing shear rates due to the orientation of mesogen axes upon shearing. Less energy is thus needed for processing thermotropic LCPs than isotropic thermoplastics. The high orientation times permit a freezing-in of the mesogen orientation in injection molding, for example. Because of the higher than usual moduli of elasticity and tensile strengths, such LCPs are also called *self-reinforcing polymers*.

The first self-reinforcing polymer was the copolyester X7 G with 60 mol% *p*-hydroxybenzoyl and 40 mol% terephthaloyl glycol units. It is no longer produced because the less expensive glass-fiber-reinforced saturated polyesters possess similar properties. Xydar and Vectra are, however, industrially produced:







Polymeric side-chain LCs can serve for the thermooptical storage of information. A guided laser beam increases the temperature locally, whereupon phase transformations occur. The change of order can then be frozen-in on cooling below the glass transition temperature. The resolution is ca. 0.3 μm.

1.3.6. Block Copolymers [13]

Block copolymers consist of two and more blocks of constitutionally or configurationally different monomeric units (e.g., A_n-B_m, $A_n-B_m-A_n$). In most cases these blocks are thermodynamically or kinetically immiscible because their homopolymers A_n, B_m, etc., are not miscible. The demixing of block copolymers cannot proceed, however, to macroscopic phase separations because the blocks are chemically coupled. Similar blocks of different block copolymer molecules can thus only aggregate and form domains in a matrix of the other blocks. This phenomenon is called microphase separation.

Three different applications of block copolymers are known: Polymeric detergents, thermoplastic elastomers, and compatibilizers for

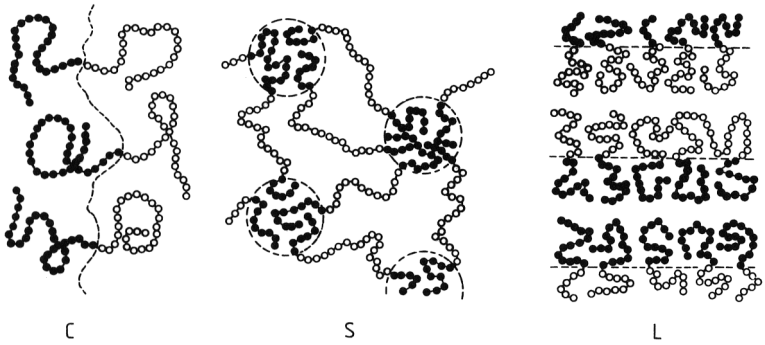


Figure 14. Arrangement of A_n blocks (with A units •) and B_m blocks (with B units ○) in diblock (C, L) and triblock copolymers (S)
C: compatibilizers at an interface - - -; S: spherical A_n domains in continuous matrix B_m; L: lamellae of A_n and B_m

blends. Polymeric detergents consist of hydrophilic and hydrophobic blocks. Examples are the multiblock copolymers from watersoluble ethylene oxide blocks $[-(OCH_2CH_2)_n-]$ and water-insoluble propene oxide blocks $-[OCH_2CH(CH_3)]_n-$. The hydrophobic blocks associate in water, which produces high viscosities.

A similar action is exerted by *compatibilizers* for nonmiscible blends of A_n and B_m polymers. These polymers are A_p-B_q diblock copolymers: The A_p block resides in the A_n phases and the B_q block in the B_m ones. Compatibilizers thus anchor the two types of phases (Fig. 14).

Thermoplastic elastomers [14] consist of tri- or multiblock copolymers. Triblock copolymers $S_n-B_m-S_n$ possess a soft center polybutadiene block$-B_m-$(glass transition temperature below use temperature) and two hard end polystyrene blocks S_n-(glass transition temperature above use temperature). Below certain *m/n* ratios, styrene blocks form spherical microdomains in a continuous matrix of butadiene blocks. These spherical domains thus act as cross-linking units in an elastomer (Fig. 14, S). The hard domains "melt" above their glass transition temperatures, and the block copolymers can then be processed like thermoplastics.

The morphology of *diblock copolymers* is governed mainly by the relative spatial requirements of the blocks. Both blocks, if independent, would form unperturbed random coils. If the unperturbed volumes of both blocks are of equal size, all A_n blocks would line up in one layer and all B_m blocks in another because the blocks are (1) coupled to each other and (2) incompatible. The A_n layer faces another A_n layer, where the A_n blocks are coupled to B_m blocks, etc. (Fig. 14, L). The diblock polymers thus form lamellae with a thickness of two coil diameters. Similar structures result for triblock polymers $A_r-B_m-A_r$, where $r = n/2$.

If the volume of the A_n blocks is much lower than the volume of the B_m blocks, then the A_n blocks can no longer be packed into layers without violating the demand for tightest packing or deviating from the shape of unperturbed coils. Both possibilities are energetically unfavorable, and the smaller A_n blocks thus cluster together and form spherical domains in a continuous matrix of the larger B_m blocks. If the A_n blocks are somewhat larger (but not big enough to form lamellae), then cylinders would result (Fig. 15).

A great number of thermoplastic elastomers of both the triblock and the multiblock type is known [15]. Their chemical structures range from $(styrene)_n-(butadiene)_m-(styrene)_n$ triblock copolymers to polyether–urethane multiblock polymers, ethylene–propene copolymer–polyolefin blends, polyether–esters, and graft copolymers of butyl rubber on polyethylenes.

1.3.7. Ionomers

Ionomers are copolymers from primarily hydrophobic monomers with small amounts

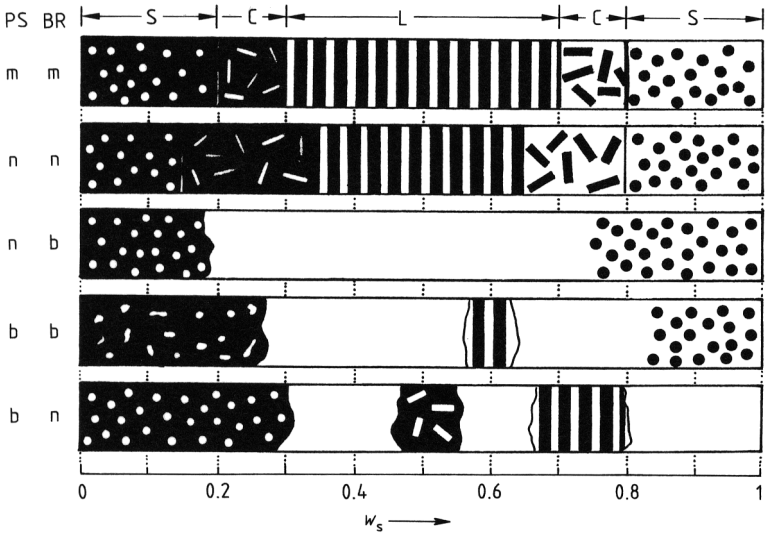
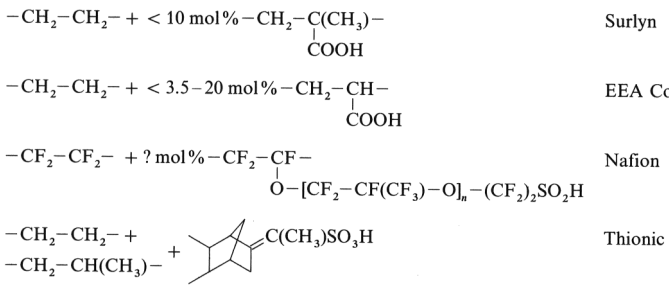


Figure 15. Morphology of styrene–butadiene diblock copolymers as a function of the mass fraction of the styrene units. White: polystyrene blocks (PS); black: polybutadiene blocks (BR). The block length distribution may be (m) molecularly homogeneous (theory), (n) narrow, or (b) broad
S = Spherical domains, C = cylinders (rods), L = lamellae (layers). Upper row: Predictions of Meier theory; rows 2–5: schematic after experimental results of many authors
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of ionic comonomers. The ionic groups may be in the main chain or in substituents. Four different types of ionomers are produced commercially.

rubber. Both EEA and Nafion are used as acids, whereas Surlyn and Thionic are obtained by aftertreatment that leads to sodium or zinc salts.



Surlyn, EEA, and Nafion are synthesized by direct copolymerization of the corresponding monomers. Thionic results from the postpolymerization sulfonation (< 5%) of the diene units (usually 5-ethylidene-2-norbornene) of the primary ethylene–propene–diene (EPDM)

The introduction of ionic groups into hydrophobic polymers leads to ion associations and subsequently to microphase separations. The ion association is controlled by the coordination number of the ions; that is, sodium ions with valence 1 and coordination number 6 are as

good cross-linkers as zinc ions with valence 2. Cross-linking by ions does not occur via ion pairs but via clusters and domains of many ions. These ionic bonds dissociate at higher temperature, and the ionomers can then be processed like thermoplastics. At lower temperature, they behave either as thermoplastic elastomers (T_G of polymer segments lower than use temperature) or as "reversible" thermosets (T_G of segments higher than use temperature).

1.4. Gels

Chemically lightly cross-linked polymers swell upon addition of solvent to form gels. The maximum degree of swelling results from the attempt of segments located between cross-linking sites to attain their energetically most favored coil dimensions which in turn is counteracted by the elastic retraction due to cross-links. Physically cross-linked polymers behave in the same way if the physical cross-links (crystallites, ion clusters, etc.) survive the dissolution process.

The latter phenomenon is utilized in poly (vinyl chloride) pastes. The strong dipole–dipole interactions between C−Cl bonds leads to associations of chain segments which at room temperature resist dissolution by plasticizers such as phthalates, adipates, sebacates, or citrates. Heating of PVC with these plasticizers and subsequent cooling leads to gelation by formation of a lightly physically cross-linked network. Plasticized PVC thus behaves like an elastomeric material. The physical cross-links dissociate at higher temperature, and the resulting PVC paste can be processed with extruders or roll mills.

1.5. Polymer Surfaces [16]

1.5.1. Structure

Outer layers of solid or liquid polymers do not exhibit, in contrast to air, water, metal surfaces, etc., the same average composition as the interiors of these polymers. Groups or segments with the lowest Gibbs interfacial energy will reside preferentially at the surface or interface. Surface structures may also be altered by chemical attack during processing or on prolonged use (e.g., by oxidation) or by physical processes such as transcrystallization.

This behavior can be studied by a wide variety of new spectroscopic methods, for example, the concentration of immediate surface groups by Fourier transform infrared spectroscopy (FT-IR); the composition of the upper 0.3–0.5 nm layer by ion scattering spectroscopy (ISS, LEIS); of the upper 1–10 nm by photoelectron spectroscopy [UPS, PE (S)], electron spectroscopy for chemical analysis (ESCA, XPES, XPS, IEE), and Auger spectroscopy (AES).

These methods have shown that poly-(2-vinylpyridine) and poly(4-vinylpyridine) have much more hydrophobic surfaces than their chemical structure indicates: CH_2- and CH-groups face the surface; pyridine residues (C_5H_4N), the interior. Imide–carbonyl residues of polyimides, on the other hand, are preferentially found at the surface and aromatic rings in the interior. The surface is enriched by siloxane residues in polycarbonate–polydimethylsiloxane block copolymers but by styrene units in polystyrene–poly(ethylene oxide) block copolymers. Because the surface energy depends on the contact (air, water, metals, etc.) and also on kinetic effects (thermal history, solvents, etc.), one and the same polymer may possess various surface compositions and thus also surface properties.

1.5.2. Interfacial Tension

Interfacial tension is the force that acts at the interface between two phases; it is called surface tension for the interface condensed phase–gas phase.

Surface tensions γ_{lv} of liquid polymers against air decrease with the two-third power of the molar mass according to

$$\gamma_{lv} = \gamma_{lv}^{\infty} + K_e \times M^{-2/3}$$

They do not vary markedly with temperature. Typical values (at 150 °C) range from 13.6 mN/m (polydimethylsiloxane), 22.1 mN/m (it-polypropylene), 28.1 mN/m (polyethylene), and 33.0 mN/m poly(ethylene oxide). At present, no correlation of these surface tensions with chemical constitution is possible because the

surface structures of liquid polymers are unknown.

Interfacial tensions between two liquid polymers are always lower than surface tensions. They are low for two apolar polymers but higher if one polymer or both of them are polar. For example, the interfacial tension of polyethylene–it-polypropylene is only 1.1 mN/m, but that of polyethylene–poly(ethylene oxide) is 9.5 mN/m and poly(ethylene oxide)−polydimethylsiloxane 9.8 mN/m.

The interfacial tensions between solid polymer and air are generally unknown. They do not differ markedly, however, from the critical surface tensions determined by the *Zisman method*. In this method, the liquid–air surface tensions of various liquids are plotted against the cosine of contact angles cos θ of these liquids against air and extrapolated to cos $\theta \rightarrow 0$. The resulting "critical" surface tensions of polymers are always lower than the surface tension of water: Polytetrafluoroethylene, 18.5; polyethylene, 33; poly(vinyl alcohol), 37; polyamide 66, 46; and urea–formaldehyde resins, 61 mN/m. Fluorinated polymers have especially low critical surface tensions. They are not wetted by water (72 mN/m) or oils and fats (20–30 mN/m) and are therefore used as surface coatings to prevent sticking.

1.5.3. Adsorption

Macromolecules possess many adsorbable groups and segments. The type of adsorption depends on the adsorption energy per segment (group), the concentration of adsorbable macromolecules, and the duration of the experiment.

"Adsorption equilibria" are established in minutes to hours at smooth surfaces but may take days to attain at rough surfaces or powders. The adsorption time increases with the concentration and molar mass of the polymer.

Polymer coils tend to overlap even in fairly dilute solutions: The adsorbed polymer layers are almost always multilayers, except for the adsorption of oligomers ($X < 10$–100) or from very dilute solutions (volume fractions $< 10^{-4}$–10^{-3}). At higher concentrations or molar masses, adsorbed amounts and structures of polymer layers are mainly kinetically controlled. Reorganization may occur with time; for example, the adsorption of polar polymers at polar surfaces can change from an initial loose loop structure to a more compact, flat covering. The layer of poly(ethylene oxide) adsorbed on chromium surfaces is only ca. 2 nm thick and so tightly packed that the refractive index of the adsorbed layer is identical with that of the crystalline polymer. The thickness of the surface layer of polystyrene of $M = 176\,000$ g/mol adsorbed from a 5 mg/mL solution in the thermodynamically bad solvent cyclohexane is however about 27 nm (i.e., identical with the end-to-end distance in the unperturbed state). The physical structures of adsorbed polymers obviously play an important, yet widely unknown, role in many technological applications of polymers.

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Plastics, General Survey, 4. Polymer Composites

ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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1. Overview

The term composite has various meanings. In general, it denotes a complex material in which two or more distinct substances combine to produce some properties not present in any individual component. In biomaterials, it means any two joined materials (e.g., polymer-coated titanium parts). In engineering, composites are more narrowly defined as physical admixtures of various materials that are present as distinct phases. The term "phase" is used here in the descriptive sense, not in the thermodynamic one. The engineering term "composite" thus includes only heterogeneous composites. Heterocomposites can be further subdivided into nanocomposites (dispersed phase has at least one dimension smaller than 100 nm), microcomposites (dispersed phase in the micrometer to millimeter range), and macrocomposites. Polymer composites are defined as composites in which at least one component is of a polymeric nature. In accordance with the general definition of a composite and in contrast to the engineering use of the word, the term "polymer composite" is often used to cover not only heterogeneous mixtures of a polymer and another material (minerals, fibers, other plastics, elastomers, etc.), but also homogeneous (single-phase) materials of two polymers (homogeneous polymer blends). Such polymer composites are a subgroup of "multicomponent polymer systems", which also include copolymers (two or more types of monomeric units chemically bound together).

Polymer composites occur naturally (wood, bamboo, lobster shells, bone, muscle tissue, etc.) or are manufactured synthetically. Synthetic polymer composites can also be subdivided into single-phase (homogeneous) and multiphase (heterogeneous) composites. Further subdivisions may be according to the second component's size (microcomposites, macrocomposites), chemical nature (air, low molar mass plasticizer, elastomer, plastic, mineral), geometry (particulate, fiber, platelet, fabric), and macroconformation (if polymeric: coil, rod), etc. (see Fig. 1). Most of these subclasses have different technical names

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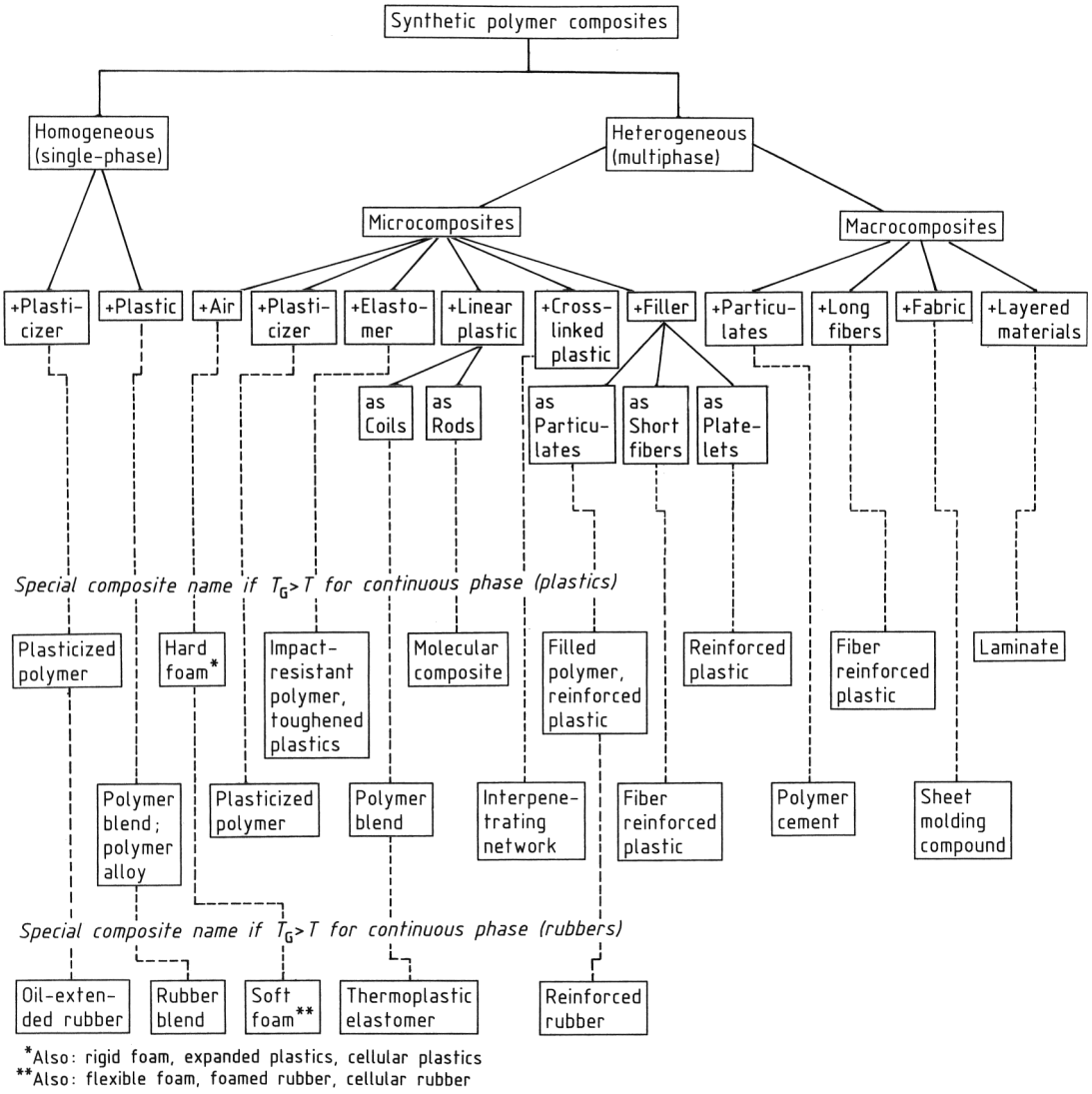


Figure 1. Classification of polymer composites of a base polymer (matrix polymer) with other materials (plasticizer, plastic, air, long fiber, layered materials). Some of these materials have their molecules in different shapes (coils, rods) or have various outer shapes (particulates, short fibers, platelets). Adopted from [1]

depending on whether the glass transition temperature of the continuous phase is above (plastics) or below (rubbers) the use temperature. The same name is often given to various subtypes.

A mixture of two (or more) different polymers is often called a *blend* when both polymers are either above (rubber) or below (plastics) their glass transition temperatures. Blends are distinguished from composites of two polymers such as polymer–fiber-reinforced or rubber-toughened plastics. The term blend is sometimes restricted to mean only "incompatible polymer mixtures", whereas compatible polymer mixtures are called polymer alloys. The latter term is, however, occasionally more narrowly used for mixtures of two crystallizable polymers.

Table 1. Names of simple mixing rules

Field	Property exponent in generalized mixing law		
	$n = 1$	$n = 0$	$n = -1$
Mathematics	arithmetic mean	harmonic mean	geometric mean
Chemical engineering	rule of mixtures	logarithmic mixture rule	inverse rule of mixtures
Mechanical engineering	Voigt model		Reuss model
Electrical engineering	parallel		series
Materials science	upper bound		lower bound

The term *miscibility* refers to admixtures on the molecular level (nanometer range), that is true thermodynamic solubility. It is sometimes used more loosely for any polymer mixture that exhibits only one glass transition temperature. *Compatibility* denotes the ability of admixtures to be blended to heterogeneous microcomposites that do not separate into macroscopic phases.

2. Mixture Rules

The composition dependence of properties Q of composites can often be described by mixture rules. The *generalized simple mixing law* relates Q to the fractions f_A=1−f_B of components A and B with properties Q_A and Q_B:

$$Q^n = Q_A^n \cdot f_A + Q_B^n \cdot f_B \quad (1)$$

The generalized simple mixing law is usually applicable to single-phase composites without specific interactions of its components and to two-phase systems with regularly dispersed discrete phases of "infinite" dimensions. It includes three special cases that are known by different names in different fields (Table 1) and are illustrated in Figure 2.

The *rule of mixtures* (n = 1) applies, for example, to various moduli if both components behave elastically. An example is Young's modulus parallel to the fiber direction for

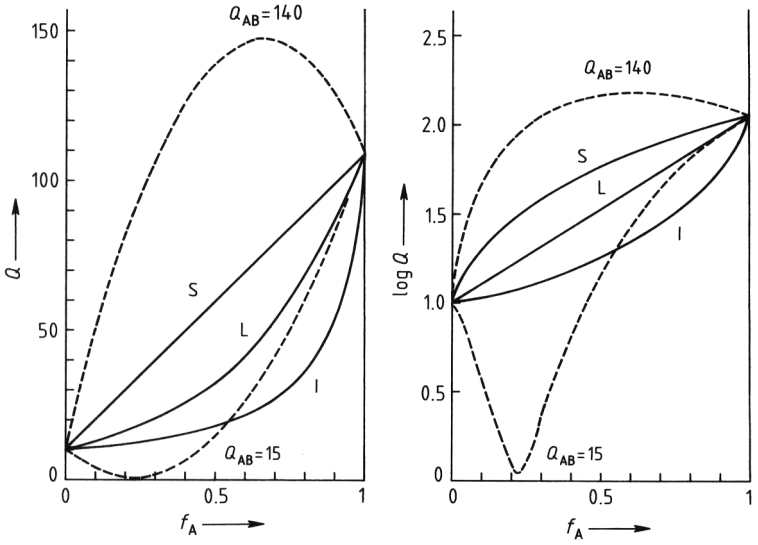


Figure 2. Mixing laws for composites with Q_A = 110 and Q_B = 10: left: $Q = f(f_A)$; right: log $Q = f(f_A)$
Simple mixing laws with interaction parameter
Q_{AB} = 0 (S = simple mixing law; L = logarithmic mixing law; I = inverse mixing law
- - - Composites with interaction parameters Q_{AB} = 140 and 15, as indicated

epoxide resins reinforced with long glass fibers (see below). The same composites follow the *inverse rule of mixtures* ($n = -1$) if the modulus is measured perpendicular to the fiber direction and no slippage occurs. The *logarithmic mixture rule*

$$\log Q = f_A \cdot \log Q_A + f_B \cdot \log Q_B \quad (2)$$

is obtained from Equation 1 for $n = 0$ after some mathematical manipulation. The only known case concerns the permeation of oxygen through ABS resins. The proper fraction f_i in Equations 1 and 2 is always the volume fraction. If mass fractions are used instead, deviations from the curves shown in Figure 2 occur, which may be confused with either deviations from additivity or specific interactions.

True deviations from the upper bound S and lower bound I (Fig. 2) may be caused by irregularities in phase distributions (discrete phases) or phase continuities (continuous phases), phase alignments (anisotropic phases), bonding (adhesion), or nonuniform stresses. The resulting functions always lie between the upper and the lower bound if specific interactions are absent. Many empirical, semiempirical, and theoretical expressions have been proposed for such composites. A widely used function is the Halpin–Tsai equation

$$Q = Q_B \cdot \frac{1 + K_1 K_2 f_A}{1 - K_2 f_A}; K_2 = \frac{Q_A - Q_B}{Q_A + K_1 Q_B}$$

where K_1 is an adjustable constant. The Halpin−Tsai equation gives the lower bound for $K_1 \to 0$ and the upper bound for $K_1 \to \infty$. Particulate fillers often have $K_1 \approx 0$, and fiber-reinforced plastics $K_1 \approx 2\ L/d$, where $2\ L/d$ is the aspect ratio of the fiber.

Specific interactions between components can be considered by an additional interaction term. This term is differently defined, for example:

$$Q = Q_A f_A + Q_B f_B + K_i f_A f_B;$$
$$K_i = 2(2Q_{AB} - Q_A - Q_B)$$

where the property term Q_{AB} is taken at $f_A = f_B = 1/2$. The value Q_{AB} may be an interaction parameter between components A and B in homogeneous mixtures or the property of the interphase between A and B phases in heterogeneous mixtures. The upper bound for absent interactions or interphases is retrieved for the condition $Q_{AB} = (Q_A + Q_B)/2$. The functions for $Q_{AB} \neq (Q_A + Q_B)/2$ may lie fully or partially outside the range between upper and lower bounds (Fig. 2); that is synergistic effects (above the upper bound) or antagonistic effects (below the lower bound) may be present. They may also show maxima and minima, depending on the relative magnitudes of Q_{AB}, Q_A, and Q_B. Maxima or minima that exceed the highest property value (either Q_A or Q_B) are sometimes considered the true criteria for synergistic and antagonistic effects, respectively.

3. Filled Polymers

3.1. Microcomposites

The addition of fillers (low thermal expansion) to polymers (high thermal expansion) reduces the proportion of the latter and thus the shrinkage of plastics on processing (Table 2). The melt flow is also lower. Heat deflection temperatures (HDT) of amorphous polymers are either the same as those of unfilled plastics or no more than ca. 10 K higher (Fig. 3, group a), probably because of the increased viscosity of the filled plastic. The HDTs of amorphous thermoplastics are almost identical with glass transition temperatures.

The HDTs of crystalline polymers depend on a number of factors. Unfilled or particulate-filled crystalline polymers show HDTs that are

Table 2. Effect of fillers on some properties of amorphous (A) and crystalline (C) thermoplastics [(↑) weak increase, ↑ increase, ↑↑ strong increase, (↓) weak decrease, ↓ decrease, ↓↓ strong decrease]

Property	Extenders		Reinforcing agents	
	A	C	A	C
Shrinkage	↓	↓	↓	↓
Heat deflection temperature		(↑ ↓)		↑
Melt flow	↓	↓	↓	↓
Young's modulus	(↑)	(↑)	↑	↑
Flexural modulus	↑	↑	↑	↑↑
Fracture strength	↓	↓	↑	↑
Brittleness	↑	↑	↑↓*	↑↓*

* Tough plastics become more brittle, and brittle plastics become tough.

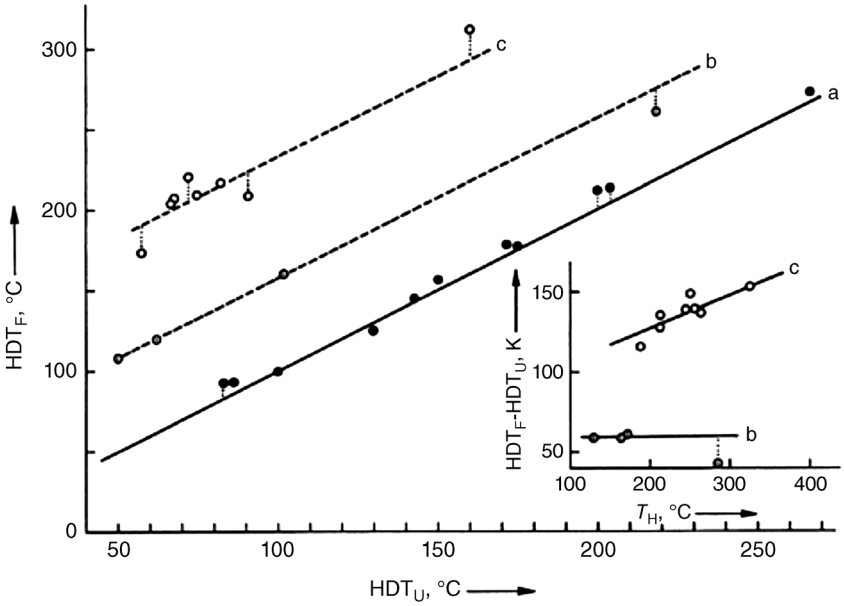


Figure 3. Heat deflection temperatures HDT_F of thermoplastics filled with 30 wt% short glass fibers as a function of heat deflection temperatures HDT_u of the corresponding unfilled polymers, both at 1.85 N/mm^2 (ISO/R 75 A)
(•) Amorphous polymers; (⊙, ○) crystalline polymers; solid line: $HDT_F = HDT_u$; broken lines: empirical
a) Amorphous polymers; b) Apolar crystalline polymers; c) Polar crystalline polymers
Insert: Difference $HDT_F - HDT_u$ as function of melting temperatures T_M of unfilled crystalline polymers

often considerably lower than their melting temperature. Upon fiber-filling, HDTs of crystalline polymers increase strongly; they may reach values near the melting temperatures. This behavior is thought to be due to additional polymer crystallization near, or polymer adsorption on, the fiber surface, epitaxial layers have been found to extend from the filler up to 150 nm into the matrix. The surface layers overlap; the resulting physical network reduces creep.

Two groups of HDTs of glass-fiber-filled crystalline polymers can be distinguished (Fig. 3). The HDTs of group b are about 50–60 K above those of their unfilled counterparts. This group comprises apolar polymers such as polyethylene, polypropylene, and poly(phenylene sulfide); polyoxymethylene also belongs to group b because its oxygen groups are buried deep inside compact helical structures, which are thus apolar on their surfaces. The difference in HDTs of filled and unfilled group b polymers does not vary with melting temperature. Group c includes polar crystalline polymers (polyesters, polyamides, etc.). For this group, the difference in HDTs of filled and unfilled polymers increases with the melting temperature of the unfilled polymer.

Young's moduli of thermoplastics increase with filler content (Fig. 4). The increase is small for spheroidal fillers (glass spheres, chalk), stronger for platelets (kaolin, talc), and strongest for fibers (glass). Short fibers are usually added in amounts of ca. 30 wt%, which corresponds to ca. 17 vol% for glass fibers ($\rho = 2.55$ g/cm^3) in an average polymer ($\rho \approx 1.2$ g/cm^3). Higher fiber content often leads to packing problems since the maximum volume fraction of three-dimensional randomly packed rods with $L/d = 20$ is already ca. 25% (glass fibers typically have diameters d = 10–20 μm and lengths of ca. 0.2 mm after injection molding). Particulate fillers can be added in far greater amounts without sacrificing properties because maximum packing densities of spheres are, for example, 0.745 for the hexagonally most dense and 0.637 for the randomly most dense packing.

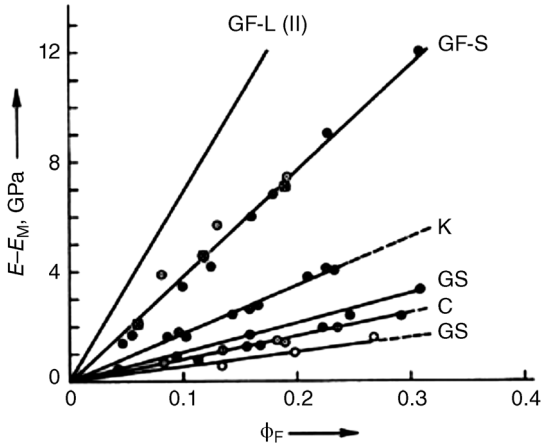


Figure 4. Influence of the volume fraction ϕ_F of fillers on the difference in Young's moduli of filled thermoplastics (E) and their polymer matrices (E_M)
GS = glass spheres; C = chalk; K = kaolin; GF = glass fibers; (S = short; L = long)
○ = polyethylene; (⊙) = polypropylene; ⊗ = polyoxymethylene; ⊕ = poly(butylene terephthalate); • = polyamide 6
The solid line for GF-L (‖) corresponds to the simple mixing law. From data of [2]

Young's moduli E of filled materials can be described by a modified mixing law

$$E = E_M\phi_M + f\,E_F\phi_F = E_M + (f\,E_F - E_M)\cdot\phi_F \quad (3)$$

where f is an adjustable parameter. The data in Figure 4 can be described with $f = 0.39 \pm 0.03$ (chalk), 0.66 ± 0.04 (kaolin), and 1.61 (talc). The effect of 30 wt% of short glass fiber was tested in 14 thermoplastics, and f was found to be 0.57 ± 0.04. These numbers increase with the specific area of the fillers, which are given as 0.3–2.2 (ground limestone), 0.5–1 (glass fibers), 6–22 (kaolin), and 6–17 m^2/g (talc) [3]. Composites obviously increase in stiffness as the contact between filler and polymer segments increases. Good adhesion is not necessary, since E is measured for strains approaching zero.

The adjustable parameter f of Equation 3 adopts a physical meaning for short fiber reinforced plastics. In such composites, forces are transferred to the hard fiber from the soft matrix if (i) the Young's modulus of the fiber is greater than the Young's modulus of the matrix ($E_F > E_M$), (ii) the fiber length L_F exceeds a certain critical value $L_{F,crit}$, and (iii) the shear strength in the matrix is smaller than the shear strength between fiber and matrix (the fiber would be otherwise pulled out of the matrix unless the fiber breaks). In this case, $f = 1 - [L_{F,crit}/(2\,L_F)]$.

Fracture strengths are, however, measured for maximum strains. The failure mode of filled thermoplastics is matrix dominated. Electron micrographs show that at low fiber contents, planar cracks spread through the matrices and debonded fibers are pulled out of either surface; the matrix must thus adhere well to the filler.

The tensile strength σ_B at break is given by the rule of mixtures ($\sigma_B = \sigma_F\,\phi_F + \sigma'_{M'}\,\phi_M$) where $\sigma'_{M'}$ is the tensile stress of the matrix upon application of a load σ_B to the composite. This relationship applies if (i) the tensile strength σ_B is greater than the contribution $\sigma_M\,\phi_M$ of the matrix component to the total tensile strength σ_B (that is $\sigma_B > \sigma_M\,\phi_M$), and (ii) the volume fraction ϕ_F of the fiber exceeds a certain minimum value ($\phi_F > \phi_{F,min}$).

Particulate fillers usually strongly reduce the fracture strengths of composites of amorphous thermoplastics, whereas those of crystalline polymers are reduced less or not at all. *Short fibers* generally increase the fracture strengths by factors of 1.5–2 for amorphous and crystalline polymers alike. Rigid PVC is an exception because its fracture strength is reduced on fiber-filling. The moduli and strengths can be further enhanced if coupling agents are used, which improves the bonding between fiber and matrix (e.g., silanes for glass-fiber-filled polymers).

3.2. Molecular Composites

The problem of insufficient bonding between fiber and matrix can be dramatically reduced if so-called molecular composites are used. These materials are dispersions of semiflexible (rodlike) polymer molecules with mesogenic units in chemically similar polymer matrices, e.g., poly(*p*-phenylenebenzobisthiazoles) in polybenzimides (→ Plastics, General Survey, 1. Definition, Molecular Structure and Properties, Section 5.6.2 Theoretical Fracture Strength). The mesogens are not truly molecularly dissolved; rather, they form microdomains in the matrix. The segment axes are randomly

distributed in these domains if the molecular composites are formed from polymer solutions with total polymer concentrations c below the critical isotrope phase–mesophase concentration $c_{i/n}$. Microdomains show mesophase behavior if films or fiber are formed at $c > c_i/_n$. Such microcomposites have excellent moduli and fracture strengths (Fig. 2).

3.3. Macrocomposites

Polymer macrocomposites are heterogeneous composites of polymers and "macro"-sized additives. Examples are polymer concrete, composition board, long fiber-reinforced polymers, and plywood.

Polymer concrete is composed of polymer [usually polyester or poly(methyl methacrylate)], aggregate (sand, ground limestone, etc.), and other additives (dyes, etc.); it does not contain cement. *Polymer–concrete hybrids* include polymer–cement hybrids (cement is partially replaced by polymers) and polymer-impregnated concrete (conventional concrete saturated with a monomer that is polymerized in place). Polymer concretes have higher moduli and higher tensile and compressive strengths than ordinary concretes. They are not vulnerable to damage by freeze-thaw cycles.

Composition boards are panel products. They include particleboard, fiberboard, hard board from flakes or shearings, etc. The fillers are mainly wood products; the resins, urea–formaldehyde (interior applications), and polyurethanes or phenolic resins (exterior).

Long-fiber-filled polymer macrocomposites range in structure from polymers filled with "long" fibers 6–12 mm in length to fiber strands and mats filled with polymers. The filler content can often reach 65 wt%. Upon application of tensile stress, local stress concentrations are transferred by shear forces onto the plastic–fiber interface and distributed over the much greater fiber surface area. The fibers must therefore bond well to the plastic (use of coupling agents) and must have a certain length to avoid slipping.

Young's moduli of long glass-fiber-reinforced epoxide resins follow the simple mixing law if the tensile stress is in the fiber direction (Fig. 5). The

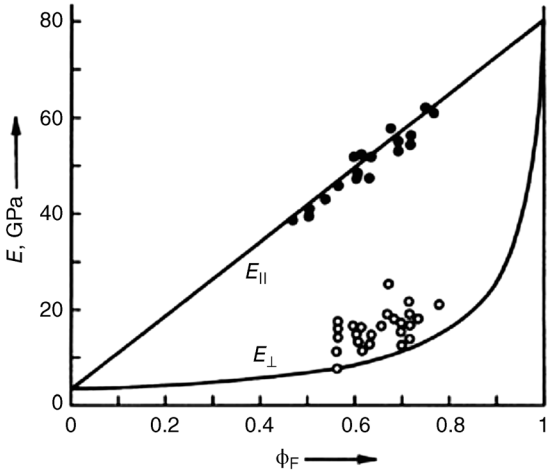


Figure 5. Young's moduli of epoxy–glass-fiber composites parallel (∥) and perpendicular (⊥) to the fiber direction

inverse mixing law is not observed as well for stresses perpendicular to the fiber direction since some fibers bend under stress.

The simple mixing law corresponds to $f = 1$ in Equation (3). For long fibers, f has the meaning of an orientation factor. It becomes 1/6 for fibers distributed three-dimensionally at random, 1/2 for 90° cross-plies measured in either fiber direction, and 3/8 for a uniform, planar distribution of fibers.

This group of macrocomposites also includes prepregs (fiber mats soaked with unsaturated polyester resins) and the composites generated by filament winding (wound filaments saturated with epoxies or unsaturated polyesters), both of which are subsequently polymerized.

3.4. Nanocomposites [4–6]

Polymeric nanocomposites are defined as multiphase materials in which at least one dimension of the dispersed or continuous phase is smaller than 100 nm. This includes organic–inorganic hybrid materials as well as "all-polymer" nanocomposites in which matrix and reinforcing phase consist of the same polymer. In contrast to micro- and macrocomposites, most polymers are allocated due to the presence of nanostructures at interfaces that affect the chain mobility and entanglement. Hence, the properties of interfacial polymers substantially differ from those of bulk polymers,

especially regarding their thermal, mechanical, electrical, optical, and biological properties. For instance, polymeric nanocomposites can be optically transparent, exhibit improved stiffness, high surface gloss, high scratch resistance, and even electrical conductivity. Three different strategies lead to polymeric nanocomposites: (i) Dispersion of functional nanofillers in a polymer matrix, (ii) formation of organic–inorganic hybrid polymers, and (iii) oriented polymer crystallization.

Nanofiller Dispersion [4–8]. Since the 1990s, significant progress in nanotechnology has made a large variety of nanometer-scaled inorganic and organic fillers as well as nanofibers commercially available for nanocomposite preparation (see Section 2.2.4 Extending and Functional Fillers, in Plastics, General Survey, 2. Production of Polymers and Plastics). When the size of inorganic fillers is reduced, a transition from the inorganic solids to the molecules takes place. Molecular nanofillers include nanosilica, such as POSS (polyhedral oligomeric silsesquioxane); 2D carbon polymers, such as graphene; and multifunctional hyperbranched polymers with nanometer dimensions.

Nanometer-scaled silica spheres, prepared by a flame process, are known as pyrogenic silica of around 5 nm diameter, which is widely applied as thixotropic agents in coatings, adhesives, and sealants. Due to the shear-sensitive formation of hydrogen bridges between silanol groups at the silica particle surface, silica percolation networks are destroyed upon shearing, thus accounting for shear thinning. This thixotropic effect, caused by less than 0.5 wt% silica nanoparticles, prevents sedimentation of fillers in formulated thermoset systems. Moreover, functionalized silica fillers play an important role in improving scratch resistance in coatings. Nanosilica together with disulfide-functional silane coupling agents are used for the preparation of silica–rubber nanocomposites.

For many years, carbon black nanoparticles have been commercially employed to improve electrical conductivity of plastics and coatings. This is important for antistatics and electromagnetic interference shielding. Compared to micron-sized carbon black, the percolation threshold of nanocarbon black is much lower, which drastically reduces the amount of carbon black required for achieving electrical conductivity. Highly anisotropic carbon nanofillers, such as carbon nanotubes and graphene, further reduce the percolation threshold. Moreover, both carbon nanotubes and ultrathin but micron-sized graphene enable combining electrical conductivity with improved matrix reinforcement. Alignment of graphene in a polymer matrix improves barrier resistance to permeation of gas and liquids ("labyrinth effect") together with improved electrical conductivity and matrix reinforcement. Another approach to improved barrier resistance combined with halogen-free flame retardency and matrix reinforcement employs organophilic layered silicates. When layered silicates are made organophilic by cation exchange of sodium cations for alkyl ammonium cations, they can be intercalated and exfoliated during polymer melt compounding. The family of organophilic nanofillers is rapidly expanding.

Inorganic—Organic Hybrids [4, 9, 10]. Polymer hybrids combine the properties typical for ceramics with facile processing typical for polymers. Sol–gel chemistry is employed to equip inorganic particles and resins with reactive groups that enable efficient covalent coupling with various polymers. For example, functionalized alkoxysilanes are cocondensed with tetraethoxysilane and other metal alkoxides, such as zirconates and aluminates to produce reactive liquid oligomers or reactive nanoparticles. They are mixed and cured together with thermoset resins to form nanostructured polymer–ceramic hybrids. Sol–gel coatings are well known for their extraordinary scratch resistance. Moreover, sol–gel chemistry is used to functionalize inorganic nanoparticles by incorporating initiator and transfer agents, which enables covalent attachment of polymer chains by "grafting-from" and "grafting-to" processes. Polymer grafting of nanoparticles greatly facilitates nanoparticle dispersion and prevents undesirable agglomeration.

Self-Reinforcing Plastics and All-Polymer Nanocomposites [11, 12]. Going well beyond the scope of liquid crystalline polymers and conventional nanocomposites, the self-reinforcement of polymers does not require

mesogens as comonomers and eliminates the special handling and safety precautions related to the use of potentially hazardous alien nanoparticles and nanofibers. Moreover, such all-polymer nanocomposites, in which both the matrix and the reinforcing phase consist of the same polymer, have much lower mass and are much easier to recycle than conventional polymer composites. This is highly advantageous for applications in sustainable lightweight engineering. Key concept for achieving self-reinforcement is the oriented polymer crystallization during processing. Whereas one-dimensional crystallization affords in situ aligned polymer nanofibers, the two-dimensional crystallization produces nanosheets and all-polymer multilayer composites. Because this nanostructure formation of polymers does not require nanofibers and nanoparticles, nanometer-scaled particles will not be emitted. In contrast to many other nanocomposites, all-polymer nanocomposites are environmentally benign. In one strategy, oriented films are laminated or coextruded to produce multilayer all-polymer nanocomposites. In another strategy, multilayer all-polymer nanocomposites are produced by pressure- and flow-induced crystallization near the melting temperature of thermoplastics. Extrusion of polyethylene containing ultrahigh molecular mass polyethylene (UHMWPE) close to the PE melting temperature can afford shish-kebab-like aligned UHMWPE nanofibers. However, because UHMWPE has very high viscosity, the incorporation of UHMWPE in PE reactor blends has been restricted to a few percent. Exploiting advanced multisite ethylene polymerization catalysis, it became possible to incorporate much larger amounts of UHMWPE into reactor blends without impairing processing. Because no entanglement with HDPE takes place, the nanometer-scaled UHMWPE forms a low viscosity phase separated melt and elongates during processing. Because the lower HDPE fraction crystallizes much faster, it crystallizes onto UHMWPE nanofibers to produce shish-kebab-like UHMWPE fibers in conventional melt processing without narrowing the processing window. The development of self-reinforcing plastics and all-polymer nanocomposites, which do not require the addition of (nano)fillers and fibers, holds great promise for the sustainable development of lightweight engineering plastics.

4. Homogeneous Blends [13, 14]

Mixtures of polymers with other polymers are called polymer blends (→ Polymer Blends). Such blends may be composed of two thermoplastics (plastic blends), two elastomers (rubber blends), a plastic filled with an elastomer as the dispersed phase (rubber-modified plastics), an elastomer with a plastic as the dispersed phase (polymer-filled elastomer), or a plastic filled with a polymer melt or a low molar mass liquid (plasticized polymers). Whether or not these blends are truly miscible on a molecular level depends on the thermodynamics of the systems.

4.1. Thermodynamics

If two components 1 and 2 are mixed, entropy S, enthalpy H, and volume V change. In many cases, volume changes can be neglected and the Gibbs energy of mixing is given by the changes in enthalpy and entropy: $\Delta G_{mix} = \Delta H_{mix} = T \cdot \Delta S_{mix}$. These changes can be calculated by the Flory–Huggins theory, which assumes that the mixture can be modeled by a three-dimensional lattice on which the monomeric units (or solvent molecules) can be placed. Each monomeric unit experiences the same force field; the theory is thus a mean-field theory. The assumption of a constant force field is fairly well fulfilled for polymer blends and concentrated polymer solutions but not for dilute solutions.

The entropy and enthalpy of mixing are calculated separately. Entropies are calculated for ideal solutions (zero mixing enthalpy); all environment-dependent entropy changes are thus zero (translational, vibrational, and inner rotational entropies do not change). Units can however be arranged relative to each other in many ways; however, there is a combinatorial entropy that is also called "configurational entropy" in statistical mechanics.

The mixing of two components is modeled as a quasi-chemical reaction. The mixing enthalpy is thus determined by the change in interaction energies and the number and type

of nearest neighbors. Enthalpy and entropy terms are added to give the molar Gibbs energy of mixing:

$$(\Delta G_{mix})^m/RT = \chi \cdot \phi_1\phi_2 + \phi_1 \cdot \ln\phi_1 + (X_1/X_2) \cdot \phi_2 \cdot \ln\phi_2$$

which, on differentiation with respect to the molar amounts of the components, yields the chemical potentials, for example, of component 1

$$\Delta\mu_1 = RT\{\chi \cdot \phi_2^2 + \ln(1-\phi_2) + [1-(X_1/X_2)] \cdot \phi_2^2\}$$

where χ is the parameter for the interaction between component 1 and component 2 (usually with numerical values between 0 and 2), also called the Flory–Huggins parameter. All three terms in brackets must be considered if a polymer 2 is mixed with a solvent 1, for example, a plasticizer ($X_1 \ll X_2$). If both components are polymers however, then $X_1 \approx X_2$ and the entire entropy contribution comes from the relatively small logarithmic term. Thus little combinatorial entropy is gained on mixing two polymers, and the miscibility is determined mainly by the mixing enthalpy, that is, by the term $\chi\,\phi_2^2$.

Phase separation occurs if the curve $(\Delta G_{mix})^m = f(\phi_2)$ (at T = const.) has a shape that can be touched at two points by a tangent. The compositions at these points are ϕ_2' and ϕ_2'' (with $\phi_2' < \phi_2''$). Two phases exist for the unstable range $\phi_2' < \phi_2 < \phi_2''$, which is separated from the stable ranges $\phi_2 < \phi_2'$ and $\phi_2'' > \phi_2$ by the so-called binodal. The unstable range itself is subdivided by the spinodal into two metastable ranges and one unstable one. Spinodals are characterized by inflection points in the Gibbs energy–composition functions and extremal values in the chemical potential–composition functions. Maximum, minimum, and inflection point become identical at the critical point, which is defined by a zero value of the second derivative of the chemical potential

$$\partial^2\Delta\mu_1/\partial\phi_2^2 = RT \cdot [2\chi - (1-\phi_2)^{-2}] = 0 \qquad (4)$$

This critical point is characterized by a critical volume fraction $\phi_{2,crit} = 1/(1+X_2^{1/2})$ and a critical interaction parameter $\chi_{crit} \approx (1/2) + (1/X_2)^{1/2}$.

The temperature dependence of χ is approximately

$$\chi \approx A + (B/T) \qquad (5)$$

where A and B are system-dependent constants; B is positive for endothermal mixtures [i.e., χ increases with increasing temperature and a homogeneous solution exists above an "upper critical solution temperature" (UCST)]. Other systems are homogeneous only below a "lower critical solution temperature" (LCST). The demixing is correspondingly either enthalpy (UCST) or entropy (LCST) induced.

The terms UCST and LCST do not indicate the absolute position of demixing temperatures since some systems show LCST > UCST (Fig. 6). Depending on the system, either an hourglass-type diagram or a closed miscibility gap is shown.

4.2. Plastification

Plastification of a plastic is the flexibilization of the material either by added plasticizers (external plastification) or by incorporated flexibilizing comonomer units (internal plastification).

The molecular action of plasticizers consists of a flexibilization of chain segments, which can have various causes. *Polar plasticizers* increase the proportion of *gauche* conformations in polar chains, thus decreasing rotational barriers. *Primary plasticizers* can dissolve helical structures and crystalline regions if they are thermodynamically good solvents. Furthermore both *primary and secondary plasticizers* are diluents; their addition increases the distance between polymer segments and thus decreases the activation energy needed for cooperative movement of segments. Solvation does not per se increase chain flexibility, however, because solvent shells act as substituents and increase the rotational barriers.

The molecular effect of an increase in chain flexibility by plasticization is measured as a decrease of glass transition temperatures (Fig. 7). Small molecules are better plasticizers than bigger ones of similar chemical constitution. The plasticizer efficiency decreases with increasing thermodynamic "goodness" of the

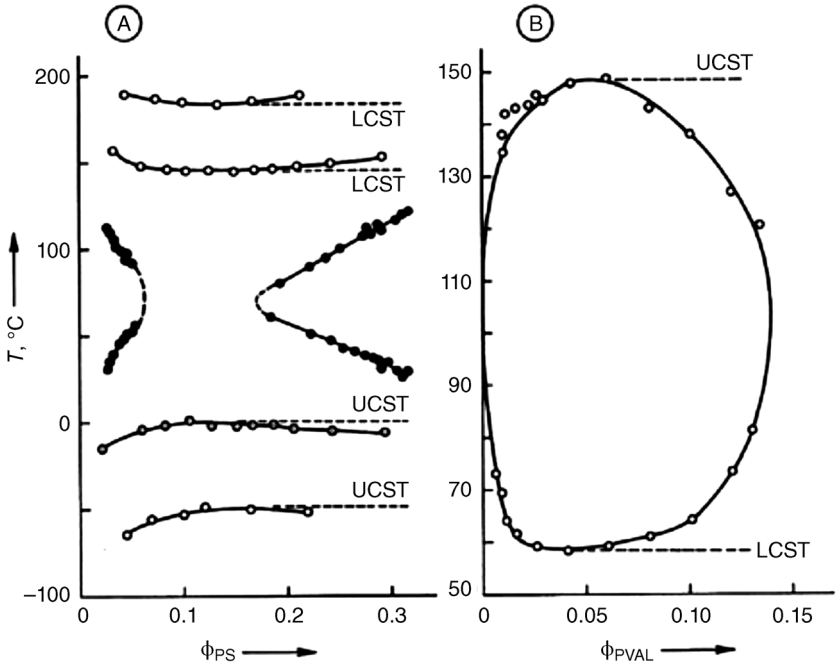


Figure 6. Phase separation temperature as function of polymer–solvent composition
A) Polystyrenes with various molar masses in acetone; B) Poly(vinyl alcohol-*co*-vinyl acetate) (93 : 7) in water
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plasticizer for the polymer (greater interaction, i.e., bigger solvation). Good plasticizers with respect to lowering glass transition temperatures are thus small molecules that act as theta solvents. These plasticizers are however bad for technological applications because they bleed (transport of plasticizer to the surface of the plastic), migrate (transport of plasticizer into another contacting material), or are extractable (e.g., transport into packaged foods). These transport phenomena can be reduced if polymer plasticizers are used. Increasing molar masses lead to decreasing thermodynamic compatibility, however (see below). Technical plasticizers are therefore in most cases a compromise between thermodynamic plasticizer efficiency and kinetically hindered plasticizer transport.

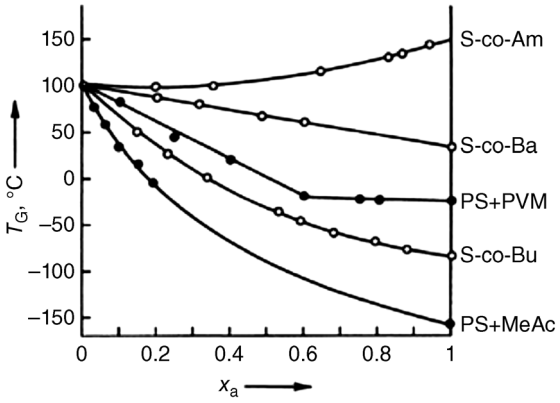


Figure 7. Glass transition temperatures of (●) polystyrene plasticized with methyl acetate (MeAc) or poly(vinyl methyl ether) (PVM) and (○) copolymers of styrene with butadiene (Bu), butyl acrylate (Ba), or acryl amide (Am)

Plastification can also be followed by the changes of certain mechanical properties such as lowering of fracture strength, increase of elongation, and decrease of tensile moduli. Such methods sometimes show "anti-plasticizations" at low plasticizer concentrations (Fig. 8) (e.g., increases of moduli). Glass transition temperatures are not increased, however. The effect thus cannot be the result of increased segment mobility. It may be due to a healing of microvoids in amorphous polymers such as polystyrene or

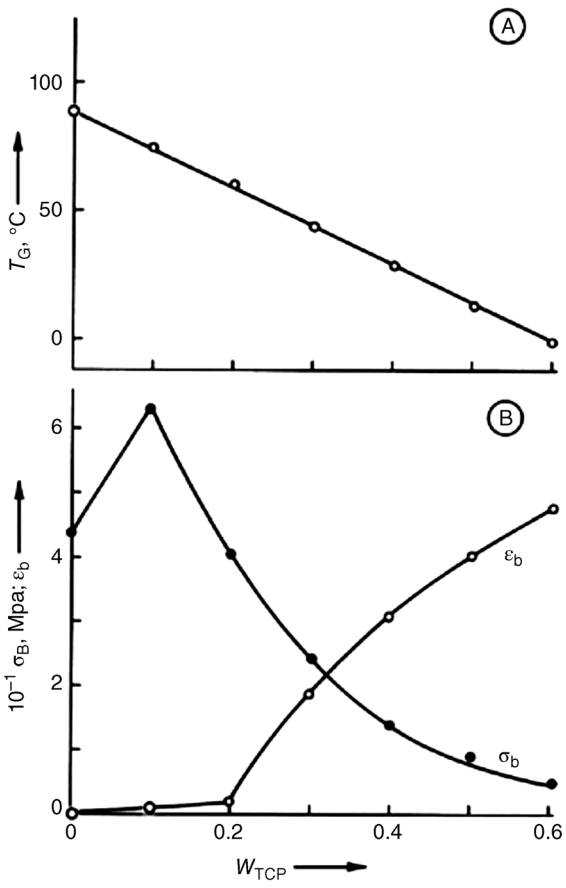


Figure 8. A) Glass transition temperature T_G and B) fracture strength σ_B and elongations ε_B at break of a poly(vinyl chloride) plasticized with tricresyl phosphate (TCP) Reprinted with permission by Hüthig and Wepf Publ., Basel [16]

to additional crystallization of slightly crystalline polymers, such as poly(vinyl chloride).

4.3. Rubber Blends [13, 14, 17, 18]

About 75% of all elastomers are employed as blends. Heterogeneous blends of natural (rubber–styrene)–butadiene rubber or (*cis*-butadiene rubber–styrene)–butadiene rubber are used mainly for tire treads since they reduce abrasion. Homogeneous blends are more rare. They possess only one glass transition temperature which, for 50 : 50 blends, is an average of the glass transition temperatures of the two parent polymers. Heterogeneous blends exhibit two glass transition temperatures, both practically identical to those of the parent polymers. Homogeneous blends are usually formed if the difference in solubility parameters is smaller than 0.7 $cal^{1/2}$ $cm^{-3/2}$ (1.44 $J^{1/2}$ $cm^{-3/2}$).

4.4. Plastic Blends

Plastic blends are usually immiscible because the combinatorial entropy of mixing is too small (high molar masses) and the enthalpy changes on mixing are often positive. Miscibility is observed for three types of systems:

1. Chemically similar polymers, for example, polystyrene–poly(*o*-chlorostyrene), showing both LCST and UCST
2. Systems having specific interactions between different components, for example, polystyrene–poly(vinyl methyl ether); these systems show only LCSTs
3. Systems consisting of oligomers, for example, oligo(ethylene oxide)–oligo(propylene oxide); these systems possess only UCSTs

Homogeneous polymer blends show only single glass transition temperatures; the composition dependence of these T_G's can be described by the simple rule of mixtures. Two-phase systems always show two glass transition temperatures if the phase diameters are greater than ca. 3 nm. Transparency, on the other hand, is no indication of a single-phase blend since opacity can be observed only if the refractive indices of the two phases are sufficiently different and if the phase diameters are greater than ca. one-half the wavelength of incident light. The presence of two phases in clear specimens can often be detected with electron microscopy by special staining techniques.

Modified PPO, a blend of poly(2,6-dimethylphenylene oxide) and polystyrene, is the industrially leading *homogeneous blend*. Blends of poly(vinyl chloride) with poly(methyl methacrylate), poly(ethylene-co-vinyl acetate) or chlorinated polyethylene are also said to be one-phase systems.

5. Heterogeneous Blends [13, 14, 17, 18]

5.1. Compatible Polymers

Two polymers may be thermodynamically immiscible but still mechanically compatible. These compatible blends are two- or multiphase systems that show multiple glass transition temperatures, which do not change with composition. The components do not separate, however, under mechanical stress during the expected life of the product. Such mechanical compatibilities can be improved or introduced by the addition of diblock polymers. One block of these diblock polymers is compatible with one phase type of the heterogeneous blend and the other one with the other type (→ Plastics, General Survey, 3. Supermolecular Structures). The two blocks need not necessarily be chemically identical with the two parent polymers, that is, a compatibility of poly (A) and poly (B) can be achieved not only by addition of poly (A)−*block*-poly (B) but also by poly (A)−*block*-poly (C) if the C block is either miscible with poly (B) or can form mixed crystals with poly (B).

5.2. Blend Formation

Heterogeneous polymer blends can be produced by mixing together two polymers (as melts, lattices, or in solution) or by in situ polymerization of a monomer in the presence of a dissolved polymer.

The energy taken up during *melt mixing* is used for flow processes and for the generation of surfaces of new microdomains. After some time, a steady state is established and the domain size becomes constant. No macroscopic demixing occurs because of the low diffusion coefficients resulting from the high viscosities.

Latex blending consists of the mixing of aqueous dispersions of two polymers. Far lower temperatures and lower shear fields can be employed compared to melt blending. The good mixing of the latex particles remains after coagulation. The domain size is, however, restricted to the size of the latex particles themselves; it is not altered by subsequent melting of the coagulate.

Solution blending involves the mixing of two polymer solutions. Miscible polymers can be blended to domains of molecular size. Solutions of immiscible polymers demix, however, at very low concentrations, sometimes under fractionation with respect to molar masses. Domains grow further on solvent removal by distillation or freeze drying.

In situ polymerization involves solutions or gels of polymers in monomers, which are subsequently polymerized. The in situ polymerization of styrene in a styrenic polydiene solution, which leads to rubber-toughened polystyrene (HIPS) is most important industrially. The polymerization of a cross-linkable monomer in a gel of a cross-linked rubber in the very same monomer results in interpenetrating networks.

Various blending processes produce blends with very different properties (Fig. 9). The high notched impact strengths of the polymerization-blended materials (line P) are caused by a strong anchoring of phases due to the formation of graft copolymers of styrene on polybutadiene and cross-linking within the rubber domains, both caused by free-radical initiators. Such processes are less prevalent during melt blending (radical formation by high shearing at elevated temperature) (line M) and latex blending (low

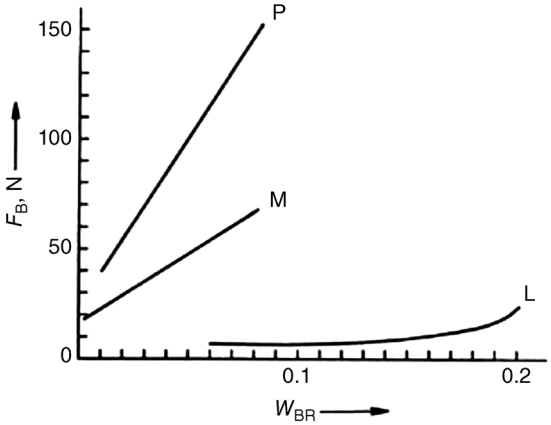


Figure 9. Impact strength with notch F_B as function of the mass concentration w_{BR} of *cis*-1,4-polybutadiene in its blends with polystyrene. P = in situ polymerization of styrene; M = melt blending; L = latex blending
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shearing at ambient temperature) (line L). In situ polymerization is thus the method of choice for unsaturated rubber (easy cross-linking and grafting by chain transfer) and monomer–rubber pairs with favorable Q, e-values for copolymerizations. In all other cases, blends are formed by melt mixing.

5.3. Toughened Plastics

Rubber-modified plastics (toughened plastics, high-impact plastics) consist of rubber domains dispersed in plastic matrices. The domain size varies with the blending process. Typical values are ca. 0.1 μm for melt-blended poly(vinyl chloride)–acryl rubber and 1 μm for polystyrene–polybutadiene. The domains are often multiphased; small plastic domains are imbedded in the rubber domains (Fig. 10). The morphologies depend strongly on the blending process. During stirred in situ polymerizations, phase inversions often occur if the amount of newly formed plastic approaches that of the incipient rubber. During phase inversion, already present plastic particles may be embedded in the newly formed rubber domains.

Rubber-toughened plastics are valued because of their improved impact strength. On impact, very many crazes are formed near the equators of the rubber particles. The crazes propagate until they encounter an obstacle (e.g., rubber particle or shear band) or until the stress concentration at the tip of the craze becomes very low. Many small crazes result, and the stress is evenly distributed if the rubber phase is cross-linked and binds well to the thermoplast phase [e.g., by in situ formed graft copolymers (HIPS)]. In contrast, stress peaks concentrate at a few defect points in normal thermoplasts.

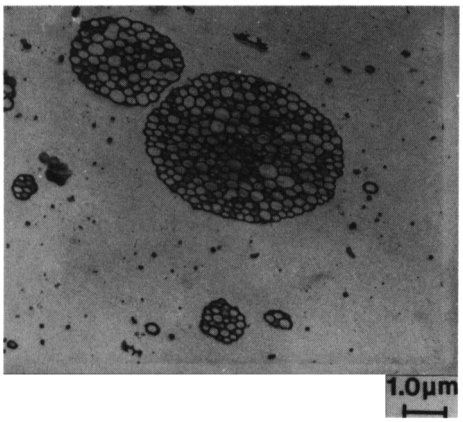


Figure 10. Rubber domains in high-impact polystyrene by in situ free-radical polymerization of styrenic polybutadiene solutions
Reprinted with permission by Society of Plastics Engineers [20]

5.4. Thermoplastic Elastomers (→ Thermoplastic Elastomers)

Thermoplastic elastomers (elastoplastics, thermoplastics, plastomers) are processed like thermoplastics but applied like elastomers. Their unique properties follow from their molecular structures; their chains consist of "soft" and "hard" segments in block, graft, or segmented copolymers composed of monomeric units A and B. The A and B segments are mutually incompatible and form locally separated regions. With a well-designed molecular architecture, domains of the "hard" A segments (transition temperature > service temperature) act as physical cross-links in the continuous matrix of the "soft" B segments (transition temperature < service temperature) (→ Plastics, General Survey, 3. Supermolecular Structures Section 3.6). Such transition temperatures may be glass transition temperatures in amorphous polymers or melting temperatures in partially crystalline polymers. The A segments attain mobility above these transition temperatures and the elastoplasts become processible.

Thermoplastic elastomers comprise linear triblock polymers of the polystyrene–*block*-polydiene–*block*-polystyrene type; radial, star, or "teleblock" polymers of the same monomeric units; urethane segment or block copolymers with polyester or polyether soft segments; polyesteramides and polyesteretheramides; graft copolymers of butyl rubber on polyethylene, vinyl chloride on poly(ethylene-co-vinyl acetate), styrene–acrylonitrile on saturated acryl rubbers, and various ionomers.

Thermoplastic elastomers can also be produced by "dynamic vulcanization." The

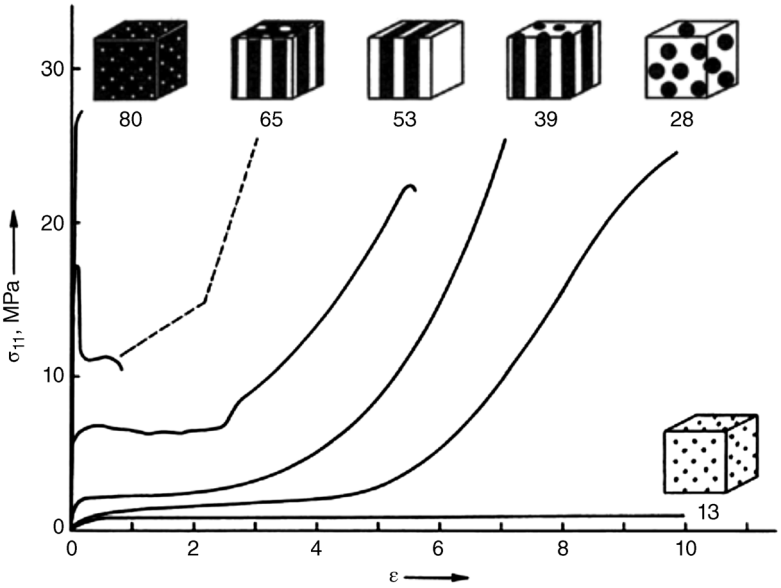


Figure 11. Stress–strain curves and morphologies of styrene–butadiene–styrene triblock polymers with various styrene contents
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mastication of blends of conventional rubbers and crystalline poly(α-olefins) leads to chain scissions. The resulting macroradicals cross-link the rubber domains.

The mechanical properties of thermoplastic elastomers are determined mainly by their morphologies. In styrene–butadiene–styrene triblock polymers, for example, morphologies are governed by the spatial requirements of the various blocks (→ Plastics, General Survey, 3. Supermolecular Structures, Section 3.6). With a low content of hard styrene segments, small spherical polystyrene microdomains are formed in the soft polybutadiene matrix. These microdomains act as physical cross-linkers. The distances between the domains are large, and the polymer behaves as a weakly linked elastomer with correspondingly high extension (Fig. 11). The domains are larger and their distances are shorter at 28% styrene units and the polymer strengthens (stiffens). The stiffening becomes stronger for rodlike styrene domains (39% S). Lamellar morphologies (53% S) show an "unruly" behavior initially because of reorientation of lamellae. At even higher styrene content, the polymer behaves as a plasticized tough thermoplast (65% S) or almost like polystyrene itself (80% S).

6. Expanded Plastics (→ Foamed Plastics) [21, 22]

Expanded plastics (foams, foamed plastics, cellular plastics) are blends of plastics with air. They are subdivided according to their rigidity, their cell structure, and the nature of the parent plastics. Rigid expanded plastics are used mainly for thermal insulation, and flexible foams for damping and cushioning materials.

The rigidity ("hardness") of expanded plastics follows the properties of the parent polymers. Phenolic and urea resins thus yield brittle-rigid plastics; polystyrene and hard poly(vinyl chloride), tough-rigid; and polyethylenes, polyurethanes, and plasticized PVC, semirigid to flexible foams. The elastic moduli of expanded plastics decrease approximately proportional to their polymer content (simple mixing law). Because the stiffness of

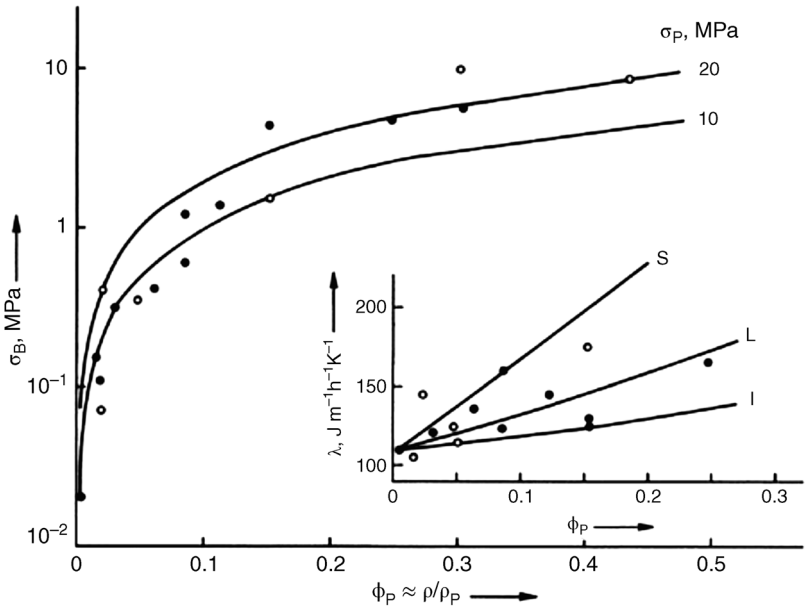


Figure 12. Tensile strengths of expanded plastics as a function of the volume fraction of the rigid (●) or flexible (○) parent polymers P
Solid lines indicate a) Simple mixing law for σ_p = 20 MPa; b) Simple mixing law for σ_p = 10 MPa;
Insert: Thermal conductivities (for λ_p=700 and λ_{air} = 110 J (m^{-1} h^{-1} K^{-1}) of rigid (●) and flexible (○) plastic foams
S: Simple mixing law; L: Logarithmic mixing law; I: Inverse mixing law

an article increases with the third power of the wall thickness, the gases in expanded plastics work as enhancers that reduce material costs and weights.

Tensile strengths of foamed plastics also follow the simple mixing law. Because the tensile strengths of gases are diminishingly small, tensile strengths σ_B of foamed plastics are determined by the volume fraction ϕ_p and strengths $\sigma_{B,p}$ of the plastics themselves [i.e., $\sigma_B \approx \sigma_{B,p} \cdot \phi_p = \sigma_{B,p} \cdot (\rho/\rho_p)$] (Fig. 12). Compression strengths follow a similar simple mixing law.

The cell structure can be open, closed, or mixed. Open-celled foams are always air filled, regardless of the blowing or expanding gases used for foam manufacture. The trapped gases in closed-cell structures can be exchanged with the surrounding air only by slow diffusion through the polymer matrix. Because thermal conductivities of low-density foams ($\rho_p < 0.3$) obey, to a first approximation, a logarithmic mixing law, they are considerably affected by the thermal conductivities of trapped gases [($\lambda = 93$ J m^{-1} h^{-1} K^{-1} (nitrogen), 56 J m^{-1} h^{-1} K^{-1} (CO_2), 26.4 J m^{-1} h^{-1} K^{-1} (CCl_3F)]. The gas exchange is considerably reduced in integral skin foams (dense skin, low-density core) and in syntactic foams (plastics filled with hollow spheres; spheres may be made of glass, ceramics, or plastics and contain either gases or a vacuum).

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Plastics, General Survey, 5. Plastics and Sustainability

ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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1. Plastics and Environment [1–5]

During the first decade of the 21st century, more plastics were produced than during the entire 20th century. The plastics production rapidly increases and follows the growth of the world population. Originally introduced as rather poor imitation of natural materials, such as silk, natural rubber, and ivory, modern plastics have emerged as advanced materials with tailored property profiles, which is unparalleled in nature. Synthetic polymers are engineered to meet the demands of diversified technologies ranging from food packaging to textiles, shelter, communication, mobility, and health care. Plastics play an important role in daily life. Without plastics, the high quality of modern life with secure supply of food, water, and energy would not be feasible. Highly cost-efficient and versatile polymeric materials have made hightech affordable for people of all income groups. At present, plastics production consumes around 5% of the world's fossil resources, which is equivalent to about 60% of the petrochemical production. At present around 90% of the world's fossil resources are burned in energy production accompanied by severe emission of carbon dioxide, which contributes to global warming and climate change. The emission of greenhouse gases, i.e., carbon dioxide and methane, is also being referred to as carbon footprint. More than 30% of durable plastics are used in packaging, such as bags, wraps, and bottles, all of which possess short product life of a few months. According to the statistics of the U.S. Environmental Protection Agency (EPA), around 251×10^6 t of municipal trash composed of paper (27.4%), food wastes (14.5%), yard trimmings (13.5%), plastics (12.7%), metals (8.9%), rubber, leather, and textiles (8.7%), wood (6.3%), and glass (4.6%) were created in the United States in 2012. Archaeological studies of landfills have revealed that the biodegradation processes of synthetic polymers and biopolymers are very slow in landfills, especially in the absence of light, air, and water. Some buried newspapers could be read after residing for 25 years in a landfill. Clearly, recycling and incineration are the only possible ways for disposing of plastics. Because most plastics have an oillike, high energy content, plastic wastes are valuable raw materials that need to be reused. While in 2012 the plastics recycling and energy recovery reached 61.9% in Europe, it was around 9% in the United States (for comparison: paper recycling reaches 50% in

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the United States). When plastic recycling fails, the consequences of littering are clearly visible in nature. Driven by marine and wind currents, nontoxic plastics debris together with hazardous chemical sludge accumulate in the ocean, in particular in a region known as the northern pacific garbage vortex. Addressing high sustainability is an important issue in plastics development. As stated in 1987 by the Brundtland Commission of the UN General Assembly, sustainability means meeting the needs of the present without compromising the ability of future generations to meet their own needs. High resource-, eco-, and energy efficiency of plastics together with their low carbon footprint and high energy content, typical for the large-scale commodity plastics, holds great promise for achieving high sustainability. Efficient plastics recycling, exploiting renewable feedstocks, and especially tailoring advanced polymeric materials for sustainable development are important tasks in the plastics industry.

2. Green Polymer Chemistry [6, 7] and Life Cycle Assessment [8]

According to the definition by Anastas, important elements of green chemistry include high resource effectiveness by maximizing the content of raw materials in the product; clean and lean production processes; catalytic reactions at ambient temperature and pressure; preventing wastes and reducing greenhouse gas emissions; high safety standards; no use of auxiliary substances, such as organic solvents, blocking groups etc.; low energy demand of production and processing; no health and environmental hazards by substituting toxic chemicals; using renewable resources; low carbon footprint; and controlled product life cycles with effective waste recycling. This definition of "green" is not at all synonymous with biomaterials and biotechnology.

An important tool for assessing the environmental impact of materials is the life cycle analysis, which is also referred to as ecobalance, cradle-to-grave analysis, and life cycle assessment (LCA). LCA addresses the environmental aspects of all stages of a product's life time from feedstock recovery to monomer and polymer manufacturing, processing, distribution, use, maintenance, disposal, and recycling. Taking into account all relevant materials and energy inputs and output together with environmental aspects, the following LCA ranking of plastics was determined in 2010, yielding the best marks for polyolefins:

1. Polypropylene (PP),
2. High-density polyethylene (HDPE),
3. Low-density polyethylene (LLDPE).

The LCA ranking of bio-based polylactic acid (rank 9) was similar to that of PVC (rank 7). According to LCA, converting petrochemical plastics into green plastics by using renewable feedstocks lowers the LCA ranking. The success of polyolefins, such as PP, HDPE, and LLDPE is clearly associated with significant progress made in polyolefin production since the 1950s. The polyethylene life cycle is displayed in Figure 1. Produced in solvent-free catalytic polymerization processes with low energy demand using a highly active stereospecific catalysts, polyolefins are readily tailored to meet the demands of diversified applications ranging from food packaging to baby diapers, carpets, and automotive bumpers. Modern reactor granule technology produces pellet-sized polyolefin particles, which eliminates pelletizing extrusion. The heat of polymerization can be used as power generator. No water and no purification are required. This is in contrast to biotechnology processes and to pulping. The latter has very high water demand and produces byproducts, such as organic compounds and salts. Compared with paper, LLDPE packaging has much lower mass and is easy to process by blow molding. After completing their product life, polyolefins are readily recycled by mechanical, feedstock, and energy recycling. As hydrocarbon resins, they have oillike energy content. On heating above 300°C, they are converted into oil and gas, which are valuable sources for feedstocks and energy. The raw materials of polyolefins are highly flexible. Virtually any carbon source, ranging from oil, gas, and coal to biomass and bioethanol, can be employed in polyolefin production.

From the LCA it is apparent that the substitution of plastics packaging by paper and other materials would substantially increase mass, energy demand, and greenhouse gas emission.

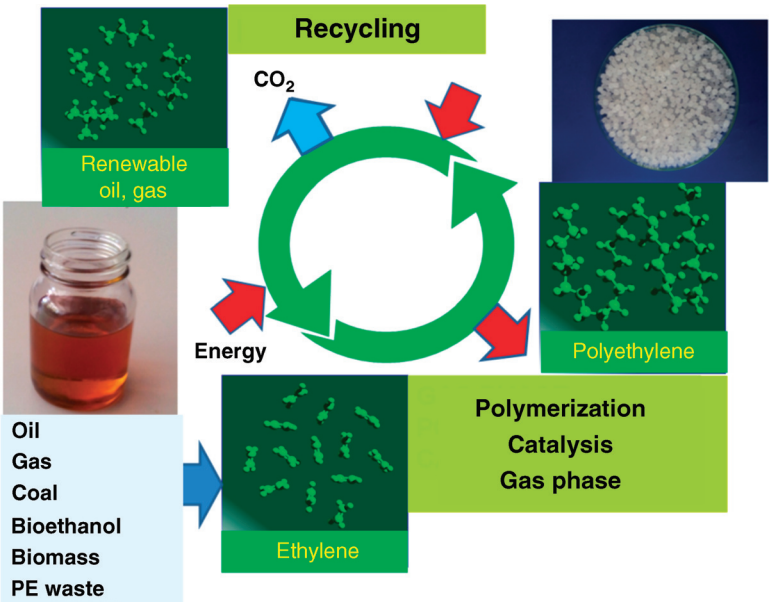


Figure 1. Life cycle of polyethylene

Contrary to the public opinion, increased use of plastics reduces the greenhouse gas emission, whereas the substitution of plastics by other materials would have a stringent detrimental environmental impact and drastically enhance greenhouse gas emissions. At the end of their service life, plastics wastes are too valuable to be thrown away.

3. Plastics Waste Recycling

3.1. Mechanical Recycling [9, 10]

For identification and for facilitating their recycling, plastic products bear special codes consisting of label with three broken arrows, arranged in a triangle, and a number, sometimes also combined with letters and/or bar code. The numbers and letter combinations indicate the type of plastics. The letter combinations are not always identical with the acronyms and abbreviations recommended by ISO, ASTM, DIN, IUPAC, etc., for the same polymers. The following number and letter codes are used:

- 1 = PET [poly(ethylene terephthalate)]
- 2 = HDPE (high-density polyethylene)
- 3 = PVC [poly(vinyl chloride)]
- 4 = LDPE (low-density polyethylene)
- 5 = PP (polypropylene)
- 6 = PS (polystyrene)
- 7 = for all other plastics, including multilayered materials

Different waste management systems have been established to collect and sort wastes from different applications, such as packaging, automotive, electronics, and construction. A large variety of waste-pretreatment and sorting technologies are in place including shredding, magnetic separation, flotation, and air separation assisted by plastics identification by spectroscopy, such as near infrared sensing.

Especially when plastics wastes are clean and composed of as single type of plastics, mechanical recycling is attractive. In thermoplastics mechanical recycling, wastes are sorted, purified, and extruded to produce granulates. For example, mechanical recycling converts PET bottle waste into new PET bottles or PET textile fleeces for jackets. Due to polymer ageing by degradation and autoxidation during product life and recycling, most recycled plastics are somewhat inferior with respect to the corresponding virgin plastics. Therefore, most

recycled plastics are blended together with virgin polymers in mechanical recycling. Because most polymers are highly immiscible, mechanical recycling of mixed plastics wastes produces blends, which require the addition of compatibilizers. Because cross-linked plastics do not melt, they can be recycled by grinding. Recycled thermoset resin powders or ground rubber are used as organic fillers for thermoset or rubber formulations.

3.2. Feedstock Recycling [10, 11]

During pyrolysis plastics are broken down at elevated temperatures in the absence of air to produce liquid and gaseous fragments. Thermolysis is of particular interest for recycling highly polluted complex plastic mixtures. In the case of PVC, HCl is formed and removed by washing the thermolysis gases with water. Hydrocarbons, such as polyolefins, are readily thermolyzed to produce oil and gas in essentially quantitative yields. Plastics, such as polyoxymethylene and poly(methyl methacrylate) are thermally depolymerized to recover the corresponding monomers. On thermolysis, carbohydrates decompose to form a considerable amount of water and ashes. Whereas pyrolysis requires rather high temperatures, typically above 500°C, catalytic liquefaction converts biomass and plastics wastes into diesel fuel at temperature well below 500°C. In this process, water is catalytically converted into hydrogen, which improves the yield of low molecular mass hydrocarbons by hydrogenation. In sharp contrast, hydrogenation of plastics wastes and distillation residues in oil refinery require much higher hydrogen pressure and temperature. The presence of hydrogen increases the amount of liquid hydrocarbon. In the case of biomass and biopolymers, anaerobic digestion can be employed to convert biowastes into methane or bioethanol. Lignocellulose from forestry and agricultural wastes is an attractive source of sugar that serves as raw material for biorefineries without competing with food production.

When small amounts of oxygen are present, gasification by incomplete combustion converts plastics into a mixture of carbon monoxide and hydrogen (syngas), which can be used as feedstock for producing a variety of chemicals and monomers in refineries. Similar to the Fischer–Tropsch process for coal-to-liquid conversion, this process can also be applied to biomass (biomass-to-liquid conversion) and plastics wastes. Moreover, syngas is of interest as reducing gas for metal oxide ores in steel mills, thus substituting oil and gas. Polycondensates, such as polyesters and polyurethanes are readily cleaved by hydrolysis and glycolysis, thus recovering monomers useful in polycondensation reactions.

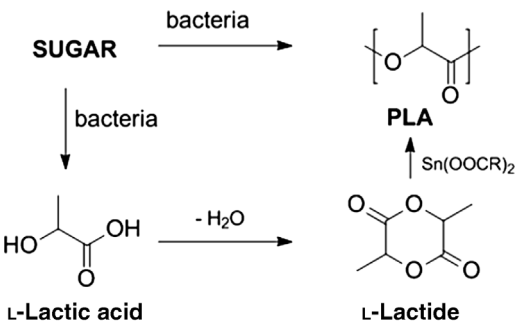
3.3. Energy Recycling [9–11]

Taking into account the high energy content and hydrocarbon nature of commodity plastics, in many countries incineration is the preferred method for municipal waste recycling, which does not need extensive sorting and purification of the plastics wastes. In fact, the plastics wastes represent an attractive source of energy for the combustion of municipal wastes, which contain components with much less energy content. In contrast to inorganic wastes and biomass, commodity plastics do not form large amounts of ashes but completely decompose to produce gas and heat. For many years, public fears concern the formation of dioxin by waste incineration. Today, the incineration off-gases are carefully purified to remove gaseous and dustlike particulate pollutants. This includes the catalytic conversion of dioxin and furan traces. Incineration is the preferred process for disposing of hazardous wastes containing microorganisms, toxins, or chemicals.

3.4. Biodegradation and Bio-based Plastics [7, 12–16, 17] (→ Polymers, Biodegradable)

In the early 1900s, all plastics were bio-based because carbohydrates and proteins were the only industrially available feedstocks for plastics production. Because abundant biopolymers, such as cellulose, are infusible and insoluble, extensive chemical modifications are required to enable

melt and solution processing of cellulosics. Within very short time during the first half of the 20th century, the emerging highly versatile and low-cost synthetic plastics, based on fossil feedstocks and petrochemistry, have outperformed biopolymers and conventional bio-based plastics. In spite of the ongoing commercial significance of natural rubber, claiming 40% of the rubber market, and the successful development of wood plastics compounds and natural fiber reinforced composites, the total biopolymer share of the annual world's plastics production is still below 5%. However, there is a renaissance of the use of renewable and natural resources as well as the development of biopolymers. In view of the dwindling fossil resources, which are rapidly being depleted in energy production, the shift from fossil to renewable resources is thought to safeguard plastics production against an expected future oil crisis. Moreover, the growing consumers' concerns regarding global warming and the fear that a collapse of the biosphere is imminent, stimulate the surging demand for renewable and bio-based products. Because most natural polymers still fail to match the performance of synthetic polymers, synthetic plastics are rendered "green" and bio-based by using renewable raw materials for the production of monomers. For example, bioethanol is converted into ethylene and propene, which are polymerized in highly efficient gas phase processes to afford "green" polyolefins, which have properties equivalent to petrochemical polyolefins. In contrast to bacterial poly-L-lactic acid (PLA), which requires separation of PLA from cell proteins and water recovery, the solvent-free ring-opening polymerization of bio-based dilactide affords much better control of polymer properties, such as crystallization rate and shear thinning.



In life cycle assessment, most bio-based products have lower performance with respect to the corresponding petrochemical products due to the additional process steps. Moreover, in many industrialized countries the biomass supply is insufficient to substitute oil in energy and plastics production. PLA, polyolefins, or paper are not completely biodegradable in landfill, especially when air and water are absent. In contrast to the public opinion, biodegradation and bioerosion, which are highly dependent on the climate, do not instantaneously degrade biopolymers to produce carbon dioxide and water. Instead, biodegradation makes polymers brittle. They disintegrate to form tiny particles, invisible for human eyes, which are carried away by wind or rain and serve as breeding ground for spores and bacteria. Because the label "biodegradable" stimulates consumers to carelessly dump wastes and ignore recycling efforts, biodegradable plastics are contra productive to recycling. Moreover, the high energy content of polymers is wasted during biodegradation in landfill. Hence, biodegradable polymers do not seem to be the universal solution to the plastics waste problem. Yet, they offer prospects for special applications like bioresorbable implants, surgical sutures, drug release, as well as agricultural films and packaging. Today, it is well recognized that the surging biomass demand in bioenergy production, accompanied by extensive farming of energy crops, endangers both the biosphere and the food supply of the rapidly growing world population. Many industrialized countries do not have enough biomass to serve the need of both energy and plastic production.

3.5. Plastics from Carbon Dioxide [7, 18] (→ Carbon Dioxide 12.4.10. Polymers from Carbon Dioxide)

In order to prevent a conflict with food production, several successful attempts have been made to exploit the direct chemical fixation of carbon dioxide in plastics production. Because carbon dioxide is the energy sink in the combustion process, it must be activated in order to be useful in polymer production. In copolymerization this is achieved by reacting

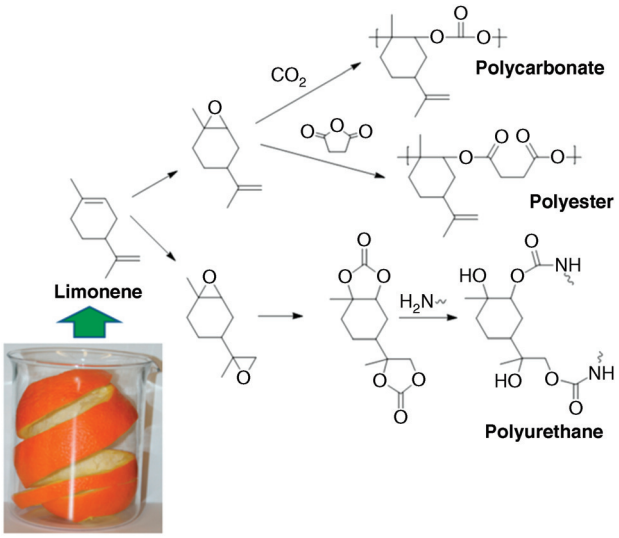


Figure 2. Bio-based polyesters, polycarbonates, and nonisocyanate polyurethanes from orange peels
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carbon dioxide with energy-rich highly strained oxirane and oxetane rings, thus producing polyfunctional cyclic carbonates and linear polycarbonates. Dihydroxy-terminated poly(propylene ether carbonates) are of special interest as polyols in polyurethane synthesis. Polyfunctional cyclic carbonates, prepared by reacting epoxy resins with carbon dioxide, are attractive intermediates for the isocyanate- and phosgene-free production of hydroxyl-functional polyurethanes (NIPU for nonisocyanate polyurethane). Biowastes, such as orange peels can be used as a source of limonene, which upon oxidation and carbonation affords mono- and difunctional cyclic carbonates as intermediates for bio-based polyesters and NIPU (Fig. 2). Electrochemical processes are developed to exploit excess renewable energy supplied by wind mills and solar power plants to convert carbon dioxide into methane, which is useful as chemical storage of renewable energy, as fuel, and as intermediate for the production of chemicals and plastics.

4. Polymers for Sustainable Development [7]

In many ways plastics serve the needs of sustainable development. Produced in highly energy- and resource-efficient polymerization processes, plastics have low carbon footprint and preserve high oillike energy content. After completing their product life, they are mechanically recycled or serve as valuable source of energy and feedstocks. This attractive balance of low energy demand during production and processing combined with low carbon footprint and high energy content is typical for all large-volume commodity and most engineering plastics and rubbers, amounting to more than 90% of the world's plastics production. Among them, hydrocarbon plastics, such as polypropylene and polyethylene, produced by solvent-free catalytic polymerizations processes, meet the demands of green chemistry and achieve top rankings in life cycle assessment. Moreover, plastics have a low mass and are corrosion resistant. In lightweight engineering and packaging, polymeric materials contribute to considerable weight savings, thus reducing fuel consumption and dioxide emission in transportation. Moreover, unparalleled by other materials, plastics are highly versatile with respect to tailoring property profiles, processing, and applications. Owing to their low mass together with thermal and electrical insulation, plastics contribute to high energy efficiency and secure the supply of food, water, and energy. Although plastics consume around 5%

of fossil fuels, they help to preserve close to 20% oil by thermal insulation and mass reduction in transportation. As advanced functional materials and integrated into systems, polymers bring high resource efficiency to a variety of applications ranging from lightweight engineering to health care. For example, as filters and membranes, functional plastics enable water and air purification, water desalination, and recovery of precious metals from wastes. This unique combination of high cost-, eco-, resource-, and energy efficiency with high versatility typical for most plastics holds great promise for sustainable development.

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Plastics, Analysis

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ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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1. Introduction

The polymeric chains of most industrially and economically important plastics are built up from only a small number of elements: mainly C, H, O, N, Cl, F, and Si. Nevertheless, plastics analysis constitutes an extremely complicated and wide-ranging field that requires the application of many chemical and physical analytical methods.

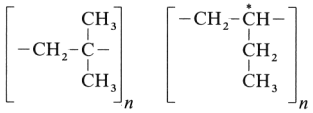
The subject of plastics analysis is treated here in terms specifically of the analysis of polymer chains. Most plastics – that is to say, materials formulated on the basis of synthetic polymers – contain significant amounts of additives such as pigments, plasticizers, stabilizers, and fillers, but analysis of these secondary components constitutes a separate field of study. In certain cases the desirable properties of a particular plastic arise only during the course of subsequent thermal or mechanical treatment associated with shaping or molding. There has also been increasing interest in the determination of polymer degradation products and monomer residues.

The fundamental problem in plastics analysis is the heterogeneity of macromolecular materials with respect to molecular mass and the numerous isomeric possibilities open to a polymeric chain.

For example, vinyl chloride is a gas under normal conditions, but its lower oligomers are liquids, and poly(vinyl chloride) is a solid. Thus the physical, physicochemical, and applications characteristics of a particular batch of poly(vinyl chloride), such as solubility, crystallinity, strength, and elasticity, are a function not only of the structure of the polymeric chain, but also of the degree of polymerization.

Isomerism. The empirical formula obtained by elemental analysis (see Section 4) is generally of little help in the precise identification of a plastic or a polymer. This is due to the constitutional, configurational, and conformational isomerism characteristic of a polymer chain, which is reflected in a structure that can be described at primary through quaternary levels. Thus, an empirical formula such as $(C_4H_8)_n$ is equally valid for achiral polyisobutene and its positional isomer poly(1-butene), which contains a series of pseudoasymmetric carbon atoms (C^*).

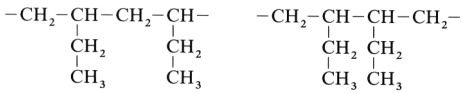
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Poly(isobutene) Poly(1-butene)

Polymolecularity in a polymer is another form of constitutional isomerism, which results from the stochastic character of the polymerization reaction but can also arise from decomposition, aging, or cross-linking reactions that occur during processing or utilization. The determination of polymolecularity is discussed in Chapter 5.

Another source of constitutional isomerism may be the way in which monomer units are linked, although head-to-tail linkage usually predominates. An example is poly(1-butene):



head-to-tail head-to-head

Apart from the nature of polymer end groups and the extent of branching, the sequence of structural units within the polymer chain is also of major importance. Analysis of sequential structure is treated in Section 4.3 and Chapter 6.

Plastics that contain pseudoasymmetric carbon atoms in their polymer chains, such as poly (1-butene), can also exhibit *configurational isomerism*. The sequence of such pseudoasymmetric C atoms has a major effect on properties such as melting point, glass transition temperature, and crystallinity. There is also isomerism of the *cis – trans* type to be considered in the case of unsaturated polydienes, whose structural units include C=C double bonds. The number of possibilities for isomerism – and thus the analytical challenge – increases dramatically on moving from homopolymers to copolymers. Analysis of configurational isomers is the subject of Section 6.2.

As a result of the wide diversity in types of plastic materials and the range of potential problems, it is impossible to describe a single general scheme for polymer analysis. Both the number of questions that might be raised regarding the nature of a completely unknown polymer and the catalog of applicable analytical methods are very extensive. However, it is often possible to monitor product quality by determining a single structural property by means of a standardized analytical method. The scope and complexity of an analytical investigation is thus a direct function of the nature of the question.

The most superficial description of an unknown plastic must include some characterization of the *primary structure :* chemical composition, molecular mass and molecular mass distribution, and the sequential arrangement of subunits. This leads to the following series of analyses for identifying an unknown plastic:

1. Determination of solubility (Chap. 2)
2. Isolation of macromolecular components (Chap. 2)
3. Preliminary tests for polymer identification (Chap. 3)
4. Chemical analysis (Chap. 4)
5. Molecular mass determination (Chap. 5)
6. Sequence analysis (Chap. 6)
7. In the case of a copolymer, analysis of chemical heterogeneity (Chap. 7)

For a discussion of structure at the secondary through quaternary levels (e.g., conformation, orientation, and crystallinity), see → Plastics, Properties and Testing.

Literature. Plastics analysis is treated in detail in various standard works [1–26]. There also exists an extensive specialized literature [27–63] devoted to specific problems (e.g., analysis of silicones [51], or fiber-reinforced plastics [52], which is further supplemented by tabular works [53] and data from handbooks [54–57]. The review literature should be consulted for more recent developments in plastics analysis, especially with respect to highly specialized questions [58], [59]. For the analysis of selected additives, see [60–63].

2. Polymer Isolation

Solubility is the basis for preliminary separation of a plastic into polymer components and additives. Insoluble fillers and pigments can be removed from a polymer solution by filtration or centrifugation. A plastic that is received in the form of a solution, emulsion, or suspension must first be dried by evaporation of low

molecular mass solvents; nonvolatile additives remain in the residue.

A polymeric material that is to be extracted or brought into solution for analytical investigation should be first converted into the most finely divided state possible. Prior freezing of plastic or elastic samples in liquid nitrogen often facilitates size reduction.

Solubility. Polymers and solvents are miscible only if the corresponding free energy of mixing is negative [64], [65]:

$$\Delta G_{cm^3} = \frac{RT}{V_s}\left(\Phi_s \ln\Phi_s + \frac{\Phi_p}{m}\ln\Phi_p + \mu\Phi_s\Phi_p\right) \quad (1)$$

G_{cm^3} Gibbs free energy of mixing per cm^3 solution
V_s Molar volume of solvent
Φ Volume fraction (s = solvent; p = polymer)
m Ratio of molar volumes of polymer and solvent
μ Constant

The interaction parameter μ is a function of temperature that takes into account the enthalpy of mixing. Miscibility can be anticipated for any polymer – solvent system in which $\mu<0.5$. In the case of an amorphous polymer it is possible to ignore, to a first approximation, the change in entropy, which is the justification for focusing here strictly on the enthalpy of mixing. In the expression:

$$\Delta H_{cm^3} = \Phi_s\Phi_p\left[(E_s/V_s)^{1/2} - (E_p/V_p)^{1/2}\right]^2 \quad (2)$$

ΔH_{cm^3} Enthalpy of mixing for 1 cm^3 solution
Φ Volume fraction
E Molar cohesion energy
V Molar volume

the term E/V is referred to as the cohesion energy density, from which can be derived the solubility parameter $\delta = \sqrt{E/V}$. The following list gives δ values for various polymers and solvents.

Polymers	
Polyethylene	7.9
Polyisoprene	7.9
Polyisobutylene	8.05
Styrene rubber	8.60
Polybutadiene	8.6
Polystyrene	8.7
Neoprene	9.2
Poly(dimethyl siloxane)	9.4
Nitrile rubber	9.5
Poly(vinyl chloride)	9.7
Poly(methyl methacrylate)	10.2
Cellulose acetate	10.9
Nylon 66	14.5
Poly(vinyl alcohol)	23.4
Solvents	
Heptane	7.43
Diethyl ether	7.70
Cyclohexane	8.25
Carbon tetrachloride	8.62
Benzene	9.21
Chloroform	9.40
Chlorobenzene	9.70
Acetonitrile	9.75
Acetone	9.89
Dichloromethane	10.04
Carbon disulfide	10.10
Dioxane	10.15
Methanol	14.48
Water	23.41

Solubility can be expected when polymer and solvent have comparable solubility parameters. Such δ values provide useful orientation in a search for a suitable solvent, although many exceptions are known, attributable to such factors as molecular mass, degree of branching and cross-linking, configuration, and crystallinity.

Precipitation. A considerable degree of polymer purification can often be achieved by precipitation with a precipitating agent, a process that may need to be repeated several times. However, some oligomers may remain in solution, as a result of which precipitation may cause a change in the molecular mass distribution.

If a plastic and a solvent have different δ values the plastic will be insoluble in that solvent. Therefore, addition of such a solvent to a polymer already dissolved in another solvent should lead to precipitation. Methanol is a poor solvent for most polymers but miscible with many other organic solvents, so it is frequently used as a precipitating agent. Generally, the lower the molecular mass of a plastic, and the more atactic or amorphous it is, the higher its solubility. Raising the temperature also leads to an increase in solubility. Appropriate solvents and precipitating agents have been established empirically for a wide range of plastics; for a tabular summary see [53].

If precipitation proves unsuccessful for the removal of additives it is usually necessary to resort to preparative chromatography [66–68].

Extraction. Plastics can be extracted with organic solvents either in a Soxhlet apparatus or in a high-pressure extractor with supercritical solvents such as CO_2. Extraction is the method of choice for pretreatment of an insoluble plastic. A prerequisite to success is finding an extractant that will dissolve the additives at the temperature of operation but act as a nonsolvent for polymeric components. If necessary, several extractants can be utilized in sequence, although inorganic fillers or pigments that are insoluble in organic solvents will always remain in the sample after extraction (see Table 1).

3. Preliminary Tests for Polymer Identification

Once a set of macromolecular components has been isolated, characterization can begin on the basis of physical methods. Powerful and rapid spectroscopic procedures are now available for establishing chemical structure, although their successful utilization presupposes access to the required instrumentation and an appropriate data base. In the absence of such information it may still be possible to narrow the range of structural possibilities in relatively simple ways.

Analysis is most straightforward for soluble polymers. A material consisting of a mixture of various polymers must first be separated into its macromolecular components, preferably by preparative chromatography [66–71] or precipitation. Such a separation may prove problematic in the case of a copolymer, since separability then becomes a function of heterogeneity with respect to both molecular mass and chemical composition of the polymer molecules (see Chap. 7).

Density. Density measurements are conducted either with a pycnometer or on the basis of buoyancy. A rough determination of density can be made by introducing an unknown sample into a series of nonsolvents of known density. By using Figure 1, the nature of the material can then be established with a reasonably high degree of certainty. Crystalline polymers are generally denser than amorphous materials. Density can also be affected by the presence of fillers. Density measurements on plastic materials that contain entrapped gases (e.g., foams) must be preceded by melting or precipitation.

Combustion Characteristics. The combustibility of a plastic can be investigated in the flame of a Bunsen burner. Apart from distinguishing between flammable and inflammable materials, it is also important to observe whether a substance burns only while it is in the flame or if burning persists outside the flame as well. Table 2 provides an overview of flammability characteristics for various plastics.

Thermal Degradation. Pyrolysis behavior and the characteristics of a pyrolyzate give further information on the nature of an unknown plastic. The sample is heated to redness in a pyrolyzer (Fig. 2). Volatile products are either condensed or collected in a cotton wool filter. Approximately 100 mg of sample is sufficient for this analysis.

The nature and odor of a pyrolyzate can be characteristic for a particular polymer. Highly volatile pyrolyzates are produced by polystyrene, polyisobutene, polybutadiene, and polyacrylates. Oily, resinous, or waxy products arise from polyethylene, polypropylene, and poly(1-butene) as well as from copolymers of styrene with butadiene and acrylonitrile. Black carbonaceous residues result from the pyrolysis of cellulose and its derivatives, as well as from poly(vinyl chloride) and resins.

Formation of ammonia suggests a polyamide or a resin based on urea, melamine, aniline, or casein. Pyrolyzate with a pungent odor is released by poly(vinyl chloride), polyacrylates, and poly(vinyl formates).

The combination of pyrolysis with hydrogenation of the resulting fragments, followed by gas chromatographic separation and identification,can provide considerable information on the sequential structure of a polymer (see Section 6.3).

4. Chemical Analysis

4.1. Heteroelements and Functional Groups

Heteroelements. In conjunction with quantitative analysis for the principal elements C and H, the potassium fusion test for heteroelements remains a very important analytical technique [3] (see Table 3). Roughly 100 mg of a finely divided plastic is fused in a test tube with a pea-sized portion of potassium, heated to a red glow,

Table 1. Solubility of common plastics and polymers [14]*

Plastic/polymer	Soluble in	Insoluble in
Alkyd resin	chlorinated hydrocarbons, lower alcohols, esters	hydrocarbons
Amine – formaldehyde resin, cured	benzylamine (60 °C), ammonia	
Methyl cellulose	water, dilute sodium hydroxide, dichloromethane, methanol	acetone, ethanol
Cellulose esters	ketones, esters	aliphatic hydrocarbons, water
Cellulose nitrate	lower alcohols, acetic esters, ketones	ether, benzene, chlorinated hydrocarbons
Chlorinated rubber	esters, ketones, carbon tetrachloride, tetrahydrofuran	aliphatic hydrocarbons
Chloroprene rubber	toluene, chlorinated hydrocarbons	alcohols
Polychlorotrifluoroethylene	hot fluorinated solvents	all common solvents
Poly(vinyl chloride)	dimethyl formamide, tetrahydrofuran, cyclohexanone	alcohols, butyl acetate, dioxane, hydrocarbons
Chlorinated poly(vinyl chloride)	dichloromethane, cyclohexane, benzene, tetrachloroethylene	
Poly(vinylidene chloride)	tetrahydrofuran, ketones, butyl acetate, dimethylformamide (hot), chlorobenzene	alcohols, hydrocarbons
Acrylonitrile – butadiene – styrene copolymer	dichloromethane	alcohols, water, aliphatic hydrocarbons
Styrene – butadiene copolymer	ethyl acetate, benzene, dichloromethane	alcohols, water
Rubber	chlorinated and aromatic hydrocarbons	oxygen-containing solvents
Polytetrafluoroethylene	fluorocarbon oil (hot)	all solvents
Poly(vinyl fluoride)	above 110 °C: cyclohexanone, propylene carbonate, dimethyl sulfoxide, dimethylformamide	
Poly(vinylidene fluoride)	dimethyl sulfoxide, dioxane	
Phenolic resin	alcohol, ketones	chlorinated hydrocarbons, aliphatic hydrocarbons
Polyacrylamide	water	alcohols, esters, hydrocarbons
Polyacrylonitrile	dimethylformamide, butyrolactone nitrophenol, dimethyl sulfoxide, mineral acids	alcohols, esters, ketones, formic acid, hydrocarbons
Polyacrylates	aromatic hydrocarbons, esters, chlorinated hydrocarbons, acetone, tetrahydrofuran	aliphatic hydrocarbons
Polymethacrylates	aromatic hydrocarbons, dioxane, chlorinated hydrocarbons, esters, ketones	ether, alcohols, aliphatic hydrocarbons
Polyamides	phenols, formic acid, conc. mineral acids	alcohols, esters, hydrocarbons
Polybutadiene	aromatic hydrocarbons, cyclohexane, dibutyl ether	alcohols, esters
Polycarbonates	chlorinated hydrocarbons, dioxane, cyclohexanone	alcohols, aliphatic hydrocarbons, water
Polyesters, unsaturated, uncured	ketones, styrene, acrylic esters	aliphatic hydrocarbons
Poly(ethylene terephthalate)	cresol, conc. sulfuric acid, chlorophenol	
Polyethylene	dichloroethylene, tetralin, hot hydrocarbons	polar solvents, alcohols, esters
Poly(ethylene glycol)	chlorinated hydrocarbons, alcohols, water	aliphatic hydrocarbons
Polyformaldehyde	hot solvents, phenols, benzyl alcohol, dimethylformamide	alcohols, ketones, esters, hydrocarbons
Polyisoprene	benzene	alcohols, ketones, esters, hydrocarbons
Polypropylene	at high temperature: aromatic and chlorinated hydrocarbons, tetralin	alcohols, esters, cyclohexanone
Polystyrene	aromatic and chlorinated hyrocarbons, pyridine, ethyl acetate, methyl ethyl ketone, dioxane, tetralin	alcohols, water, aliphatic hydrocarbons
Polyurethane	tetrahydrofuran, pyridine, dimethylformamide, formic acid, dimethyl sulfoxide	ether, alcohols, benzene, water, hydrogen chloride (6 N)
Poly(vinyl acetal)	esters, ketones, tetrahydrofuran	methanol, aliphatic hydrocarbons
Poly(vinyl formal)	dichloroethane, dioxane, glacial acetic acid, phenols	aliphatic hydrocarbons
Poly(vinyl acetate)	aromatic and chlorinated hydrocarbons, acetone, methanol, esters	aliphatic hydrocarbons
Poly(vinyl alcohol)	formamide, water	ether, alcohols, esters, ketones, aliphatic and aromatic hydrocarbons

* For comprehensive table, see [14].

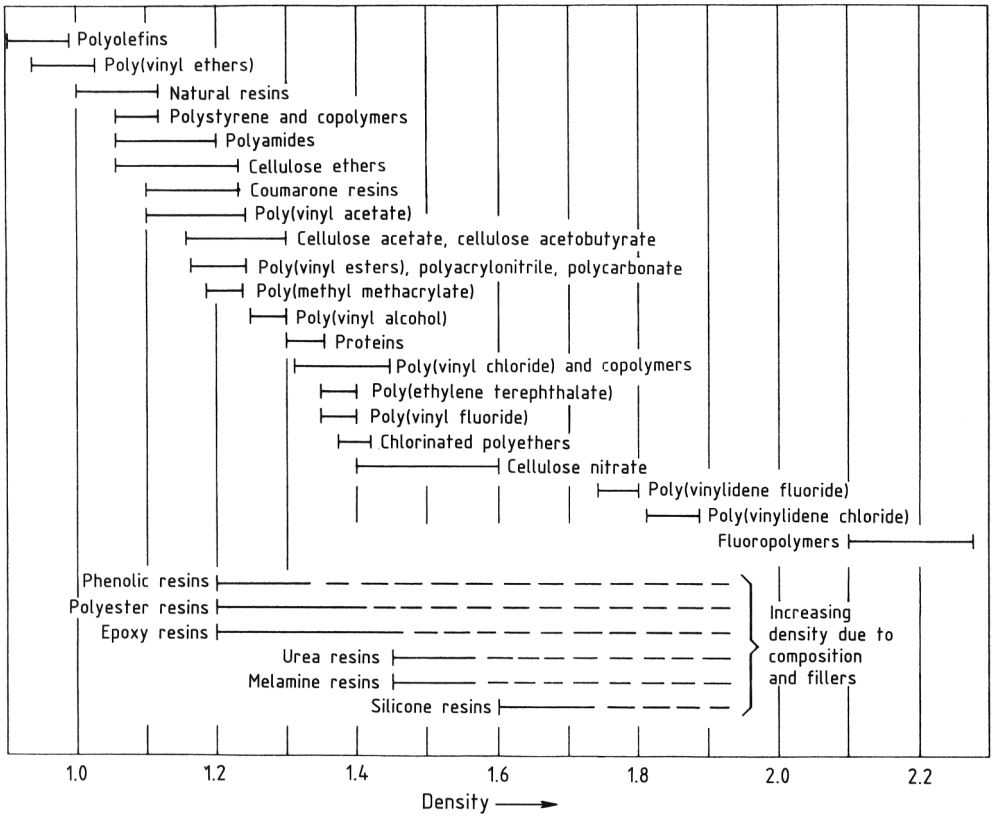


Figure 1. Density of plastics [62]

and then quenched in 10 cm^3 of water. The resulting solution is filtered and divided into six equal portions for the identification of Cl, F, N, S, P, and Si.

Chlorine. The filtrate is acidified with HNO_3 and treated with $AgNO_3$ solution; a white precipitate soluble in ammonia indicates chlorine.

Table 2. Flammability of plastics and polymers [14]

Nonflammable	Self-extinguishing	Flammable
Polychlorotrifluoroethylene	poly(vinyl chloride)	polyolefins
Polytetrafluoroethylene	vinyl chloride copolymers	polystyrene
Chlorinated poly(vinyl chloride)	poly(vinyl fluoride)	copolymers of styrene
Urea resins	polyvinylcarbazole	poly(vinyl ethers)
Melamine resins	polyvinylpyrrolidone	poly(vinyl esters)
Silicone resins	polyacrylonitrile	poly(vinyl alcohol)
	filled phenolic, epoxy, and polyester resins	polyacrylates
		polyamides
		polycarbonates
		poly(ethylene terephthalate)
		polyurethanes
		cellulose
		alkyd, coumarone, phenolic, epoxy resins

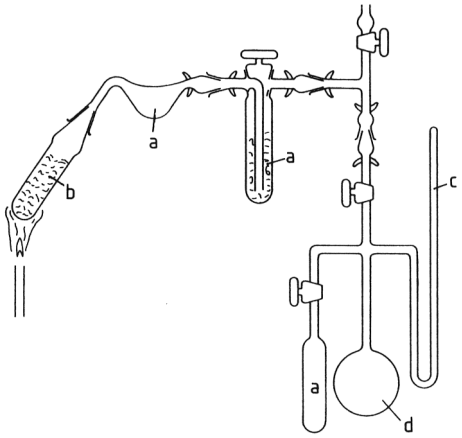


Figure 2. Pyrolysis of plastics by vacuum distillation [3] a) Condensate traps; b) Sample; c) Manometer; d) IR sample cell

Fluorine. After acidification with HCl the solution is treated with $CaCl_2$ solution; a white precipitate of CaF_2 is characteristic of fluorine.

Nitrogen. The solution is treated with a spatulafull of $FeSO_4$, boiled, cooled, and a few drops of $FeCl_3$ solution are added. A precipitate of Prussian blue upon acidification with HCl indicates nitrogen.

Sulfur. The cold solution is treated with a freshly prepared solution of sodium prussiate. A deep violet color represents a positive test for sulfur.

Phosphorus. Acidification of the solution with HNO_3 and addition of a few drops of ammonium molybdate solution results in a yellow precipitate in the presence of phosphorus.

Silicon. The polymer sample is boiled with a mixture of sulfuric and nitric acids and then evaporated. The residue is pyrolyzed to SiO_2, which is fumed with a mixture of sulfuric and hydrofluoric acids. Appearance of a white precipitate on a moist piece of black paper is evidence of silicon.

Functional Groups. Chemical tests for heteroelements are supplemented by tests for specific functional groups. In addition to establishing the presence of C=C double bonds by Br_2 addition, determination of the saponification number is useful. For this purpose a known amount of plastic is dissolved in alcohol, benzene, or toluene, and refluxed for 2 – 3 h with a known excess of 1 N KOH. The excess alkali is then determined by back-titration with 1 N HCl. The saponification number is defined as the number of milligrams of KOH consumed per gram of polymer. Many polymers containing no heteroelements other than oxygen can be distinguished on the basis of

Table 3. Chemical analysis of common polymers [14]

Elements (other than C and H)	Polymers
None	polymerized hydrocarbons (e.g., polyethylene, polypropylene, polybutadienes, polystyrene, poly(methyl styrene), poly(vinyl benzene), butadiene – styrene copolymer)
O	Carbohydrates (e.g., celluloses, starches), phenol – formaldehyde resins, phenol – ether resins, phenol – furfural resins, phthalic esters and related compounds, alkyds, poly(vinyl esters), poly(allyl esters), polyacrylic and related esters, polycarbonates, aliphatic polyesters, epoxy resins, aldehyde resins, poly(vinyl alcohol)
N (O)	cellulose nitrate, polyacrylonitrile and copolymers, polyacrylamide, nylons and other polyamides, poly(ethylene imines), urea – formaldehyde resins, melamine – formaldehyde resins, polyurethane, polyester – urethane
Cl (O)	Chlorinated polyhydrocarbons, poly(vinyl chloride), poly(vinylidene chloride), poly(vinyl chloride acetate), polychloroacrylates, chlorinated alkyds
F (O)	polytetrafluoroethylene, poly(vinyl fluoride)
F, Cl	Polychlorotrifluoroethylene
S (O)	alkyl polysulfides, polysulfones, thiophenol condensates
N, S	thiourea – formaldehyde resins
Cl, S	thioplastics, vulcanized neoprenes
N, S, P	casein, protein
Si	silicones
Ti	poly(titanic esters)
B	poly(boric esters)
N, P, Cl	poly(phosphonitrilic halides)

Table 4. Saponification number of plastics, resins, and polymers [6]

< 20	100 – 200	> 200
Polyolefins	natural resins	polyacrylates
Methyl cellulose	alkyd resins	polymethacrylate
Polystyrene		poly(vinyl acetate)
Poly(vinyl alcohol)		cellulose esters
Phenol – formaldehyde resins		poly(butylene terephthalate)
Natural and synthetic rubber		polycarbonates
Poly(vinyl chloride)		
Chlorinated poly(vinyl chloride)		
Polyamides		
Natural waxes		

their saponification numbers, as indicated in Table 4.

A specific color reaction between a plastic and dichloroacetic acid sometimes serves as a rapid and simple means of identification [3].

4.2. Separation and Identification Schemes

A simple identification scheme based on polymer pyrolysis is illustrated in Table 5.

Figure 3 shows a more elaborate scheme that uses a set of solubility tests, and combines pyrolysis with both thin-layer chromatography and chemical identification. Specific tests applied to the pyrolyzate result in identification of a particular plastic. In the case of a copolymer, various isomeric possibilities with respect to the principal chain require that chemical analysis be supplemented by physical methods of structure determination. Purely chemical methods may also fail to distinguish clearly between a copolymer and a blend of two homopolymers.

If detailed and unambiguous structural analysis is required spectroscopic methods should be used. Not only do they often allow nondestructive testing of the sample, they also give considerably more information than elemental analysis, particularly with regard to structural subunits and their sequence within the polymer chain (see Sections 4.3 and 6.2).

4.3. Spectroscopic Methods

Infrared spectroscopy (IR) [72–77] is now a very important tool in the routine analysis of plastics, both for establishing macromolecular composition and for identifying additives.

The IR portion of the electromagnetic spectrum can be divided into three regions:

Table 5. Pyrolysis of polymers [14]

Observations	Tests	Conclusions
Smell of burnt paper	vapors burn with characteristic flame – yellow with little smoke	cellulose
+ smell of acetic acid		cellulose acetate
+ smell of butyrates		cellulose butyrate
Smell of acetic acid	fumes; acidic to indicator paper	acetate polymers
Cyanide		polyacrylonitrile
Smell of burning vegetation	test vapor with damp universal indicator paper; alkaline vapors	polyamides (nylon), polyurethanes, protein-type resins
Smell of formaldehyde		urea – formaldehyde
+ amine-like smell		melamine – formaldehyde
+ phenolic smell		phenol – formaldehyde
Sweetish odor		methacrylate and related compounds
Acrid odor	allow vapors to impinge on a glass rod moistened with silver nitrate solution; cloudy precipitate	poly(vinyl chloride) and its copolymers; natural and synthetic chlorinated rubbers, chloroprene and chlorinated polyolefins
+ heavy black ash	allow vapors to impinge on a glass rod moistened with silver nitrate solution; cloudy precipitate	probably poly(vinylidene chloride)
Sulfurous	allow vapors to impinge on a glass rod moistened with barium chloride solution; cloudy precipitate	sulfur-containing rubbers, etc.

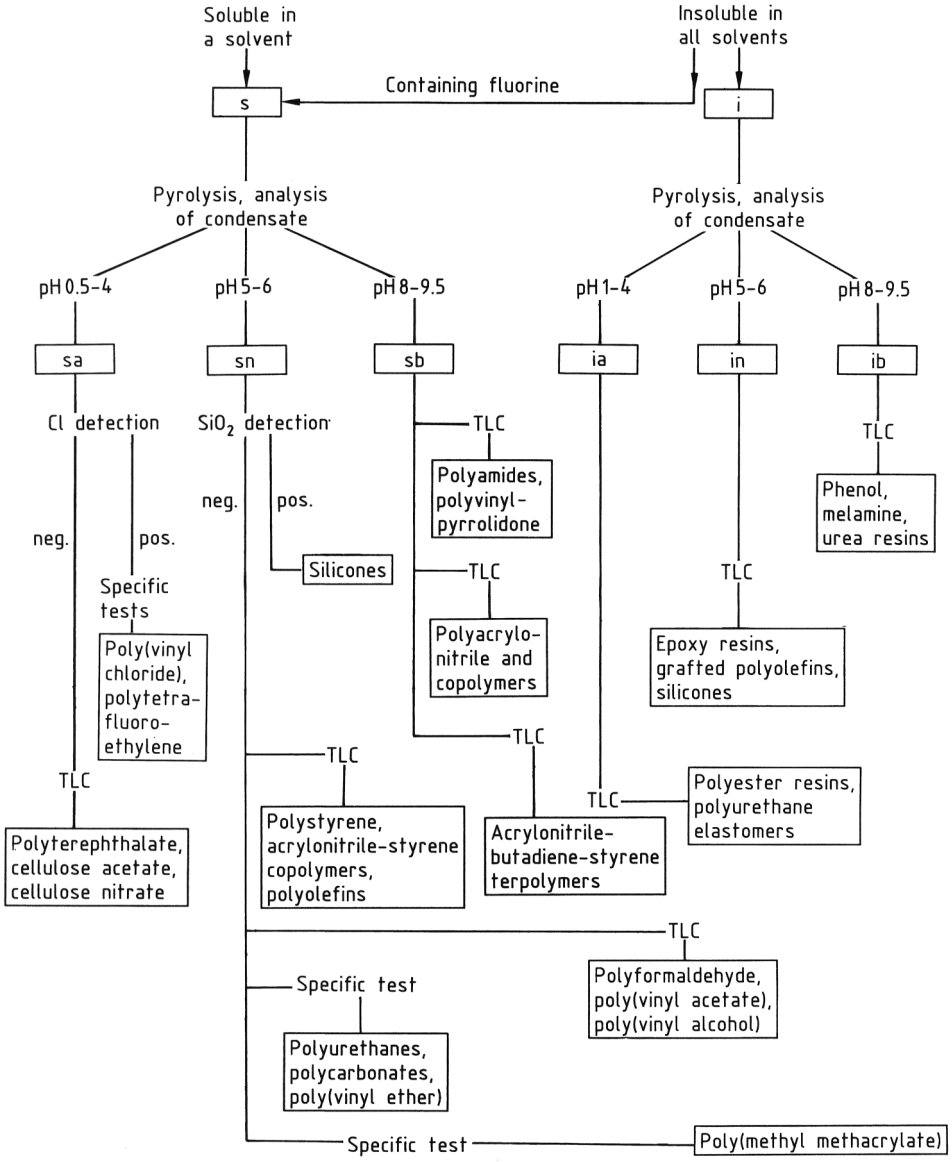


Figure 3. Identification of plastics (simplified; for further details, see [70], [71])
Solubility test with the solvents: water, tetrahydrofuran, dimethylformamide, xylene, formic acid, nitrobenzene
s = soluble; i = insoluble; a = acid; n = neutral; b = basic

Near IR (NIR)	0.76 – 2.5 μm, 13 200 – 4000 cm^{-1}
Mid IR (MIR)	2.5 – 50 μm, 4000 – 200 cm^{-1}
Far IR (FIR)	50 – 1000 μm, 200 – 10 cm^{-1}

Plastics analysis can be performed in all three regions, but MIR is preferred for routine work. Each structural element in a polymer chain has associated with it several absorption lines at various positions in the spectrum, corresponding to the number and type of IR-active vibrational modes (Table 6). For a macromolecule with a degree of polymerization P and a structural unit that consists of N atoms, $3NP - 5 \cong 3PN$ vibrations can be anticipated. However, the number of vibrations actually observed is considerably

Table 6. Positions of characteristic IR bands [3]

Polymer	Position of band, μm
Homopolymers	
cis-1,4-Polybutadiene	3.31 – 6.06 – 7.12 – 7.64 – 8.07 – 9.82 – 12.8. . . .12.9 – 13.5 – 14.5
trans-1,4-Polybutadiene	7.48 – 8.09 – 9.49 – 10.3. . .10.4 (double band) – 12.93
1,2-Polybutadiene	5.47 – 6.10 – 7.32 – 8.10 – 10.07 – 11.0 – 12.3. . . .12.4
Copolymers	
Butadiene – styrene	6.12 – 6.7 – 10.8 – 10.35 – 10.99 – 13.2 – 14.3
Butadiene – methyl methacrylate	5.8 – 7.25 – 8.38 – 8.75 – 10.3 – 10.95 – 13.1
Butadiene – acrylonitrile	4.48 – 6.1 – 10.3 – 10.9

smaller, so that, contrary to what might be expected, polymers are not completely opaque to infrared radiation. By using group theory together with symmetry considerations, it can be shown that $3N - 4$ fundamental vibrations are expected for a linear polymer chain.

In practice, direct assignment of the large number of observable vibrations that still remain is not always feasible. The coupling of molecular vibrations is generally so weak that a spectrum of an unknown polymer can usually be identified most easily by comparing it with spec-tra of low molecular mass model compounds, or with spectra of polymers of known structure. In those cases in which inter- or intramolecular coupling is evident, however, the IR spectrum can provide important additional structural information (Figs. 4 and 5) and the sequence of structural units (Table 7) [3].

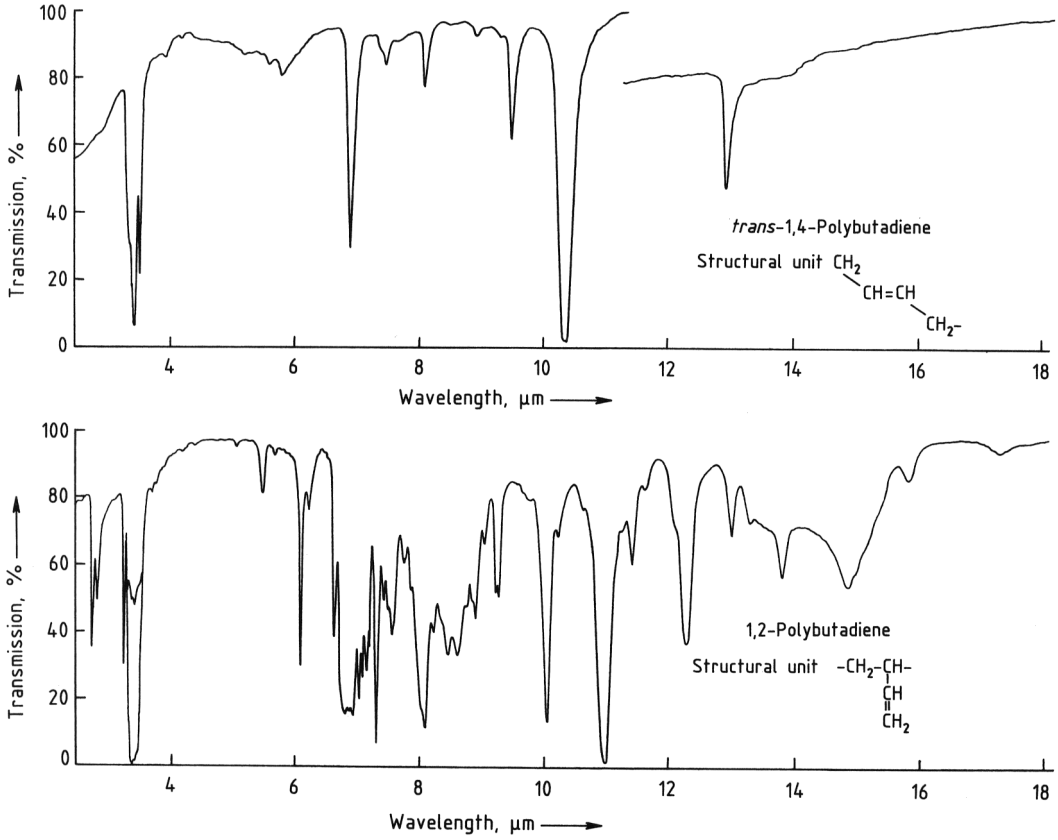


Figure 4. IR spectra of polybutadiene [3]

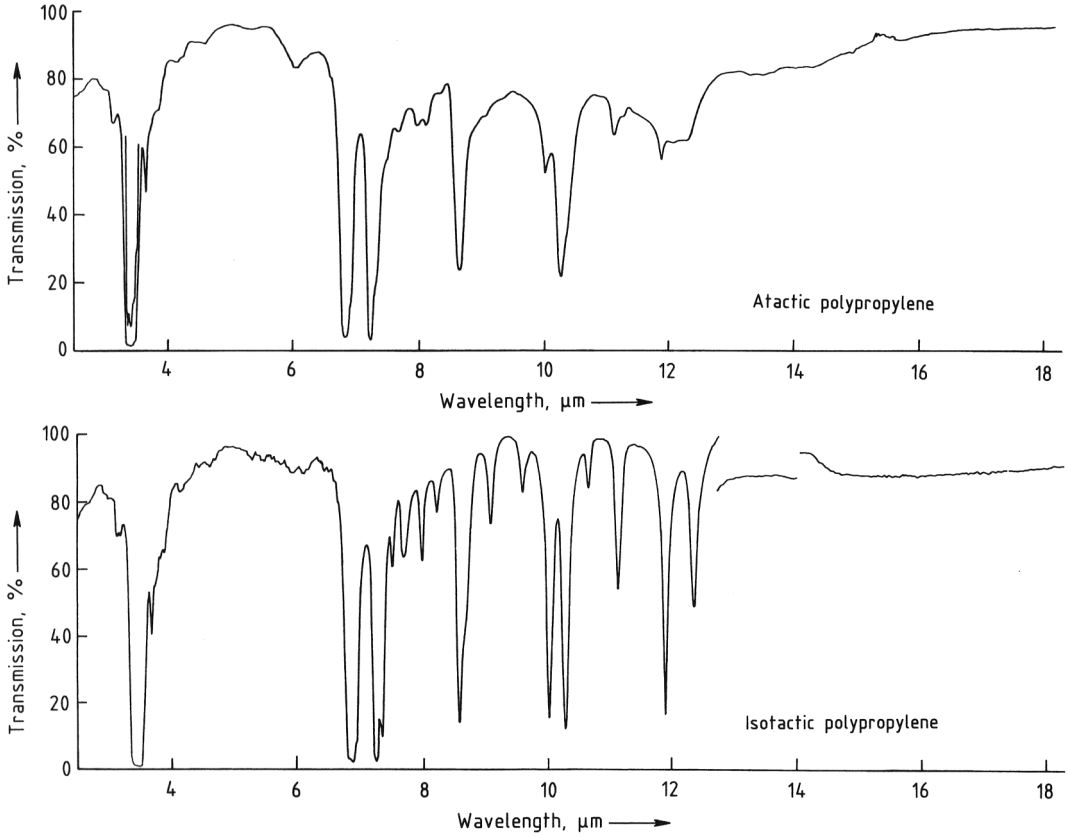


Figure 5. IR spectra of polypropylene [3]

Table 7. Chain structure of ethylene – propylene copolymers from IR spectra [3]

Wavelength, µm	Structure	Sequence of monomer units*
12.25	$-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-$	polypropylene units in ht polymerization
13.3	$-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-$	polypropylene units in tt polymerization equivalent to ethylene unit between two propylene units in hh polymerization
13.6	$-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-$	ethylene unit between two propylene units in ht polymerization
13.7	$-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-CH_2-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-$	ethylene unit between two propylene units in tt polymerization two ethylene units between two propylene units in hh polymerization
13.83	$-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-CH_2-CH_2-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-$	two ethylene units between two propylene units in ht polymerization

*hh = head-to-head; tt = tail-to-tail; ht = head-to-tail.

Extensive spectral catalogs are now available containing tables of group frequencies [3]. Nevertheless, one should never rely too heavily on an analysis based solely on spectral comparisons. Confirmatory tests should be conducted as well. Elemental analysis (Section 4.1) and other physical methods such as NMR spectroscopy (Section 6.2) are especially recommended.

Quantitative Spectroscopy. IR spectra of polymers are preferably recorded with highly automated Fourier transform instruments (FT-IR).

Spectra of soluble plastics can be recorded in largely IR-transparent solvents such as carbon disulfide, carbon tetrachloride, and dichloromethane. However, the preferred method is to examine a polymer film, prepared either as a thin section or cast directly as a film. A film can also be prepared from a solution evaporated on a sodium chloride plate. A film thickness of ca. 10 μm is usually adequate for a reliable measurement.

An insoluble plastic can also be analyzed in the form of a fine powder. In this case the sample is first mixed with a powdered alkali metal halide (potassium bromide) and then compressed into a pellet.

The ATR (attenuated total reflection) method [77] allows IR analysis to be carried out on the surface of a plastic sample. The method is based on examining IR radiation that has been reflected from a plastic surface in contact with an IR-transparent substance of lower refractive index. Selective absorption results in a spectrum analogous to a transmission spectrum. Multiple total reflection techniques increase the sensitivity of the analysis [3].

Other Spectroscopic Methods. Comprehensive reviews are provided in [9] and [33]. Methods for detecting traces of metals in plastics include flame photometry [1] and atomic absorption spectroscopy, applicable in both the visible and ultraviolet regions of the spectrum.

Elemental analysis and the spectroscopic methods so far discussed provide results that correspond to averages over an entire plastic sample. In the case of plastics containing inorganic pigments (titanium white, cadmium yellow) or fillers (glass fibers, carbon black) information on the distribution of the additives is often required. Appropriate analytical methods here include X-ray fluorescence spectroscopy and especially the electron beam microprobe. The latter method employs an electron beam to probe systematically the nature of a plastic surface. Adjusting the analyzer so that it corresponds to X-ray lines of a particular element (e.g., silicon in the glass beads of a filler) gives a picture of the local concentration distribution of that particular element (Fig. 6). The resolution of an electron microprobe is ca. 1 μm. Elements of atomic number > 5 can be detected with a sensitivity up to 100 ppm (ca. 10^{-14} g/cm^3).

5. Molecular Mass Determination

Introduction. Molecular masses for industrially important polymers extend to values as high as 10^6.

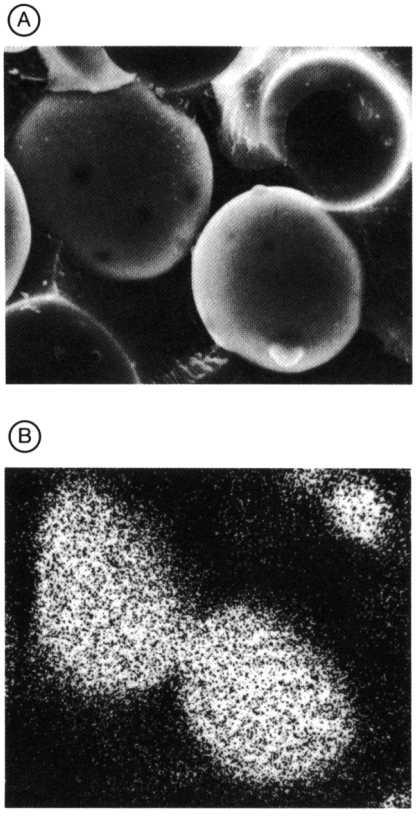


Figure 6. Scanning electron micrograph of the fracture plane of a phenol – formaldehyde resin filled with glass beads (A) and identification of silicon by X-ray fluorescence (B) Magnification × 300

Methods of molecular mass determination can be divided into two categories: absolute and relative [78–104]. Evaluation based on an absolute method involves in addition to experimental data (e.g., osmotic pressure, intensity of dispersed light) only such universal factors as the gas constant. The most important absolute methods are membrane osmosis, vapor pressure osmosis, combined sedimentation and diffusion, sedimentation equilibrium, and light scattering [78], [79], [83], [87].

Membrane osmosis is based on the equilibrium established by a membrane separating a polymer solution from pure solvent. Molecular mass determination by combined sedimentation and diffusion requires analysis of two types of material transport within a polymer solution: (1) sedimentation under the influence of a powerful centrifugal field, and (2) free diffusion. Alternatively, establishment of a stationary state in an analytical cell under the influence of a weak centrifugal field and consideration of the resulting equilibrium between sedimentation and diffusion also permits calculation of an absolute molecular mass. The method of light scattering requires the analysis of the intensity of Tyndall light as a function of the angle of observation.

Relative methods also involve polymer properties that are dependent upon molecular mass, but ones that do not lend themselves to direct conversion into unique molecular mass values. Essential to this approach is a calibration curve, prepared by using an absolute method. The most important relative methods utilize intrinsic viscosity (Staudinger index) or gel permeation chromatography (GPC). The experimental results in both cases depend not only on molecular mass but also on the conformation of polymer molecules in solution.

Since polymerization reactions are stochastic processes, most polymer samples are polymolecular. Standard separation methods do not allow the separation of macromolecules differing in degree of polymerization by only a single monomeric unit. For this reason, all absolute methods for molecular mass determination give characteristic mean values. Investigation of the molecular heterogeneity of a polymer must therefore include two discrete steps: (1) separation of the polymer components, and (2) determination of molecular mass for the separated components. Both ultracentrifugation and gel chromatography are effective for separating homopolymers of differing molecular mass, so these methods are widely used in the determination of molecular mass distribution.

Average Molecular Masses. Each molecule of solute in a solution makes an equal contribution to the osmotic pressure regardless of molecular mass. Osmotic analysis of a polymer thus gives the number-average molecular mass $\overline{M}_n$. If n_i is the number of moles of molecules with molecular mass M_i, the corresponding mass concentration will be $n_i = c_i/M_i$. It therefore follows that:

$$\overline{M}_n = \frac{\sum_i n_i M_i}{\sum_i n_i} = \frac{\sum_i c_i}{\sum_i c_i M_i} \tag{3}$$

Dispersion of light depends on the molecular mass, and therefore gives the weight-average molecular mass $\overline{M}_w$:

$$\overline{M}_w = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i} = \frac{\sum_i c_i M_i}{\sum_i c_i} \tag{4}$$

In a molecularly uniform polymer $\overline{M}_w = \overline{M}_n$, whereas for a polymolecular sample $\overline{M}_w > \overline{M}_n$. The discrepancy becomes greater the broader the mass distribution. The molecular nonuniformity U

$$U = (\overline{M}_w/\overline{M}_n) - 1 \tag{5}$$

is a measure of the molecular heterogeneity so long as the samples compared have similar molecular mass distributions. In some cases, samples with differing molecular mass distributions may actually have identical values of $\overline{M}_w$ and $\overline{M}_n$, a consequence of the fact that Equations (3) and (4) are based on summations.

Not all analytical methods lead to simple mean values such as $\overline{M}_w$ and $\overline{M}_n$. A more general definition of an average $\overline{M}$ is

$$\overline{M}_\beta = \frac{\sum_i c_i M_i^\beta}{\sum_i c_i M_i^{\beta-1}} \tag{6}$$

For $\overline{M}_n$, $\beta = 0$, whereas $\beta = 1$ for $\overline{M}_w$. Depending upon the experimental method, the mean that is determined may have $\beta > 1$ or an exponent β with a fractional value. For example, the method that combines sedimentation velocity with diffusion leads to a mean somewhat smaller than $\overline{M}_w$, and the same is true for the intrinsic viscosity $[\eta]$.

5.1. Absolute Methods

5.1.1. Membrane Osmometry

The osmotic pressure Π of a solution is a function of the chemical potential μ_1 and partial molar volume V_1 of the solvent:

$$\Pi = -\Delta\mu_1 / V_1 \tag{7}$$

The molecular mass is derived from the Vant'Hoff equation, which applies to ideal solutions

$$\Pi = \frac{RTc}{\overline{M}_n} \tag{8}$$

The assumption of ideality for a polymer solution is valid only in exceptional cases. Nonideality of a solution results in an osmotic pressure and, therefore, an apparent molecular mass that depends upon the concentration of the solute, a consequence of the differing spatial demands of solvent and polymer molecules. However, the additional enthalpy and entropy terms that determine μ_1 may cancel out at the so-called Θ temperature, resulting in a pseudoideal solution. The Θ temperature is of major significance in the determination of molecular masses and molecular mass distributions of polymers. Such Θ systems are in fact known for a large number of polymers [53]. At the Θ temperature, plotting Π/c versus c gives a line parallel to the c axis. The advantage of acquiring data at the Θ temperature is that this permits measurement of the molar mass distribution at a single concentration.

An example is given in Figure 7 for the case of polystyrene dissolved in cyclohexane. The molecular-mass-independent Θ temperature in this case is 34 °C. Increasing the temperature leads to an additional term for the osmotic pressure, reflecting the effect of the chemical potential. Lowering the temperature makes this term negative. The nonideal concentration dependence observed at temperatures other than the Θ temperature can be represented by a power series in c:

$$\frac{\Pi}{c} = \frac{RT}{M_n} + A_2 c + \ldots . \tag{9}$$

As shown in Figure 7, the molecular mass $\overline{M}_n$ can be determined by extrapolation to $c \rightarrow 0$.

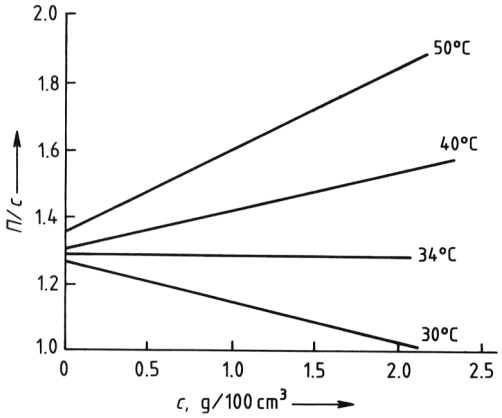


Figure 7. The dependence of osmotic pressure on temperature [21]

Experimental Technique. In an osmometer, such as that illustrated schematically in Figure 8, a polymer solution and a pure solvent are separated by a semipermeable membrane, ideally one that permits passage only of the solvent. Each of the chambers is surmounted by a capillary. The difference in chemical potential between the two chambers creates an osmotic pressure Π, which can be quantified in terms of a difference in height Δh of the liquid in the two capillaries. Equilibration of the osmotic pressure may require from several hours to several days. Automatic osmometers eliminate the need for waiting until equilibrium has been achieved.

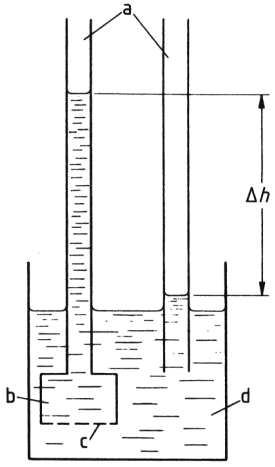


Figure 8. Schematic of a membrane osmometer [21]
a) Capillaries; b) Polymer solution; c) Membrane; d) Pure solvent

Instead, a servo-activated device applies an external pressure continuously to the solution chamber, and the magnitude of the pressure required to maintain equivalence is taken as a quantitative measure of the osmotic pressure Π. Another type of osmometer utilizes chambers with fixed volumes, permitting direct evaluation of Π by means of anelectronic pressure sensor.

Since the osmotic pressure decreases with increasing molecular mass, the scope of membrane osmometry is limited by the minimum detectable pressure, corresponding to a molecular mass of at most 10^6. The reliability of an osmotic determination is largely a function of the permeability of the membrane. If molecules of low molecular mass (e.g., oligomers, foreign solvent introduced during precipitation) can enter the solvent chamber then the apparent value for the molecular mass of the polymer will lie above $\overline{M}_n$. The extent of such error is a function of membrane permeability and the proportion of foreign molecules.

Osmosis is not limited to molecular mass determination on homopolymers. It is also the method of choice for copolymers regardless of the sequence of structural units or the extent of chemical heterogeneity, because osmotic pressure is a function only of the number of molecules present, irrespective of their chemical structures.

5.1.2. Lowering of Vapor Pressure

Vapor Pressure Osmometry. According to Raoult's law, the ratio of the vapor pressure of a pure solvent p_1^0 to that of a solution p_1 is equal to the mole fraction of the solvent x_1:

$$p_1/p_1^0 = x_1 = 1 - x_2 \tag{10}$$

x_2 mole fraction of solute and the relative decrease in vapor pressure is:

$$\Delta p_1/p_1^0 = x_2 = \frac{n_2}{n_1} \tag{11}$$

n_1 number of moles of solvent
n_2 number of moles of solute

In a vapor-pressure osmometer, solvent distills, a consequence of the difference in vapor pressure exerted by solvent and solution, onto droplets of solution. The heat of condensation is measured, which for an ideal system is proportional to the number of moles of dissolved polymer (i.e., with a constant sample size, inversely proportional to the molecular mass). The range of applicability of vapor-pressure osmometry is thus a function of the precision and sensitivity with which temperature differences can be measured. Determinations of this type are possible up to $\overline{M}_n = 10^4$. The results must be extrapolated to infinite dilution, as in the case of membrane osmometry, and for the same reasons.

Freezing Point Depression, Boiling Point Elevation. The relative decrease in vapor pressure of a polymer solution can also be determined by measuring the depression of freezing point ΔT_f or elevation of boiling point ΔT_b. The corresponding cryoscopic and ebullioscopic methods are based on the relationship that exists between vapor pressure and temperature, as given by the Clausius – Clapeyron equation:

$$dp/dT = \Delta H/\Delta V \cdot T \tag{12}$$

ΔH heat of vaporization
ΔV volume change on evaporation

The ebullioscopic method is the more important in practice. Molecular masses are derived from the equation:

$$\frac{\Delta T_b}{c} = \frac{RT^2}{\overline{M}_n} \cdot \frac{\overline{M}_1}{\Delta H_s} \tag{13}$$

$\overline{V}_1$ specific volume of solvent
H_s specific heat of vaporization of solvent

The term $RT^2 \times \overline{V}_1/\Delta H_s$ is the ebullioscopic constant K for a particular solvent.

5.1.3. Ultracentrifugation

Combined Sedimentation and Diffusion. Sedimentation rates are measured by subjecting a polymer solution to a high centrifugal acceleration in an ultracentrifuge, depicted schematically in Figure 9. The centrifugal acceleration is expressed as $\omega^2 r$, where ω is angular velocity and r is the distance from the axis of rotation [83–85]. Centrifugal force causes dissolved molecules to be sedimented at the bottom of the sample cell as a function of molecular mass and conformation in solution. Directed material transport is opposed by forces of friction. With F as the molar coefficient of friction, $\overline{V}_2$ the partial specific volume of the solute, and ϱ_1 the

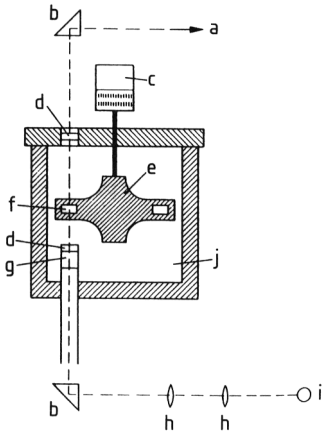


Figure 9. Schematic of an ultracentrifuge [21] a) Camera; b) Prism; c) Motor; d) Window; e) Rotor; f) Sample cell; g) Filter; h) Condenser; i) Light source; j) Vacuum chamber

density of the solvent, the following equation of motion is applicable:

$$M(1-\bar{V}_{2\varrho 1}) = F\frac{t}{\omega^2 r} = F \cdot s \tag{14}$$

The sedimentation constant s thus represents a rate of sedimentation through a uniform field. At infinite dilution, Einstein's law is applicable, providing a relationship between the coeffficient of friction F and the diffusion constant D:

$$F = RT/D \tag{15}$$

Equations (14) and (15) can be combined to give the Svedberg equation:

$$M = \frac{s_0}{D_0} \cdot \frac{RT}{(1-\bar{V}_{2\varrho 1})} \tag{16}$$

By combining the results obtained in separate sedimentation and diffusion experiments it is possible to eliminate the effect of the coefficient of friction on both transport processes. In this way, determination of molecular mass via the Svedberg equation becomes an absolute method. The procedure requires optimization of the rotational speed of the centrifuge as well as the choice of a suitable solvent [53]. For sedimentation measurements, the density of the polymer must be greater than that of the solvent. The transport velocity for the polymer in a centrifuge cell is measured by detecting either the UV spectrum or the refractive index of the polymer.

As in all experiments involving molecular mass determination, concentration dependencies must also be considered. If measurements are not made at the Θ temperature, then a series of s and D at various concentrations must be measured. The corresponding concentration dependencies can be expressed as:

$$\frac{1}{s} = \frac{1}{s_0}(1 + k_s c) \tag{17}$$

$$D = D_0(1 + k_D c) \tag{18}$$

The resulting molecular mass is a mean that arises from averaging the two measured variables; its value is close to $\overline{M}_w$. The method is applicable over the molecular mass range 10^4 – 10^7 [83].

Sedimentation Equilibrium. If the rotational velocity of a centrifuge is so adjusted that a mass-transport equilibrium is established between sedimentation and diffusion, then during the time interval dt the same number of molecules will migrate through a cross-section of the cell in the direction of the cell floor (due to sedimentation) as toward the axis of rotation (due to diffusion). This equilibrium follows the relationship:

$$\frac{\partial c}{c} = \frac{M(1-\bar{V}_{2\varrho 1})\omega^2 r \mathrm{d}r}{RT} \tag{19}$$

Integration between r_1 and r_2 leads to an equation for determining the molecular mass:

$$M = \frac{2RT\ln(c_1/c_2)}{(1-\bar{V}_{2\varrho 1})\omega^2(r_2^2 - r_1^2)} \tag{20}$$

Equation 20 is applicable only to an ideal system and requires extrapolation to $c \rightarrow 0$ for a real system.

The nature of the resulting mean is dependent upon the method used for interpreting the experiment. In the simplest case the z-mean, corresponding to $\beta = 2$ in Equation (6) is obtained. The range of applicability is extremely large, extending from monomers to molecular masses of 10^6. Analyses involving high molecular mass require long periods of time for the establishment of equilibrium. The time factor can be reduced by utilizing cells with low fill heights together with a multicell rotor. Solvents are selected on the same basis as in sedimentation transport.

5.1.4. Light Scattering

Introduction. The electric field associated with a light wave causes the electron shells of a polymer molecule to vibrate with a frequency corresponding to that of the monochromatic excitation beam. Excited molecules then emit scattered light in all directions at a wavelength λ_0 identical to that of the primary irradiation (the Tyndall effect) [86–88].

The intensity I of a light beam passing through a nonabsorbing polymer solution is reduced relative to the initial intensity I_0 by an amount equivalent to the light that is scattered. The overall scattering intensity attributable to N molecules within a unit volume (1 cm^3) is expressed by the turbidity number τ:

$$\tau = \frac{I}{I_0} = \frac{128}{3}\pi^5 N \lambda_0^4 \alpha^2 \tag{21}$$

The polarizability α of a substance is a function of its refractive index n:

$$\alpha = \frac{1}{N}\frac{n^2 - 1}{4\pi} \tag{22}$$

Combining Equations (21) and (22) leads to:

$$\tau = \frac{I}{I_0}\frac{32}{3}\pi^3 \frac{(n^2 - 1)^2}{N\lambda_0^4} \tag{23}$$

The above equations apply strictly only to gases but can also be used for dilute solutions of polymers. For an ideal solution, the scattering intensity is a function of the difference between the refractive index of the solvent n_1 and that of the dissolved polymer n, introduced as the refractive index increment $\partial n/\partial c$ [53]. Replacing the number of macromolecules by the mass concentration c and the molecular mass $\overline{M}_w$ leads to the expression:

$$\frac{\tau}{c} = M\frac{32}{3}\pi^3 \frac{n_1^2}{N_A\lambda_0^4}(\partial n/\partial c) \tag{24}$$

N_A is the Avogadro number from which the weight-average molecular mass $\overline{M}_w$ of an unknown polymer can be calculated. Equation (24) contains no term for scattering due to the solvent, so this must be subtracted from the overall scattering τ of the polymer solution. The value of τ is determined in practice by measuring the intensity of laterally scattered radiation as a function of the angle Θ. All measurements and their interpretation are influenced by the dimensions and shapes of the dissolved macromolecules relative to λ_0.

Macromolecules Smaller than λ/20. If the solute molecules responsible for scattering are small relative to the wavelength of the source they can be treated as point sources of radiation. This is the case for flexible chain molecules up to the dimension λ/20. If the irradiating light is polarized in a plane perpendicular to the plane of observation, the resulting intensity I_θ of light scattered through an angle Θ is independent of the angle of observation Θ. In this case the relative scattering intensity R_θ per unit volume and distance r for any angle of observation Θ is a function of the turbidity number τ according to:

$$R_\Theta = \frac{r^2 I_\Theta}{I_0} = \frac{3}{8\pi}\tau \tag{25}$$

where I_0 is the intensity of the incident light. Introducing the optical constant K,

$$K = 4\pi^2 \frac{n_1^2}{N_A\lambda_0^4}(\partial n/\partial c) \tag{26}$$

which is characteristic of a particular system and wavelength leads to an equation applicable to a dilute ideal solution. This defines the molecular mass as a function of the amount of light scattered through an angle Θ, an expression which is also appropriate for pseudoideal systems (see Section 5.2.1):

$$K\frac{c}{R_\Theta} = \frac{1}{\overline{M}_w} \tag{27}$$

Analogous to the situation with osmotic pressure, the concentration dependence of the reduced scattering intensity for real polymer solutions is taken into account by the Debye relationship:

$$K\frac{c}{R_\Theta} = \frac{1}{\overline{M}_w} + 2A_2 c + \ldots. \tag{28}$$

where A_2 is the second virial coefficient of the osmotic pressure. In this case $\overline{M}_w$ is established by measurement of a concentration series and then extrapolating to infinite dilution.

Macromolecules larger than λ/20 can no longer be regarded as point oscillators because of interference with the laterally scattered light. Path differences and, therefore, the amount of interference quenching of the scattered radiation

increase with increasing angle of observation and with increasing size of the macromolecules. However, at an angle of 0° – where direct measurement is of course impractical – no interference occurs, so Equation (27) remains valid even for large molecules. The angular dependence of scattering intensity for large macromolecules is a function not only of molecular size but also of shape and molecular heterogeneity. These factors are accounted for in the equation for $\overline{M}_w$ by the scattering function P_θ:

$$K\frac{c}{R_\Theta} = \frac{1}{P_\Theta \overline{M}_w} + \frac{2A_2 c}{P_\Theta} + \dots \quad (29)$$

For statistically entangled, uniform macromolecules with a mean distance of $\sqrt{h^2}$, the following expression is applicable to P_θ:

$$P_\Theta^{-1} = 1 + (8\pi^2/9\lambda_0^2) \cdot h^{-2} \cdot \sin^2(\Theta/2) \quad (30)$$

Scattering functions have been computed for a wide range of molecular shapes [86], [87]. Their utility extends beyond providing a correction factor for use in determining $\overline{M}_w$. Quantitative evaluation of the angular dependence of the scattering function also provides additional information on macroscopic conformation (size and shape) of the dissolved macromolecules. It follows from Equations (29) and (30) that:

$$K\frac{c}{R_\Theta} = \frac{1}{\overline{M}_w} + D \cdot \sin^2(\Theta/2) + 2A_2 c + \dots \quad (31)$$

where

$$D = \frac{1}{\overline{M}_w} \cdot \frac{8\pi^2}{9\lambda_0^2} \cdot h^{-2} \quad (32)$$

The determination of the molecular mass of a large macromolecule by means of Equation (31) involves extrapolation to $\Theta \rightarrow 0$ and $c \rightarrow 0$ with the aid of a Zimm diagram, as shown by the example in Figure 10. Here the expression Kc/R_θ is plotted simultaneously against the concentration c and the angular function $\sin^2(\Theta/2)$. This facilitates both of the required extrapolations, which are linear and intersect the ordinate at $1/\overline{M}_w$. In a similar way one can also evaluate the concentration dependence of the virial coefficient A_2 and the angular dependence of the molecular dimension $\sqrt{h^2}$. The method of light scattering is applicable up to a molecular mass of 10^8.

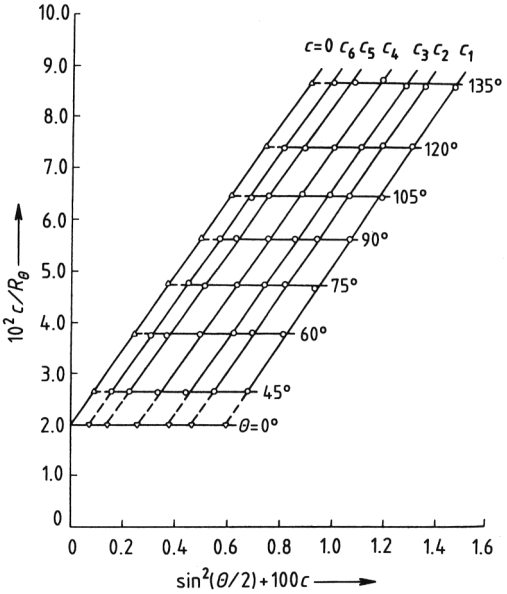


Figure 10. Zimm diagram of polytetrahydrofuran ($\overline{M}_w = 2.26 \times 10^6$) in 2-propanol ($T = 317$ K) [87]

Molecular Masses of Copolymers. Equation (28) for $\overline{M}_w$ assumes a macromolecular system with a uniform index of refraction; in other words, it is strictly valid only for homopolymers. A copolymer, on the other hand, consists of structural units that differ chemically, and thus would be expected to differ with respect to refractive index as well. Each component makes its own characteristic contribution to the overall scattering through the term $(\partial n/\partial c)^2$.

The refractive index increment for a copolymer is a function of the mass fractions m_A and m_B of the individual components and the refractive index increments of the corresponding homopolymers:

$$(\partial n/\partial c)_{AB} = m_A(\partial n/\partial c)_A + m_B(\partial n/\partial c)_B \quad (33)$$

The measured scattering intensity for a copolymer therefore depends not only on molecular mass but also on chemical composition.

The molecular mass of a copolymer that is heterogeneous both chemically and in degree of polymerization can be determined by conducting light-scattering experiments in at least three solvents [88]. Considerable experimental effort is required, but it is possible to establish in this way a mean mass $\overline{M}_w$ and thereby the nonuniformity U.

The equations used in studying homopolymers can also be applied to chemically heteregeneous copolymers provided structural units in the latter are isorefractive. This is the case to a good approximation, for example, with ethylene – propylene copolymers.

Experimental Technique. Figure 11 illustrates the design of a light-scattering apparatus. The measurement requires total absence of dust from the solutions and the cuvettes. Solutions can be purified by filtration or ultracentrifugation. The refractive index increment is determined by means of a differential refractometer. In order to achieve a high scattering intensity it is important that the refractive indices of solvent and solute differ as much as possible.

5.2. Relative Methods

Intrinsic Viscosity. Even a low concentration of macromolecules leads to a significant increase in the viscosity of a solvent. The increase observed for a given amount of a particular polymer depends not only upon molecular mass but also upon the dimensions of the molecules in solution. Macroconformation for a statistically entangled macromolecule is a function of both solvent and temperature. Use of intrinsic viscosity for characterizing a molecular mass requires that the experiment be conducted at constant temperature [53], [89–91]. The intrinsic viscosity $[\eta]$ (Staudinger index) is defined as:

$$[\eta] = \lim_{\substack{c \to 0 \\ G \to 0}} \left[\frac{\eta_{sp}}{c} \right] \tag{34}$$

This represents a limiting value for the reduced specific viscosity η_{sp} for a concentration $c \to 0$ and a shear rate $G \to 0$. Extrapolation to $c \to 0$ can be accomplished graphically by plotting η_{sp}/c against η_{sp} or c. In most cases a linear relationship results. The reduced viscosity is determined by measuring the flow times t for the solution and t_1 for the solvent, leading to:

$$\eta_{sp} = \frac{t\varrho - t_1\varrho_1}{t_1\varrho_1} \tag{35}$$

ϱ, ϱ_1 Density of solution and solvent, respectively

At low concentration $\varrho_1 = \varrho$, so this can be simplified to:

$$\eta_{sp} = \frac{t - t_1}{t_1} \tag{36}$$

Extrapolation to $G \to 0$ can be dispensed with for the low molecular mass range and by employing an Ubbelohde viscometer with a low shear rate. Large macromolecules tend to become partially oriented upon passage through a capillary as a consequence of a reduction in frictional resistance by solvent shearing. This structural viscosity is taken into account by measuring the viscosity of a solution as a function of the applied pressure p. An Ostwald viscometer is convenient for the purpose. Extrapolation to $G \to 0$ can be accomplished graphically by plotting η_{sp} against p. Linear extrapolation is possible here as well. Automatic viscometers have also been developed. These devices take into account the role played by shear rate as well as measuring the flow time.

The relationship between intrinsic viscosity $[\eta]$ and molecular mass for a linear, statistically entangled thread-like chain molecule is given by the Kuhn expression:

$$[\eta] = KM^{\alpha} \tag{37}$$

A log – log plot of $[\eta]$ versus $\overline{M}_{w,n}$ gives a straight line with slope α. The value of the exponent depends upon the flexibility of the entanglement. It approaches 1 in a thermodynamically favorable solvent. The minimum value of 0.5 is obtained with Θ systems (cf. Section 5.2.1). Representative values of α lie in the range 0.6 – 0.9. The intrinsic viscosity $[\eta]$ leads to a mean of the form:

$$M_{\eta} = \left[\frac{\sum_i c_i M_i^{\alpha}}{\sum_i c_i} \right]^{1/\alpha} \tag{38}$$

This is identical to $\overline{M}_w$ when $\alpha = 1$, but it becomes increasingly smaller as α decreases.

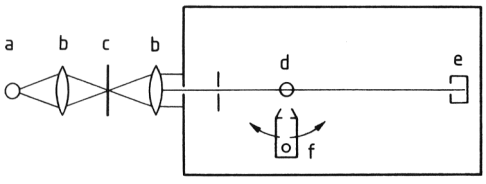


Figure 11. Schematic of a light-scattering apparatus
a) Light source; b) Collimator; c) Filter and polarizer; d) Sample cell; e) Light trap; f) Photomultiplier

For this reason it is advantageous to calibrate the intrinsic viscosity $[\eta]$ by means of an absolute method such as light scattering. Figure 12 illustrates $[\eta] - M$ calibration curves for various temperatures and solvents in the case of polystyrene. For additional systems see [53].

Relative molecular mass determination on the basis of viscometry is of major technical importance. Absolute methods are preferable for reasons of time and expense only with polymers for which an expression corresponding to Equation (35) has yet to be established. Relative methods provide reliable results whenever there is reasonable agreement between the molecular mass distributions of the reference and the sample.

5.3. Determination of Molecular Mass Distribution

Introduction. The nonuniformity U is incapable of providing an unambiguous characterization of polymolecularity. Samples with identical values of $\overline{M}_w$ and $\overline{M}_n$ may differ in their molecular mass distributions. The polymolecularity of a polymer sample can be established fully only by fractionation. In a batch separation procedure the total mass of polymer molecules in the system is represented in terms of an integral distribution over a discrete set of molecular masses between M_0 and M_i:

$$J_w(M) = \sum_{M_0}^{M_i} w_i \Delta M \tag{39}$$

Equation (39) describes a step function which progresses in steps of the monomer mass dM. A corresponding experimental measurement assumes prior molecular mass evaluation of the various fractions with molecular mass M_i. However, changes in physical characteristics for similar macromolecules differing only in size are so small that isolation of a fraction containing only molecules of a single degree of polymerization is essentially impossible. In a continuous separation method the step function of Equation (39) is replaced by a continuous integral distribution function:

$$J_w(M) = \int_{M_0}^{M_i} w(M)\mathrm{d}M \tag{40}$$

with the normalization:

$$J_w(M) = \int_0^{\infty} w(M)\mathrm{d}M = 1 \tag{41}$$

The first derivative of this expression is the differential molecular mass distribution, which provides a mass fraction for macromolecules in the increment M+dM:

$$w(M) = \frac{\mathrm{d}J_w(M)}{\mathrm{d}M} \tag{42}$$

Experimental determination of a molecular mass distribution thus always entails use of a method of separation combined with molecular mass analysis of the individual fractions.

Polymers can be separated by taking advantage of macromolecular properties that depend exclusively on molecular mass, including solubility (precipitation fractionation) and sedimentation rate. Chromatographic procedures have also assumed considerable practical importance.

Precipitation Fractionation. The solubility of a polymer depends not only on the nature of the structural units present, but also on molecular mass. This characteristic of polymer solutions serves as the basis for a simple and effective approach to establishing a molecular mass distribution. The process begins with a ca. 1 % solution of a polymer, to which is slowly added dropwise with stirring a precipitating agent, usually methanol. Turbidity is observed after the addition of a certain amount of the precipitating agent. The mixture is then warmed slightly to restore complete dissolution. Subsequent lowering of the temperature again leads to precipitation. After some period of time the

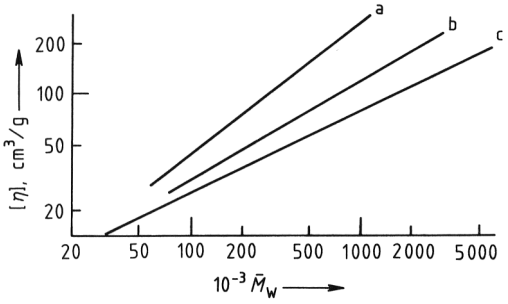


Figure 12. Logarithmic plot of viscosity versus molecular mass of polystyrene a) In benzene (T = 290 K); b) In methyl ethyl ketone (T = 290 K); c) In cyclohexane (T = 305 K)

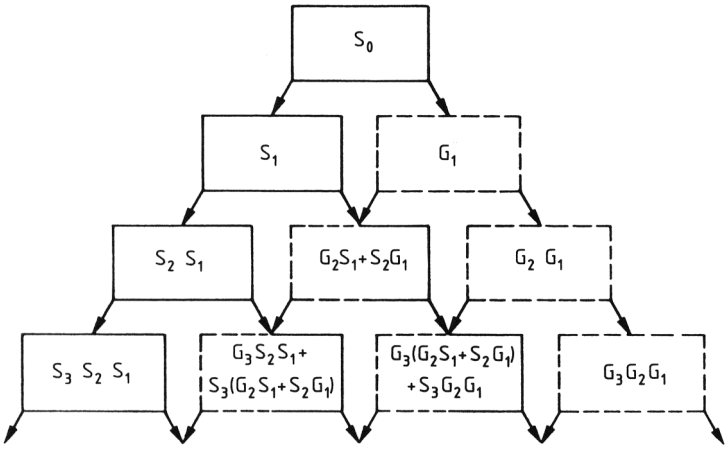


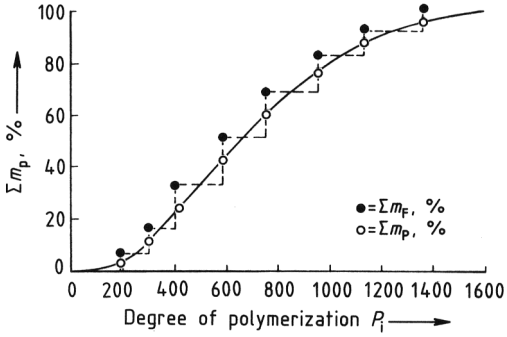
Figure 13. Schematic fractionation of polymers by dissolution and precipitation [9]
S = Solution; G = Gel

system separates into a polymer-rich gel phase (G_1) and a polymer-poor sol phase (S_1). In most cases the polymer is the more dense component, so the gel phase collects at the bottom of the precipitating vessel. Evaporation of this phase gives the polymer fraction with the highest molecular mass. The sol S_1 is then treated with additional precipitating agent leading to a second stage of separation, etc. This procedure allows the isolation of up to 10 fractions from a single polymer sample. Fractions do not consist exclusively of molecules with uniform molecular masses, however, but instead contain components with both higher and lower masses as well. Even repetition of the process will not alter this situation [92], [93].

In order to improve the fractionation the gel phase G_1 can be treated again with precipitating agent, producing another sol phase that can be combined with S_1 subfractionation procedure. The triangular fractionation method illustrated schematically in Figure 13 represents another effective approach to fractionation.

Once a set of fractions has been isolated the corresponding masses must be determined, along with mass fractions relative to the total sample. Molecular masses are determined by one of the methods described in Sections 5.2 and 5.3. The results permit one to construct a molecular mass distribution consistent with Equation (39) (Fig. 14).

Precipitation fractionation is a very simple procedure. Its chief limitation lies in the small



Analysis of typical fractionation data

Fraction	Degree of polymerization P_i	wt% of fraction m_F	Σm_F, %	Σm_p, %
VIII	190	6.4	6.4	3.2
VII	300	9.0	15.4	10.9
VI	420	17.2	32.6	24.0
V	585	17.6	50.2	41.4
IV	755	18.5	68.7	59.4
III	955	13.5	82.2	75.5
II	1140	9.7	92.0	87.0
I	1370	8.1	100.0	95.0

Figure 14. Molecular mass distribution by dissolution fractionation [21]
m_F = mass fraction of a fraction; m_p = mass fraction with degree of polymerization P_i

number of fractions generated, which might, for example, fail to reveal a bimodal character of the molecular mass distribution. The time required for separating the gel phases can also be very great, especially since the sol phase increases in volume at each stage in the process, requiring the use of large amounts of solvent. Nevertheless, precipitation has the advantage compared to preparative chromatography that it represents an economical source of gram-quantity fractions, which can in turn serve as starting points for analyzing a polymer by other methods (e.g., configurational analysis with NMR; see Section 6.2).

Gel permeation chromatography (GPC) is a form of liquid column chromatography in which carrier solvent is passed at a constant rate through a column consisting of cross-linked polymer beads previously allowed to swell in the same solvent. The total volume V_t of the column includes the volume occupied by both mobile (V_0) and stationary (V_x) phases. Only a portion of V_x is actually utilized in the separation process: the pore volume V_p [94–103].

Figure 15 shows a simplified model of the separation process. Separation occurs on the basis of the hydrodynamic volume of a given macromolecule, which is in turn a function of molecular mass. It is this volume that governs the extent to which the macromolecule can permeate into the pore structure of a suitably dimensioned microporous gel.

The sample that is to be separated is introduced onto the top of the column as a solution in the mobile phase. Polymer molecules then distribute themselves between the mobile phase V_0 and the pore volume of the stationary phase V_p on the basis of a diffusion-driven equilibrium defined by their hydrodynamic volumes and the pore diameter of the gel. As solvent flows through the column, large molecules are unable to penetrate into the gel matrix due to their diameters, so these are eluted first within the elution volume V_0. By contrast, molecules with diameters smaller than the pore openings diffuse into the interiors of the pores. The smaller the macromolecule the more deeply it is able to penetrate into the stationary phase, and the more its progress is retarded relative to solvent flow outside the pores. In the absence of special interactions between the polymer and the surface of the stationary phase, the observed order of elution and the corresponding elution volume V_e will be a function only of molecular size. Small macromolecules capable of passing freely between V_p and V_0 are eluted last. The difference between the elution volumes for totally excluded molecules and the smallest macromolecules present corresponds to V_p.

The *gel chromatogram* is generated by measuring the polymer concentration in the eluate as a function of elution volume. The polymer concentration can be measured by monitoring the refractive index and/or ultraviolet absorption of the eluate. Larger columns can be used for

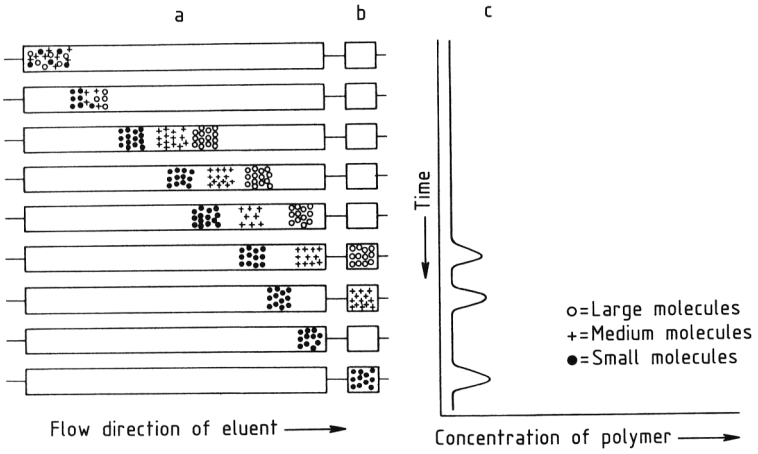


Figure 15. Principle of polymer fractionation by size exclusion chromatography (SEC) [31] a) Column; b) Detector; c) Detector signal

preparative GPC, providing an effective alternative to precipitation fractionation.

Even for a completely homogeneous fraction, the quality of the column packing and effects of axial diffusion during the separation process cause peak broadening. An elution curve can be calibrated by chromatography of a set of uniform polymers with known masses determined by an absolute method, as illustrated in Figure 16. The linear portion of the elution curve is described by the function:

$$\log M = \log M_a - AV_e \tag{43}$$

where M_a is the molecular mass above which separation is impossible and A is a constant specific to a particular system and apparatus. This method is applicable within the molecular mass range $10^2 - 10^6$.

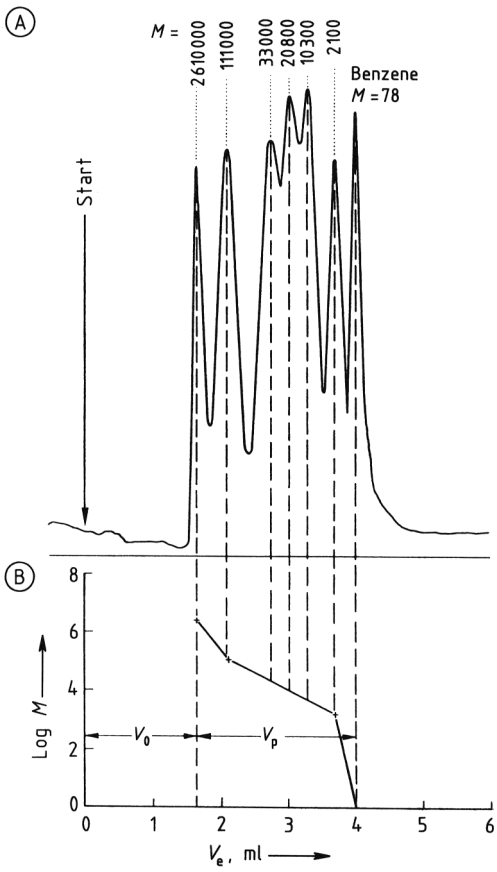


Figure 16. Chromatogram (A) and calibration curve (B) for SEC [96]
V_0 = Volume of eluent in column; V_p = pore volume; V_e = volume of eluate

The relationship shown in Figure 16 between elution volume V_e and molecular mass M is strictly valid only for a particular homologous series of polymers, and it must be established with the aid of calibration samples. If the intrinsic viscosity $[\eta]$ is used to take into account hydrodynamic volumes of polymers that differ chemically by plotting $[\eta]M$ vs. V_e, the result is a universal elution curve applicable to multiple polymer systems. Within its range of linearity GPC can be used as a relative method for the determination of molecular mass [98].

Evaluation. Gel chromatograms often consist of several broad, unsymmetrical, and overlapping peaks, as illustrated by the example of polypropylene adipate in Figure 17. If the relationship between detector signal and polymer concentration is known, mass fractions w (M) can be computed from the corresponding surface areas in the chromatogram of a series of oligomers. Equation (39) is then used to construct a step distribution function for the various molecular masses. It is not possible in the high molecular mass range to isolate fractions with uniform molecular mass. The typical gel chromatogram must instead be regarded as a superposition of uniform fractions characterized by differing molecular masses. The problem in interpretation is therefore to distinguish the contribution to peak broadening that can be attributed directly to molecular mass distribution in the sample from peak-broadening effects inherent in the system.

The chromatogram of a single fraction can be described as a Gaussian curve of the form:

$$f(V) = A(h/\sqrt{\pi})\exp[-h^2(V - V_{max})^2] \tag{44}$$

where V_{max} is the elution volume at the maximum of the curve, h represents the breadth of the Gaussian curve, and A is the area under the chromatogram. For a system of i fractions each with area A_i:

$$f(V) = \sum_i A_i(h_i/\sqrt{\pi})\exp[-h_i^2(V - V_{max,i})^2] \tag{45}$$

If the number of fractions is very large, or if the chromatogram cannot be resolved into uniform fractions in the high molecular mass range, the summation A_i can be replaced by the continuous function w (Y). For h=constant it follows that:

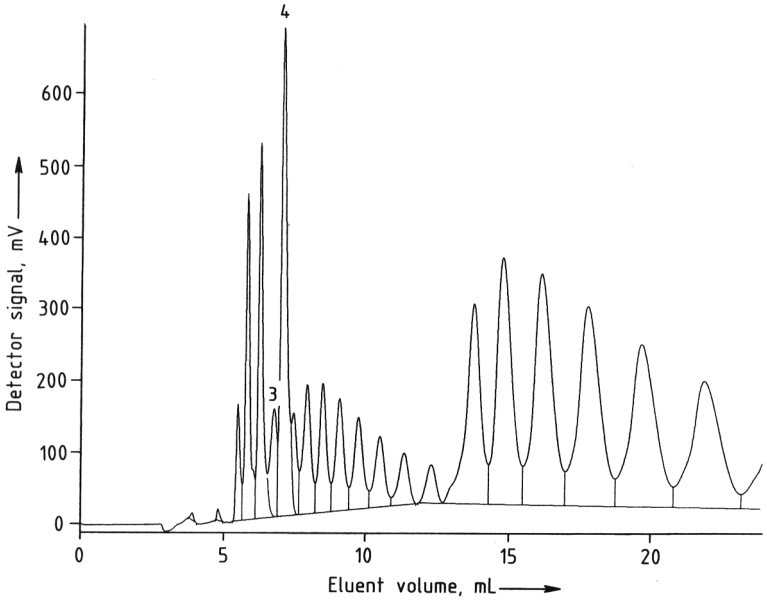


Figure 17. Fractionation of oligomers of different size and composition [101]
Chromatographic separation for coupling with NMR detection (see Fig. 29). Sample: polypropylene adipate; Eluent: D_2O/methanol-d_4; Column: Chromegabond 5 μm

$$f(V) = \int w(Y)(h/\sqrt{\pi})\exp[-h^2(V+Y)^2] \quad (46)$$

where $w(Y)$ represents a chromatogram from which diffusion broadening has been removed. This can in turn be transformed into the molecular mass distribution by using a calibrated elution curve; various methods are available for this [99].

A second and very effective approach for determining a molecular mass distribution entails greater experimental effort: extrapolation to zero of the data from a gel chromatogram of a polymer in terms of both concentration and elution velocity [100].

GPC is a very flexible analytical method as a result of the availability of a wide variety of column packings and solvents. Calibration curves permit coverage of a molecular mass range extending from oligomers up to 10^6. GPC coupled with GC has become the most important method for the identification and molecular mass determination of oligomers.

Ultracentrifugation. The sedimentation constant

$$s_0 = \left(\frac{\dot{r}}{\omega^2 r}\right)_{\tau \to 0, M, T, S} \quad (47)$$

where $\dot{r} = dr/dt$ describes the rate of sedimentation (extrapolated to $c \to 0$) in a uniform field for a macromolecule of molecular mass M in the solvent S at temperature T. The dependency upon molecular mass is expressed by:

$$s_0 = kM^{\alpha} \quad (48)$$

A log – log plot of the experimental results gives a straight line. The observed value of the exponent is a function of the thermodynamic quality of the solvent. The smallest values are associated with sedimentation systems in which $\alpha = 0.5$. Numerous relationships based on Equation (48), calibrated by using absolute methods, have been tabulated [53]. For this reason the determination of molecular mass by sedimentation is also important as a relative method (for the absolute method, see Section 5.2.3).

Recording the polymer concentration during sedimentation as a function of time and location gives a set of curves in which the information relevant to molecular mass distribution is initially masked by other parameters influencing the separation process. Methods for determining molecular mass distribution by ultracentrifugation are described in detail in [78], [79], [83–85].

Ultracentrifugation is capable of producing forces up to 400 000 *g*. The lower limit for establishing a molecular mass distribution is $M = 10^4$. The unmatched flexibility of ultracentrifugation with respect to relative and absolute mass determinations as well as sample separation comes at the expense of high investment and operating costs, factors which must be taken into account in any comparison with GPC.

6. Determination of Sequential Structure

Introduction. The properties and applications of plastics are determined largely by the primary structures of their mainly linear macromolecules, which are formed by the sequential coupling of a single monomer or several chemically distinct species (see Chap. 7). One important type of problem in plastics analysis derives from the numerous types of isomerism, a situation that becomes increasingly complex in the case of co- and multipolymers [1], [104–109]. The sequence of two structural characteristics A and B can be block-like, alternating, or random. Structural units comprising *configurational sequences* of a single monomer contain pseudoasymmetric carbon atoms. Such polymers can be classed as isotactic (meso, m), syndiotactic (racemic, r), or atactic (random distribution of m and r linkages). Table 8 provides a summary of possible configurational sequences for discrete groups of three (triads) and five (pentads) structural units. The number of possible sequences *N* increases dramatically with the sequence length *n*:

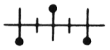
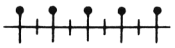
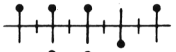
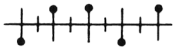
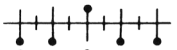
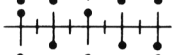
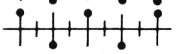
Sequence length *n*:	2	3	4	5	6
Sequences *N* (*n*):	2	3	6	10	20

If addition of a new monomer unit occurs independently of the structure of the growing chain, then the probability *P* for a particular sequence can be shown to be $P_r = 1 - P_m$. One speaks in this case of Bernoulli statistics [107].

Configurational sequences also arise in the 1,4 addition of 1,3-dienes such as butadiene. The resulting polymer chain contains one C=C double bond per structural unit, which may have either the *cis* or *trans* configuration. The term *constitutional sequences* refers to the situation

Table 8. Tactical sequences in poly- α-olefins [3]

The monomer unit $-CH_2-CHR-$ is symbolized by .

	Sequence	Symbol	Probability
Triads	mm		P_m^2
	mr		$2P_m(1-P_m)$
	rr		$(1-P_m)^2$
Pentads	mmmm		P_m^4
	mmmr		$2P_m^3(1-P_m)$
	rmmr		$P_m^2(1-P_m)^2$
	mmrm		$2P_m^3(1-P_m)$
	mmrr		$2P_m^2(1-P_m)^2$
	rmrm		$2P_m^2(1-P_m)^2$
	rmrr		$2P_m(1-P_m)^3$
	mrrm		$P_m^2(1-P_m)^2$
	rrrm		$2P_m(1-P_m)^3$
	rrrr		$(1-P_m)^4$

in which identical monomer units are capable of bonding in different ways (see Table 8). *Compositional sequences* are characteristic of copolymers into which two different comonomers have been incorporated [108].

6.1. NMR Spectroscopy

The most useful technique for the analysis of sequences in polymer chains is NMR spectroscopy. It often facilitates quantitative evaluation of even the smallest structural details of a polymer. For a comprehensive treatment of the fundamentals of NMR, see [109–119], [121]; general principles are treated in [106]. Nuclei that are important in the analysis of polymers by NMR are listed in Table 9; they suffice for characterizing all the important types of polymers.

Nuclear magnetic resonance spectroscopy of polymers exploits the fact that the resonance frequencies of the investigated nuclei depend strongly on the constitutional, configurational, and conformational structure of the polymer. Each structural feature plays a role, so that each

Table 9. NMR properties of nuclei important in the analysis of plastics [115]

Nucleus	Natural abundance	NMR frequency in 1 T magnetic field, MHz	Sensitivity relative to proton	Magnetogyric moment	Spin
^{1}H	99.9844	42.577	1.000	2.79270	1/2
^{2}H (D)	0.0156	6.536	0.00964	0.85738	1
^{13}C	1.108	10.705	0.0159	0.70216	1/2
^{14}N	99.635	3.076	0.00101	0.40357	1
^{15}N	0.365	4.315	0.00104	− 0.28304	1/2
^{17}O	0.037	5.772	0.0291	− 1.8930	5/2
^{19}F	100	40.055	0.834	2.6273	1/2
^{29}Si	4.70	8.460	0.0785	− 0.55477	1/2
^{31}P	100	17.235	0.0664	1.1305	1/2
^{35}Cl	75.4	4.172	0.00471	0.82089	3/2
^{37}Cl	24.6	3.472	0.00272	0.68329	3/2

of the sequences listed in Table 8 is associated with specific resonance signals. Primary structures have been assigned for a large number of polymers in solution on the basis of ^{1}H and ^{13}C NMR spectroscopy [3], [104], [113], and NMR spectroscopy of heteroelements is gaining in importance [115].

Poly(Vinyl Chloride). The ^{13}C NMR spectrum of poly(vinyl chloride) is an example of a simple atactic polymer.

In Figure 18 configurative sequences corresponding to those listed in Table 8 can be identified. Configurational differentiation is possible for sequences of up to seven successive monomer units.

Polybutadiene. The ^{13}C NMR spectrum of polybutadiene is particularly instructive with respect to the effectiveness of the NMR method. Butadiene molecules can be linked in either a 1,4 or a 1,2 configuration

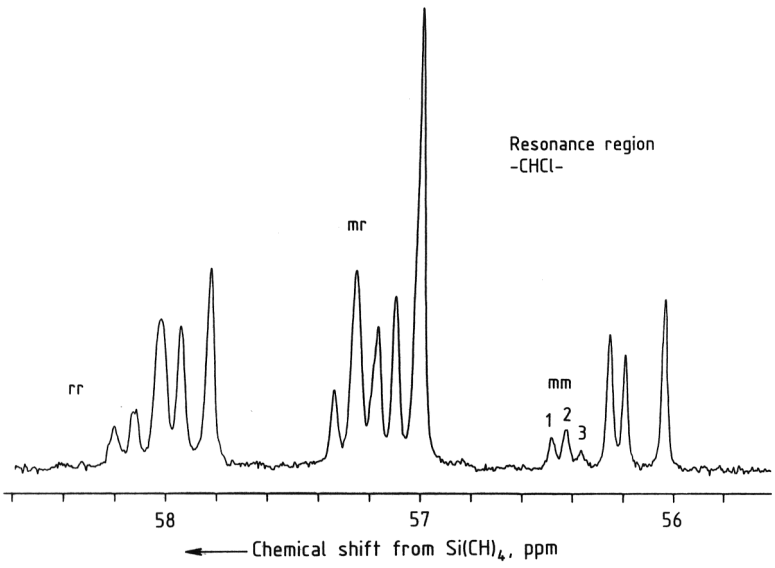


Figure 18. 67.88 MHz ^{13}C NMR spectrum of poly(vinyl chloride)
The signals 1 – 3 indicate configurational sequences (see Table 8) of up to 7 monomer units, rmmmmr, mmmmmr, and mmmmmm, respectively. Solvent: tetrahydrofuran-d_8; Temperature: 373 K; Broadband decoupling

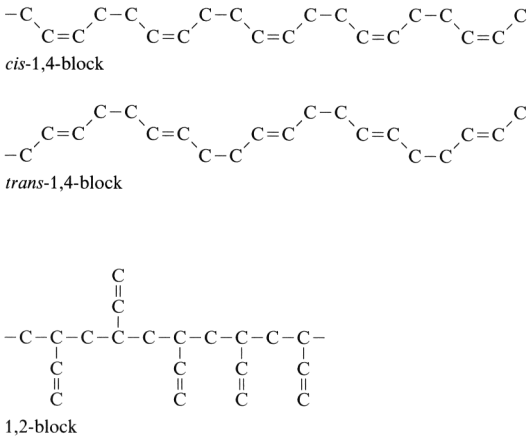


Figure 19 A shows a ^{13}C NMR spectrum of a mixture of *cis*-1,4- and *trans*-1,4-polybutadiene. Separate resonance signals are observed in the C=C double bond region for each of the possible structures. The transition from *cis* to *trans* and vice versa during isomerization of the polymers can also be observed by means of NMR spectroscopy (Fig. 19 B and C).

Depending on the polymerization conditions, polybutadiene can contain both 1,4 and 1,2 linkages. In the NMR spectrum (Fig. 20) it is possible to identify all eight of the possible triad sequences for combinations of *cis* (c), *trans* (t), and 1,2 (v) linkage between monomer units.

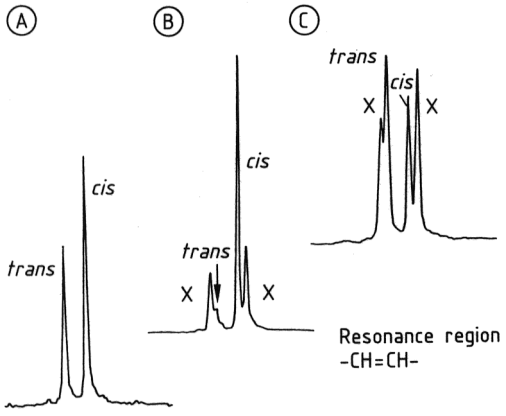


Figure 19. 67.88 MHz ^{13}C NMR spectrum of 1,4-polybutadiene
x = transition from *cis* to *trans* sequences; Solvent: deuterochloroform; Temperature: 300 K; All samples with random sequence distribution A) Mixture of *cis*- and *trans*-1,4-polybutadiene; B) *cis*- with 20 % *trans*-1,4-polybutadiene sequences; C) 1,4-Polybutadiene with *cis* and *trans* sequences (1: 1)

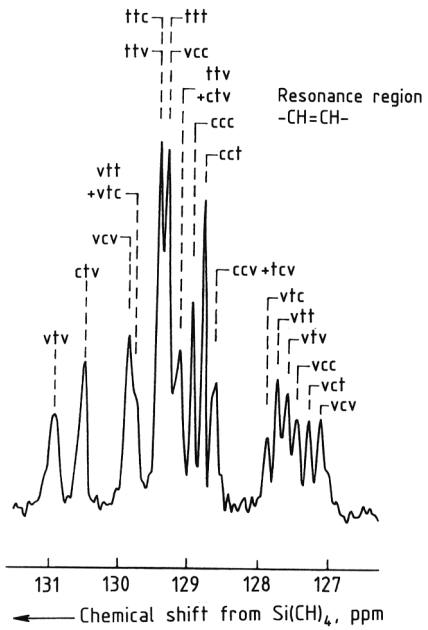


Figure 20. ^{13}C NMR spectrum of polybutadiene with 1,4- and 1,2-sequences
Conditions and sequence distribution as in Figure 19

Evaluation of the spectrum reveals that monomer addition in this sample was independent of the structure of the previously formed chain.

The 1,2 linkage of two butadiene units corresponds formally to an α-olefin, and it is in this way that the ^{13}C NMR spectrum in Figure 21 must be interpreted with respect to the configurative sequences listed in Table 8. The results are consistent with a Bernoulli distribution of the sequences. The observed distribution depends upon the polymerization conditions.

2D NMR Spectroscopy. Two-dimensional NMR spectroscopy allows the investigation of the nature of magnetic interactions between adjacent nuclides. Verifying the presence of a bond between particular nuclides significantly simplifies the interpretation of an NMR spectrum. Figure 22 illustrates a typical coupling experiment [111], [114] conducted on a fluorine-containing polymer [119].

3D NMR spectroscopy is a tomographic procedure for solid polymers. In addition to providing primary structural information on insoluble polymers it can also be used to test the quality of finished products made of plastic.

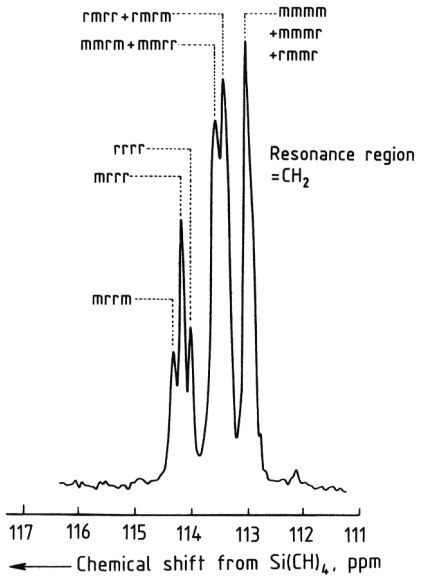


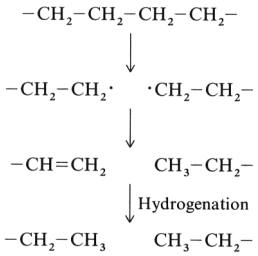
Figure 21. ^{13}C NMR spectrum of 1,2-polybutadiene at 67.88 MHz
Conditions and sequence distribution as in Figure 19

From a methodological standpoint 3D NMR bridges the gap between structural analysis and quality control. Figure 23 shows the structure of a polybutadiene molding [120].

6.2. Pyrolysis Gas Chromatography

The pyrolytic methods described in Chapter 3 can be combined with gas chromatography [122–125] and mass spectrometry [126] to provide an extremely sensitive analysis of the chain structure of a polymer. Pyrolysis conditions are chosen such that the chain fragments released contain up to 30 monomer units, requiring temperatures of 500 – 800°C. The nature and number of observed fragments depends not only on the empirically determined experimental conditions but also on the composition and structure of the polymer (structural units, branching, tacticity, and sequence in the case of copolymers).

The pyrolysis of polyethylene proceeds as shown in Scheme **1**. Simultaneous hydrogenation of the fragments often greatly simplifies the resulting pyrogram. The pyrogram of polyethylene consists exclusively of *n*-alkanes (Fig. 24). The presence of isoalkanes in a pyrogram is evidence for branching of the polymer



Scheme 1. Pyrolysis of polyethylene

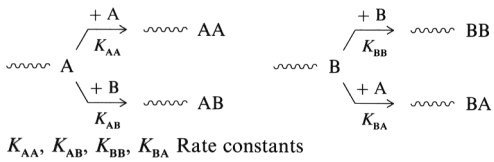
chain. Under constant experimental conditions, each polymer gives a characteristic pyrogram, permitting structural assignment by comparison with standard pyrograms from structurally defined polymers. In favorable cases it is sometimes possible to identify stereoisomeric fragments [126] (Fig. 25).

Use of isotopically labeled polymers permits the application of pyrolysis chromatography in kinetic investigations (depolymerization, sequences in copolymers).

7. Determination of Chemical Heterogeneity

Methods that combine the online detection of chemical structure and molecular mass distribution are of growing importance.

Molecular Heterogeneity of Copolymers. Copolymerization of the monomers A and B can be described in terms of four different growth reactions:



Monomers typically differ in their reactivity towards a growing chain. The reactivity relationship can be expressed in terms of two copolymerization parameters:

$$r_A = \frac{K_{AA}}{K_{AB}};\ r_B = \frac{K_{BB}}{K_{BA}} \tag{49}$$

It follows for a radical copolymerization that the structure of emerging copolymer will vary as

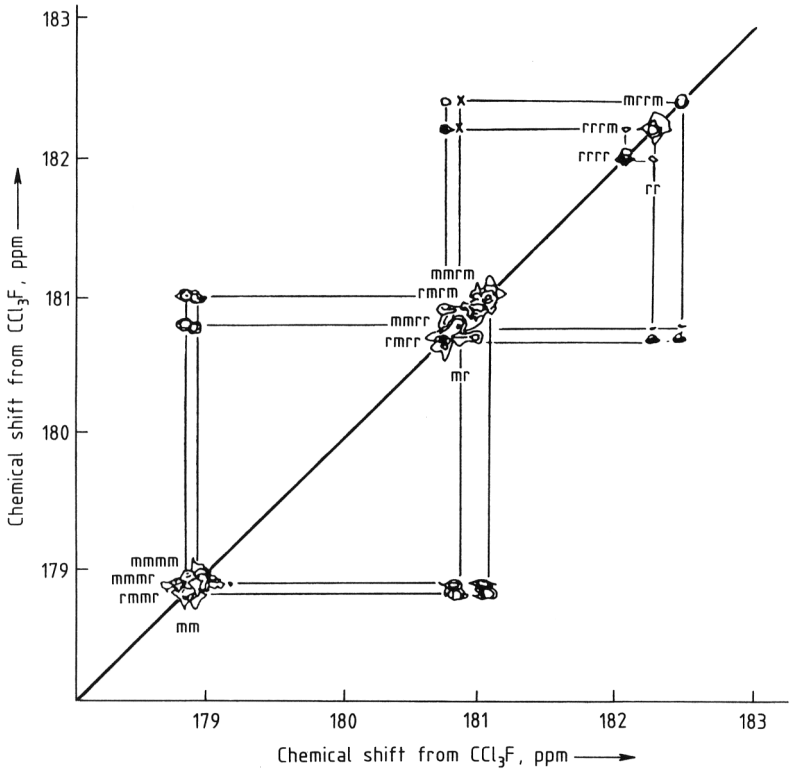


Figure 22. Two-dimensional ^{19}F NMR spectrum of poly(vinyl fluoride) [119]
Contour map of two-dimensional (refers to two different observation frequencies) J-correlated ^{19}F NMR spectrum. Sequences of five monomer units are assigned unambiguously

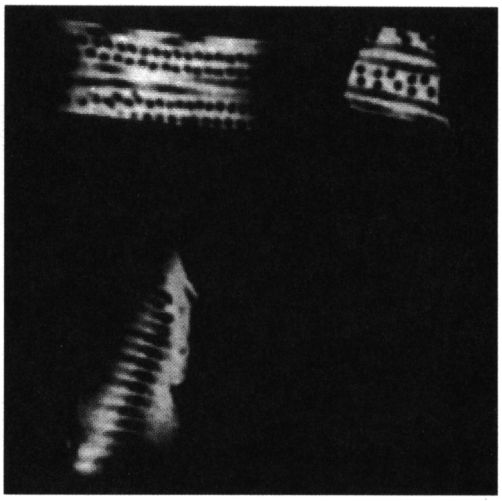


Figure 23. NMR micrograph of filled synthetic rubber [120]
Three-dimensional (refers to space coordinates) ^{1}H NMR spectrum of a sample of reinforced tire rubber. Position of inhomogeneously distributed cord can be located without degradation of sample

a function of the extent of conversion:

$$\frac{m_A}{m_B} \sim \frac{A}{B} \cdot \frac{r_A A + B}{r_B B + A} \tag{50}$$

A, B	mole fractions of monomers A and B in initial monomer mixture
m_A, m_B	mole fractions of monomers A and B in copolymer

Generally, the macromolecules of a copolymer are heterogeneous with respect to molecular mass, chemical composition, and sequential structure. The differential distribution for a typical copolymer with respect to molecular mass and chemical composition is illustrated in Figure 26. Macromolecules with a particular molecular mass M_1 vary in their composition m_B. By the same token, molecules of a particular composition m_B exhibit a molecular mass distribution. Such a distribution function for a copolymer cannot be established by a single method of separation, since the

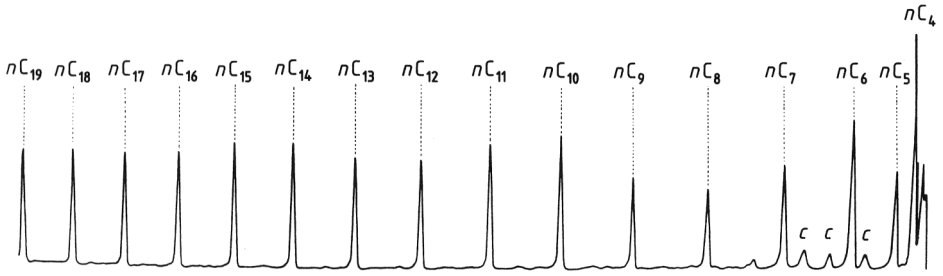


Figure 24. Pyrogram of polyethylene in a hydrogen atmosphere [124]
n = Linear olefins; c = Cyclic olefins

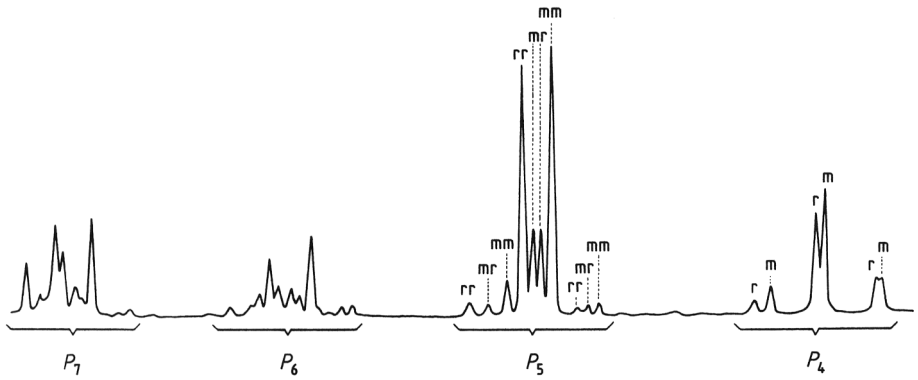


Figure 25. Pyrogram of isotactic polypropylene in a hydrogen atmosphere [124]
$P_4 - P_7$ = Degree of polymerization. For assignment of configurational sequences, see Table 8

experimental parameter that distinguishes one molecule from another is no longer determined only by molecular mass, but also by chemical composition and sequential structure. As a result, several structure-specific separation techniques must be used.

This condition can be met to a first approximation by the application of turbidity titration to eluate fractions obtained by gel permeation chromatography (see Gol Permeation Chromatography (GPC)). A copolymer sample is first separated by gel chromatography to give a series

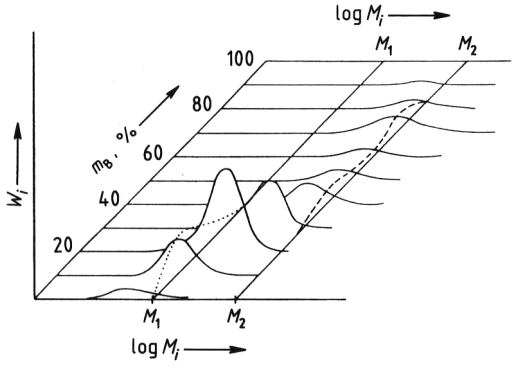


Figure 26. Heterogeneity of copolymer [9]
W_i = Frequency of the macromolecules with molecular mass M_i and chemical composition m_B

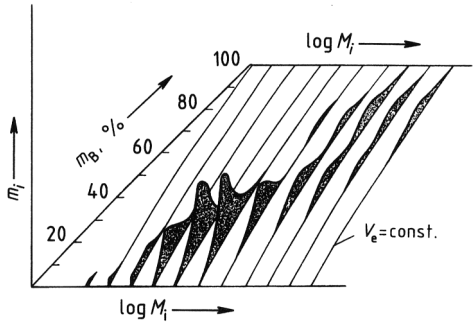


Figure 27. Distribution function of copolymer [9]
Methods: SEC and turbidity titration
m_i = Fraction of copolymer AB with molecular mass M_i and composition m_B; V_e= GPC elution volume

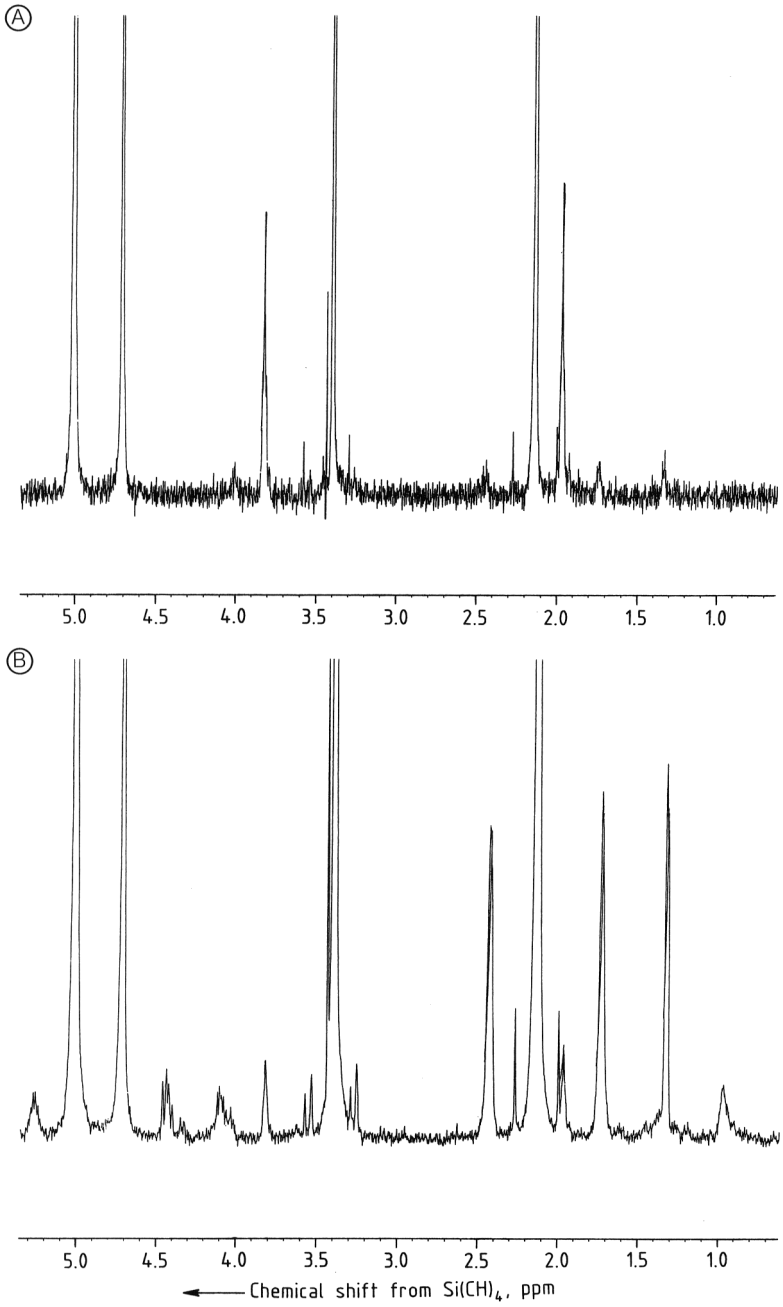


Figure 28. 500 MHz ^{1}H NMR spectrum of fractions from LC-NMR [127]
Online NMR spectra of the fractions 3 (A) and 4 (B) from Figure 17. The chemical structure of different components can be identified by analysis of the NMR spectrum.

of fractions containing molecules of comparable hydrodynamic volume, but not necessarily with the same molecular mass. Under certain conditions subsequent turbidity titration – essentially a precipitation fractionation monitored on the basis of light scattered laterally at an angle of 90°C (see Section 5.2.4) – makes it possible to determine the chemical composition of the polymer. Here

both the amount of precipitant and the rate of precipitant addition are characteristic of the composition of the copolymer, whereas these factors are largely insensitive to molecular mass. The result is a differential distribution function for the copolymer, as shown in Figure 27 [9].

Structural Heterogeneity of Oligomers. Coupling of gradient HPLC and NMR spectroscopy opens up new ways for the online analysis of polymerization reactions. This method is applicable to polymers containing heteroelements such as ^{19}F, ^{31}P etc. The minimal amount of substance for detection of a fraction is ca. 30 μg. The spectra in Figure 28 demonstrate the considerable potential of the method [127].

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Polymerization Processes, 1. Fundamentals

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ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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1. Introduction

Plastics have shaped our modern life, and various types of synthetic polymers are found everywhere in our daily life. Polymers are macromolecules, usually possessing molecular mass larger than 10 000, built up by a large number of small molecules called monomers. There is no significant meaning in the number "10 000", but the term oligomer is often used for polymers with molecular mass smaller than several thousand. Chemical reactions to combine monomers into polymers are called polymerization. The extraordinary versatility of synthetic polymers results from the complexities of polymer structures. The most fundamental polymer structure is determined during the polymerization processes, and therefore, the understanding of the processes is crucially important to produce high quality polymer products.

In the polymerization processes, monomer molecules that move around freely are joined together to form polymers. In general, the entropy change of polymerization ΔS is negative. In order for the free energy change, $\Delta G = \Delta H - T\Delta S$, to be negative, the enthalpy change ΔH must be negative, meaning that the polymerization processes are exothermic. In addition, the viscosity of the reaction system becomes very high as the polymerization proceeds, due to the entanglements of polymer chains, which tends to result in the incomplete mixing and drastic decrease in the heat transfer coefficient during polymerization. Therefore, failure in temperature control may lead to runaway reactions. The control of polymerization processes is a challenging field for the process

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engineers; however, at the same time, it is highly rewarding because the polymer properties are usually very sensitive to the processes used and good operation may turn commodity polymers into high quality specialty polymers.

In this article, some of fundamental elements to understand the polymerization reactions and their mathematical representations are discussed, focusing attention mainly on the polymerization rate and molecular mass distribution (MMD).

2. Polymerization Mechanisms and Kinetics

Polymerization mechanisms are conveniently divided into two categories, step and chain polymerization. Polymerizations in which the polymer chains grow step-wise by reactions that connect any two molecular species are step polymerizations. Polymerizations in which a polymer chain grows only by reaction of monomers with a reactive chain end of the growing chain are chain polymerizations. It is important to note that this is a classification of reaction mechanisms, not of the structure of the repeating unit, since the same polymer could be synthesized either by step or chain polymerization. Officially, IUPAC recommends classifying polymerization reactions into four categories, chain polymerization, condensation chain polymerization, polycondensation, and polyaddition. However, it is still convenient to use the terms, step and chain polymerization to start learning polymerization processes, and these terms are used in this article. The relationships of various definitions are summarized in Table 1 [1]. The terms, step-growth and chain-growth polymerizations have long been used. Although the meanings are the same, for brevity and the modern preference [2], step polymerization and chain polymerization are used in this article.

Generally, polymer physical properties can differ significantly depending on the polymerization mechanism, and this is often due to the difference in molecular mass, i.e., polymers synthesized by chain polymerization often have higher molecular masses. In step polymerization, the size of polymer molecules increases at a relatively slow rate over a much longer period of time. With step polymerization, the reactions that link monomers, oligomers, and polymers involve the same reaction mechanism, and any two molecular species (monomer, oligomer, or polymer) can be coupled. The growth of a polymer chain proceeds slowly from monomer to dimer, trimer, tetramer, and so on, until full-sized polymer molecules are formed at high monomer conversions. Polymer chains continue to grow from both ends throughout the polymerization and, therefore, both chain lifetimes and polymerization times are usually of the order of hours.

Chain polymerization is a chain reaction of the active center, radical or ion, and addition of monomer to the active center is very fast. Once an active center is created, a polymer chain grows rapidly, and when the growing chain is deactivated by a termination reaction, the polymer chain is dead and no longer takes part as a reactant in the polymerization solely producing linear polymer molecules. Except for living polymerization, in which chain transfer and termination reactions are eliminated, polymer molecules generally grow to full size in a timescale that is much smaller than the time required for high conversion of monomer to polymer. In the case of chain polymerization, unreacted monomer is clearly distinct from polymer, and normally, monomers are not included in

Table 1. Classification of polymerization reactions

	Terms used in this article	Chain polymerization	Step polymerization
	Growth mechanism	monomers reacting with active polymer chains	molecules of all sizes reacting together
	Reaction type	chain reaction	usually non-chain reaction
Stoichiometry	With low-molar-mass byproduct	condensative chain polymerization	polycondensation
	Without low-molar-mass byproduct	chain polymerization	polyaddition

the polymer molecular mass distribution. On the other hand, in step polymerization there is no clear distinction between polymers and monomers, and monomers are included in the polymer molecular mass distribution.

3. Kinetics of Step Polymerization

In step polymerization, there is generally only one type of chemical reaction that links molecules of all sizes. Some of the typical chemical reactions are esterification, amidation, the formation of urethanes, and aromatic substitution. The growth reaction in step polymerization can be represented by the general reaction:

$$m\,\text{mer} + n\,\text{mer} \rightarrow (m+n)\text{mer} \tag{1}$$

The kinetic study of such reactions would be extremely difficult if the rate constant for the coupling reaction depended on the size of both species. Fortunately, various kinetic studies have shown that the rate constant is effectively independent of chain length except perhaps for oligomers. This is often referred to as the concept of equal reactivity of functional groups.

Consider the example of step polymerization shown below.

$$n\text{A} - \text{A} + n\text{B} - \text{B} \rightarrow [\text{A} - \text{A} - \text{B} - \text{B}]_n \tag{2}$$

In the case of the polyesterification of a diol and a diacid, A may be a hydroxyl group and B may be a carboxyl group, although the low molecular mass condensation byproduct is not shown. As shown later, an almost exact equivalence in the number of functional groups is necessary to obtain polymers with high molecular weight. In the case of exact stoichiometric ratio of the two types of functional groups, i.e., [A] = [B], the polymerization rate or the rate of disappearance of functional groups is given by

$$-\frac{1}{V}\frac{\mathrm{d}(V[\text{A}])}{\mathrm{d}t} = k[\text{A}][\text{B}] = k[\text{A}]^2 \tag{3}$$

except for self-catalyzed polymerization, in which case the rate is third order in monomer. The self-catalyzed polymerization may not be a useful reaction from the practical point of view of productivity. Neglecting the volume (V) change during polymerization, integration of Equation (3) gives

$$\frac{1}{1-p} = 1 + k[\text{A}]_0 t \tag{4}$$

where $[\text{A}]_0$ is the initial (at $t = 0$) concentration of A groups, and p is the conversion of functional groups, which is defined as

$$p = (N_{\text{A}_0} - N_{\text{A}})/N_{\text{A}_0} \tag{5}$$

where N_{A_0} and N_{A} are the total number of moles of A groups at $t = 0$ and at any later time t, respectively, i.e., $N_{\text{A}_0} = V_0[\text{A}]_0$ and $N_{\text{A}} = V[\text{A}]$.

Consider the number-average chain length of the reaction mixture $\overline{P}_{\text{n}}$, which is simply given by the following ratio:

$$\overline{P}_{\text{n}} = \frac{(\textit{total number of monomeric units})}{(\textit{total number of molecules})} \tag{6}$$

Note that in the case of step polymerization, monomer molecules are also counted in both denominator and numerator.

For the polymerization of A-A and B-B type monomers, if $[\text{A}]_0 = [\text{B}]_0$ holds, the total number of monomeric units in the reaction system, which is the numerator of Equation (6) is $N_{\text{A}_0}/2 + N_{\text{B}_0}/2 = N_{\text{A}_0}$. On the other hand, because the total number of molecules decreases by one each time a bond is formed, the total number of molecules is given by $N_{\text{A}_0} - \left(N_{\text{A}_0} - N_{\text{A}}\right) = N_{\text{A}}$, and therefore:

$$\overline{P}_{\text{n}} = \frac{N_{\text{A}_0}}{N_{\text{A}}} = \frac{1}{1-p} \tag{7}$$

Equation (7) shows that very high conversions are necessary to obtain large chain lengths. For example, $\overline{P}_{\text{n}}$ is only 20 even when the conversion is as large as $p = 0.95$, and $p = 0.99$ is required to obtain $\overline{P}_{\text{n}} = 100$.

Combining equations (4) and (7) gives:

$$\overline{P}_n = 1 + k[\text{A}]_0 t \tag{8}$$

which shows that $\overline{P}_{\text{n}}$ increases linearly with time. In terms of conversion of functional groups p, $\overline{P}_{\text{n}}$ increases significantly only at the final stage of polymerization as shown in

Equation (7). The assumption with respect to time that $\overline{P}_n$ also increases rapidly in the final stage, is not so as shown in Equation (8). Because the melt viscosity increases with 3.4 power of molecular mass [3], the viscosity does increase tremendously at the final stage even with respect to time, but the $\overline{P}_n$-value does not. In fact, the increase in viscosity makes it difficult to remove condensation byproduct, which may lead to a slower increase in $\overline{P}_n$ with respect to time during the final stage of polymerization.

Equation (7) assumes an exact stoichiometric ratio of unity. If a slight excess of one bifunctional monomer is used, all chain ends will eventually consist of the group present in excess. Assuming $N_{A_0} < N_{B_0}$, and defining the stoichiometric imbalance α by $\alpha = N_{A_0}/N_{B_0}$. The total number of monomer molecules initially present is given by $\left(N_{A_0} + N_{B_0}\right)/2 = N_{A_0}(1 + 1/\alpha)/2$. Now consider the situation at conversion p. Note that p is usually defined with respect to the deficient group, so that p is defined for A groups in this example. Because the total number of molecules decreases by one each time a bond is formed as in the exact stoichiometric case, the total number of molecules is given by $\left(N_{A_0} + N_{B_0}/2 - N_{A_0}p\right) = \left[N_{A_0}(1 - p) + N_{B_0}(1 - \alpha p)\right]/2$. Therefore, Equation (6) leads to:

$$\overline{P}_n = \frac{1 + 1/\alpha}{1 - p + (1 - \alpha p)/\alpha} = \frac{1 + \alpha}{1 + \alpha - 2\alpha p} \tag{9}$$

When $\alpha = 1$, Equation (9) reduces to Equation (7). As conversion p approaches unity, $\overline{P}_n$ goes to $(1 + \alpha)/(1 - \alpha)$. Thus if $\alpha = 0.99$, the maximum number-average chain length attainable is only 199. This example illustrates the importance of precise control of the stoichiometric ratio in order to obtain a desired chain length.

In general, in order to produce high molecular mass polymers by step polymerization, the system must satisfy the following requirements:

1. Very accurate control of the stoichiometric ratio of functional groups
2. Absence of side reactions
3. Availability of high-purity monomers
4. Reasonably high polymerization rate
5. Little tendency towards cyclization reactions

4. Basic Concepts of Molecular Mass Distribution (MMD)

The representative MMDs used in polymer science are the distribution on a number and a mass basis. A convenient way to understand the concept of the MMD, or equivalently, the chain length distribution, is to consider the fraction of polymer with chain length r, as the probability of finding r-mer in the polymer mixture. The random sampling technique [5] is a convenient method to elucidate the difference of the number and mass basis. Figure 1 shows the concept of selection on a number and a mass basis. Suppose there are an infinite number of polymer molecules. The number fraction distribution is obtained when polymer molecules are sampled by selecting chain ends randomly, as shown in

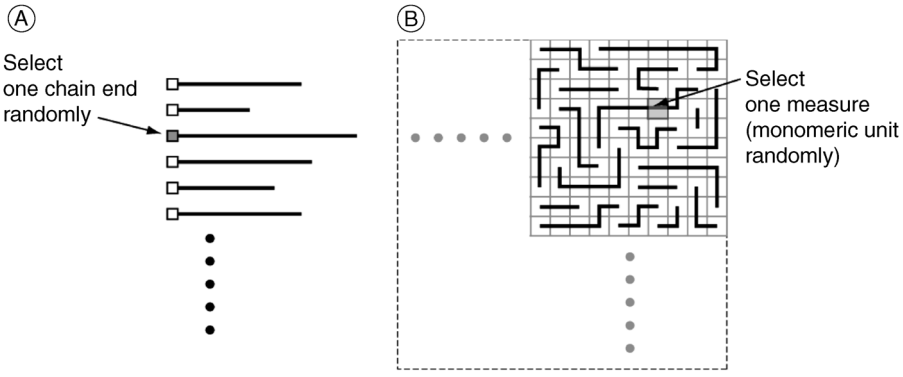


Figure 1. Concept of the chain length distribution on a number basis (A) and on a mass basis (B), from the point of view of the random sampling technique

Figure 1A. The number-average chain length is the expected chain length of a polymer molecule selected. On the other hand, suppose that all polymer molecules are embedded into 2D space, so that each monomeric unit occupies one measure (Fig. 1B). When one measure, or equivalently, one monomeric unit is chosen randomly, the polymer molecule that involves this particular unit is selected on a mass basis.

Consider the chain length distribution formed in an ideal step polymerization, in which the probability of connecting the next unit is given by p for all units. The number fraction distribution can be obtained by selecting chain ends randomly, as shown in Figure 2A. The polymer molecule having r units must have (r-1) linkages, and at the same time, the final unit must not be connected. Therefore, the probability of finding polymer with length r is given by:

$$N(r) = p^{r-1}(1-p) \tag{10}$$

Obviously, the mass fraction distribution $M(r)$ can be calculated from the number fraction distribution, as follows:

$$M(r) = \frac{rN(r)}{\sum_{r=1}^{\infty} rN(r)} = rp^{r-1}(1-p)^2 \tag{11}$$

On the basis of the random sampling technique, the above equation can be obtained with the following reasoning. Suppose a polymer molecule has been chosen by selecting one monomeric unit randomly, as shown in Figure 2B. This polymer molecule contains (r - 1) linkages, and both chain ends must not be connected. In addition, the same polymer molecule could have selected by selecting any monomeric units in the chain, and there are r selection possibilities. Therefore, the probability of finding polymer with length r on a mass basis, which is equal to the mass fraction distribution, is given by:

$$M(r) = rp^{r-1}(1-p)^2 \tag{12}$$

The chain length distribution represented by Equation (10) on a number basis and Equation (12) on a mass basis is called the most probable distribution [4]. The most probable distribution is formed when the probability of connecting next unit is a constant, and is the most fundamental distribution of synthetic polymers. When the number-average chain length is large enough, i.e., $p \to 1$, the distribution can be represented by the following continuous functions, by using the relationships, $p^{r-1} \cong \exp[-(1-p)r]$ and Equation (7).

$$N(r) = \frac{1}{\overline{P}_n}\exp\left(-\frac{r}{\overline{P}_n}\right) \tag{13}$$

$$M(r) = \frac{r}{(\overline{P}_n)^2}\exp\left(-\frac{r}{\overline{P}_n}\right) \tag{14}$$

The mass average chain length is the expected chain length when one polymer molecule is selected on a mass basis. The averages can always be obtained from the distribution functions, however, for the most probable distribution, the mass-average chain length can be obtained by using Figure 2, just arithmetically as follows. In Figure 2B, the connection statistics are completely the same as that for Figure 2A, when approaching the randomly selected unit from the right, which shows the number-based selection. Therefore, the

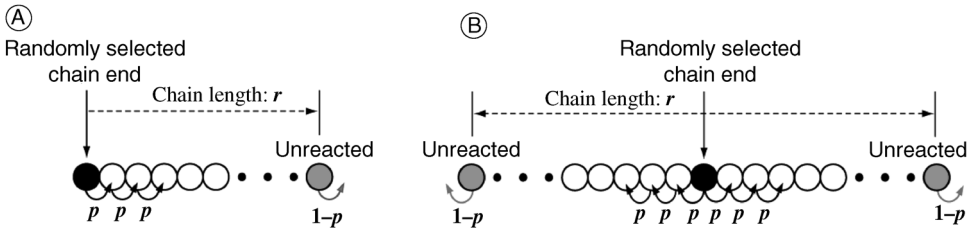


Figure 2. Number (A) and mass (B) fraction distribution of polymers formed in step polymerization

expected chain length from the right direction starting from the randomly selected unit is $\overline{P}_n$. Similarly, approaching from the left direction from the randomly selected unit, the connection statistics are again the same as for Figure 2A, and the expectation is $\overline{P}_n$. Remembering that the randomly selected unit is counted twice, the mass-average chain length of the most probable distribution is given by:

$$\overline{P}_M = 2\overline{P}_n - 1 = \frac{1+p}{1-p} \tag{15}$$

On the basis of the random sampling technique, it is obvious that the polydispersity index $\overline{P}_M/\overline{P}_n$ of the most probable distribution is practically equal to 2, when the chains are long enough.

Figure 3A shows the most probable distribution profiles on a number basis $N(r)$, and on a mass basis $M(r)$. There are a greater number of smaller chains and $N(r)$ is simply an exponentially decreasing function. On the other hand, a peak appears on a mass basis $M(r)$. The peak chain length conforms to the number average chain length $\overline{P}_n$, which is 100 in the case shown in Figure 3.

The most probable distribution is most frequently seen distribution in synthetic polymers. The most probable distribution is obtained if the probability of connecting the next unit is the same for all units in a chain. Therefore, this type of distribution is obtained if the reactivity of all functional groups is equal and independent of the chain length. In step polymerization, the most probable distribution is obtained not only for the cases with complete equilibrium, but also or the cases with irreversible polymerization in a batch reactor starting from monomer.

In free-radical polymerization, the polymer radicals follow the most probable distribution, as shown in Section 6.2.2. Another example includes the degradation of polymer chains. Starting from any kind of distribution, random degradation leads to the formation of the most probable distribution [6–8]. Irreversible depolymerization by chain-end scission (unzipping) also leads to the formation the most probable distribution [9]. Because of the random nature of synthetic polymer formation, it can be found everywhere in polymer science, except for the living polymers.

The chain length distribution profiles are often represented by using a logarithm of chain length as an independent variable. In the measurement of MMDs using size exclusion chromatography (SEC, also known as gel permeation chromatography, GPC), the MMD is commonly given by the mass fraction distribution whose independent variable is the logarithm of molecular mass. Now consider how to convert independent variable to the logarithm of it. Note that the MMD or its equivalent chain length distribution is the probability density distribution, and it is always the area that represents the probability. The mass fraction of polymers whose chain length is between a and b is given by:

$$\int_a^b M(r)dr = \int_{\log_{10}a}^{\log_{10}b} M(\log_{10}r)d(\log_{10}r) \tag{16}$$

This is a simple problem on the change of variables. By using the relationship, $\log_{10}r = \ln r/\ln 10$, one obtains $dr = r\ln 10 d(\log_{10}r)$. By

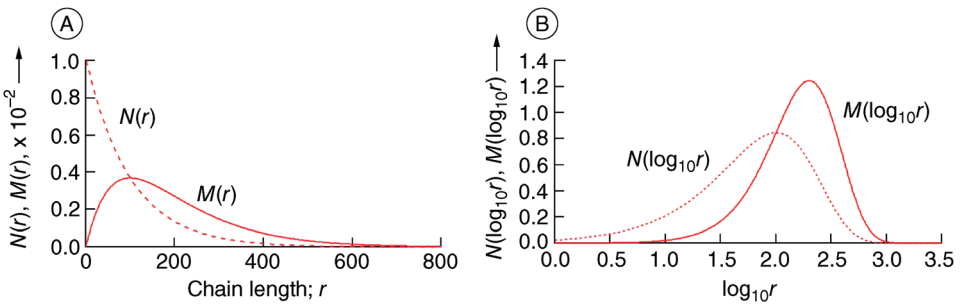


Figure 3. Most probable distribution profiles plotted as a function of chain length r (A), and as a function of the logarithm of r (B), for $\overline{P}_n = 100$

substituting into Equation (16),

$$\int_{\log_{10}a}^{\log_{10}b} M(r)r\ln 10\, d(\log_{10}r) = \int_{\log_{10}a}^{\log_{10}b} M(\log_{10}r)\, d(\log_{10}r) \qquad (17)$$

Equation (17) shows the transformation rule, represented by:

$$M(\log_{10}r) = M(r)r\ln 10 \qquad (18)$$

Figure 3B shows the most probable distribution, plotted as a function of $\log_{10}r$. Both number and mass fraction distribution possess a peak. The peak chain length is $\overline{P}_n$ for $N(\log_{10}r)$, and $\overline{P}_w$ for $M(\log_{10}r)$.

All 4 curves in Figure 3 show the same most probable distribution, and the physical meaning is completely the same, although appearances of the profiles are significantly different. When discussing the MMDs, one needs to clarify (1) whether the distribution is on the number basis or on the mass basis, and (2) whether the independent variable is a normal scale or a logarithmic scale.

The chain length distributions can be converted to the MMDs in a straightforward manner, simply bearing in mind that it is the area that represents the probability. Assuming the molecular mass of monomeric unit is m, the molecular mass is given by $M_M = mr$. When the independent variable is a normal scale, the x-axis is enlarged m times ($M_M = mr$), while the y of the polymer-axis is made smaller by m times, i.e., $N(M_M) = N(r)/m$ and $M(M_M) = M(r)/m$. On the other hand, when the independent variable is changed to $\log_{10}M_M$ from $\log_{10}r$, only the reading of the x-axis is shifted by $\log_{10}m$, i.e., $\log_{10}M_M = \log_{10}r + \log_{10}m$, while the value of y-axis is the same, $N(\log_{10}M_M) = N(\log_{10}r)$ and $M(\log_{10}M_M) = W(\log_{10}r)$.

5. Chain Polymerization

Chain polymerization is initiated by a reactive species, R_{in}^*, produced from an initiator or catalyst I.

$$I \xrightarrow{k_d} nR_{in}^* \qquad (19)$$

Depending on the type of active center, chain polymerization can be divided into free-radical, anionic, and cationic polymerization. The reactive species R_{in}^* adds to a monomer to form a new active center, and monomer molecules are added to the active center successively. This process is called the propagation reaction:

$$R_{in}^* \xrightarrow{+M} P_1^* \xrightarrow{+M} P_2^* \xrightarrow{+M} P_3^* \cdots \qquad (20)$$

where M represents a monomer molecule, and P_r^* is an active polymer molecule with chain length r. In general, the propagation reaction is represented by:

$$P_r^* + M \xrightarrow{k_p} P_{r+1}^* \qquad (21)$$

In chain polymerization, only molecules with an active center can propagate, so that polymer molecules once formed may be considered dead polymer for linear chain polymerization. Dead polymer molecules do not take part as reactants thereafter. The active center is always on the chain end when linear chains are being produced exclusively. Polymer chain growth is terminated at some point by termination. Bimolecular termination between active centers occurs only in free-radical polymerization.

Carbon–carbon double bonds and the carbon–oxygen double bond in aldehydes and ketones are the two main types of functional groups that undergo chain polymerization. The polymerization of the carbon–carbon double bond is much more important, as most commercial monomers with carbon–carbon double bonds readily undergo free-radical polymerization (an important exception is propene). The carbonyl bond is not generally susceptible to polymerization by radical initiators due to its highly polarized structure. Another reason is that most of the carbonyl monomers (except formaldehyde) possess very low ceiling temperatures [10], the temperature above which active polymer chains depolymerize rather than grow.

Most of the commercial vinyl monomers (CH_2=CHX and CH_2=CXY, and monomers in which fluorine is substituted for hydrogen) can be polymerized with free radicals. Whether a vinyl monomer can be polymerized by anionic or cationic mechanisms strongly depends on the type of monomer. Monomers with

electron-donating groups attached to the doubly bonded carbon atoms form stable carbenium ions and polymerize best with cationic initiators. Conversely, monomers with electron-withdrawing substituents form stable carbanions and require anionic initiators. It should be noted that ions of low stability might be expected to react with carbon–carbon double bonds; however, in many cases they cannot be formed or else are easily consumed by side reactions.

6. Free-Radical Polymerization

As one of the most representative examples of chain polymerization, the kinetics of free-radical polymerization is discussed in detail. Controlled/living radical polymerization, whose IUPAC name is "reversible-deactivation radical polymerization" [11], also belongs to free-radical polymerization; however, it possesses a living nature and will be discussed in Chapter 8.

6.1. Elementary Reactions

Generally, free-radical polymerization consists of four types of elementary reaction; initiation, propagation, termination, and chain transfer reactions.

1. Initiation reactions, which continuously generate radicals during polymerization.

$$\mathrm{I} \xrightarrow{k_\mathrm{d}} n\mathrm{R}^\bullet_\mathrm{in} \tag{22}$$

$$\mathrm{R}^\bullet_\mathrm{in} + \mathrm{M} \xrightarrow{k_\mathrm{i}} \mathrm{R}^\bullet_1 \tag{23}$$

   The stoichiometric coefficient n is two for the thermal decomposition of initiators. A free-radical $\mathrm{R}^\bullet_\mathrm{in}$ derived from the initiator is called a primary or initiator radical.

2. Propagation reactions, which are responsible for the growth of polymer chains by addition of monomer to a radical center.

$$\mathrm{R}^\bullet_r + \mathrm{M} \xrightarrow{k_\mathrm{p}} \mathrm{R}^\bullet_{r+1} \tag{24}$$

   where $\mathrm{R}^\bullet_r$ is a polymer radical (or macroradical) of chain length r.

3. Bimolecular termination reactions between two radical centers, which give a net consumption of radicals. These consist of disproportionation (Eq. 25) and combination (Eq. 26).

$$\mathrm{R}^\bullet_r + \mathrm{R}^\bullet_s \xrightarrow{k_\mathrm{td}} \mathrm{P}_r + \mathrm{P}_s \tag{25}$$

$$\mathrm{R}^\bullet_r + \mathrm{R}^\bullet_s \xrightarrow{k_\mathrm{tc}} \mathrm{P}_{r+s} \tag{26}$$

   where P_r is a polymer molecule of chain length r and does not have a radical center.

4. Chain transfer to small molecules that causes the cessation of the growth of polymer radicals while generating small transfer radicals simultaneously. Chain-transfer reactions do not give a net consumption of radicals, and if the transfer radicals are as reactive as polymer radical (or more reactive) these reactions should not affect the polymerization rate or monomer consumption rate when the bimolecular termination reactions are chemically controlled. Chain-transfer reactions to small molecules reduce the size of polymer radicals and therefore would increase bimolecular termination rates when these reactions are diffusion controlled.

$$\mathrm{R}^\bullet_r + \mathrm{X} \xrightarrow{k_\mathrm{fX}} \mathrm{P}_r + \mathrm{X}^\bullet \tag{27}$$

$$\mathrm{X}^\bullet + \mathrm{M} \xrightarrow{k'_\mathrm{p}} \mathrm{R}^\bullet_1 \tag{28}$$

   X may be monomer, a solvent molecule, or a chain-transfer agent. When X is a polymer molecule, polymer molecules with long-chain branches are formed. Long-branch formation is discussed separately in Section 9.2.

The sequence of elementary reactions in Equations (22–28) result in total radical concentrations of the order 10^{-9}–10^{-5}mol/L for most commercial polymerizations. Since polymer molecules with high molecular masses are produced from the very start of polymerization, the reacting solution can be quite viscous over most of the monomer conversion range. The high viscosities not only cause problems in mixing and heat removal, but also can affect reaction rates (reactions such as bimolecular termination of polymer radicals).

Free-radical polymerization is the most commonly used method for the synthesis of polymers from vinyl and divinyl monomers. Some typical monomers which readily undergo free-radical polymerization are ethylene, styrene, vinyl chloride, vinylidene chloride, acrylonitrile, vinyl acetate, methyl methacrylate, methyl acrylate, acrylamide, etc. Of all chain polymerization processes, it is the most widely studied and best understood.

6.1.1. Initiation

Free radicals may be generated in a monomer in a number of ways. Some of representative methods to generate free radicals are as follows.

1. Thermal decomposition of initiators.
   Chemical initiators, such as azo and peroxide compounds, are added to the monomer in low concentrations (usually < 1 wt% based on monomer). When heated, the initiator decomposes, generating radicals which act as active centers for monomer addition. For example, organic peroxides (ROOR′) decompose thermally by O–O bond cleavage to produce two initiator radicals as follows.

$$\mathrm{ROOR'} \rightarrow \mathrm{RO}^{\bullet} + \mathrm{R'O}^{\bullet} \tag{29}$$

2. Redox initiation.
   This is a method to generate radicals by an oxidation–reduction reaction. The advantage of using this method is that it is possible to generate radicals at lower temperature, normally 0-50°C.
3. Irradiation.
   Irradiation with UV, high-energy electrons, and γ-rays can initiate polymerization with or without the presence of initiators. Radiation initiation has been used widely for polymer modification (chain scission, long-chain branching, cross-linking, and grafting). These radiation processes are characterized by a zero activation energy for radical generation and as a consequence a low activation energy for polymerization. Therefore, they are effective at both low and high temperatures.
4. Thermal polymerization.
   It is known that some types of monomers, such as styrene (and some substituted styrenes such as *p*-methylstyrene) and methyl methacrylate generate free radicals at elevated temperatures in the absence of a free-radical initiating system.

The most often used method of free-radical generation is to use the thermal decomposition of initiators, and the kinetics of initiation is discussed for such systems, represented by:

$$\mathrm{I} \xrightarrow{k_d} 2\mathrm{R}^{\bullet}_{in} \tag{30}$$

where k_d is a thermal decomposition rate constant with units of inverse time, most often s^{-1}. This is a first order reaction, and the change in the number of moles of initiator N_I for a batch reactor is given by:

$$dN_I/dt = -k_d N_I \tag{31}$$

For isothermal decomposition (isothermal polymerization) Equation (31) can be integrated analytically to obtain:

$$N_I = N_{I_0} \exp(-k_d t) \tag{32}$$

where N_{I_0} is the number of moles of initiator at time $t = 0$.

The half-life of an initiator is given by:

$$t_{1/2} = -\ln(0.5)/k_d = 0.693/k_d \tag{33}$$

Equation (33) shows that the knowledge of k_d for an initiator permits calculation of the initiator half-life $t_{1/2}$. In reverse, it is possible to determine k_d from $t_{1/2}$, and they are equivalent. Since k_d has an Arrhenius temperature dependence, k_d and $t_{1/2}$ both depend on temperature. Activation energies for peroxides and azo initiators are ca. 120 kJ/mol, so the decomposition rate is highly temperature dependent, and the useful temperature range is quite small (decomposition rate is either too fast or too slow outside the useful temperature range, which normally spans about 30°C).

To complete the initiation step, the initiator radicals ($R^{\bullet}_{in}$) must add to the double bond of a monomer molecule to generate a polymer

radical of unit chain length $R_1^\bullet$. In most polymerizations, this step (Eq. 23) is much faster than the rate of initiator decomposition (Eq. 22). The homolysis of the initiator is the rate-determining step in the initiation sequence, and the initiation rate R_I is given by:

$$R_I = 2k_d f[I] \tag{34}$$

where f is the initiator efficiency. The coefficient 2 comes from the two initiator radicals which are generated from a single initiator decomposition. The initiator efficiency is defined as the fraction of radicals produced by initiator decomposition that initiate polymer radicals. Some primary radicals may react with themselves or with other molecules to form stable species that do not form polymer radicals. The initiator efficiency usually has values in the range 0.2–1.0 at low monomer conversions, where polymer concentrations are low.

The major cause of low initiator efficiency is recombination of the radical pairs before they diffuse apart, which is called the cage effect. When an initiator decomposes, the primary radicals $R_{in}^\bullet$ are nearest neighbors for about $10^{-10}-10^{-9}$ s. During this interval they are surrounded by a "cage" of solvent and monomer molecules through which they must diffuse to escape from the cage. Since reactions between radicals are extremely fast, there is reasonable probability that reaction between primary radicals occurs. Direct recombination may simply regenerate the original initiator molecules, but other reactions can also occur that consume initiator radicals without forming polymer chains. In particular, since azo initiators decompose with the elimination of a nitrogen molecule, recombination of the primary radicals results in the formation of a stable molecule that cannot generate radicals, and thus there may be a significant decrease in initiator efficiency. Efficiency decreases with increasing viscosity of the reaction medium. Thus f decreases during the course of polymerization and may approach zero at very high polymer concentrations where the diffusion coefficient of primary radicals in the "cage" is very small [12, 13], which may result in stoppage of bulk polymerization at below 100% monomer conversion.

When selecting an initiator type, in general the magnitude of the decomposition rate constant, water and oil solubility, stability of initiator fragments on chain ends, and other factors should be considered. Another important point is the activity of the initiator radical center towards the abstraction of atoms (e.g., hydrogen atoms) from the polymer backbone. This can lead to chain scission, long-chain branching, and possibly crosslinking.

6.1.2. Propagation

The propagation reaction (Eq. 24) controls both the rate of growth and the structure of the polymer chain. Monomers which undergo free-radical polymerization are commonly monosubstituted or 1,1-disubstituted ethylenes, CH_2=CHX or CH_2=CXY. With 1,1-disubstituted ethylenes both substituents should not be large, since propagation would be sterically hindered. 1,2-Disubstituted ethylenes are normally considered very difficult to polymerize since the approach of the propagating radicals to a monomer is sterically hindered. 1,2-Disubstituted ethylenes can, however, often be incorporated into copolymers.

Due to steric and resonance effects, vinyl monomers predominantly undergo head-to-tail addition. In certain cases when the substituents are small and do not have large resonance stabilizing effects, head-to-head propagation may occur. For example, approximately 16% head-to-head placement has been reported for poly(vinyl fluoride) [14].

In free-radical polymerization, chain microstructure is largely independent of initiation mechanism and initiator type. Polymers produced by free-radical polymerization are largely atactic. The slight preference for syndiotactic over isotactic placement is caused by steric and/or electrical repulsion between substituents in the chain, although at high temperatures their effects are progressively diminished, due to thermal motion. For example, the fraction of syndiotactic diads of poly(vinyl chloride) changes from 0.67 to 0.51 as the synthesis temperature increases from −78°C to 120°C [15]. For methyl methacrylate, it is 0.86 at −40°C and 0.64 at 250°C [16, 17].

For most chain polymerization conditions, either free-radical or ionic, the propagation

reactions can be considered irreversible. However, it is important to bear in mind that the rate of depropagation becomes significant at elevated temperature [18, 19]. The ceiling temperature T_c, which is the temperature above which active polymer chains depolymerize rather than grow, is reached when the propagation and depropagation rates are equal. Note that the ceiling temperature T_c is not a singular value but is a function of monomer concentration. At any temperature, a concentration of monomer exists at which polymerization/depolymerization is at equilibrium. The existence of this equilibrium concentration prevents monomer conversion reaching 100%. Normally, this equilibrium monomer concentration is very low. A notable exception is α-methylstyrene whose T_c for 100% monomer concentration is 61°C, and the equilibrium monomer concentration at 25°C is 2.2 mol/L [20].

In a strict sense, the propagation rate constant k_p changes with chain length. The first propagation step could be much faster than the long chain propagation reactions. However, experimental results have shown that k_p is independent of chain length for chain lengths larger than about 5 for many monomer types [21]. When producing polymers with high molecular masses, the chain-length dependence could be neglected. The propagation rate constant k_p is relatively insensitive to the viscosity of the system, except at very high polymer concentrations [13, 22].

On the basis of the elementary reaction shown in Equation (24), the propagation rate R_p is represented by:

$$R_p = k_p[M][R^\bullet] \tag{35}$$

where k_p is the propagation rate constant, [M] is the monomer concentration, and $[R^\bullet]$ is the total polymer radical concentration, i.e., $[R^\bullet] = \sum_{r=1}^{\infty}[R_r^\bullet]$. When the chain lengths of produced polymers are long enough, monomer consumption other than propagation is negligibly small, and Equation (35) is directly equal to the polymerization rate for usual free-radical polymerizations (long-chain approximation).

For a batch polymerization, the time development of monomer conversion, x can calculated from:

$$\frac{dx}{dt} = k_p(1-x)[R^\bullet] \tag{36}$$

The average number of monomer units added to a single radical in a second, $\overline{n}_M$ is given by:

$$\overline{n}_M = R_p/[R^\bullet] = k_p[M] \tag{37}$$

Usually, $k_p[M]$ is quite large, and one would understand that a single polymer chain can be formed within a couple of seconds in free-radical polymerization. The average time needed to add a monomer unit to a radical center can be estimated by $1/k_p[M]$.

6.1.3. Termination

Bimolecular termination in free-radical polymerization is either by disproportionation (Eq. 25) or by combination (Eq. 26). In the disproportionation termination, the terminal double bonds could be formed. However, these double bonds are often both substituted and usually inactive toward free-radical polymerization. Even when they are active, the reaction of the terminal double bonds can be neglected until the polymerization proceeds to a high conversion region where the terminal double bond fraction among the residual double bonds is noticeable.

Termination by combination and disproportionation can occur simultaneously, and the relative importance of these two modes of termination depends most importantly on the monomer type, and secondary on the polymerization temperature. For methyl methacrylate, combination and disproportionation are both important at low temperature, with disproportionation becoming the dominant mode at high temperatures [23].

Distinction of disproportionation and combination is important when discussing the MMD, but for the description of polymerization rate, only the sum of these reaction rates is needed, and the overall termination rate constant k_t can be used.

$$k_t = k_{td} + k_{tc} \tag{38}$$

There are two types of definition for the termination rate constant. One school of thought, such as the compilation of *Polymer Handbook* and also in this article, employs the expression for the termination reaction rate R_t,

which is the radical consumption rate as follows.

$$R_t = k_t[R^\bullet]^2 \tag{39}$$

Another school of thought uses to add coefficient 2:

$$R_t = 2k_t[R^\bullet]^2 \tag{40}$$

Equation (40) is based on the argument that two radicals are consumed by a single termination reaction. On the other hand, when the combination of possible radical pairs is considered, the coefficient 2 disappears. In a termination reaction, two radicals are chosen as a pair. Within a system consisting N radicals, the possible combination is $N(N-1)/2 \cong N^2/2$. When the fate of each radical is considered faithfully, $R_t = 2k_t[R^\bullet]^2/2 = k_t[R^\bullet]^2$.

Each conversion for termination rate constant can be employed as long as used consistently, but these two cannot be mixed. The termination rate constant given by Equation (39) is exactly twice as large as k_t in Equation (40). Careful attention should be paid when deciding which conversion of termination rate constant is used when reading published papers. As mentioned later, Equation (39) is preferable, in order to avoid mistakes in building up the population balance equations.

Because bimolecular termination reactions are intrinsically very fast, these reactions are likely to be diffusion controlled when they involve radical centers on polymeric reactants. The autoacceleration of polymerization rate that is a consequence of diffusion-controlled termination is usually called the gel effect or Trommsdorff–Norrish effect. Figure 4 illustrates the autoacceleration in rate for the polymerization of methyl methacrylate [24]. The interpretation proposed was that the increase in rate is a consequence of a decrease in the rate of termination, due to the large increase in viscosity of the reacting medium, thus giving an increase in radical concentration.

Originally, upon examination of the autoacceleration of the conversion–time curve, it was thought that the termination reaction only became diffusion controlled at some monomer conversions greater than zero and that this occurred when the polymer chains were

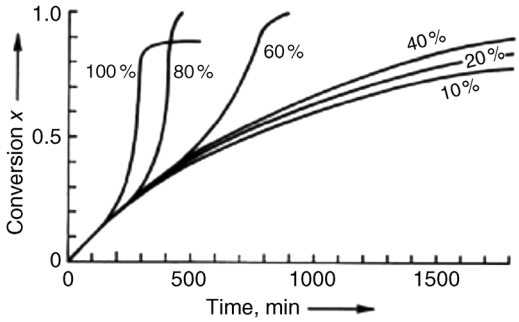


Figure 4. Conversion development for the polymerization of methyl methacrylate in benzene initiated by benzoyl peroxide at 50°C. Different curves are for various initial monomer concentrations in solvent [24]

sufficiently entangled (with a sufficient number of physical entanglement points). It is now recognized that the bimolecular termination reactions may be diffusion controlled even at zero monomer conversion (zero polymer concentration) [25, 26]. This interpretation would be reasonable, because the bimolecular termination constants for polymeric systems are 10^6–10^8 in $Lmol^{-1}s^{-1}$, while those for small molecules are 10^9–10^{10} in solution. When bimolecular termination is diffusion controlled, the chain-length dependent, bimolecular termination is dominated by interactions between short chains and long chains [27, 28].

Strictly, the termination rate constant should depend on the size of the polymeric radical reactants, the concentration and molecular mass distribution of the accumulated polymer, solvent type, temperature, etc. [29] Considering the complexity of the mechanisms of diffusion-controlled termination reactions, a practical way is to use an empirical approach for reactor calculations [30–32]. For example, k_t may be approximated by:

$$k_t = k_t^0 exp\left[-\left(A_1 x + A_2 x^2 + A_3 x^3\right)\right] \tag{41}$$

where x is the monomer conversion, k_t^0 is the termination rate constant at zero monomer conversion ($x = 0$), and A_1, A_2, A_3 are adjustable parameters. The adjustable parameters A_1, A_2, A_3 are usually estimated by fitting the isothermal conversion–time curve, for a given set of polymerization conditions.

6.1.4. Chain Transfer to Small Molecules

During free-radical polymerization, chain transfer to small molecules X may occur. The small molecule may be an initiator, a monomer, a chain-transfer agent, a solvent, an inhibitor, or an impurity. In general, these chain-transfer reactions can be represented by Equations (27) and (28).

When k'_p in Equation (28) is approximately zero (i.e., $X^\bullet$ is a stable radical) X is called an inhibitor. If k'_p is smaller than the propagation rate constant k_p, X is called a retarder. For an added agent to be a chain-transfer agent, k'_p must be approximately equal to k_p (or $k_p < k'_p$, if chain length is large enough). Therefore, the chain-transfer agent reduces the molecular mass but does not affect rates of polymerization.

Monomer is always required in polymerization, and chain transfer to monomer cannot be totally eliminated. The monomer transfer constant $C_m(=k_{fm}/k_p)$ is normally rather small, i.e., $C_m = 10^{-5}$–10^{-4}, but without other chain stoppage mechanism, it may dominate the dead polymer formation. The value of C_m places an upper limit on the average polymer molecular mass that can be obtained with a given monomer, i.e., $\overline{P}_{n,Max} = 1/C_m$.

Consider a batch polymerization with an added chain-transfer agent, CTA. Neglecting the volume change during batch polymerization, the consumption rate of CTA is given by:

$$\frac{d[CTA]}{dt} = k_{fCTA}[CTA][R^\bullet] \tag{42}$$

From Equations (36) and (42), one obtains:

$$\frac{d[CTA]}{dx} = C_{fCTA}\frac{[CTA]}{(1-x)} \tag{43}$$

where C_{fCTA} $(=k_{fCTA}/k_p)$ is the chain-transfer constant. Equation (43) can be solved to obtain:

$$\frac{[CTA]}{[CTA]_0} = (1-x)^{C_{fCTA}} \tag{44}$$

where $[CTA]_0$ is the initial CTA concentration.

Figure 5 shows the calculated results. It is possible to think that CTA with a larger chain transfer constant is effective in reducing the polymer chain length. However, as shown in Figure 5, with a larger C_{fCTA}-values, the CTA is used up in the earlier part of polymerization, and the chain length is uncontrolled in the later stage of polymerization. When $C_{fCTA} = 1$, the ratio [CTA]/[M] is kept constant during a batch polymerization, and the average chain length is kept constant if the chain transfer reaction dominates the dead polymer formation.

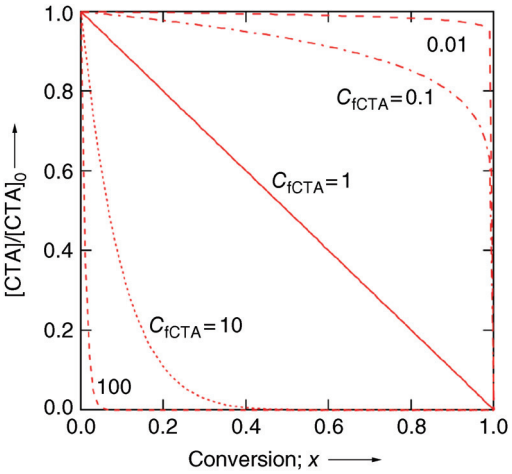


Figure 5. CTA concentration change during batch polymerization

6.2. Kinetics of Free-Radical Polymerization

Bearing in mind the elementary reactions discussed in Section 6.1, consider a free-radical polymerization consisting of the following elementary reactions.

Initiation

$$I \xrightarrow{k_d} 2R^\bullet_{in} \tag{45}$$

$$R^\bullet_{in} + M \xrightarrow{k_d} R^\bullet_1 \tag{46}$$

Propagation

$$R^\bullet_r + M \xrightarrow{k_p} R^\bullet_{r+1} \tag{47}$$

Chain transfer to monomer

$$R^\bullet_r + M \xrightarrow{k_{fm}} P_r + R^\bullet_1 \tag{48}$$

Chain transfer to small molecule, X

$$R_r^{\bullet} + X \xrightarrow{k_{tX}} P_r + X^{\bullet} \quad (49)$$

$$X^{\bullet} + M \xrightarrow{k'_p} R_1^{\bullet} \quad (50)$$

Termination by disproportionation

$$R_r^{\bullet} + R_s^{\bullet} \xrightarrow{k_{td}} P_r + P_s \quad (51)$$

Termination by combination

$$R_r^{\bullet} + R_s^{\bullet} \xrightarrow{k_{tc}} P_{r+s} \quad (52)$$

Complexities in dealing with free-radical polymerization come from the fact that the elementary reactions (45)–(52) occur simultaneously.

The polymer radical with chain length unity, $R_1^{\bullet}$ is formed in elementary reactions (46), (48), and (50). The chemical structure of these three types of radical is different; however, the effect of chain ends on the chemical reactivity of a radical center diminishes well before the chain length becomes large enough to be called a "polymer". One does not have to distinguish these species, except for the production of oligomers.

When dealing with the kinetics of free-radical polymerization, the following assumptions are usually made, without any explicit statement. If any other assumption is employed, it is usually stated clearly.

1. All rate constants are independent of chain length. Note, however, the kinetic rate constants may change with time.
2. Chain lengths are sufficiently large that the total rate of monomer consumption may be equated to the rate of monomer consumption by the propagation reactions alone. This is often called the long-chain approximation (LCA).
3. Radicals generated in chain-transfer reactions propagate with monomer rapidly and thus do not affect the polymerization rate.
4. The stationary-state hypothesis (SSH) is valid for radical reactions. The rates of radical generation and consumption are balanced very quickly.

6.2.1. Polymerization Rate

With the long-chain approximation, the polymerization rate is already represented by Equation (35). However, the total radical concentration $[R^{\bullet}]$ is usually too small to measure directly. In addition, the recipe of polymerization has to be decided before starting experiments, and therefore, $[R^{\bullet}]$ needs to be represented by the concentrations of the basic ingredients.

Looking at the elementary reactions (45)–(52) carefully, it is shown that the change in the number of radicals occurs only in the initiation and termination steps. Therefore, the balance equation for the total radical concentration is given by:

$$\frac{d[R^{\bullet}]}{dt} = R_I - R_t = 2k_d f[I] - k_t[R^{\bullet}]^2 \quad (53)$$

Note that $k_t = k_{td} + k_{tc}$, and the definition of k_t is Equation (39), not Equation (40).

By using the stationary-state hypothesis (SSH) for the total radical concentration, $d[R^{\bullet}]/dt=0$,

$$[R^{\bullet}] = \sqrt{\frac{2k_d f[I]}{k_t}} \quad (54)$$

Note that the SSH, $d[R^{\bullet}]/dt = 0$ does not mean that the radical concentration is constant throughout the polymerization. As shown in Equation (54), $[R^{\bullet}]$ changes with [I], k_d, f, and/or k_t during polymerization. The SSH means that the rates of radical generation and consumption are balanced much faster than the time required for the changes in the other concentrations and parameters.

By substituting Equation (54) into Equation (35), one obtains:

$$R_p = \left(\frac{k_p}{k_t^{0.5}}\right)(2k_d f[I])^{0.5}[M] \quad (55)$$

Equation (54) can be obtained also by using the population balance equations for radicals having different chain lengths. For the radicals

with chain length unity,

$$\frac{d[R_1^\bullet]}{dt} = R_I + k_{fm}[M]\sum_{r=1}^{\infty}[R_r^\bullet] + k'_p[X^\bullet][M] - k_p[R_1^\bullet][M] - k_{fm}[R_1^\bullet][M] - k_{fX}[R_1^\bullet][X] - (k_{tc}+k_{td})[R_1^\bullet][R^\bullet] \quad (56)$$

Note if the conversion for termination rate constant represented by Equation (40) instead of Equation (39) is used, the coefficient 2 is needed in the final term. In this term, only one molecule of $R_1^\bullet$ is consumed in a single termination reaction, and it is difficult to logically explain why the coefficient 2 is needed. Equation (39) may be better to use in building the population balance equations to avoid mistakes.

For the radicals with chain length r (≥ 2),

$$\frac{d[R_r^\bullet]}{dt} = k_p[R_{r-1}^\bullet][M] - k_p[R_r^\bullet][M] - k_{fm}[R_r^\bullet][M] - k_{fX}[R_r^\bullet][X] - (k_{tc}+k_{td})[R_r^\bullet][R^\bullet] \quad (57)$$

Invoking the SSH for each radical and summing up for all chain lengths,

$$\frac{d[R^\bullet]}{dt} = \sum_{r=1}^{\infty}\frac{d[R_r^\bullet]}{dt} = R_I + k'_p[X^\bullet][M] - k_{fX}[R^\bullet][X] - (k_{tc}+k_{td})[R^\bullet]^2 = 0 \quad (58)$$

Using the SSH also for $X^\bullet$, $k'_p[X^\bullet][M] = k_{fX}[R^\bullet][X]$, and therefore:

$$R_I = (k_{tc}+k_{td})[R^\bullet]^2 \qquad \text{or} \qquad [R^\bullet] = \sqrt{R_I/k_t} \quad (59)$$

which agrees with Equation (54).

6.2.2. Molecular Mass Distribution

Invoking the SSH for Equations (56) and (57), one obtains:

$$[R_1^\bullet] = \frac{R_I + k_{fm}[M][R^\bullet] + k'_p[X^\bullet][M]}{k_p[M] + k_{fm}[M] + k_{fX}[X] + (k_{tc}+k_{td})[R^\bullet]} = \frac{(k_{tc}+k_{td})[R^\bullet] + k_{fm}[M] + k_{fX}[X]}{k_p[M] + k_{fm}[M] + k_{fX}[X] + (k_{tc}+k_{td})[R^\bullet]}[R^\bullet] \quad (60)$$

$$[R_r^\bullet] = \frac{k_p[M][R_{r-1}^\bullet]}{k_p[M] + k_{fm}[M] + k_{fX}[X] + (k_{tc}+k_{td})[R^\bullet]} \qquad (r \geq 2) \quad (61)$$

Note that the relationships, $R_I = (k_{tc} + k_{td})[R^\bullet]^2$ and $k'_p[X^\bullet][M] = k_{fX}[R^\bullet][X]$ are used in deriving the final form of Equation (60).

Equations (60) and (61) hold at each instant. As discussed using Equation (37), a single polymer molecule in free-radical polymerization is formed within a couple of seconds, while it usually takes several hours to obtain high conversion of monomer to polymer. Therefore, the concentrations and kinetic rate constants involved in Equations (60) and (61) can be considered constant during the time required for the formation of a single polymer chain, which shows that $[R_r^\bullet]$ is represented by a geometric progression.

Let us introduce the following dimensionless groups:

$$\tau = \frac{R_{td}+R_f}{R_p} = \frac{k_{td}[R^\bullet] + k_{fm}[M] + k_{fx}[X]}{k_p[M]} \quad (62)$$

$$\beta = \frac{R_{tc}}{R_p} = \frac{k_{tc}[R^\bullet]}{k_p[M]} \quad (63)$$

where

$R_p = k_p[R^\bullet][M]$; propagation rate

$R_{td} = k_{td}[R^\bullet]^2$; rate of termination by disproportionation

$R_{tc} = k_{tc}[R^\bullet]^2$; rate of termination by combination

$R_f = k_{fm}[R^\bullet][M] + k_{fX}[R^\bullet][X]$; rate of chain transfer.

The values of τ and β can be considered constant during the formation of a single chain. Note that in order to produce polymers with sufficient chain lengths, both τ and β must be much smaller than unity, i.e., $\tau \ll 1$ and $\beta \ll 1$.

By using τ and β, Equations (60) and (61) reduce to:

$$[R_1^\bullet] = \frac{\tau+\beta}{1+\tau+\beta}[R^\bullet] \quad (64)$$

$$[R_r^\bullet] = \frac{1}{1+\tau+\beta}[R_{r-1}^\bullet] \qquad (r \geq 2) \quad (65)$$

Equation (65) shows the probability of connecting the next unit, $p = 1/(1+\tau+\beta)$ is constant for chains formed within a very small time interval. As clarified in Chapter 4, the most probable distribution is obtained when the probability of connecting the next unit is the same for all units in the sequence of the chain, and therefore, the number and mass fraction

distribution of polymer radicals are given by the following most probable distribution.

$$N^{\bullet}(r) = p^{r-1}(1-p) \tag{66}$$

$$M^{\bullet}(r) = rp^{r-1}(1-p)^2 \tag{67}$$

Note that $p = 1/(1+\tau+\beta)$ and $(1-p) = (\tau+\beta)/(1+\tau+\beta)$. Referring to Equations (7) and (15), the number- and mass-average chain length of polymer radicals are given respectively by:

$$\overline{P}^{\bullet}_{n} = \frac{1}{1-p} = \frac{1+\tau+\beta}{\tau+\beta} \cong \frac{1}{\tau+\beta} \tag{68}$$

$$\overline{P}^{\bullet}_{M} = \frac{1+p}{1-p} = \frac{2+\tau+\beta}{\tau+\beta} \cong \frac{2}{\tau+\beta} \tag{69}$$

If one uses the continuous functions given by Equations (13) and (14), the distributions are given by:

$$N^{\bullet}(r) = (\tau+\beta)\exp[-(\tau+\beta)r] \tag{70}$$

$$M^{\bullet}(r) = r(\tau+\beta)^2\exp[-(\tau+\beta)r] \tag{71}$$

Now, consider the instantaneous mass fraction distribution of dead polymers, i.e., the mass fraction distribution of dead polymers formed within a small time interval. On the basis of the random sampling technique, represented by Figure 1, the mass fraction distribution can be obtained by randomly selecting one monomeric unit in the chain. Figure 6 shows the random selection of a polymer radical, just before the dead polymer formation. Because this polymer radical is selected on a mass basis, the chain length distribution is given by $M^{\bullet}(r)$. With probability $\tau/(\tau+\beta)$, the dead polymer chain is formed by disproportionation termination or chain-transfer reaction. In this case, the formed dead polymer length is the same as the original polymer radical, i.e., $M_{\tau}(r) = M^{\bullet}(r)$. On the other hand, with probability $\beta/(\tau+\beta)$, the dead polymer chain is formed by combination termination. In this case, the chain length of the dead polymer chain is longer than the original polymer radical.

Figure 7 shows the schematic representation of the combination termination. Neglecting the chain length dependence of bimolecular termination reaction, the partner is selected by choosing a radical center randomly, i.e., by choosing a chain end randomly. This is the selection process based on a number, as was shown in Figure 1. Therefore, given the chain is formed by combination termination, the probability to obtain dead polymer chain having length r is given by:

$$\begin{aligned} M_{\beta}(r) &= \sum_{s=1}^{r-1} M^{\bullet}(s)N^{\bullet}(r-s) \\ &\cong \int_0^r M^{\bullet}(s)N^{\bullet}(r-s)ds = (\tau+\beta)^3\exp[-(\tau+\beta)r]\int_0^r s\,ds \\ &= \frac{r^2}{2}(\tau+\beta)^3\exp[-(\tau+\beta)r] \end{aligned} \tag{72}$$

Therefore, the instantaneous mass fraction distribution is given by:

$$\begin{aligned} M_{\text{inst.}}(r) &= \frac{\tau}{\tau+\beta}M_{\tau}(r) + \frac{\beta}{\tau+\beta}M_{\beta}(r) \\ &= (\tau+\beta)\left\{\tau + \frac{\beta}{2}(\tau+\beta)r\right\} r\exp[-(\tau+\beta)r] \end{aligned} \tag{73}$$

The mass-average chain length of the dead polymer formed instantaneously, $\overline{P}_{M,\text{inst.}}$ can be calculated from the mass fraction distribution,

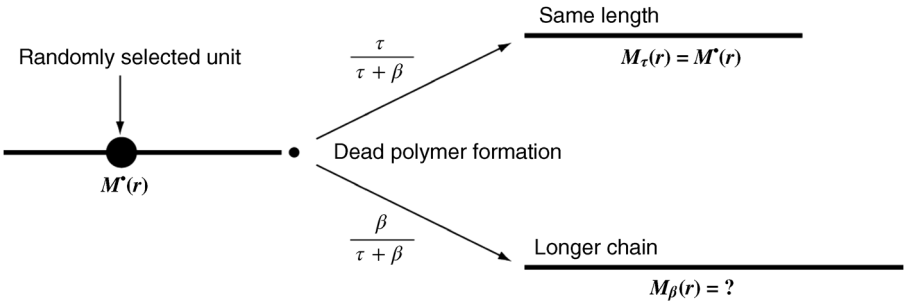


Figure 6. Process of dead polymer chain formation

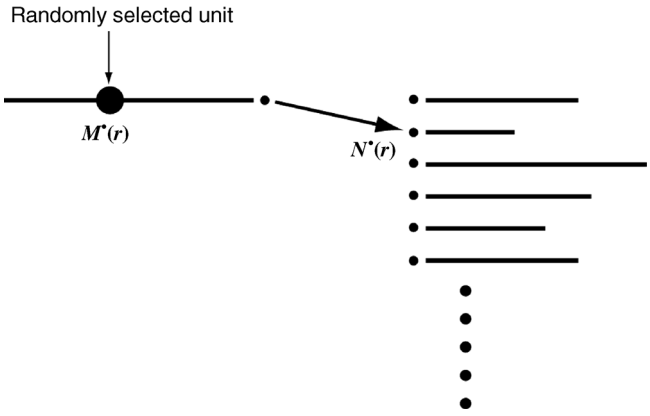


Figure 7. Schematic representation of the process of combination termination

but on the basis of the random sampling technique, it can be obtained as follows.

As was shown in Figure 6, the expected chain length of the randomly selected polymer radical is $\overline{P}_M^{\bullet}$, because it is selected on a mass basis. Only with combination termination, whose probability is $\beta/(\tau+\beta)$, does the chain length increase. As shown in Figure 7, the expected chain length of the partner is $\overline{P}_{\mathrm{n}}^{\bullet}$. Therefore, the mass-average chain length of the dead polymer chains, $\overline{P}_{M,\mathrm{inst.}}$ is given by:

$$\overline{P}_{\mathrm{w,inst.}} = \overline{P}_{\mathrm{w}}^{\bullet} + \frac{\beta}{\tau+\beta}\overline{P}_{\mathrm{n}}^{\bullet} = \frac{2}{\tau+\beta} + \frac{\beta}{(\tau+\beta)^2} = \frac{2\tau+3\beta}{(\tau+\beta)^2} \tag{74}$$

Note that the number and mass average chain lengths of radicals are given by Equations (68) and (69), respectively.

Next consider the number-average chain length of the dead polymer chain formed instantaneously, $\overline{P}_{\mathrm{n,inst.}}$. Figure 8 shows a schematic representation of a random sampling of a dead polymer chain on a number basis, i.e., one dead polymer chain end is selected randomly. Note that the number of dead polymer chains becomes smaller than that for polymer radicals because of the combination termination. Just before the dead polymer formation, the number ratio of the polymer radicals causing the τ-process and β-process is τ:β. When one dead polymer chain end is selected randomly, the expected chain length of the radical part is $\overline{P}_{\mathrm{n}}^{\bullet}$. Only with combination termination (β-process), whose probability is $(\beta/2)/(\tau+\beta/2)$ as shown in Figure 8, does the chain length increase. The expected chain length of the coupled part is $\overline{P}_{\mathrm{n}}^{\bullet}$, because the active radical center is chosen randomly. Therefore, the expected chain length when one dead polymer chain end is selected randomly, which is the number-average chain length of the dead polymer chains, $\overline{P}_{\mathrm{n,inst.}}$ is given by:

$$\overline{P}_{\mathrm{n,inst.}} = \overline{P}_{\mathrm{n}}^{\bullet} + \frac{\beta/2}{\tau+\beta/2}\overline{P}_{\mathrm{n}}^{\bullet} = \frac{\tau+\beta}{\tau+\beta/2}\overline{P}_{\mathrm{n}}^{\bullet} = \frac{1}{\tau+\beta/2} \tag{75}$$

The polydispersity index (PDI) for polymer produced instantaneously is given by:

$$\mathrm{PDI}_{\mathrm{inst.}} = \frac{\overline{P}_{\mathrm{M,inst.}}}{\overline{P}_{\mathrm{n,inst.}}} = \frac{(2\tau+3\beta)(\tau+\beta/2)}{(\tau+\beta)^2} \tag{76}$$

If $\beta = 0$, i.e., termination by combination does not occur, the polydispersity index takes on the maximum value, PDI = 2. On the other hand, if $\tau = 0$, i.e., chain termination is solely by bimolecular termination through combination, PDI takes on the minimum value, 1.5. Note that the combination termination makes MMD narrower. This is because although the combination termination makes the number-average chain length twice as large as that of polymer radicals $\overline{P}_{\mathrm{n,inst.}} = 2\overline{P}_{\mathrm{n}}^{\bullet}$, it makes the mass-average only 1.5 times larger than for polymer radicals $\overline{P}_{M,\mathrm{inst.}} = \overline{P}_M^{\bullet} + \overline{P}_{\mathrm{n}}^{\bullet} = 1.5\overline{P}_M^{\bullet}$, as was shown in Figure 7.

Figure 9 shows some examples of the calculated instantaneous mass fraction distribution profiles, with $\tau+\beta = 0.002$. Because the

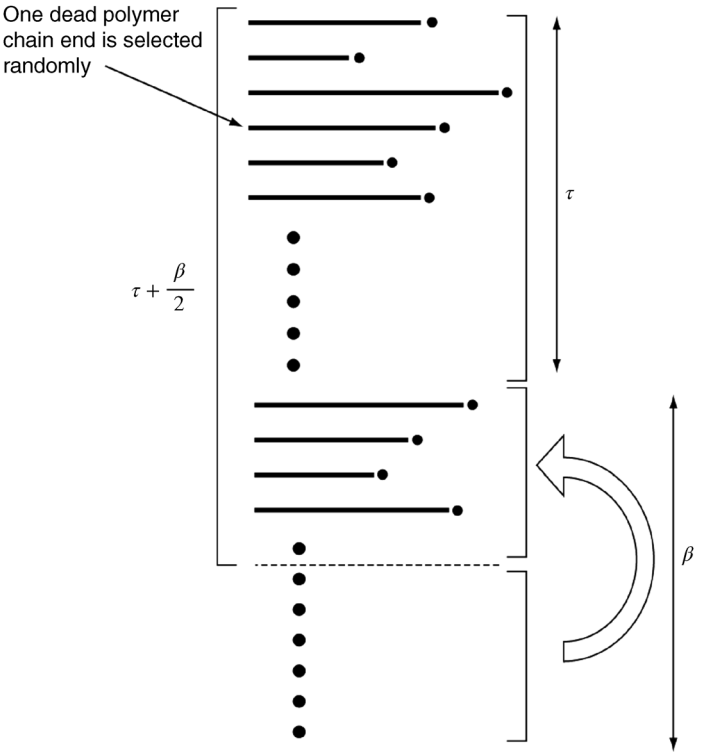


Figure 8. Derivation of number-average chain length, based on the random sampling technique

mass fraction distribution of the polymer radicals is given by Equation (71), the distributions of polymer radicals are the same for all three cases. The difference of chain length distribution of dead polymer molecules is caused by the contribution of dead polymer formation by combination termination, whose probability is represented by the ratio, $\beta/(\tau+\beta)$. One would notice that the distribution becomes narrower as the contribution of combination termination becomes significant.

The chain length distribution derived here gives the instantaneous distribution, which is formed within a very small time interval. In linear free-radical polymerization the polymer molecules once formed are inert and do not react further. In general, since the concentrations of monomer, initiator, and chain-transfer agent change with time, the chain length distribution of the accumulated polymer is broader than the instantaneous distribution. The accumulated mass fraction distribution $M_{\text{accum.}}(r)$ and its mass-average $\overline{P}_{M,\text{accum.}}$ for batch polymerization are given by:

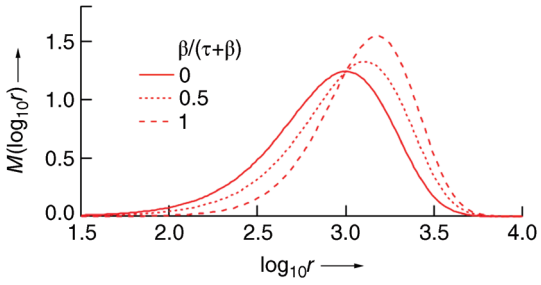


Figure 9. Instantaneous mass fraction distribution. The chain length distributions of polymer radicals are the same for all three cases, with $\tau+\beta=0.002$, while the formation mechanism of dead polymer chains is different

$$M_{\text{accum.}}(r) = \frac{1}{x}\int_0^x M_{\text{inst.}}(r)\,\mathrm{d}x$$

$$= \frac{1}{x}\int_0^x (\tau+\beta)\left\{\tau+\frac{\beta}{2}(\tau+\beta)r\right\} r\exp[-(\tau+\beta)r]\,\mathrm{d}x \qquad (77)$$

$$\overline{P}_{M,\text{accum.}} = \frac{1}{x}\int_0^x \overline{P}_{M,\text{inst.}}\,\mathrm{d}x = \frac{1}{x}\int_0^x \frac{2\tau + 3\beta}{(\tau+\beta)^2}\,\mathrm{d}x \tag{78}$$

where x is the monomer conversion to polymer. The conversion is based on mass, and therefore, simple integration by conversion leads to the accumulated properties. Note that τ and β change with time, i.e., with conversion x.

For the calculation of number-average, the definition given by Equation (6) should be revisited. The number of polymer chains within a conversion interval dx can be evaluated by $\mathrm{d}x/\overline{P}_{\text{n,inst.}}$, and the number-average chain length of the accumulated polymers is given by:

$$\overline{P}_{\text{n,accum.}} = \frac{x}{\displaystyle\int_0^x \frac{\mathrm{d}x}{\overline{P}_{\text{n,inst.}}}} = \frac{x}{\displaystyle\int_0^x \left(\tau + \frac{\beta}{2}\right)\mathrm{d}x} \tag{79}$$

The accumulated molecular mass properties can be calculated for semi-batch and continuous reactors in a similar manner. In an ideal continuous stirred tank reactor (CSTR), the concentration of every component is kept constant, and the chain length distribution produced is the instantaneous distribution, which is the narrowest. On the other hand, however, because the polymerization in a CSTR proceeds with a high polymer concentration, the polymer transfer reaction may not be neglected, which could make the distribution broader.

6.3. Effect of Temperature

In free-radical polymerization initiated by the thermal decomposition of an initiator, the polymerization rate is given by Equation (55), and the effect of temperature can be estimated by the change in the ratio of three rate constants, $k_\text{p}\,(k_\text{d}/k_\text{t})^{0.5}$. Since each kinetic rate constant is considered to follow the Arrhenius equation, the activation energy of polymerization E_R is given by:

$$E_\text{R} = E_\text{p} + \frac{E_\text{d}}{2} - \frac{E_\text{t}}{2} \tag{80}$$

where E_p, E_d, E_t are the activation energies for propagation, initiator decomposition, and bimolecular termination. Typical values for E_p, E_d, E_t are 30, 120, and 15 kJ/mol, respectively. Therefore, E_R is 82.5 kJ/mol and this is largely due to the high activation energy for initiator decomposition. The large activation energy for polymerization means that the rate of polymerization increases strongly with increasing temperature. With redox initiation, E_d is ca. 40 kJ/mol and therefore E_R is considerably smaller at 42.5 kJ/mol. With radiation initiation, E_d is close to zero and E_R is 22.5 kJ/mol, and the effect of temperature is not very significant.

Now consider the effect of temperature on the molecular mass of polymer obtained. For a simple example, consider the case where $\tau \ll \beta$, that is, termination by combination produces most of the polymer chains. Equation (74) gives:

$$\overline{P}_{M,\text{inst.}} \propto \frac{1}{\beta} = \frac{k_\text{p}[\text{M}]}{k_\text{tc}(2k_\text{d}f[\text{I}]/k_\text{tc})^{0.5}} \propto \frac{k_\text{p}}{(k_\text{tc}k_\text{d})^{0.5}} \tag{81}$$

The activation energy for average chain lengths E_L is given by:

$$E_\text{L} = E_\text{p} - \frac{E_\text{d}}{2} - \frac{E_\text{t}}{2} \tag{82}$$

Using the same activation energies used the above, E_L is -37.5 kJ/mol. The average chain length decreases with increasing temperature when initiators are used and bimolecular termination controls the polymer chain lengths. With radiation initiation, E_L is 22.5 kJ/mol and molecular mass increases moderately with temperature.

When chain transfer reactions dominate in the production of polymer chains, E_L is given by:

$$E_\text{L} = E_\text{p} - E_\text{f} \tag{83}$$

where E_f is the activation energy for the chain-transfer reaction. E_f depends on the type of chain transfer agent, but often $E_\text{p} - E_\text{f} < 0$, and therefore, the chain length may decrease with increasing temperature when chain transfer to small molecules controls the dead polymer formation.

7. Copolymerization

Copolymerization permits the synthesis of an almost unlimited number of polymer types and is therefore often used to obtain a better balance

of properties for commercial applications. Copolymers may be synthesized by chain and step polymerization. In step polymerization, different monomers with the same type of functional group generally show only minor differences in reactivity. As a result, most copolymers prepared by step polymerization contain essentially random placements of repeat units, with the composition of the copolymers essentially the same as those of the original monomer mixture.

In contrast, strong selective effects often occur in chain copolymerizations, and the composition of the copolymer formed may differ greatly from the composition of the original monomer mixture. This section deals exclusively with chain copolymerization.

7.1. Copolymer Composition

The composition of copolymers cannot be determined from a knowledge of the homopolymerization rates of each monomer. In 1944, the instantaneous copolymer composition equation was proposed independently by several researchers by assuming that the chemical activity of a propagating chain depends solely on the terminal monomer unit on which the active center is located [33–36]. This model is called the terminal model, and the copolymer chain can be considered as a first-order Markov chain. For binary systems, the following four propagation reactions are possible.

$$P^*_{m,n,1} + M_1 \xrightarrow{k_{11}} P^*_{m+1,n,1} \tag{84}$$

$$P^*_{m,n,1} + M_2 \xrightarrow{k_{12}} P^*_{m,n+1,2} \tag{85}$$

$$P^*_{m,n,2} + M_1 \xrightarrow{k_{21}} P^*_{m+1,n,1} \tag{86}$$

$$P^*_{m,n,2} + M_2 \xrightarrow{k_{22}} P^*_{m,n+1,2} \tag{87}$$

where $P^*_{m,n,1}$ is a live copolymer chain with m units of monomer 1 (M_1) and n units of monomer 2 (M_2) bound in the polymer chain and with the active center located on terminal monomer unit 1.

The reactivity of the propagating species may be affected by the penultimate monomer unit. In such cases, the model is referred to as the penultimate model or a second-order Markov chain, and propagation consists of eight reactions. Although the penultimate effects could be found in the sequence of units in chain, the copolymer composition is usually represented, at least approximately, by the terminal model. Higher order Markov chain could be used, but the number of propagation rate constants increases exponentially. For the nth order Markovian model consisting of m types of monomer, the necessary number of propagation rate constants is m^{n+1}.

It is customarily assumed that the propagation rate constants are independent of chain length and that the chains are sufficiently large (long-chain approximation, LCA). The LCA includes the approximation that monomer consumed in reactions other than propagation is negligible and that the SSH is valid for each type of active center; i.e., the rate of formation of any type of active center is equal to its rate of consumption.

Consider a binary copolymerization whose propagation reactions follow the terminal model. Our present concern is to develop the instantaneous copolymer composition equation, so that the active species does not have to be distinguished by the size. The total concentration of active center of type 1 is given by:

$$[P^*_1] = \sum_{m=1}^{\infty}\sum_{n=1}^{\infty}[P^*_{m,n,1}] \tag{88}$$

The active center of type 1 is created solely by Equation (86). Equation (84) does not lead to an increase in the amount of P^*_1, because the number of active centers is not changed by the reaction. Similarly, the active center of type 1 is consumed solely by Equation (85), and therefore, the population balance of P^*_1 is given by:

$$\frac{d[P^*_1]}{dt} = k_{21}[P^*_2][M_1] - k_{12}[P^*_1][M_2] \tag{89}$$

Invoking the SSH provides:

$$k_{21}[P^*_2][M_1] = k_{12}[P^*_1][M_2] \tag{90}$$

The instantaneous copolymer composition is equal to the ratio of the consumption rates of M_1 and M_2. The specific polymerization rates of

monomers 1 and 2 are given by:

$$-\frac{d[M_1]}{dt} = k_{11}[P_1^*][M_1] + k_{21}[P_2^*][M_1] \quad (91)$$

$$-\frac{d[M_2]}{dt} = k_{12}[P_1^*][M_2] + k_{22}[P_2^*][M_2] \quad (92)$$

Let F_1 and F_2 be the mole fractions of monomers 1 and 2 in the copolymer produced instantaneously.

$$\frac{F_1}{F_2} = \frac{-d(V[M_1])}{-d(V[M_2])} = \frac{k_{11}[P_1^*][M_1] + k_{21}[P_2^*][M_1]}{k_{12}[P_1^*][M_2] + k_{22}[P_2^*][M_2]} \quad (93)$$

By using Equation (90) and eliminating concentrations of active centers, one obtains:

$$\frac{F_1}{F_2} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2]([M_1] + r_2[M_2])} \quad (94)$$

where r_1 and r_2 are the reactivity ratios defined respectively by:

$$r_1 = \frac{k_{11}}{k_{12}} \quad (95)$$

$$r_2 = \frac{k_{22}}{k_{21}} \quad (96)$$

By using the mole fractions of unreacted monomer, $f_1 = [M_1]/([M_1]+[M_2])$ and $f_2 = 1-f_1$, Equation (94) can also represented by:

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \quad (97)$$

Equation (94), or equivalently, Equation (97) represents the composition of monomeric units bound into polymer chains in a small time interval, which is called the instantaneous copolymer composition. In free-radical polymerization, because each polymer chain is formed instantaneously, the instantaneous copolymer composition equation shows the composition of each polymer molecule. On the other hand, in the case of living polymerization, this is an imaginary composition of monomer molecules bound into different polymer chains instantaneously when such monomer molecules are collected.

Figure 10 shows the calculated results of the copolymer composition for various reactivity ratio pairs. Except for the azeotropic point, the copolymer composition is different from the monomer composition, which results in a compositional drift during copolymerization. In free-radical polymerization, the compositional drift occurs among polymer chains born at different times. For living polymers, it occurs along a polymer chain. The compositional drift during batch polymerization will be discussed later.

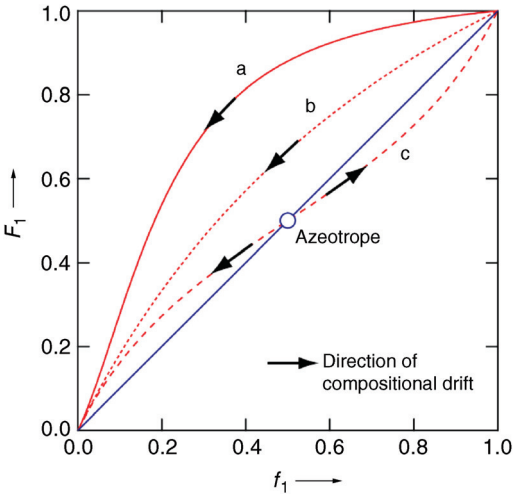


Figure 10. Instantaneous copolymer composition for various reactivity ratio pairs
(a) $r_1 = 10$, $r_2 = 0.5$, (b) $r_1 = 2$, $r_2 = 0.5$, and (c) $r_1 = 0.5$, $r_2 = 0.5$.

Now consider free-radical polymerization, in which dead polymer chains are formed instantaneously and the instantaneous copolymer composition represents the composition of each polymer molecule. In this case, the instantaneous copolymer composition equation introduced here is strictly valid only for infinitely long chains. For finite chains, there exists statistical variations of composition, as well as the chain length distribution. For longer chains, say chain length $r > 20$, Equation (97) is practically equal to the average composition of the instantaneous polymers, $F_{1,av}$. For the oligomers, the effect of initiation and chain stoppage mechanism cannot be neglected, and it may not appropriate to use the copolymer composition equation [37–39].

For copolymer chains produced instantaneously, in general, there is a bivariate distribution of composition and chain length. Except for oligomers, Stockmayer's bivariate distribution of chain length and composition is a

convenient equation to apply for a binary copolymerization with the terminal model [40]. The Stockmayer bivariate distribution, $M(r,F_1)$ consists of the product of mass-based chain length distribution $M(r)$ and the composition distribution $Comp(F_1|r)$, which is represented by the conditional probability given the chains with length r.

$$M(r,F_1) = M(r)Comp(F_1|r) \tag{98}$$

The composition distribution $Comp(F_1|r)$ is given by the following Gaussian distribution, whose average is $F_{1,\mathrm{av}}$ and the variance is inversely proportional to chain length r, as follows:

$$Comp(F_1|r) = \frac{1}{\sqrt{2\pi\sigma^2}}\exp\left[-\frac{(F_1 - F_{1,\mathrm{av}})^2}{2\sigma^2}\right] \tag{99}$$

$$\sigma^2 = \frac{F_{1,\mathrm{av}}\,F_{2,\mathrm{av}}\,K}{r} \tag{100}$$

$$K = \sqrt{1 + 4F_{1,\mathrm{av}}\,F_{2,\mathrm{av}}(r_1r_2 - 1)} \tag{101}$$

where the average composition, $F_{1,\mathrm{av}}$ can be determined from the copolymer composition equation, Equation (97). Extension of the bivariate distribution to the multicomponent polymerization can be found elsewhere [38, 39, 41].

Figure 11 shows the effect of chain length on the copolymer composition distribution. For chains with $r = 50$, the composition distribution is quite large and polymers with ca. $F_1 = 0.3$ to 0.7 exist in the instantaneous distribution. The distribution becomes narrower as the chain length increases. Figure 12 shows an example

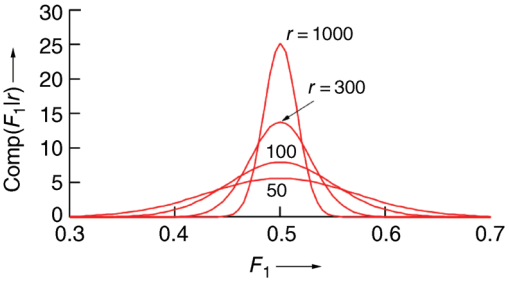


Figure 11. Instantaneous copolymer composition distribution calculated with $r_1r_2 = 1$ and $F_{1,\mathrm{av}} = 0.5$

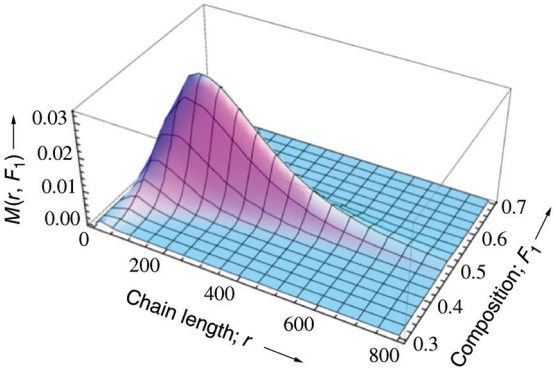


Figure 12. Bivariate distribution of chain length and composition, with $\overline{P}_{\mathrm{n,inst.}} = 100$, $r_1r_2 = 1$ and $F_{1,\mathrm{av}} = 0.5$

of the bivariate distribution in a 3D form. This is the instantaneous distribution profile, and the distribution of accumulated polymers is obtained by the integration of instantaneous distribution. The chain length distribution formed in copolymerization, $M(r)$ will be discussed in the next section.

In a batch copolymerization, the compositional drift can be calculated as follows. Let N_{M} be the number of moles of total unreacted monomer. When a small amount of monomer is polymerized, the decrease in monomer 1 must be equal to the increase in M_1 units in polymer, and therefore:

$$\Delta(N_{\mathrm{M}}f_1) = F_1\Delta N_{\mathrm{M}} \tag{102}$$

From Equation (102), one obtains the following differential equation:

$$\frac{df}{dN_{\mathrm{M}}} = \frac{F_1 - f_1}{N_{\mathrm{M}}} \tag{103}$$

By using total monomer conversion, $x = \left(N_M^0 - N_M\right)/N_M^0$, where N_M^0 is the initial moles of total amount of monomer,

$$\frac{df_1}{dx} = \frac{f_1 - F_1}{(1-x)} \tag{104}$$

One can calculate the monomer composition by solving Equation (104) with the initial condition, $f_1 = f_1^0$ and $F_1 = F_1^0$ at $x = 0$. Obviously, the copolymer composition equation is needed, i.e., Equation (97) for the terminal model with a binary system, to solve Equation (104). The

accumulated copolymer composition, $\overline{F}_1$ can be calculated from:

$$\overline{F}_1 = \frac{f_1^0 - (1-x)f_1}{x} \tag{105}$$

Note that $\overline{F}_1 = F_1^0$ at $x = 0$.

If the terminal model is applicable to a binary system, Equation (104) can be integrated analytically to obtain the following equation [42, 43]:

$$x = 1 - \left(\frac{f_1}{f_1^0}\right)^a \left(\frac{f_2}{f_2^0}\right)^b \left(\frac{f_1^0 - d}{f_1 - d}\right)^c \tag{106}$$

where

$$a = r_2/(1 - r_2),$$
$$b = r_1/(1 - r_1),$$
$$c = (1 - r_1 r_2)/\{(1 - r_1)(1 - r_2)\},$$
$$d = (1 - r_2)/(2 - r_1 - r_2).$$

On the other hand, however, because f_1 is not given explicitly by x in Equation (106), it may be straightforward to solve Equation (104) numerically, rather than using Equation (106).

One method to avoid compositional drift is to use an ideally micromixed continuous stirred tank reactor. In this case, Stockmayer's bivariate distribution of chain length and composition will be obtained directly. Another method to avoid compositional drift is to use semi-batch operation in which monomers are fed to maintain a constant ratio of monomer concentrations in the reactor [44, 45].

7.2. Kinetics of Free-Radical Copolymerization

Consider the kinetics of free-radical copolymerization of monomers M_1 and M_2, assuming the terminal model is applicable. Important elementary reactions are:

Initiation

$$I \xrightarrow{k_d} 2R^{\bullet}_{in}$$

$$R^{\bullet}_{in} + M_1 \xrightarrow{k_1} R^{\bullet}_{1,0,1}$$

$$R^{\bullet}_{in} + M_2 \xrightarrow{k_2} R^{\bullet}_{0,1,2}$$

Propagation

$$R^{\bullet}_{m,n,1} + M_1 \xrightarrow{k_{11}} R^{\bullet}_{m+1,n,1}$$

$$R^{\bullet}_{m,n,1} + M_2 \xrightarrow{k_{12}} R^{\bullet}_{m,n+1,2}$$

$$R^{\bullet}_{m,n,2} + M_1 \xrightarrow{k_{21}} R^{\bullet}_{m+1,n,1}$$

$$R^{\bullet}_{m,n,2} + M_2 \xrightarrow{k_{22}} R^{\bullet}_{m,n+1,2}$$

Chain transfer to monomer

$$R^{\bullet}_{m,n,1} + M_1 \xrightarrow{k_{fm,11}} P_{m,n} + R^{\bullet}_{1,0,1}$$

$$R^{\bullet}_{m,n,1} + M_2 \xrightarrow{k_{fm,12}} P_{m,n} + R^{\bullet}_{0,1,2}$$

$$R^{\bullet}_{m,n,2} + M_1 \xrightarrow{k_{fm,21}} P_{m,n} + R^{\bullet}_{1,0,1}$$

$$R^{\bullet}_{m,n,2} + M_2 \xrightarrow{k_{fm,22}} P_{m,n} + R^{\bullet}_{0,1,2}$$

Chain transfer to small molecule, X

$$R^{\bullet}_{m,n,1} + X \xrightarrow{k_{fX,1}} P_{m,n} + X^{\bullet}$$

$$R^{\bullet}_{m,n,2} + X \xrightarrow{k_{fX,2}} P_{m,n} + X^{\bullet}$$

$$X^{\bullet} + M_1 \xrightarrow{k'_1} R^{\bullet}_{1,0,1}$$

$$X^{\bullet} + M_2 \xrightarrow{k'_2} R^{\bullet}_{0,1,2}$$

Termination by disproportionation

$$R^{\bullet}_{m,n,1} + R^{\bullet}_{r,s,1} \xrightarrow{k_{td,11}} P_{m,n} + P_{r,s}$$

$$R^{\bullet}_{m,n,1} + R^{\bullet}_{r,s,2} \xrightarrow{k_{td,12}} P_{m,n} + P_{r,s}$$

$$R^{\bullet}_{m,n,2} + R^{\bullet}_{r,s,2} \xrightarrow{k_{td,22}} P_{m,n} + P_{r,s}$$

Termination by combination

$$R^{\bullet}_{m,n,1} + R^{\bullet}_{r,s,1} \xrightarrow{k_{tc,11}} P_{m+r,n+s}$$

$$R^{\bullet}_{m,n,1} + R^{\bullet}_{r,s,2} \xrightarrow{k_{tc,12}} P_{m+r,n+s}$$

$$R^{\bullet}_{m,n,2} + R^{\bullet}_{r,s,2} \xrightarrow{k_{tc,22}} P_{m+r,n+s}$$

where $R^{\bullet}_{m,n,1}$ is a polymer radical with m units of monomer 1 (M_1) and n units of monomer 2 (M_2) bound in the polymer chain with active

center located on monomer unit 1. $P_{m,n}$ is a dead polymer molecule with m units of monomer 1 and n units of monomer 2. The polymerization rate, R_p is given by:

$$R_p = k_{11}[R_1^\bullet][M_1] + k_{12}[R_1^\bullet][M_2] + k_{21}[R_2^\bullet][M_1] + k_{22}[R_2^\bullet][M_2] \quad (107)$$

where $[R_1^\bullet]$ is the total concentration of polymer radical of type 1 explicitly defined by Equation (88). By using the mole fractions, $f_1 = [M_1]/([M_1]+[M_2])$ and $\phi_1^\bullet = [R_1^\bullet]/\left[[R_1^\bullet] + [R_2^\bullet]\right]$, Equation (107) can be written as:

$$R_p = \left(k_{11}\phi_1^\bullet f_1 + k_{12}\phi_1^\bullet f_2 + k_{21}\phi_2^\bullet f_1 + k_{22}\phi_1^\bullet f_2\right)[R^\bullet][M] \quad (108)$$

where [M] and $[R^\bullet]$ are the total concentrations of monomer and radical, respectively, explicitly defined by $[M] = [M_1] + [M_2]$ and $[R^\bullet] = [R_1^\bullet] + [R_2^\bullet]$.

Therefore, by defining the pseudo-kinetic rate constant for propagation, $k_p = k_{11}\phi_1^\bullet f_1 + k_{12}\phi_1^\bullet f_2 + k_{21}\phi_2^\bullet f_1 + k_{22}\phi_1^\bullet f_2$, the explicit expression of the polymerization rate, $R_p = k_p[R^\bullet][M]$ becomes the same as that for homopolymerization. In general for the multicomponent polymerization consisting of N components, the pseudo-kinetic rate constants can be defined as follows:

Propagation

$$k_p = \sum_{i=1}^{N}\sum_{j=1}^{N} k_{ij}\phi_i^\bullet f_j \quad (109)$$

Chain transfer to monomer

$$k_{fm} = \sum_{i=1}^{N}\sum_{j=1}^{N} k_{fm,ij}\phi_i^\bullet f_j \quad (110)$$

Chain transfer to small molecule, X

$$k_{fX} = \sum_{i=1}^{N} k_{fX,i}\phi_i^\bullet \quad (111)$$

Termination by disproportionation

$$k_{td} = \sum_{i=1}^{N}\sum_{j=1}^{N} k_{td,ij}\phi_i^\bullet\phi_j^\bullet \quad (112)$$

Termination by combination

$$k_{tc} = \sum_{i=1}^{N}\sum_{j=1}^{N} k_{tc,ij}\phi_i^\bullet\phi_j^\bullet \quad (113)$$

By application of the above pseudo-kinetic rate constants, a multicomponent polymerization reduces to a homopolymerization, and therefore Equations (73–79) are all applicable for copolymerization. With appropriate definitions for pseudo-kinetic rate constants, this method may also be usefully applied when copolymerization kinetics follow the penultimate model [46]. Note that for copolymerization, τ and β in Equations (73–79) change with the progress of polymerization not only by the change in the concentrations but by the change in the pseudo-kinetic rate constants.

8. Living Polymerization

Living polymerization is strictly defined as the chain polymerization from which chain termination and irreversible chain transfer are absent [11]. Practically, however, polymers are considered as living if their end groups retain the propensity of growth for at least as long a period as needed for the completion of an intended synthesis, or any other desired task [47]. Living polymerization was first reported for ionic polymerization, more specifically in the anionic polymerization [48]. Unlike radical polymerization, bimolecular termination between active centers does not occur in ionic polymerization. Termination of an active center on a polymer chain occurs by reaction with the counterion, solvent, monomer, or other species. If the termination and chain-transfer reactions are suppressed effectively, living polymerization proceeds. Often, the initiation reactions are very fast, and the initiator is consumed in the early stages of polymerization before the polymer chains have grown much beyond oligomeric size. Living polymerization was made possible also in cationic polymerization [49, 50]. In cationic living polymerization, monomers are not added one by one to an active center, but reversible deactivation occurs and monomer molecules are added to an active center during intermittent active period. In

free-radical polymerization, bimolecular termination reactions between polymer radicals are inevitable, and therefore, it cannot be living polymerization in a strict sense, but by utilizing the reversible deactivation, living polymers in a practical sense can be synthesized [51–53]. Living polymerization has been made possible for all three types of active centers in chain polymerization, i.e., anion, cation, and radical.

Conventionally, polycondensation proceeds with step polymerization. However, by preventing the reaction between monomer and by making monomer react only with the propagating polymer chain end, it has become possible to conduct living polycondensation [54, 55]. Ideally, monomers are added to an activated polymer chain end one by one in this case.

8.1. Ideal Living Polymerization

In this section, the kinetic characteristics of the ideal living polymerization where the initiation reactions are instantaneous and monomers are added one by one to an active center without reversible deactivation processes are considered. The effect of reversible deactivation will be discussed in the next section.

Suppose active centers are created instantaneously with concentration [P*]. The polymerization rate is represented by:

$$R_p = k_p[P^*][M] \tag{114}$$

In the absence of termination, [P*] may be kept constant, and $k_p[P^*]$ could be regarded as a constant. In this case, Equation (114) can be integrated to give:

$$\int_0^x \frac{dx}{1-x} = k_p[P^*] \int_0^t dt \tag{115}$$

or

$$\ln \frac{1}{1-x} = k_p[P^*]t \tag{116}$$

where x is the monomer conversion to polymer, $x = ([M]_0 - [M])/[M]_0$.

Note, however, Equation (116) applies for the systems with a constant concentration of the active center [P*] during polymerization, and it does not necessarily mean that the reaction system is living. Balanced rates of initiation and termination may also lead to a constant [P*]. In addition, with the reversible deactivation, which will be discussed in the next section, [P*] may change during polymerization, even when the system can be considered living polymerization.

The number-average chain length, $\overline{P}_n$ is the ratio between the total number of monomeric units incorporated into polymer and the total number of polymer chains, as represented by Equation (6). Therefore, $\overline{P}_n$ is given by:

$$\overline{P}_n = \frac{x[M]_0}{[P]} \tag{117}$$

where [P] represents the concentration of all polymer molecules, i.e., $[P] = Q_0 = \sum_{r=1}^{\infty}[P_r]$, where all polymer chains possess active centers in the present simplified model. With reversible deactivation, most of the polymer chains are dormant, but the total number of active and dormant polymer chains is kept constant for the most part of polymerization. The linear increase of $\overline{P}_n$ with respect to conversion, x is one of the most important characteristics of living polymerization.

Now consider the chain length distribution of the ideal living polymerization, by using the model shown in Figure 13. Assuming that

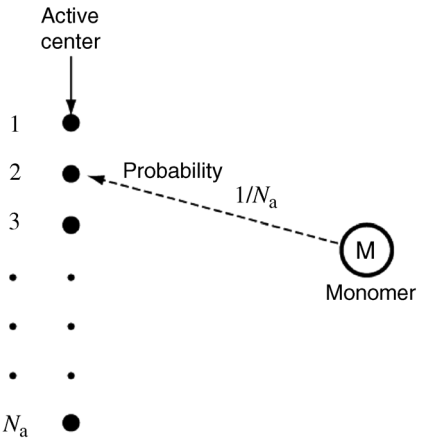


Figure 13. Model to derive the chain length distribution in ideal living polymerization. A monomer molecule is added to an active center selected randomly, with probability $1/N_a$, where N_a is the total number of growing chains having an active center

initiation is instantaneous, the total number of growing chains having an active center N_a is constant throughout the polymerization. Now a monomer molecule adds to a polymer chain as shown in Figure 13. The probability that a monomer adds to a particular polymer chain (2 in the figure) is $1/N_a$, and that it does not add to the polymer chain (2) is $1–1/N_a$. Therefore, when the total of N_M monomer units have been consumed and bound into polymer chains the probability that a randomly selected polymer chain possesses r monomer units is given by a binomial distribution:

$$N(r) = {}_{N_M}C_r \left(\frac{1}{N_a}\right)^r \left(1 - \frac{1}{N_a}\right)^{N_M - r} \tag{118}$$

where ${}_nC_k$ is the binomial coefficient, ${}_nC_k = \frac{n!}{k!(n-k)!}$.

Because $1/N_a \ll 1$ and N_M is large, the binomial distribution reduces to the Poisson distribution:

$$N(r) = \frac{e^{-\eta}\eta^r}{r!} \tag{119}$$

where $\eta = N_M/N_a$, which is equal to the number-average chain length, $\eta = \overline{P}_n$.

The mass fraction distribution $M(r)$ and the mass-average chain length $\overline{P}_M$ can be calculated, as follows:

$$M(r) = \frac{rN(r)}{\sum_{r=1}^{\infty} rN(r)} = \frac{e^{-\eta}\eta^{r-1}}{(r-1)!} \tag{120}$$

$$\overline{P}_M = \sum_{r=1}^{\infty} rM(r) = \overline{P}_n + 1 \tag{121}$$

On the basis of the random sampling technique, Equation (121) can be rationalized as follows. The mass-average chain length is the expected chain length when one monomeric unit in polymer is selected randomly, as was schematically shown in Figure 1. Now suppose that the unit shown by an arrow in Figure 14 is selected randomly. The expected chain length other than the randomly selected units is $\overline{n}_1 + \overline{n}_2$, as shown in Figure 14. Except for this randomly selected unit, we have a total of $N_M - 1$ monomer molecules initially. The expected length, $\overline{n}_1 + \overline{n}_2$ is equal to the number-average chain length when $N_M - 1$ monomer molecules are distributed randomly, through the process shown in Figure 13. Obviously, $N_M \gg 1$, and $N_M - 1 \cong N_M$. Therefore, the expected length of a single chain distributed as shown in Figure 13 must be equal to $\overline{P}_n$, and $\overline{n}_1 + \overline{n}_2 = \overline{P}_n$. By including the randomly selected unit, the equation, $\overline{P}_M = \overline{P}_n + 1$ holds.

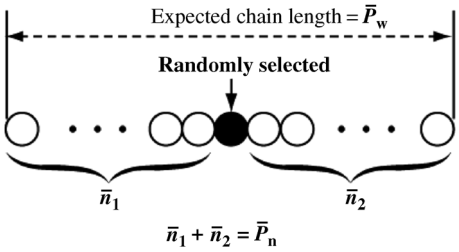


Figure 14. Weight-average chain length of the ideal living polymerization, derived on the basis of the random sampling technique

From Equation (121), the polydispersity index is given by:

$$\text{PDI} = \frac{\overline{P}_M}{\overline{P}_n} = 1 + \frac{1}{\overline{P}_n} \tag{122}$$

With sufficiently large average chain length, the PDI approaches unity.

On the other hand, in order for the Poisson distribution to be valid, the rate of initiation must be much faster than that of propagation. Slow initiation may lead to significant broadening of the MMD. In anionic polymerization, active chain ends with various states whose propagation rate constant is different greatly could exist [56]. If the exchange rate between these states is slow, the MMD could become much broader than the Poisson distribution.

8.2. Reversible-Deactivation Radical Polymerization

In free-radical polymerization, the bimolecular termination reactions are inevitable. Therefore, the living polymerization in a strict sense in which the chain termination reactions are totally absent is impossible. However, if a large percentage of polymer chains are dormant and can

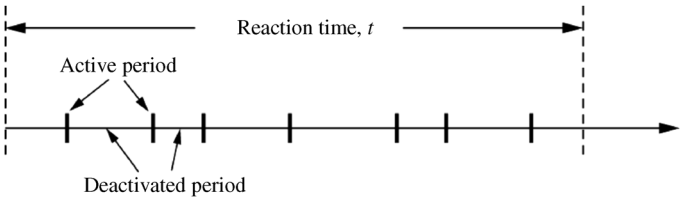


Figure 15. Schematic representation of the formation history of a polymer chain in reversible-deactivation radical polymerization (RDRP)

potentially grow further, such free-radical polymerization systems can be regarded as pseudo-living polymerization. By introducing the reversible-deactivation process in free-radical polymerization, polymers having a narrow polydispersity can be obtained, as long as the number of terminated chains is small compared with the potentially active chains.

This type of radical polymerization has been referred to as, "controlled", "controlled/living", or "living" radical polymerization. In the present article, the IUPAC name [11], reversible-deactivation radical polymerization, RDRP is used.

Because the lifetime of a generated radical in free-radical polymerization is short, normally less than a few seconds, a basic strategy to keep the chain potentially active is to distribute very short active periods throughout the whole reaction time. Figure 15 shows a schematic representation of the pseudo-living polymer formation during reversible-deactivation radical polymerization. The thickness of each vertical line represents the time length of an active period, which is typically $10^{-4} - 10^{-2}$ s, and therefore, the thickness should be much thinner than the figure shows. On the other hand, it may take hours for the whole polymerization time. From the point of view of the formation history of a chain, most of the time is spent as a deactivated form. Only when the number of added monomeric units in chain during a single active period is always unity, the formed polymers would have the Poisson distribution.

8.2.1. Polymerization Rate

Depending on the reversible-deactivation processes, various RDRPs have been proposed. RDRPs include stable-radical-mediated polymerization (SRMP), atom-transfer radical polymerization (ATRP), reversible-addition-fragmentation chain-transfer polymerization (RAFT), and degenerative-transfer radical polymerization (DTRP). The reversible-deactivation reactions are shown in Figure 16. Other elementary reactions involved are the same as the conventional free-radical polymerization, as shown in Equations (45)–(52). The deactivation in SRMP involves reversible coupling with stable (persistent) free radical, X in Figure 16. In ATRP, the deactivation of radicals involves atom transfer or reversible group transfer catalyzed often by transition-metal complexes. Both SRMP and ATRP are based on the principle in which active radicals are protected by reversible capping with a trapping agent, before termination or chain transfer occurs.

RAFT and DTRP are based on the reversible chain-transfer reactions. The kinetic chain growth process is schematically shown in Figure 17, neglecting the irreversible chain transfer reactions given by Equation (48)–(50). There are lots of dormant chains XP's, and when a radical is generated, it forms a single

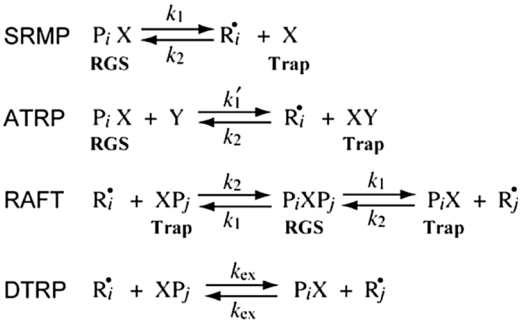


Figure 16. Reversible deactivation reaction scheme in each type of reversible-deactivation radical polymerization (RDRP). In the figure, P_iX or XP_i is the dormant polymer with chain length i. $R_i^{\bullet}$ is the active polymer radical with chain length i

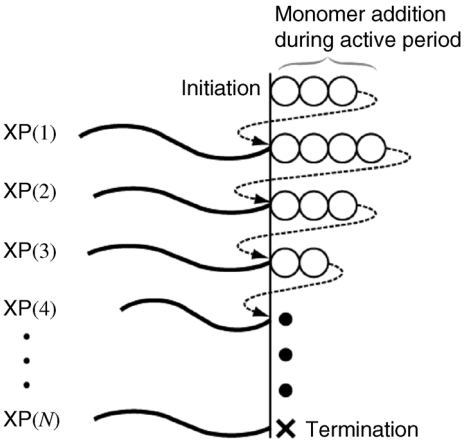


Figure 17. Schematic representation of the chain formation in RAFT and DT polymerization

kinetic chain, but this kinetic chain is separated into many small chain fractions as shown in Figure 17. The pseudo-livingness comes from the fact that an active radical is relayed to a large number of chains, N in Figure 17, before finally being stopped by bimolecular termination. If the value of N is large enough, sufficient percentage of chains are still potentially active and good livingness is kept. From the point of view of a single chain, the growth process is the intermittent chain growth, as was shown in Figure 15. This is why the theoretical MMD function is essentially the same for all RDRPs. Both RAFT and DTRP are based on the degenerative chain transfer. In RAFT it occurs by a two-step addition-fragmentation mechanism, while it is a single step in DTRP.

In order to formulate the kinetics of various types RDRPs in a unified manner, the radical generating species is represented by RGS, and the trapping agent to deactivate the active radical is represented by Trap, as shown in Figure 16. In the case of DTRP, XP (or equivalently, PX) acts as both RGS and Trap, depending on the reversible deactivation reaction type.

Similarly with Equations (35) and (114), the polymerization rate is represented by:

$$R_p = k_p[M][R^\bullet] \tag{123}$$

Unlike with Equation (114), the concentration of the active species $[R^\bullet]$ may change during polymerization. In the case of conventional free-radical polymerization, the radical concentration is determined by the balance of initiation and termination, as was shown in Equation (53). On the other hand, $[R^\bullet]$ is determined by the reversible deactivation reactions. (DTRP is a special case, as will be discussed later.)

For the calculation of polymerization rate and resulting conversion development, one can conveniently use Equation (123), by simultaneously solving differential population balance equations for various species [57]. On the other hand, however, Equation (123) does not involve concentrations of characteristic components of reversible deactivation reactions shown in Figure 16, essential to preserve the pseudo-livingness. Equation (123) may not be suitable for the prediction and control of the RDRPs, based on the reaction mechanism. The polymerization rate expression unique to the RDRPs can be derived as follows.

In order for the pseudo-living condition to be valid, the deactivation rate R_{deact} must be much larger than the bimolecular termination of active radicals R_t, i.e., $R_{deact} \gg R_t$. If not, a large amount of dead polymer chains are formed. Similarly, if the initiation reaction R_I is involved, the activation reaction in RDRP R_{act} must be much larger than R_I, i.e., $R_{act} \gg R_I$. The activation and deactivation rates are given by:

$$R_{act} = k_1[RGS] \tag{124}$$

$$R_{deact} = k_2[R^\bullet][Trap] \tag{125}$$

In the case of ATRP, k_1 is the pseudo-kinetic rate constant given by $k_1 = k'_1[Y]$. For DTRP, both R_{act} and R_{deact} are given by $k_{ex}[XP][R^\bullet]$.

Because $R_{deact} \gg R_t$, the average time interval for an active radical $\bar{t}_{R^\bullet}$ is represented as follows. The average frequency of a radical to be deactivated is given by $R_{deact}/[R^\bullet]$ s^{-1}. Therefore, the average time interval for the radical deactivation is:

$$\bar{t}_{R^\bullet} = \frac{[R^\bullet]}{R_{deact}} = \frac{1}{k_2[Trap]} \tag{126}$$

The average number of monomeric units added to a single radical was given by Equation (37). The average number of

monomeric units added to an active radical during a single active period is given by:

$$\overline{n}_M \overline{t}_{R\cdot} = \frac{k_p[M]}{k_2[Trap]} \quad (127)$$

Every time a radical is generated, $\overline{n}_M \overline{t}_{R\cdot}$ of monomeric units are added. Therefore, the polymerization rate is given by multiplying the radical generation rate and $\overline{n}_M \overline{t}_{R\cdot}$. Because $R_{act} \gg R_I$, the radical generation rate is given by R_{act}. Therefore, the polymerization rate, R_p is given by:

$$R_p = R_{act} \overline{n}_M \overline{t}_{R\cdot} = k_p[M] K \frac{[RGS]}{[Trap]} \quad (128)$$

where $K = k_1/k_2$.

Equation (128) shows the characteristic polymerization rate expression that can be applied to all of RDRPs. The living cationic polymerization that involves reversible-deactivation reactions can also be represented by this equation. For a given reaction system, a large [RGS] leads to larger polymerization rate, while a large [Trap] leads to smaller polymerization rate. Obviously, in order for the pseudo-living polymerization to be valid, the conditions, $R_{deact} \gg R_t$ and $R_{act} \gg R_I$ must be satisfied.

For DTRP, both R_{act} and R_{deact} are given by $k_{ex}[XP][R^\bullet]$, and $R_{act} \overline{n}_M \overline{t}_{R\cdot}$ reduces to $k_p[M][R^\bullet]$, resulting in Equation (123). The radical concentration is controlled by the balance of R_t and R_I, but one needs to bear in mind that the conditions $R_{deact} \gg R_t$ and $R_{act} \gg R_I$ must be valid.

In all types of RDRPs, bimolecular termination is inevitable, and longer polymerization time tends to increase the number of dead polymer chains.

Unique characteristics of RDRP conducted in a very small reaction locus, such as for the miniemulsion polymerization in which the polymerization rate might be different from the corresponding bulk polymerization, can be elucidated on the basis of Equation (128), (→ Polymerization Processes, 2. Modeling of Processes and Reactors).

8.2.2. Molecular Mass Distribution

Consider the MMD formed in RDRPs, referring to the chain formation history in which the chain growth is intermittent, as shown in Figure 15. The time length of each active period is very small in order to suppress termination reactions effectively, and the concentration changes of various components during a single active period can be neglected. Note that the duration of a single active period must be much smaller than the lifetime of a radical in the conventional free-radical polymerization. After all, RDRP is a free-radical polymerization in which the lifetime of a radical in the conventional free-radical polymerization is divided into small pieces of active periods. Therefore, the probability of connection to the next unit during a single active period would be a constant, leading to the most probable distribution. The MMD of RDRP is formed by adding a large number of short chain parts that follow the most probable distribution.

Consider SRMP as an example. The average time length of a deactivated time $\overline{t}_D$ can be obtained as follows. The frequency of activation for a particular dormant chain PX is given by $k_1[PX]/[PX]\ s^{-1}$, and therefore:

$$\overline{t}_D = 1/k_1 \qquad \text{(for SRMP)} \quad (129)$$

Equation (129) applies also for ATRP, by defining $k_1 = k'_1[Y]$. The explicit expression of $\overline{t}_D$ for each type of RDRP is summarized in Table 2. The coefficient 2 for RAFT comes from the fact that another dormant period is repeated with probability 1/2 [58].

The probability of connecting next unit during the active period for SRMP is given by:

$$p = \frac{R_p}{R_p + R_{deact}} = \frac{k_p[M]}{k_p[M] + k_2[X]} \qquad \text{(for SRMP)} \quad (130)$$

The p-values for other types of RDRPs are also shown in Table 2. The coefficient 1/2 for the reactivation rate in RAFT comes from the fact that another active period is repeated with probability 1/2 [58].

As shown in Table 2, both the average time length of a deactivated time $\overline{t}_D$ and the probability of growth during a single active period p change with the progress of polymerization. In order to highlight the important characteristics of RDRP polymers, however, let us consider a simplified case in which both $\overline{t}_D$ and p are kept constant during polymerization [59].

Table 2. Average time of deactivated period $\bar{t}_D$, and probability of connecting next unit p during the active period, for various types of RDRPs

	SRMP	ATRP	RAFT	DTRP
$\bar{t}_D$	$1/k_1$	$1/k_1 = 1/(k'_1[Y])$	$2(\bar{t}_{XP} + \bar{t}_{PXP}) = 2\left[\frac{1}{k_2[R^\bullet]} + \frac{1}{k_1}\right]$	$1/(k_{ex}[R^\bullet])$
p	$\frac{k_p[M]}{k_p[M] + k_2[X]}$	$\frac{k_p[M]}{k_p[M] + k_2[XY]}$	$\frac{k_p[M]}{k_p[M] + k_2[XP]/2}$	$\frac{k_p[M]}{k_p[M] + k_2[XP]}$

First, the chain length distribution during a single active period is considered. Figure 18 shows a schematic representation of chain growth during a single active period. Because the probability of connection p is assumed constant, the distribution is most probable. However, in the present case, the possibility of event in which no monomeric units are added must be accounted for. Similarly with the derivation of the most probable distribution, as shown in Figure 2, the number fraction distribution during a single active period, $N_{SA}(r)$ is given by:

$$N_{SA}(r) = p^r(1-p) \tag{131}$$

Obviously, the number- and mass-average chain length can be obtained from the distribution function; however, to show the versatility, the random sampling technique [5] is used here. The number-average chain length is the expected chain length when one chain end is chosen randomly. Suppose one has selected a chain that has just become active, as shown in Figure 18. The probability that a unit is connected to this active chain end is p, and if the first unit is connected, the chain length increases by one. Therefore, the expected length up to this first unit is $p \times 1$. The probability that the second unit is connected on the growing chain is p^2, and the expected number of units connected up to the second unit is $p \times 1 + p^2 \times 1$. As a consequence, the total expected length, which is equal to the number-average chain length during a single active period, $\overline{P}_{n,SA}$ is given by:

$$\overline{P}_{n,SA} = \sum_{r=1}^{\infty} p^r = \frac{p}{1-p} \tag{132}$$

The mass-average chain length is the expected length when one unit is selected randomly. Suppose a unit shown in Figure 19 has been selected randomly. Looking from the initially selected unit toward the right direction, the connection statistics is completely the same as shown in Figure 18, and therefore, the expected chain length is $\overline{P}_{n,SA}$. The same discussion applies also for the left direction. Remembering to include the initially selected unit, the mass-average chain length $\overline{P}_{M,A}$ is given by:

$$\overline{P}_{M,SA} = 2\overline{P}_{n,SA} + 1 = \frac{1+p}{1-p} \tag{133}$$

Note that the mass-average chain length is the same as the usual most probable distribution given by Equation (15), although the p-value for the usual RDRP is not very close to unity. The polydispersity index is given by:

$$\overline{P}_{M,SA}/\overline{P}_{n,SA} = \frac{1+p}{p} \tag{134}$$

In this case, the polydispersity index decreases to approach 2 when p is increased, while the usual most probable distribution leads to PDI = 1 + p which goes from 1 to 2.

Let the reaction time be t_R, then the average number of active periods, $\overline{n}_A$ is given by:

$$\overline{n}_A = t_R/\bar{t}_D \tag{135}$$

Note that $\bar{t}_D \gg \bar{t}_{R^\bullet}$ in RDRP.

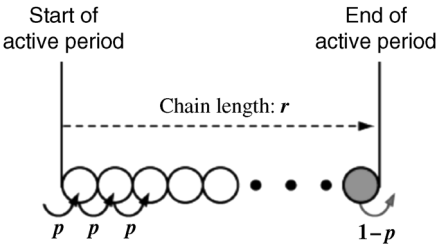


Figure 18. Schematic representation of chain growth during a single active period in RDRP

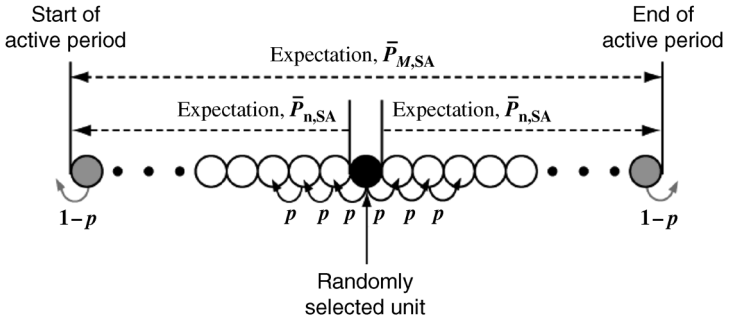


Figure 19. Derivation of the mass-average chain length during a single active period based on the random sampling technique

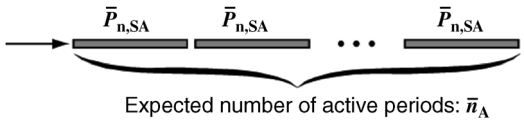


Figure 20. Derivation of the number-average chain length

When a chain end is chosen randomly, as shown in Figure 20, the expected number of active periods is $\overline{n}_A$, and the expected length formed during a single active period is $\overline{P}_{n,SA}$. Therefore, the expected length of a polymer chain when one chain end is selected randomly, which is equal to the number-average chain length, $\overline{P}_n$ is given by:

$$\overline{P}_n = \overline{n}_A \overline{P}_{n,SA} \tag{136}$$

The mass-average chain length is obtained by considering the expected chain length when one unit is selected randomly. Suppose a unit formed during a single active period at $t = t_1$ is selected, as shown in Figure 21. The expected length of this part of a polymer chain is $\overline{P}_{M,SA}$ because the selection is on a mass basis. All active periods are considered instantaneous, and therefore, the total reaction time except for the formation of this particular part of chain is still t_R, namely, $t_1 + t_2 = t_R$. The average number of active periods during the time interval t_R is $\overline{n}_A$. All other segments in this polymer chain are connected through their chain ends, and therefore, they are considered selected on the number basis. The mass-average chain length, $\overline{P}_M$ is, therefore, given by:

$$\overline{P}_M = \overline{P}_{M,SA} + \overline{n}_A \overline{P}_{n,SA} \tag{137}$$

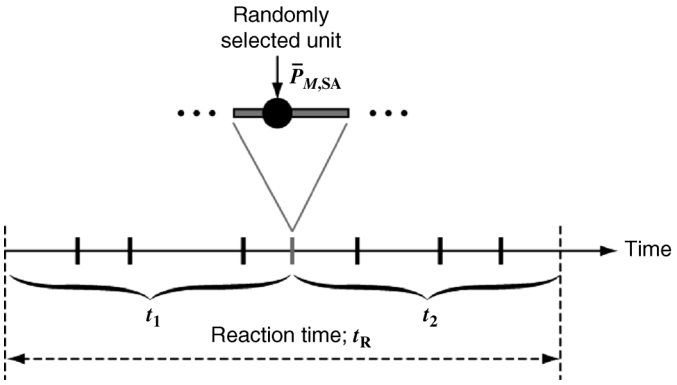


Figure 21. Derivation of the mass-average chain length

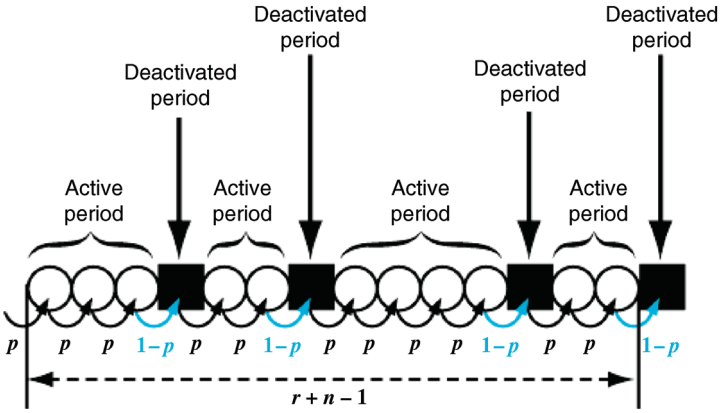


Figure 22. Schematic representation of a sequence of monomer units and deactivated periods

The polydispersity index is given by:

$$\overline{P}_M/\overline{P}_n = 1 + \frac{\overline{P}_{M,SA}}{\overline{P}_n} \tag{138a}$$

$$= 1 + \frac{1+p}{\overline{n}_A p} \tag{138b}$$

In the Poisson distribution, the PDI is $1 + 1/\overline{P}_n$ as shown in Equation (122), and therefore, the distribution given by Equation (138a) is broader than the Poisson distribution because $\overline{P}_{M,SA} > 1$.

It is usually stated that to obtain a good control in RDRP, the number of added monomeric units during a single active period must be kept small enough. Obviously, the condition, $R_{deact} \gg R_t$ is a requisite to have a good livingness, and a smaller p-value would be preferable. For a given $\overline{P}_n$-value, a smaller $\overline{P}_{M,SA}$ leads to a smaller PDI as shown in Equation (138a). The magnitude of $\overline{n}_A$ that is in the denominator of Equation (138b) has a significant effect, and by increasing the number of times of intermittent chain growth, the PDI can be made smaller. On the other hand, however, Equation (138b) also shows that if the $\overline{n}_A$-value is kept constant, a larger p-value leads to a smaller PDI. With a large p-value, the polymerization rate can also be increased. A good balance of $\overline{n}_A$ and p should be considered for commercial production.

The full chain length distribution function for the present simplified model, with constant values of $\overline{t}_D$ and p is as follows. First, consider the probability that a polymer chain with length r is formed through n times of active periods $N(r|n)$, as schematically shown in Figure 22. The probability of obtaining such a sequence of chain is $p^r(1-p)^n$. The total number of arrangements can be obtained by considering the total number of ways to place $(n-1)$ deactivated periods (depicted in square in Fig. 22) within r monomeric units. This can be done by choosing $(n-1)$ sites for the deactivated periods from the total of $(r+n-1)$ sites. Therefore, $N(r|n)$ is given by:

$$N(r|n) = {}_{r+n-1}C_{n-1}p^r(1-p)^n \tag{139}$$

Equation (139) approaches the Schulz–Zimm distribution [60, 61] (gamma distribution), sometimes used as a polymer MMD function, at $p \to 1$. In the present reaction system, however, p is usually less than 0.9, and the Schulz–Zimm distribution cannot be used instead of Equation (139).

Looking from a dormant chain, activation is a random process, similarly as in the classical examples of radioactive disintegrations, or incoming calls at a telephone exchange [62]. Therefore, the number of active periods within a given reaction time is given by the Poisson distribution. The probability that the chain experiences n times of active periods $P(n)$ is given by:

$$P(n) = \frac{(\overline{n}_A)^n e^{-\overline{n}_A}}{n!} \tag{140}$$

The derivation of Equation (140) for the present situation can be found in the appendix of [59].

The number fraction distribution, $N(r)$ is therefore given by [59]:

$$N(r) = \sum_{n=0}^{\infty} P(n)N(r|n) = (1-p)p^r \overline{n}_A e^{-\overline{n}_A} F(1+r, 2; (1-p)\overline{n}_A) \tag{141}$$

where $F(a, b; x)$ is the confluent hypergeometric function (Kummer's function of the first kind), represented by:

$$F(a, b; x) = 1 + \frac{ax}{b} + \frac{a(a+1)}{b(b+1)} \cdot \frac{x^2}{2!} + \ \ldots \tag{142}$$

The mass fraction distribution is given by:

$$M(r) = \frac{rN(r)}{\overline{P}_n} = (1-p)^2 p^{r-1} r e^{-\overline{n}_A} F(1+r, 2; (1-p)\overline{n}_A) \tag{143}$$

The fundamental distribution function for the living polymers formed in RDRP is a hypergeometric function that results from the superposition of two types of distribution, the most probable and the Poisson distribution. Another method to derive the present fundamental distribution for RDRP can be found in [63].

Figure 23 shows the calculated mass fraction distribution, $M(\log_{10} r)$. The comparison with the Poisson distribution is made at the same number-average chain lengths, $\overline{P}_n = 10$ and 100. The distribution is always broader than the Poisson distribution. At the same number-average chain length, the distribution becomes broader by increasing the p-value, i.e., by making the number of monomer addition during a single active period larger for a given $\overline{P}_n$.

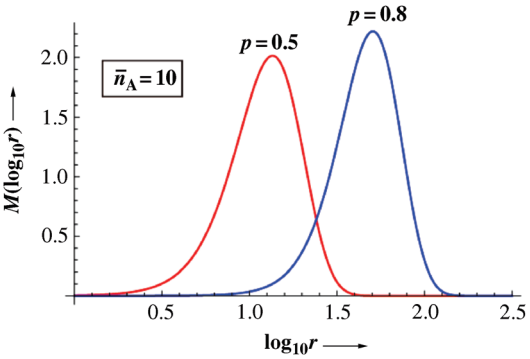


Figure 24. Mass fraction distribution of the ideal RDRP polymers when the average number of active period is set to be $\overline{n}_A = 10$

Figure 24 shows the mass fraction distribution of the ideal RDRP polymers when the average number of active period is $\overline{n}_A = 10$. If the $\overline{n}_A$-value is the same, larger p-value makes the chain longer, leading to narrower distribution, as discussed earlier. Assuming the time length of the inactive period $\overline{t}_D$ is the same for both cases, these two profiles show the MMDs at the same reaction time. Larger p-value may lead to higher productivity with a sufficiently narrow distribution.

To calculate the MMDs for more realistic cases, including termination and irreversible

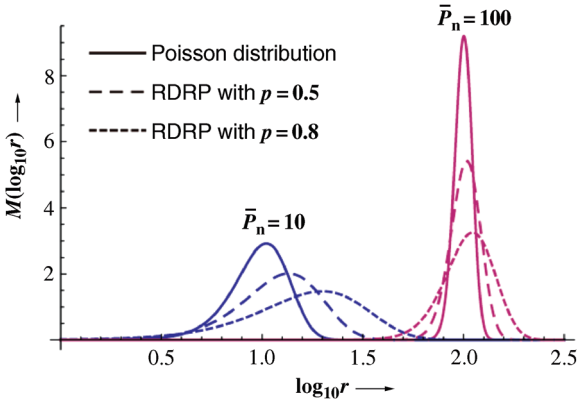


Figure 23. Mass fraction distribution for the ideal RDRP polymers and ideal living polymers (Poisson distribution), at the same number-average chain lengths, $\overline{P}_n = 10$ and 100

chain transfer reactions, deterministic approaches to solve an infinite number of differential population balance equations approximately [64, 65], or a Monte Carlo simulation method [66–68] can be applied.

9. Polymers with Branches and Crosslinks

We have, until now, considered the cases where produced polymer molecules are linear. While linear polymers are important, especially to understand the fundamentals of polymer chain formation, introduction of branches and/or crosslinks endows polymers with further versatility. However, nonlinear polymer formation is a kind of advanced topic, and in this section, discussions are made only for the most important characteristics of nonlinear polymers, assuming idealized conditions.

9.1. Crosslinked Polymers

An important characteristic of the introduction of crosslinks to linear polymer systems is the formation of a gel molecule. A gel molecule is considered to be a crosslinked polymer with infinite molecular mass, and as a consequence, a gel molecule is insoluble in any solvent under conditions where polymer degradation does not occur.

Gel is a molecule that spans the whole reaction system, and therefore, if one chooses one monomeric unit in polymer randomly, as was shown in Figure 1B, the probability of choosing a gel molecule must be larger than zero. On the other hand, because the number of polymer molecules in the system could be infinite, the probability of selecting a gel molecule on a number basis could be zero. Therefore, the onset of gelation can be recognized as a point when the mass-average degree of polymerization (chain length) $\overline{P}_M$ goes to infinity [4].

Let us consider the mass-average chain length of the whole system when crosslinks are introduced randomly to a linear polymer system, as shown in Figure 25. The linear polymer chains that constitute a crosslinked polymer system are called the primary chains. Here, we have primary chains whose mass-average chain length is $\overline{P}_{M\mathrm{p}}$. The probability for a unit (monomeric unit) to have a crosslink point is called the crosslinking density, represented by ρ in this article. Note that a crosslink point is defined as a unit to have a tri-branch point [4], and therefore, two crosslink points are formed by a single crosslinkage. In the random crosslinking considered here, the crosslinking density ρ is the same for all units.

Suppose one monomeric unit shown in Figure 26 is selected randomly from the crosslinked polymer system. Because the selection is made on a mass basis, the expected chain length of the primary chain so selected is the mass-average chain length of the primary chains, $\overline{P}_{M\mathrm{p}}$. This primary chain is considered belonging to the 0^{th} generation, as shown in Figure 26. The expected number of crosslink points on the 0^{th} generation chain is $\overline{P}_{M\mathrm{p}}\rho$, which must be equal to the expected number of primary chains belonging to the 1^{st} generation. The probability of possessing a crosslink point is the same for all units, and therefore, if one chooses a primary

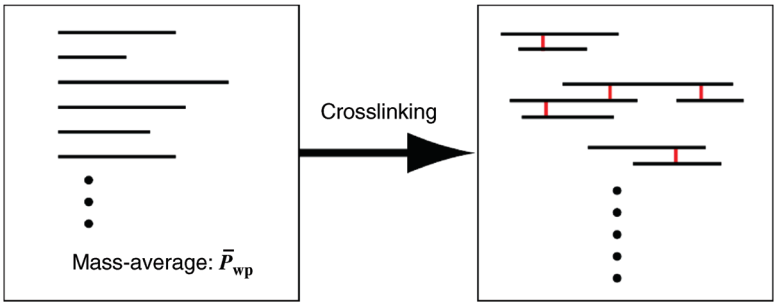


Figure 25. Schematic representation of random crosslinking of linear polymer chains

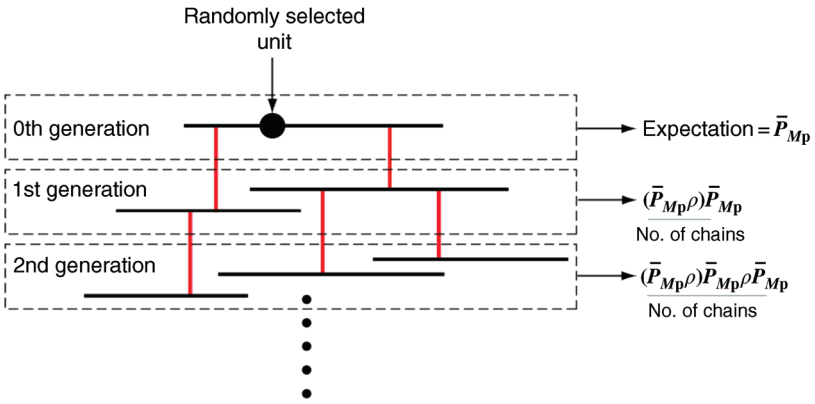


Figure 26. Derivation of the mass-average chain length $\overline{P}_M$ for a random crosslink system

chain by selecting a crosslink point randomly, the expected primary chain length so selected is the mass-average chain length, $\overline{P}_{M\mathrm{p}}$. The primary chains belonging to the 1st generation are selected by choosing crosslink points randomly, and the total expected monomeric units (chain length) belonging to the first generation is given by $\left(\overline{P}_{M\mathrm{p}}\rho\right) \times \overline{P}_{M\mathrm{p}}$.

The total expected number of crosslink points on the 1st generation chains connected to the 2nd generation is $\left(\overline{P}_{M\mathrm{p}}\rho\right)\left(\overline{P}_{M\mathrm{p}} - 1\right)\rho$. Note that $\left(\overline{P}_{M\mathrm{p}} - 1\right)$ is used here because one unit has already been used to connect with the 0th generation chain. Assuming long primary chains, $\left(\overline{P}_{M\mathrm{p}} - 1\right) \cong \overline{P}_{M\mathrm{p}}$. The number of primary chains belonging to the second generation is given by $\left(\overline{P}_{M\mathrm{p}}\rho\right)\overline{P}_{M\mathrm{p}}\rho$. The primary chains belonging to the second generation must be selected on a mass basis, and the expected size of each primary chain is again $\overline{P}_{M\mathrm{p}}$. The total expected chain length belonging to the 2nd generation is $\left(\overline{P}_{M\mathrm{p}}\rho\right)^2\overline{P}_{M\mathrm{p}}$.

Extending the present discussion to further generations, the expected chain length of the whole polymer molecule when one unit is selected randomly, which is the mass-average chain length of the whole reaction mixture, $\overline{P}_M$ is given by:

$$\begin{aligned}\overline{P}_M &= \overline{P}_{M\mathrm{p}}\left\{1 + \left(\overline{P}_{M\mathrm{p}}\rho\right) + \left(\overline{P}_{M\mathrm{p}}\rho\right)^2 + \left(\overline{P}_{M\mathrm{p}}\rho\right)^3 + \cdots\right\} \\ &= \overline{P}_{M\mathrm{p}}\sum_{i=0}^{\infty}\left(\rho\overline{P}_{M\mathrm{p}}\right)^i = \frac{\overline{P}_{M\mathrm{p}}}{1 - \rho\overline{P}_{M\mathrm{p}}}\end{aligned} \tag{144}$$

Equation (144) shows that $\overline{P}_M$ goes to infinity when the crosslinking density ρ reaches:

$$\rho_{\mathrm{gp}} = 1/\overline{P}_{M\mathrm{p}} \tag{145}$$

which is the gel point. Note that as long as the mass-average chain length of primary chains, $\overline{P}_{M\mathrm{p}}$ is kept constant, the gel point, ρ_{gp} is the same irrespective of the chain length distribution of the primary chains.

The number-average chain length, $\overline{P}_{\mathrm{n}}$ is simply the ratio of the total number of monomeric units in polymer and the number of polymer molecules, as represented by Equation (6). Because the total number of monomeric units in the system does not change with the crosslinking process, $\overline{P}_{\mathrm{n}}$ can be obtained simply by considering how the crosslinking process changes the number of polymer molecules. By introducing a single crosslinkage, the number of polymer molecules decreases by one, and the following equation holds:

$$\frac{1}{\overline{P}_{\mathrm{n}}} = \frac{1}{\overline{P}_{\mathrm{np}}} - \frac{\rho}{2} \tag{146}$$

where $\overline{P}_{\mathrm{np}}$ is the number-average chain length of the primary chains, and $\rho/2$ represents the number of crosslinkages. Remember that one crosslinkage consists of two crosslink points by definition [4]. Therefore, the number-average chain length of the crosslinked polymer system,

$\overline{P}_n$ is given by:

$$\overline{P}_n = \frac{\overline{P}_{np}}{1 - \rho\overline{P}_{np}/2} \tag{147}$$

With Equation (145), the number-average chain length at the gel point, $\overline{P}_{n,gp}$ is given by:

$$\overline{P}_{n,gp} = \frac{\overline{P}_{np}}{1 - \overline{P}_{np}/2\overline{P}_{Mp}} \tag{148}$$

Assuming the primary chain length distribution is the most probable, $\overline{P}_{Mp}/\overline{P}_{np} = 2$, and therefore, $\overline{P}_{n,gp} = (4/3)\overline{P}_{np}$. The number-average chain length is only 4/3 times as large as that of the primary chains, which is rather small, even though $\overline{P}_M$ goes to infinity.

Next, consider the mass fraction distribution of the random crosslink system. Let $M_p(r)$ be the mass chain-length distribution of the primary chains. Because the most probable distribution is the most fundamental polymer distribution, consider the case where $M_p(r)$ follows the most probable distribution, represented by Equation (14), that is:

$$M_p(r) = \frac{r}{\left(\overline{P}_{np}\right)^2}\exp\left(-\frac{r}{\overline{P}_{np}}\right) \tag{149}$$

Consider the fractional mass-based chain length distribution of the polymer molecules having k crosslinkages, $M_k(r)$ defined by:

$$M(r) = \sum_{k=0}^{\infty} M_k(r) \tag{150}$$

To obtain a polymer molecule without any crosslinkage ($k = 0$) by randomly choosing a unit, the selected primary chain must not possess any crosslink point. The fractional mass-based distribution, $M_0(r)$ is given by:

$$M_0(r) = (1-\rho)^r M_p(r) \cong \exp(-\rho r) M_p(r) \quad (\text{for } \rho \ll 1) \tag{151}$$

For the primary chains following the most probable distribution:

$$M_0(r) = \frac{r}{\left(\overline{P}_{np}\right)^2}\exp\left[-\left(\frac{1+\rho\overline{P}_{np}}{\overline{P}_{np}}\right)r\right] \tag{152}$$

Next, consider $M_1(r)$. When one unit is selected randomly, as shown in Figure 26, a polymer molecule with chain length r having one crosslinkage is obtained by connecting two primary chains with length s and $r - s$. The 0^{th} generation chain must possess one crosslink point and one $(s-1)$ uncrosslinked point. Note that any one of the units can possess a crosslink point, there are s ways of choosing a crosslink point on this chain. On the other hand, the 1^{st} generation chain must not possess any further crosslink point. Therefore, $M_1(r)$ is given by:

$$\begin{aligned} M_1(r) &= \sum_{s=1}^{r-1}\left[M_p(s)s\rho(1-\rho)^{s-1}\right]\left[M_p(r-s)(1-\rho)^{r-s-1}\right] \\ &\cong \rho(1-\rho)^{r-2}\int_0^r sM_p(s)M_p(r-s)ds \end{aligned} \tag{153}$$

For the case with $M_p(r)$ given by Equation (149):

$$\begin{aligned} M_1(r) &= \frac{\rho(1-\rho)^{r-2}}{\left(\overline{P}_{np}\right)^4}\exp\left(-\frac{r}{\overline{P}_{np}}\right)\int_0^r s^2(r-s)ds \\ &\cong \frac{r}{\left(\overline{P}_{np}\right)^2}\left(\frac{\rho\overline{P}_{np}}{2!3!}\right)\left(\frac{r}{\overline{P}_{np}}\right)^3\exp\left[-\left(\frac{1+\rho\overline{P}_{np}}{\overline{P}_{np}}\right)r\right] \end{aligned} \tag{154}$$

By continuing the present reasoning, it is straightforward to obtain the fractional mass-based distribution having k crosslinkages, $M_k(r)$ is given by [5]:

$$M_k(r) = \frac{r}{\left(\overline{P}_{np}\right)^2}\left(\frac{\left(\rho\overline{P}_{np}\right)^k}{(k+1)!(2k+1)!}\right)\left(\frac{r}{\overline{P}_{np}}\right)^{3k}\exp\left[-\left(\frac{1+\rho\overline{P}_{np}}{\overline{P}_{np}}\right)r\right] \tag{155}$$

The whole distribution consisting of all values of k is given by:

$$\begin{aligned} M(r) &= \sum_{k=0}^{\infty} M_k(r) \\ &= {}_0F_2\left(;\frac{3}{2},2;\frac{\rho r^3}{4\left(\overline{P}_{np}\right)^2}\right)\frac{r}{\left(\overline{P}_{np}\right)^2}\exp\left[-\left(\frac{1+\rho\overline{P}_{np}}{\overline{P}_{np}}\right)r\right] \end{aligned} \tag{156}$$

In Equation (152), ${}_pF_q\left[a_1, \cdots, a_p; b_1, \cdots, b_q; z\right]$ represents a generalized hypergeometric function [69] defined by:

$${}_pF_q\left[a_1, \cdots, a_p; b_1, \cdots, b_q; z\right] = \sum_{k=0}^{\infty}\frac{(a_1)_k \cdots (a_p)_k}{k!(b_1)_k \cdots (b_q)_k}z^k \tag{157}$$

where $(a)_k$ is the Pochhammer symbol defined by:

$$(a)_k \equiv \frac{\Gamma(a+k)}{\Gamma(a)} \tag{158}$$

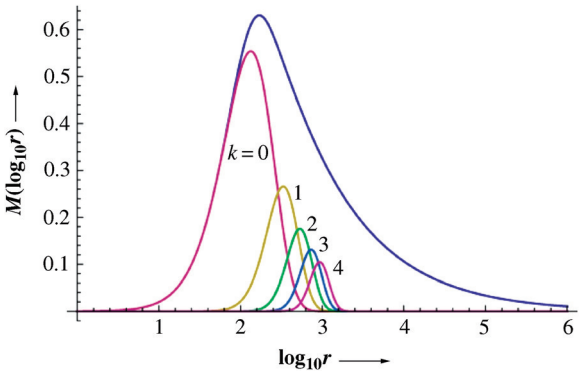


Figure 27. Calculated mass fraction distribution right at the gel point, with $\overline{P}_{\mathrm{np}} = 100$ and $\rho = 5 \times 10^{-3}$. The fractional chain length distributions containing k crosslinkages are also shown

For the actual calculation of the hypergeometric function, one can simply use a build-in function of the calculation software.

Figure 27 shows the calculated whole mass fraction distribution, Equation (156) and the fractional distribution, Equation (155) right at the gel point. Even at the gel point, the mass fraction of linear chains ($k = 0$) is the largest within the fractional MMDs.

The mass fraction of polymers containing k crosslinkages is given by:

$$M_k = \int_0^\infty M_k(r)\mathrm{d}r = \frac{(3k+1)!\left(\rho\overline{P}_{\mathrm{np}}\right)^k}{(k+1)!(2k+1)!}\left(\frac{1}{1+\rho\overline{P}_{\mathrm{np}}}\right)^{3k+2} \tag{159}$$

When the fractional MMD given by Equation (155) is normalized to make the total area of each $M_k(r)$ function unity, $M_{k,\mathrm{norm}}(r)$ is given by the following Schulz–Zimm distribution [60, 61], or equivalently, the gamma distribution:

$$M_{k,\mathrm{norm}}(r) = \frac{M_k(r)}{M_k} = \frac{\sigma^\sigma}{\overline{P}_{\mathrm{n,k}}\Gamma(\sigma)}\left(\frac{r}{\overline{P}_{\mathrm{n,k}}}\right)^\sigma \exp\left(-\frac{\sigma r}{\overline{P}_{\mathrm{n,k}}}\right) \tag{160}$$

where $\sigma = 3k + 1$, and $\overline{P}_{\mathrm{n,k}}$ is the number-average chain length of the polymers having k crosslinkages, given by:

$$\overline{P}_{\mathrm{n},k} = \frac{(3k+1)\overline{P}_{\mathrm{np}}}{1+\rho\overline{P}_{\mathrm{np}}} \tag{161}$$

For the Schulz–Zimm distribution, σ is represented by the number- and mass-average as follows:

$$\sigma = \frac{\overline{P}_{\mathrm{n},k}}{\overline{P}_{M,k} - \overline{P}_{\mathrm{n},k}} \tag{162}$$

From Equation (162), the mass-average chain length of the polymers having k crosslinkages, given by:

$$\overline{P}_{M,k} = \frac{(3k+2)\overline{P}_{\mathrm{np}}}{1+\rho\overline{P}_{\mathrm{np}}} \tag{163}$$

The PDI of the polymers having k crosslinkages is given by:

$$\overline{P}_{M,k}/\overline{P}_{\mathrm{n},k} = \frac{3k+2}{3k+1} \tag{164}$$

The PDI decreases with increasing the number of crosslinkages k, and when $k = 3$, the PDI has already become so small as 1.1.

Even with the random crosslinking, the crosslinking density of each polymer molecule is different. Each small dot in Figure 28 shows the chain length and crosslinking density of each polymer molecule generated by using a Monte Carlo simulation method [5]. The dashed line shows the crosslinking density of the whole reaction system, $\rho = 4 \times 10^{-3}$. As clearly shown in Figure 28, most of crosslinked polymer molecules are distributed around the asymptotic crosslinking density with $r \to \infty$, i.e., $\lim_{r\to\infty} \overline{\rho}(r)$, which is considered a representative value of the crosslinked polymers, rather than ρ.

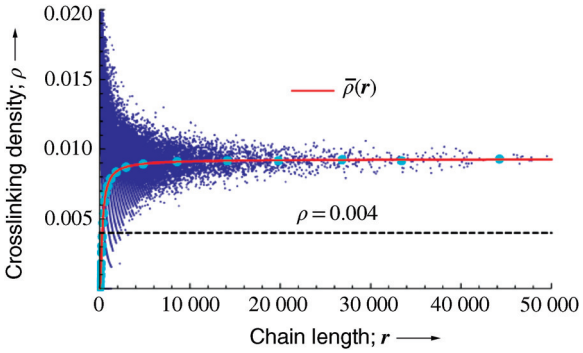


Figure 28. Relationship between crosslinking density and chain length of each polymer molecule generated by a Monte Carlo simulation (small dot), their average crosslinking density within the chain length intervals (circular symbols), with $\overline{P}_{\mathrm{np}} = 100$ and $\rho = 4 \times 10^{-3}$. The solid curve, $\overline{\rho}(r)$ is calculated from Equation (165)

The average crosslinking density of polymers having chain length r, $\overline{\rho}(r)$ can be obtained from $M_k(r)$-function, as follows:

$$\overline{\rho}(r) = \frac{\sum_{k=0}^{\infty} \frac{2k}{r} M_k(r)}{\sum_{k=0}^{\infty} M_k(r)} = \left(\frac{\rho r^2}{6\left(\overline{P}_{\mathrm{np}}\right)^2}\right) \frac{{}_0F_2\left(;\frac{5}{2},3;\frac{\rho r^3}{4\left(\overline{P}_{\mathrm{np}}\right)^2}\right)}{{}_0F_2\left(;\frac{3}{2},2;\frac{\rho r^3}{4\left(\overline{P}_{\mathrm{np}}\right)^2}\right)} \tag{165}$$

The solid curve in Figure 28 shows the calculated result of Equation (165). The value of $\lim_{r\to\infty} \overline{\rho}(r)$ can be determined from this equation, at least, numerically.

The average crosslinking density of polymers having k crosslinkages, is given by:

$$\overline{\rho}(k) = \frac{\int_0^{\infty} \left[\frac{2k}{r} M_k(r)\right] \mathrm{d}r}{\int_0^{\infty} M_k(r) \mathrm{d}r} = \frac{2k\left(1 + \rho \overline{P}_{\mathrm{np}}\right)}{(3k+1)\overline{P}_{\mathrm{np}}} \tag{166}$$

As was shown in [70], $\lim_{r\to\infty} \overline{\rho}(r) \leq \lim_{k\to\infty} \overline{\rho}(k)$, and the equality holds only right at the gel point (gp), i.e.;

$$\lim_{r\to\infty} \overline{\rho}(r)|\mathrm{gp} = \lim_{k\to\infty} \overline{\rho}(k)|\mathrm{gp} = \frac{2\left(1 + \rho \overline{P}_{\mathrm{np}}\right)}{3\overline{P}_{\mathrm{np}}} \tag{167}$$

The crosslinking density at the gel point is $\rho = 1/\overline{P}_{M\mathrm{p}}$, and therefore, the following equation holds:

$$\lim_{r\to\infty} \overline{\rho}(r)|\mathrm{gp} = 2\rho_{\mathrm{gp}} \tag{168}$$

Note that $\overline{P}_{M\mathrm{p}}/\overline{P}_{\mathrm{np}} = 2$ for the most probable distribution. At the gel point, the crosslinking density of a gel molecule just formed is twice as large as the crosslinking density of the whole system, $\rho_{\mathrm{gp}} = 1/\overline{P}_{M\mathrm{p}}$. Equation (168) is valid, irrespective of the primary chain length distribution [4].

More details on random crosslinking, including the post-gelation behavior can be found in [4–6, 70–75]. Although the random crosslinking is an idealized reaction system, the obtained results are important for understanding the fundamental characteristics of crosslinked polymer systems, at least qualitatively. In the present classical theory, the ring formation is neglected, and it is called the ring-free model. In a real system, rings would be formed. However, one needs to understand that the ring-free model is a natural consequence as long as the usual chemical kinetics is valid, in which the reaction rate is represented by the product of concentrations of functional groups. Suppose an active site is looking for a partner to react. The concentration of functional groups that can react with this active site on its own polymer molecule is zero for all sol-polymer molecules, because the mass fraction of any single sol-polymer molecule is zero. The ring formation is prohibited within sol-polymer molecules, as long as the conventional chemical kinetics is valid. On the other hand, a single gel molecule possesses a nonzero mass fraction, the intramolecular reaction or the ring formation within the gel molecule is not prohibited and is accounted for even in the ring-free model. In fact, the distribution functions shown in Equations (155) and (156) apply

to the chain length distribution of sol molecules in the post-gelation period.

An example in which rings are formed in the context of the ring-free model can be found in the cases of emulsion polymerization [76–79]. In emulsion polymerization, because the number of molecules involved in a single reaction locus is limited, each polymer molecule possesses a nonzero mass fraction, and the usual chemical kinetics naturally includes cycle formation.

9.2. Branched Polymers

There are two distinct types of branching; short-chain branching and long-chain branching. The short-chain branching is formed via backbiting reaction in free-radical polymerization, in which the active radical on the chain end abstracts a hydrogen atom intramolecularly. The backbiting is a chain transfer reaction to its own chain, and a small branch is left after the transferred radical grows. In this case, the chains consisting of only several carbons in length are the branches. High pressure free-radical polymerization of ethylene is a representative reaction to produce short-chain branches.

On the other hand, long-chain branches are formed by intermolecular reactions among polymer molecules. In free-radical polymerization, long-chain branches are formed through chain transfer reactions to other polymers and the terminal double-bond polymerization. In this section, important characteristics of long-chain branched polymers are highlighted.

Figure 29 shows an example of random branched polymer structure, formed from the primary chains having the most probable distribution. *Random branching* means that the probability of possessing a branch point is the same for all units in polymer, which provides a kind of standard structure of branched polymers. In addition, the most probable distribution is one of the most fundamental distributions in synthetic polymers, and therefore, this figure could be considered a typical structure of highly branched polymer. From the figure, a large number of relatively small branches are shown, although their lengths are much longer than the branches in the short-chain branching. In the

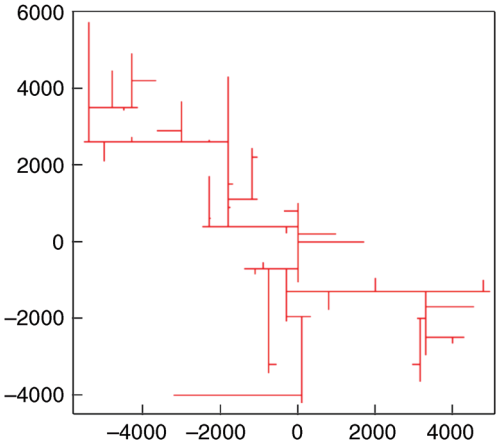


Figure 29. Representative example of a random branch polymer, in which the probability of possessing a branch point is the same for all units in chain and the primary chains follow the most probable distribution. In this particular example, the number-average chain length of primary chains is $\overline{P}_{np} = 1000$, and the chain length of this particular branched polymer is $r = 54\,000$, consisting of 46 primary chains [5]

random branched polymers, the probability of any chain end being a branch point is the same for all chain ends. In the most probable distribution, smaller chains are larger in number, as was shown in Figure 3A, and these smaller chains tend to become the branch chains. A longer chain possesses a larger number of units in it, and therefore, the probability of having a branch point is larger for longer chains and longer chains tend to become the backbone chains. Note that only one of two chain ends of a primary chain can be connected to a backbone chain in the present discussion. If both chain ends are connected, they are crosslinks, not the branches, as discussed later.

The probability that a unit possesses a branch point is defined as the branching density, ρ_b. The ρ_b-value is the same for all units in the random branched polymers. On the other hand, ρ_b is not a constant in nonrandom branching. For example, in the polymer transfer reactions in free-radical polymerization, the primary chains formed at earlier stages of polymerization are subjected to branching reactions for a longer period of time, the expected branching density is larger for the primary chains born earlier [5, 80].

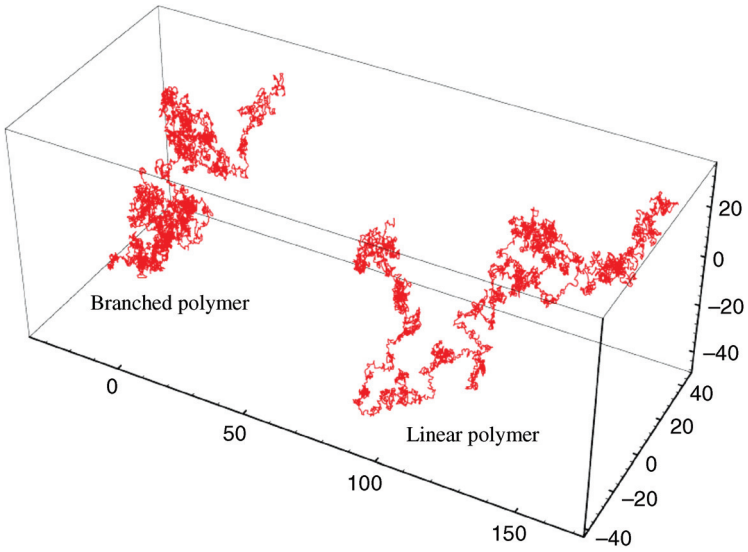


Figure 30. Examples of 3D structure of a random branch polymer and a linear polymer under unperturbed conditions. The chain lengths of both polymers are the same, $r = 6294$. The branch polymer consists of 8 primary chains [5]

Polymers containing branches/crosslinks possess smaller 3D size than linear polymers. Figure 30 shows an example of 3D structure of a random branch polymer under perturbed conditions, as well as that for a linear polymer having the same chain length $r = 6294$. The 3D size is clearly smaller for the branched polymers.

The radius of gyration $\sqrt{\langle s^2 \rangle}$ of the random branch polymer whose primary chains follow the most probable distribution is given by [81]:

$$\sqrt{\langle s^2 \rangle} = \sqrt{\langle s^2 \rangle_{\text{linear}}} \left\{ \left(1 + \frac{\overline{m}}{7} \right)^{0.5} + \frac{4\overline{m}}{9\pi} \right\}^{-0.25} \tag{169}$$

where $\overline{m}$ is the average number of branch points within the polymer molecules having the same chain length r, and $\sqrt{\langle s^2 \rangle_{\text{linear}}}$ is the radius of gyration for the linear polymers with chain length r. When using Equation (169), $\overline{m}$ is calculated from $\overline{m} = r\overline{\rho}_{\text{b}}(r)$. Similarly with the random crosslinking system shown in Figure 28, the branching density of each polymer molecules is distributed around the asymptotic value, $\lim_{r \to \infty} \overline{\rho}_{\text{b}}(r)$, not the average branching density of the whole system [82], as will be graphically shown in Figure 35. The value of $\lim_{r \to \infty} \overline{\rho}_{\text{b}}(r)$ is much more important than the average branching density of the whole reaction system. Further note that $\overline{m} = r \lim_{r \to \infty} \overline{\rho}_{\text{b}}(r)$ could be a good approximation for $\overline{m} \overset{r \to \infty}{=} r\overline{\rho}_{\text{b}}(r)$ when using Equation (169) [83].

The number-average chain length, $\overline{P}_{\text{n}}$ can be determined as follows, because the number of polymer molecules decreases by one due to the formation of a single branch point:

$$\frac{1}{\overline{P}_{\text{n}}} = \frac{1}{\overline{P}_{\text{np}}} - \rho_{\text{b}} \quad \text{or} \quad \overline{P}_{\text{n}} = \frac{\overline{P}_{\text{np}}}{1 - \rho_{\text{b}}\overline{P}_{\text{np}}} \tag{170}$$

Next, consider the mass-average chain length $\overline{P}_M$. Suppose a monomeric unit shown in Figure 31 is chosen randomly. Before considering the total expected number of monomeric units connected into this polymer molecule $\overline{P}_M$, let us consider the branched chain part in the downward direction, as shown in Figure 31.

The expected chain length of the 0^{th} generation primary chain is obviously $\overline{P}_{M\text{p}}$, because it is selected on a mass basis, as was shown in Figure 1B. The expected number of branch points on the 0^{th} generation chain is $\overline{P}_{M\text{p}}\rho_{\text{b}}$, which is equal to the number of primary chains belonging to the 1^{st} generation. Because only the chain end can be connected to the branch

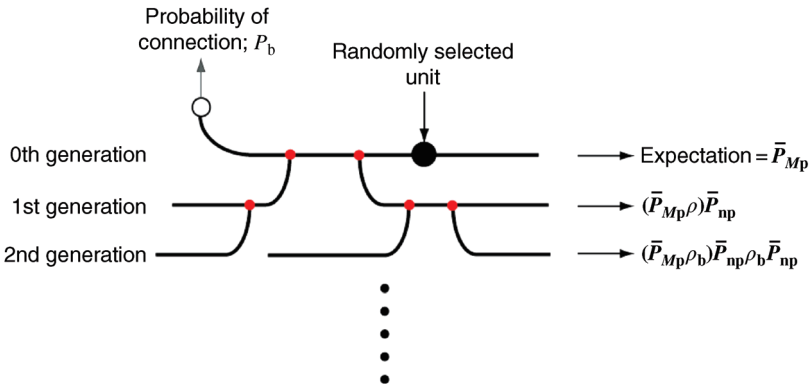


Figure 31. Schematic representation of a randomly selected polymer molecule toward the downward direction

point, the branch chains must be selected on a number basis, and therefore, the expected chain length of a branch chain is $\overline{P}_{np}$. The total chain length belonging to the 1st generation is given by $(\overline{P}_{Mp}\rho_b)\overline{P}_{np}$. Similarly, the total chain length belonging to the 2nd generation is given by $(\overline{P}_{Mp}\rho_b)\overline{P}_{np}\rho_b\overline{P}_{np}$ as shown in Figure 31. By continuing the present processes repeatedly, the total expected mass in the downward direction, $\overline{P}_{M,A}$ is given by:

$$\begin{aligned}\overline{P}_{M,A} &= \overline{P}_{Mp} + \overline{P}_{Mp}(\rho_b\overline{P}_{np}) + \overline{P}_{Mp}(\rho_b\overline{P}_{np})^2 + \cdots \\ &= \overline{P}_{Mp}\sum_{i=0}^{\infty}(\rho_b\overline{P}_{np})^i = \frac{\overline{P}_{Mp}}{1-\rho_b\overline{P}_{np}}\end{aligned} \quad (171)$$

Up to the present stage, the chains connected upward direction has not been considered. The chain end of the 0th generation primary chain is connected with probability P_b, which is given by:

$$P_b = \frac{(\textit{total number of branch points})}{(\textit{total number of primary chains})} = \frac{\rho}{1/\overline{P}_{np}} = \rho_b\overline{P}_{np} \quad (172)$$

Note that $P_b < 1$, i.e., $\rho_b\overline{P}_{np} < 1$. Therefore, $\overline{P}_{M,A}$ given by Equation (171) never goes to infinity.

Figure 32 shows the connection of a head unit of the 0th generation primary chain. Suppose the head unit is connected. The connected primary chain is selected on a mass basis, because any of the monomeric units in the system can be connected, and therefore, the expected chain length is $\overline{P}_{Mp}$. Except for the branched unit of the connected chain, there are $\overline{P}_{Mp} - 1$ units that can have a branch point. Therefore, the expected number of branch points on the connected primary chain is $(\overline{P}_{Mp} - 1)\rho_b \cong \overline{P}_{Mp}\rho_b$. Looking at Figure 31 again, one would notice that the expected chain length toward the downward direction is $\overline{P}_{M,A}$, excluding the branch unit connected from the 0th generation chain. By continuing the connection through the head unit, the total expected mass of a polymer molecule by choosing one unit randomly, which is the mass-average chain length

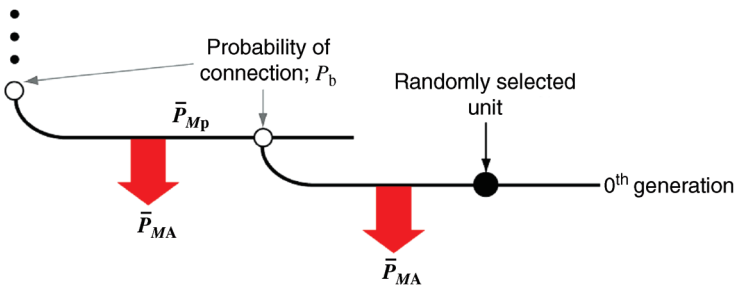


Figure 32. Schematic representation of the connection of a head unit of the randomly selected primary chain

of the whole system, $\overline{P}_M$ is given by:

$$\overline{P}_M = \overline{P}_{M,\mathrm{A}} + P_\mathrm{b}\overline{P}_{M,\mathrm{A}} + (P_\mathrm{b})^2\overline{P}_{M,\mathrm{A}} + \cdots = \overline{P}_{M,\mathrm{A}} \sum_{i=0}^{\infty} \left(\rho_\mathrm{b}\overline{P}_\mathrm{np}\right)^i = \frac{\overline{P}_{M\mathrm{p}}}{\left(1-\rho_\mathrm{b}\overline{P}_\mathrm{np}\right)^2} \tag{173}$$

The PDI of a random branched polymer system is given by:

$$\overline{P}_M/\overline{P}_\mathrm{n} = \frac{\left(\overline{P}_{M\mathrm{p}}/\overline{P}_\mathrm{np}\right)}{1-\rho_\mathrm{b}\overline{P}_\mathrm{np}} \tag{174}$$

Equation (174) shows that the PDI of random branch polymers is always larger than the PDI of the primary chains.

Note that Equations (170), (173), and (174) are valid for the random branched polymers, irrespective of the primary polymer distribution.

Because $p_\mathrm{b} = \rho_\mathrm{b}\overline{P}_\mathrm{np} < 1$, the mass-average chain length never goes to infinity, which means that gelation can never occur. In general, gelation never occurs only through branches [84], and crosslinks are required for gelation.

Figure 33 shows some examples of H-shaped (crosslinking) and T-shaped (branching) chain connection. The H-shaped chain connections, i. e., the crosslinkages are required for gelation to occur. In the case of free-radical polymerization that involves chain transfer to polymer, combination termination is required to cause gelation. Conversely, if the reaction system causes gelation, there should exist some reaction that forms the H-shaped chain connections.

As was done for the random crosslink system, consider the mass fraction distribution formed through random branching of the primary chains having the most probable distribution. By using the similar random sampling method introduced in Section 9.1, the fractional mass-based chain length distribution of the polymers possessing k branch points is given by [5, 82]:

$$M_k(r) = \left(\frac{1-\rho_\mathrm{b}\overline{P}_\mathrm{np}}{\overline{P}_\mathrm{np}}\right)\left(\frac{\left(\rho_\mathrm{b}\overline{P}_\mathrm{np}\right)^k}{k!(k+1)!}\right)\left(\frac{r}{\overline{P}_\mathrm{np}}\right)^{2k+1}\exp\left[-\left(\frac{1+\rho_\mathrm{b}\overline{P}_\mathrm{np}}{\overline{P}_\mathrm{np}}\right)r\right] \tag{175}$$

The whole distribution can be obtained by summing up for all k's:

$$M(r) = \sum_{k=0}^{\infty} M_k(r) = \left(\frac{1-\rho_\mathrm{b}\overline{P}_\mathrm{np}}{\overline{P}_\mathrm{np}}\right)\left(\frac{1}{\sqrt{\rho_\mathrm{b}\overline{P}_\mathrm{np}}}\right)\mathrm{I}_1\left(2r\sqrt{\frac{\rho_\mathrm{b}}{\overline{P}_\mathrm{np}}}\right)\exp\left[-\left(\frac{1+\rho_\mathrm{b}\overline{P}_\mathrm{np}}{\overline{P}_\mathrm{np}}\right)r\right] \tag{176}$$

where I_1 is the modified Bessel function of the first kind and of the first order.

It is interesting to note that the above equations can also be obtained by utilizing the Stockmayer bivariate distribution for the instantaneous copolymers, Equations (98–101) [85, 86].

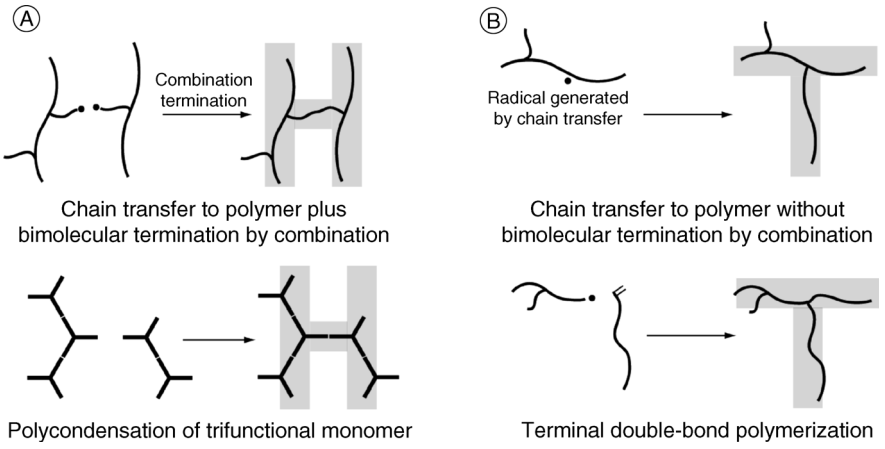


Figure 33. Examples of (A) H-shaped (crosslinking) and (B) T-shaped (branching) chain connections

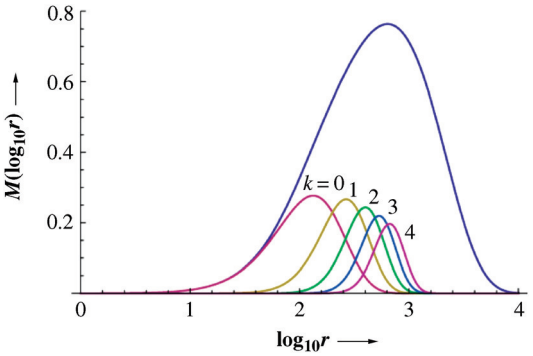


Figure 34. Calculated mass fraction distribution of random branch polymers whose primary chains follow the most probable distribution, with $\overline{P}_{np}$=100 and $\rho_b = 5 \times 10^{-3}$. The fractional chain length distributions containing k branches are also shown

Figure 34 shows the calculated mass fraction distribution of the random branched polymer system with $\overline{P}_{np} = 100$ and $\rho_b = 5 \times 10^{-3}$, by using Equations (175) and (176). Compared with a random crosslinking system shown in Figure 27, the high molecular mass tail decreases quickly, i.e., the persistence of the high molecular mass tail is a characteristic of gelling system.

The mass fraction of polymers containing k branches, M_k is given by:

$$M_k = \int_0^\infty M_k(r)\mathrm{d}r$$

$$= \frac{(2k+1)!(\rho_b\overline{P}_{np})^k(1-\rho_b\overline{P}_{np})}{k!(k+1)!}\left(\frac{1}{1+\rho_b\overline{P}_{np}}\right)^{2k+2} \quad (177)$$

Therefore, the normalization of the distribution $M_k(r)$ to make the total area unity leads again to the Schulz–Zimm distribution, as follows:

$$M_{k,\mathrm{norm}}(r) = \frac{M_k(r)}{M_k} = \frac{\sigma^\sigma}{\overline{P}_{n,k}\Gamma(\sigma)}\left(\frac{r}{\overline{P}_{n,k}}\right)^\sigma \exp\left(-\frac{\sigma r}{\overline{P}_{n,k}}\right) \quad (178)$$

where $\sigma = 2k + 1$, and $\overline{P}_{n,k}$ is the number-average chain length of the polymers having k branch points, which is given by:

$$\overline{P}_{n,k} = \frac{(2k+1)\overline{P}_{np}}{1+\rho_b\overline{P}_{np}} \quad (179)$$

For the Schulz–Zimm distribution, σ is represented by Equation (162), and therefore, the mass-average chain length of the polymers having k brach points, $\overline{P}_{M,k}$ is given by:

$$\overline{P}_{M,k} = \frac{(2k+2)\overline{P}_{np}}{1+\rho_b\overline{P}_{np}} \quad (180)$$

The polydispersity index, PDI of the polymers having k branch points is given by:

$$\overline{P}_{M,k}/\overline{P}_{n,k} = \frac{2k+2}{2k+1} \quad (181)$$

Similarly with the random crosslinking system, the PDI decreases with increasing the number of branch points k, but the PDI is slightly larger than that for random crosslinking for a given k. For example, when $k = 3$, the PDI for random branch is about 1.14 while it is 1.1 for random crosslinking.

Similarly with the random crosslinking system, the branching density of each polymer molecule is different. Each small dot in Figure 35 shows the chain length and branching density of each polymer molecule generated by

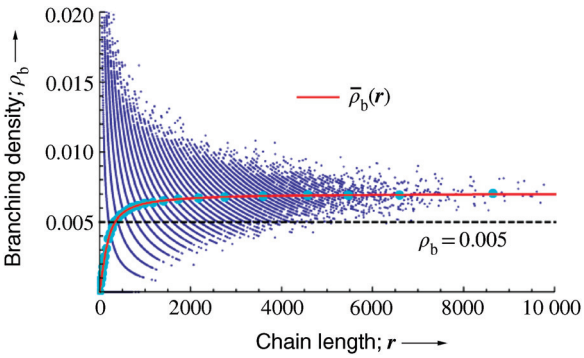


Figure 35. Relationship between branching density and chain length of each polymer molecule generated by a Monte Carlo simulation (small dot), their average crosslinking density within chain length intervals (circular symbols), with $\overline{P}_{np} = 100$ and $\rho_b = 5 \times 10^{-3}$. The solid curve, $\overline{\rho}_b(r)$ is calculated from Equation (182)

using a Monte Carlo simulation method [5]. The dashed line shows the branching density of the whole system, $\rho_b = 5 \times 10^{-3}$. Similarly with the random crosslinking case, as was shown in Figure 28, most of branched polymer molecules are distributed around the asymptotic branching density with $r \to \infty$, i.e., $\lim_{r\to\infty} \overline{\rho}_b(r)$, which is considered a representative value of the branched polymers, rather than ρ_b.

The $\overline{\rho}_b(r)$ function can be obtained from $M_k(r)$, as follows:

$$\overline{\rho}_b(r) = \frac{\sum_{k=0}^{\infty} \frac{k}{r} M_k(r)}{\sum_{k=0}^{\infty} M_k(r)} = \frac{\sqrt{\frac{\rho_b}{\overline{P}_{np}}}\, I_2\left(2r\sqrt{\frac{\rho_b}{\overline{P}_{np}}}\right)}{I_1\left(2r\sqrt{\frac{\rho_b}{\overline{P}_{np}}}\right)} \tag{182}$$

where I_2 is the modified Bessel function of the first kind and of the second order. The solid curve in Figure 35 shows the calculated result of Equation (182). The value of $\lim_{r\to\infty} \overline{\rho}(r)$ can be determined from Equation (182), at least, numerically.

The average branching density of polymers having k branch points, is given by:

$$\overline{\rho}_b(k) = \frac{\int_0^{\infty} \left[\frac{k}{r} M_k(r)\right] dr}{\int_0^{\infty} M_k(r) dr} = \frac{k\left(1 + \rho \overline{P}_{np}\right)}{(2k+1)\overline{P}_{np}} \tag{183}$$

9.3. Note on Nonlinear Polymerization

While randomly branched or crosslinked systems are important to understand the fundamental characteristics of branched or crosslinked polymer systems, real systems usually show some degrees of non-randomness in their structure and system-specific consideration is required. The number-average chain length, on the other hand, is always obtainable based on the stoichiometric investigation, because it is simply the ratio between the total number of monomeric units and the total number of polymer molecules.

Assuming that the effects of the size and/or structure dependent kinetics are negligible, the random sampling technique introduced in this article makes it possible to formulate the mass-average chain length in a matrix formula for nonrandom branching and/or crosslinking, generally represented by [87–90]:

$$\overline{P}_{\text{non-randomness}} = \overline{P}_{\text{non-randomness},0} + \mathbf{mF}(\mathbf{I} - \mathbf{M})^{-1}\mathbf{s} \tag{184}$$

where $\overline{P}_{\text{non-randomness},0}$ is the chain length of the initially selected chain or unit on a mass basis, **m** represents the mass fraction vector, **F** is the matrix showing the connection statistics from the 0^{th} to the first generation chain or unit, **I** is the identity matrix, **M** is the transition matrix representing the connection statistics among chains or units, and **s** is a vector representing the expected size of chain or unit of various species. Gelation is predicted to occur when the largest eigenvalue of the transition matrix, **M** reaches unity. One would find the similarities of Equation (184) with Equation (144) and (173).

For the calculation of average properties, the method of moments has been applied to various complex reaction systems [91–94]. The *i*th moment of the polymer distribution is defined by:

$$Q_i = \sum_{r=1}^{\infty} r^i [P_r] \tag{185}$$

For example, Q_0 describes the number of polymer molecules, and Q_1 means the total mass of polymers. The differential equations describing the time development of Q_i can be obtained by taking the population balance equations, similarly as was shown in Equations (56) and (57) for polymer radicals. Once the moments of the distributions are determined, the number- and mass-average chain length are given by:

$$\overline{P}_n = \frac{Q_1}{Q_0} \tag{186}$$

$$\overline{P}_M = \frac{Q_2}{Q_1} \tag{187}$$

The method of moments is a convenient mathematical technique to determine the averages. Because any order of moments can be obtained, one may think that it would be possible to obtain the full chain length distribution, based on the calculated moments. A numerical method to calculate the distribution from its moments by approximating the distribution as a sum of Laguerre polynomials [95, 96], or the

generalized Laguerre polynomials [97]. However, the method is limited to the distribution close to the most probable distribution, and accurate determination of the full distribution is disturbed by the amplification of oscillations in the sum of polynomials as the number of terms increases [98, 99]. In general, it is better to think that the method of moments is limited to obtain the averages, not the full distribution.

For the problems where an infinite set of differential equations describing the population balance equations can be written down, the approximate numerical solution for the full distribution may be obtained by using a discrete Galarkin method [100].

On the other hand, there are problems where the population balance equations cannot be set up. A notable example is a random scission of branched polymers [101]. All 4 types of branched polymer shown in Figure 36 possess 12 monomeric units with 4 branches. Suppose we want to have a linear polymer with 3 monomeric units by cutting one bonding. For the polymer (A), it is impossible to obtain a linear polymer with $r = 3$. On the other hand, there is one possible scission point in the polymer (B). The number of possible scission points changes with the detailed branched structure, and it is impossible to set up the population balance equations fully describing the time development during the scission reactions.

On the other hand, the random sampling technique can be applied also for such cases, as long as the size and structure dependence of branching/crosslinking/scission reaction can be neglected. With the matrix formula shown in Equation (184), the mass-average chain length can be obtained. The full chain length distribution can be obtained by application the random sampling technique to the Monte Carlo simulation method [5, 102–106]. With the Monte Carlo simulation, one can observe the structure of each polymer molecule directly on the computer screen as was shown in Figures 29 and 30, and one can determine very detailed structural information. On the basis of the detailed structural information, it is possible to determine the viscoelastic properties of branched polymers [107]. The Monte Carlo simulation technique promises to develop the computer-aided polymer design system that enables one to estimate the synthesis-structure-property relationships.

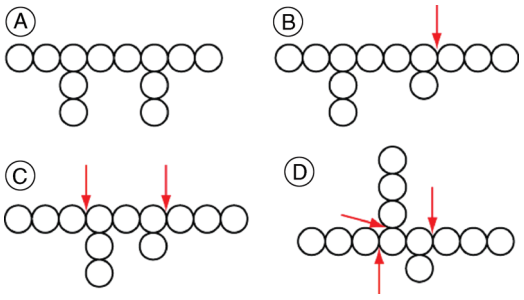


Figure 36. Possible scission point to obtain linear polymer with $r = 3$ by cutting one bonding

List of Symbols

A	functional group of reactant that reacts with B in step polymerization
A_1, A_2, A_3	adjustable parameter used for the empirical conversion dependence of k_t
ATRP	atom-transfer radical polymerization
B	functional group of reactant that reacts with A in step polymerization
C_{fCTA}	chain transfer constant of chain-transfer agent, CTA
C_{fm}	chain transfer constant of monomer
$Comp(F_1\|r)$	composition distribution of polymer molecules with chain length r
CSTR	continuous stirred tank reactor
CTA	chain-transfer agent
E_d	activation energy for initiator de composition
E_f	activation energy for chain-transfer reaction
E_L	activation energy for the average chain length
E_p	activation energy for propagation
E_R	activation energy for polymerization
E_t	activation energy for termination
f	initiator efficiency

f_1 mole fraction of monomer 1 in copolymerization

f_1^0 initial mole fraction of monomer 1 in copolymerization

F_1 mole fraction of monomer 1 bound in polymer produced instantaneously in copolymerization

$\overline{F}_1$ mole fraction of monomer 1 bound in accumulated copolymer

F_1^0 instantaneous copolymer composition of polymers formed at $x = 0$

$F_{1,av}$ average composition of polymer formed instantaneously in Stockmayer's bivariate distribution

$F(a,b;x)$ confluent hypergeometric function

${}_pF_q$ generalized hypergeometric function

GPC gel permeation chromatography

I initiator

I_1 modified Bessel function of the first kind of the first order

I_2 modified Bessel function of the first kind of the second order

k reaction rate constant

k number of crosslinkages or branch points in a polymer molecule

k_1 activation rate constant in RDRP

k_2 deactivation rate constant in RDRP

k_d initiator decomposition rate constant

k_{ex} exchange reaction rate constant in degenerative-transfer radical polymerization

k_i rate constant for monomer adding to an initiator radical

k_{ij} propagation rate constant for monomer of type *i*adding to a double bond on a monomer unit of type j (copolymerization)

k_{fCTA} rate constant for chain transfer to CTA

k_{fm} rate constant for chain transfer to monomer

k_{fX} rate constant for chain transfer to small species, X

k_p propagation rate constant

k_p' propagation rate constant for transfer radical

k_t rate constant for bimolecular termination ($=k_{tc} + k_{td}$)

k_t^0 termination rate constant at zero monomer conversion ($x = 0$)

k_{tc} rate constant for bimolecular termination by combination

k_{td} rate constant for bimolecular termination by disproportionation

K equilibrium constant ($=k_1/k_2$)

LCA long-chain approximation

m molecular mass of monomeric unit

$\overline{m}$ average number of branch points within the polymer molecules having the same chain length

M monomer

M_1 monomer of type 1 in copolymerization

M_k mass fraction of polymer molecules containing k crosslinkages or k branch points

$M(r)$ mass chain length distribution (mass-fraction of polymer molecules of length r)

$M^\bullet(r)$ mass chain length distribution of polymer radicals

$M_{accum.}(r)$ mass chain length distribution of accumulated polymer

$M_{inst.}(r)$ "instantaneous" mass chain length distribution

$M_k(r)$ fractional mass chain length distribution of polymer molecules having k crosslinkages or k branch points

$M_{k,norm}(r)$ normalized mass chain length distribution of polymer molecules having k crosslinkages or k branch points

$M_p(r)$ mass chain length distribution of primary chains

$M_\beta(r)$ "instantaneous" mass chain length distribution formed by combination termination (β-mode)

$M_\tau(r)$ "instantaneous" mass chain length distribution formed by other than combination termination (τ-mode)

MMD molecular mass distribution
$\overline{n}_A$ average number of active periods
$\overline{n}_M$ average number of monomeric units bound to an active center in a second
N_a total number of growing chains having an active center in an ideal living polymerization
N_A number of moles of A-functional groups
N_{A_0} initial number of moles of A-functional groups
N_I number of moles of initiator in the reactor
N_{I_0} initial number of moles of initiator in the reactor
N_M number of monomer molecules
$N(r)$ number chain length distribution (number-fraction of polymer molecules of length r)
$N^{\bullet}(r)$ number chain length distribution of polymer radicals
$N_{SA}(r)$ number chain length distribution formed during a single active period
p conversion of functional group in step polymerization, or the probability of connection to the next unit
[P] concentration of all polymer molecules
[P*] concentration of active center
$[P_1^*]$ concentration of active center of type 1 (copolymerization)
P_b probability that a chain end is connected to a backbone chain (branched polymer)
PDI polydispersity index ($=\overline{P}_M/\overline{P}_n$)
P_r polymer with chain length r
P_r^* active polymer molecule with chain length r
$P(n)$ probability that the chain experiences n times of active periods
$\overline{P}_n$ number-average chain length (degree of polymerization)
$\overline{P}_n^{\bullet}$ number-average chain length of polymer radicals
$\overline{P}_{n,accum.}$ number-average chain length of accumulated polymer
$\overline{P}_{n,inst.}$ number-average chain length of dead polymer chains formed instantaneously
$\overline{P}_{n,k}$ number-average chain length of polymer molecules having k crosslinkages or k branch points
$\overline{P}_{np}$ number-average chain length of primary chains
$\overline{P}_{n,SA}$ number-average chain length added during a single active period
$\overline{P}_{n,gp}$ number-average chain length at the gel point
$P^*_{m,n,1}$ live copolymer chain with m units of monomer 1 and n units of monomer 2 bound in polymer chain and with active center located on terminal unit 1
$\overline{P}_M$ mass-average chain length (degree of polymerization)
$\overline{P}_{M,A}$ expected mass-average chain length toward the downward direction in Figure 31
$\overline{P}_M^{\bullet}$ mass-average chain length of polymer radicals
$\overline{P}_{M,accum.}$ mass-average chain length of accumulated polymer
$\overline{P}_{M,inst.}$ mass-average chain length of dead polymer chains formed instantaneously
$\overline{P}_{M,k}$ mass-average chain length of polymer molecules having k crosslinkages or k branch points
$\overline{P}_{Mp}$ mass-average chain length of primary chains
$\overline{P}_{M,SA}$ mass-average chain length during a single active period in RDRP
PXP adduct radical formed in RAFT
Q_i i-th moment of polymer distribution
r polymer chain length (degree of polymerization)
r_1, r_2 reactivity ratios
$[R^{\bullet}]$ total radical concentration
R_{act} rate of activation in RDRP
RAFT reversible-addition-fragmentation chain-transfer
RDRP reversible-deactivation radical polymerization
R_{deact} rate of deactivation in RDRP
R_f rate of chain transfer
RGS radical generating species in RDRP

R_I initiation rate
R_{in}^* initiator fragment with an active center
$R_{in}^\bullet$ initiator radical
R_p propagation rate or polymerization rate
$R_r^\bullet$ polymer radical of chain length r
R_t termination rate ($=R_{tc} + R_{td}$)
R_{tc} rate of termination by combination
R_{td} rate of termination by disproportionation
$\sqrt{\langle s^2 \rangle}$ radius of gyration
SEC size exclusion chromatography
SRMP stable-radical-mediated polymerization
SSH stationary-state hypothesis
t time
$t_{1/2}$ half-life
$\bar{t}_D$ average time length of a deactivated time
t_R reaction time used for the development of MMD in RDRP
$\bar{t}_{R\cdot}$ average lifetime of a radical
T temperature
T_c ceiling temperature
Trap trapping agent in RDRP
V volume of reacting mixture
x monomer conversion
X general description of small molecule that can act as a chain-transfer agent
X trapping agent in SRMP
α stoichiometric imbalance ($= N_{A_0}/N_{B_0}$)
β kinetic dimensionless parameter ($= R_{tc}/R_p$)
Γ gamma function
ΔG free energy change
ΔH enthalpy change
ΔS entropy change
η number average for the Poisson distribution
ρ crosslinking density
ρ_b branching density
$\bar{\rho}_b(k)$ average branching density of polymer molecule having k branch points
$\bar{\rho}_b(r)$ average branching density of polymer molecule having chain length r
ρ_{gp} crosslinking density at the gel point
$\bar{\rho}(k)$ average crosslinking density of polymer molecule having k crosslinkages
$\bar{\rho}(r)$ average crosslinking density of polymer molecule having chain length r
σ standard deviation
σ parameter representing the narrowness of the Schulz–Zimm distribution
τ kinetic dimensionless parameter [$=(R_{td} + R_f)/R_p$]
$\phi_1^\bullet$ mole fraction of polymer radicals of type 1

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Polymerization Processes, 2. Modeling of Processes and Reactors

ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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1. Introduction

The polymer reactor model is accepted as a valuable tool whose use contributes significantly to all aspects of process technology for polymer manufacture. This includes process design, optimization, state estimation, and control. Through process design, polymers with a unique and desirable combination of properties can often be obtained. Process parameters such as residence time distribution (RTD) are usually not considered by polymer synthesis chemists, although RTD can influence chemical composition distribution (CCD), molecular mass distribution (MMD), long-chain branching and gel/sol ratios. In the early days of the polymer industry,

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the chemists played the major role in product and process development and scale-up. This has changed, with the process engineers now playing a significant role in all phases of commercialization of new and improved polymer products. Their broad experience with process fundamentals and computer modeling are essential to obtain high-quality products, safely and economically.

Dynamic reactor models can be used in a variety of ways. Stability and control of polymer reactors should be considered at the design stage and control problems minimized then, rather than take corrective action after the plant is built. Complex interactions which are involved in polymerization (highly nonlinear temperature and concentration effects) preclude optimal design based on experimentation alone because the cost would be prohibitive. Models can be used to identify potential sources of product variability and strategies to minimize their effects. They can also be used to store information on process technology in a concise and readily retrievable and modifiable form.

Process models are often used to train chemists, chemical engineers, and plant operators and give them a feel for the dynamics of the polymerization process. Model-based simulation that requires a large amount of calculation is now feasible with the help of modern high speed computers. Still simpler models are preferable in order to comprehend important characteristics of the polymerization processes.

The most expensive aspect of model development is the experimental estimation of model parameters; highly instrumented bench-, pilot-, and plant-scale reactors are required. Statistically designed experiments should be performed to permit efficient parameter estimation and model development. Modeling is an iterative process and the very act of developing a deterministic and/or probabilistic model permits a greater understanding of the relevant microscopic processes that occur during polymerization or polymer modification. As additional (plant, pilot-plant, and bench-scale) data become available, model structure and parameters can be updated.

The applications to various reactor operations discussed in this articles are based on the fundamentals of the polymerization models presented in (→ Polymerization Processes, 1. Fundamentals).

2. Fundamental Effects of Reactor Types

2.1. Reactor Types and Their Models

All chemical reactors, whether industrial or experimental in scale, fall into one of three broad categories: batch, semibatch (or semicontinuous), and continuous. The readers who are not familiar with these names should refer to a chemical reaction engineering textbook, such as [1]. Molecular mass and copolymer composition distributions, long-chain branching and cross-linking are affected significantly by the reactor types used, and important characteristics of polymerization reactions and reactors must be properly accounted for.

Figure 1 shows three representative ideal reactors, characterizing them on the basis of the RTD and the temporal and spatial course of the chemical reaction.

The batch reactor is a closed system, and no material enters or leaves during polymerization. In a basic modeling, it is assumed that there are no spatial variations in temperature and concentrations. Mixing at the molecular level is often called "micromixing". All fluid elements have the same reaction time in a batch reactor, which is assumed also for the plug–flow reactor (PFR). In a basic modeling, it is assumed that there are no variations in temperature and concentrations in the radial direction of a PFR, with no fluid elements overtaking or mixing with any other elements ahead or behind. The design equation for an ideal PFR is essentially the same as for a batch reactor; the reaction time in a batch reactor is changed to the length in the flow direction.

$$\text{Batch reactor}: \quad -\frac{dN_M}{dt} = R_p V \tag{1}$$

$$\text{PFR}: \quad -\frac{dF_M}{dV} = R_p \tag{2}$$

Where N_M is the number of moles of monomer in the batch reactor, F_M is the molar flow rate of monomer in a PFR, R_p is the polymerization rate, and V is the reactor volume. Note that V in a batch reactor is the whole reaction volume, while V in Equation (2) is a variable indicating

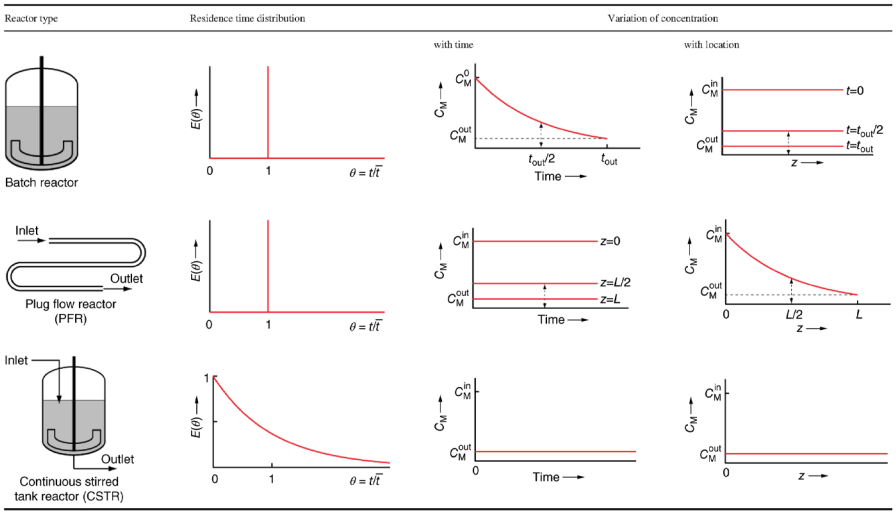


Figure 1. Schematic illustration of the course of reaction in various types of reactors $E(\theta)$ = residence time distribution function; C_M = monomer concentration; t = time; $\bar{t}$ = mean residence time; z = spatial coordinate; L = reactor length

the reactor volume up to a given location of the PFR.

With a continuous stirred tank reactor (CSTR), the micromixing is normally assumed, and when it is necessary to emphasize this, it is called the homogeneous continuous stirred tank reactor (HCSTR). At steady state, the concentrations of all components in an HCSTR are kept constant, and the polymerization proceeds at a constant rate. The design equation for an HCSTR is:

$$\text{HCSTR}: \quad \frac{F_{\mathrm{M}}^{\mathrm{in}} - F_{\mathrm{M}}^{\mathrm{out}}}{V} = R_{\mathrm{p}} \tag{3}$$

Although the concentrations are kept constant in an HCSTR, the residence time of the fluid elements have a large variation, whose residence time distribution is given by [1]:

$$E(\theta) = \exp(-\theta) \tag{4}$$

where $\theta = t/\bar{t}$ and $\bar{t}$ is the mean residence time.

Compare the reactor performance of a PFR and an HCSTR in productivity. Because the monomer conversion x in a continuous reactor is given by $x = \left(F_{\mathrm{M}}^{in} - F_{\mathrm{M}}\right)/F_{\mathrm{M}}^{in}$, the required reactor volume to make the final conversion x_{out} is given by:

$$\text{PFR}: \quad V = F_{\mathrm{M}}^{\mathrm{in}} \int_0^{x_{\mathrm{out}}} \frac{\mathrm{d}x}{R_{\mathrm{p}}} \tag{5}$$

$$\text{HCSTR}: \quad V = \frac{F_{\mathrm{M}}^{\mathrm{in}} x_{\mathrm{out}}}{R_{\mathrm{p}}} \tag{6}$$

Normally, the polymerization rate R_{p} decreases with the decrease in monomer concentration, the inverse of R_{p} is an increasing function of x, as shown in Figure 2. The area under the curve represents the required reactor volume of a PFR, while that for an HCSTR is given by the rectangular area. Obviously, $V_{\mathrm{PFR}} < V_{\mathrm{CSTR}}$, and a PFR is better in its performance. On the other hand, when the autoacceleration due to the gel effect in free-radical polymerization is significant, the $1/R_{\mathrm{p}}$ curve may show a complex behavior. If the $1/R_{\mathrm{p}}$ curve possesses a single minimum at x_{min} between $x = 0$ and x_{out}, the best choice is a train of two reactors, with the first

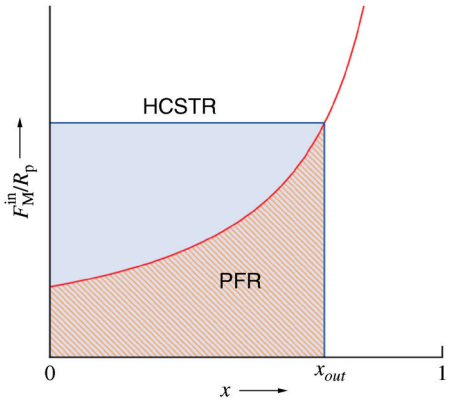


Figure 2. Necessary reactor volume to obtain polymer with conversion x_{out}

reactor being an HCSTR operated up to x_{min} and the second being a PFR.

Even when a single PFR is the best choice, the polymers may stick to the wall and it may be difficult to obtain a stable flow in a tube. In such cases, a train of HCSTRs would be the choice to approximately accomplish a plug flow. Assuming a series of N HCSTRs having the same volume, the residence time distribution function is given by [1]:

$$E(\theta) = \frac{N(N\theta)^{N-1}}{(N-1)!}\exp(-N\theta) \tag{7}$$

where $\theta = t/\bar{t}$ and the mean residence time $\bar{t} = V/v$ is calculated for the total volume of N CSTRs.

Figure 3 illustrates the calculated RTDs. By increasing the number of tanks N, the RTD

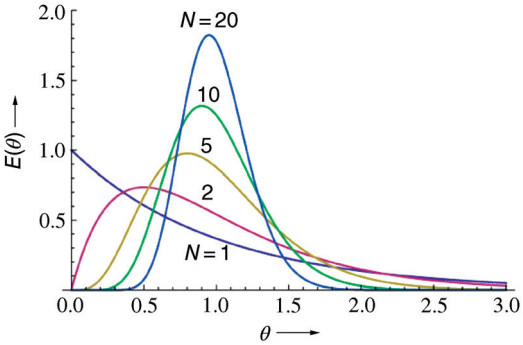


Figure 3. Residence-time distribution of the tanks-in-series model N = number of tanks; $\theta = 1$ for all fluid elements of a PFR

becomes narrower to approach that for a PFR. In fact, the tanks-in-series model is used widely as the one-parameter model to represent nonideal flow in various types of actual continuous reactors. Another notable model to represent the nonideal flow is the dispersion model [1].

In a CSTR, the micromixing condition is often not achieved in practice, however, and for this reason an alternative type of model is introduced, the segregated continuous stirred tank reactor (SCSTR) [1]. Here the fluid phase is regarded as subdivided into many small isolated compartments. Each compartment contains a large number of molecules, which are permanently confined within the limits of that compartment; therefore, the individual compartments function as miniature batch reactors with different residence times in the flow reactor. The compartments themselves are taken to be ideally mixed, with total segregation of molecules in different compartments, what is called "macromixing". Thus, the sum of all the compartments in an SCSTR have the same residence time distribution as the contents of the HCSTR, represented by Equation (4). A macroscopic mean taken over all the compartments in the effluent stream and in the reactor itself would show concentrations and temperature that are constant both spatially and with respect to time. On the other hand, a probe capable of microscopic sampling of individual compartments would reveal concentrations that varied in a statistical manner from one compartment to another. Given the high viscosity of a typical polymerizing solution it is likely that some solution polymerizations may occur in segregated systems [2]. On the other hand, however, when a CSTR is mentioned, normally, an HCSTR is envisaged unless otherwise noted about the segregation.

2.2. General Effects on the Molecular Mass Distribution (MMD)

To clarify general effects of various reactor types on the formed MMD, the linear polymerization in a homogeneous media is considered. In step polymerization and also in living polymerization, a longer reaction time, i.e., a larger residence time leads to the production of longer chains. Therefore, the variance of the residence time distribution directly influences the breadth of the MMD. In these polymerization systems, the MMD is the narrowest in a batch or a PFR. For an ideal step polymerization, the most probable distribution, whose polydispersity index (PDI) $\overline{M}_w/\overline{M}_n$ is 2, is formed (→ Polymerization Processes, 1. Fundamentals). For an ideal living polymerization, polymers having the Poisson distribution are expected (→ Polymerization Processes, 1. Fundamentals).

On the other hand, much broader MMDs are obtained for these polymerization systems when using a CSTR [3, 4], because of a broader RTD leading to a wide variation of growth time. An HCSTR and an SCSTR are compared. In an HCSTR, all chains grow in a constant environment. On the other hand, in an SCSTR, the compartments with larger residence time will possess lower monomer concentrations, leading to smaller growth rate. In addition, in the compartments with smaller residence time, the monomer concentration level is higher than in the corresponding HCSTR, leading to faster chain growth. Both high- and low-molecular-mass tails are reduced compared with the corresponding HCSTR, leading to a narrower MMD in an SCSTR [3, 4].

In step polymerization, a high monomer conversion is required to attain a high degree of polymerization (chain length). A CSTR could be used for low conversion region, however, the horizontal reactor shown later in Figure 5 (Section 3.1) whose RTD is close to a PFR, is often used for the final stage of polymerization.

In a conventional free-radical polymerization, each chain is formed in a very small time interval, and it is convenient to consider the instantaneous MMD (→ Polymerization Processes: 1. Fundamentals). The instantaneous MMD is dominated by the concentrations of the ingredients at that instant, and the residence time after the formation of dead polymer chain is not relevant. In an HCSTR at steady state, the concentration in the reactor is kept constant, as shown in Figure 1. The instantaneous MMD, which is the narrowest for a given free-radical polymerization system producing only linear polymers, is formed in an HCSTR.

On the other hand, the use of a batch or a PFR leads to a broad distribution for a conventional free-radical polymerization in which time varying instantaneous MMDs are superimposed, resulting in an accumulated MMD (→ Polymerization Processes, 1. Fundamentals). The MMD is broader in a batch or a PFR for the free-radical polymerization.

A subtle note when using an HCSTR in free-radical polymerization is that polymers may exist in a high concentration throughout the polymerization in an HCSTR, which promotes the reaction with polymers, such as chain transfer to polymer. Even for a system where the polymer transfer reaction is not significant in a batch reactor, it may have significant effects in a HCSTR. With polymer transfer reactions, the MMD becomes broader (→ Polymerization Processes, 1. Fundamentals).

Another note on the conventional free-radical polymerization is the effect of segregation on the MMD. With an SCSTR, compartments with various monomer concentrations coexist in a reactor, which makes the MMD broader. Because each compartment can be considered as an independent batch reactor, the MMD becomes broader than the batch/PFR.

In step and living polymerization, the breadth of the MMD is batch (PFR)<SCSTR<HCSTR. On the other hand for the conventional free-radical polymerization, the breadth is HCSTR<batch (PFR)<SCSTR.

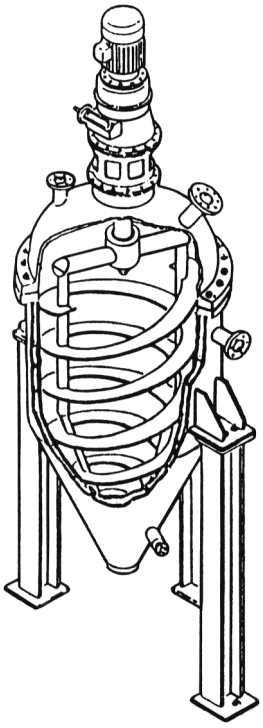


Figure 4. Vertical cone ribbon blade reactor (Mitsubishi Heavy Industries)

3. Processes and Reactor Modeling for Step Polymerization

3.1. Types of Reactors and Reactor Modeling

In step polymerization, high molecular mass polymers are usually not produced until the final stage of reactions (→ Polymerization Processes, 1. Fundamentals), so that thermal control and mixing of the reaction mixture do not present serious problems in the earlier stages. However, since the final stage of polymerization is very important for the production of polymers with high molecular mass, handling of very high viscosities and temperatures, as well as a high interfacial area to remove small molecules, are required. Various polymerization processes and reactor types, both for batch and continuous production, have been proposed. Examples of reactors for high viscosities are shown in Figures 4 and 5. Careful selection of the polymerization reactor is important to produce high-quality polymers [5, 6]. The horizontal reactor shown in Figure 5 is normally used for continuous production processes. Desirable characteristics of this type of reactor are (1) the axial flow must be close to piston flow, (2) the mixing blades must have self-cleaning performance with no dead zone, and (3) the gas-liquid interfacial area must be large enough. The item (3) is important particularly to remove condensation byproduct effectively. The rotation direction of the blades shown in Figure 5c is the opposite of that of 5a and b, which leads to a larger gas–liquid interfacial area.

The batch reactor is the most versatile reactor type and is used extensively for specialty polymers at low production volumes.

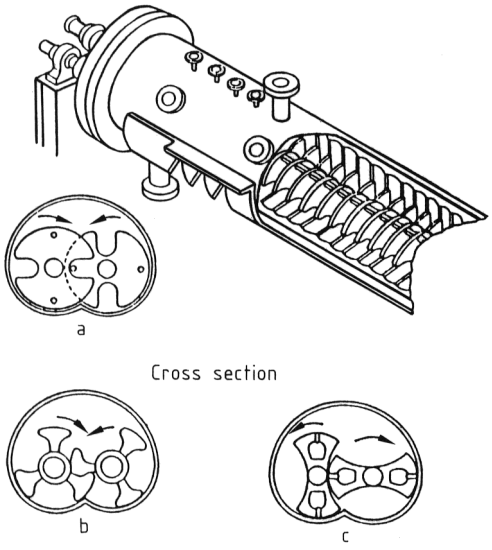


Figure 5. Horizontal high-viscosity reactor

Some examples of step polymerizations carried out in such reactors are nylon 6 (→ Polyamides); Fibers, → Fibers, 4. Polyamide Fibers), phenol–formaldehyde (→ Phenolic Resins), urea–formaldehyde, and melamine–formaldehyde (→ Amino Resins). In polycondensation reactions, it may be necessary to remove condensation products to attain sufficient conversion. When the volume of the reaction mass decreases continuously with time, such reactors can be considered as semibatch reactors. For example, in the production of poly(ethylene terephthalate), PET, because methanol or ethylene glycol evaporates during polymerization, the batchwise production of PET is considered a semibatch operation (→ Fibers, 5. Polyester Fibers). Polycondensation reactions often require high temperature, and bulk polymerization is preferred in order to suppress undesirable side reactions.

High-capacity plants often use continuous processes. The first approximation for a continuous process is a model that consists of PFRs and CSTRs in various combinations, as shown in Figure 6, although various nonideal effects such as flow pattern in the reactor, mass- and heat-transfer limitations, and residence time distribution must be considered for a detailed analysis and design of commercial reactors [1, 7–10].

The MMD of linear polymers produced by step polymerization in a batch or a PFR

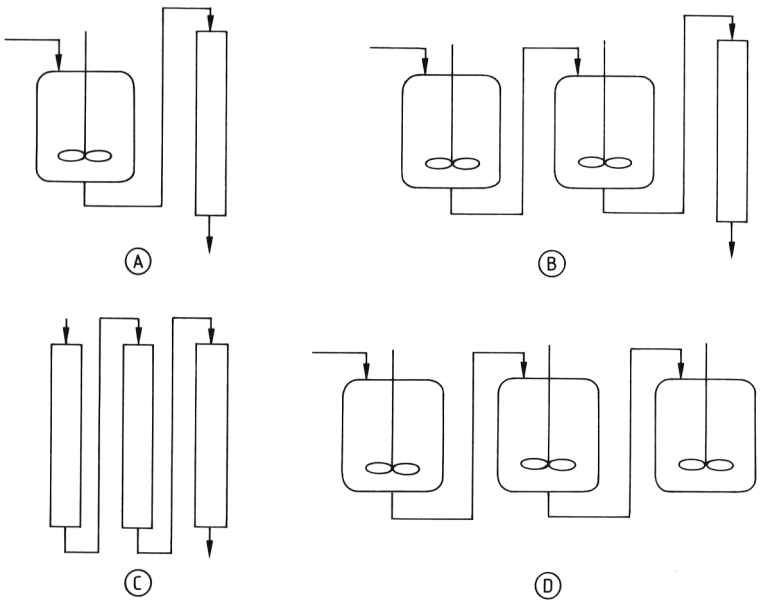


Figure 6. Representative models for continuous polymerization processes
A) CSTR + PFR; B) CSTR + CSTR + PFR; C) PFRs; D) CSTRs

basically follows the most probable distribution (→ Polymerization Processes, 1. Fundamentals). The MMD may be controlled by varying its reaction path if the reaction system is in a nonequilibrium state. Assuming irreversible step polymerization without interchange reactions, the effect of reactor types was discussed in Section 2.2. An important feature of step polymerization is that the variance of MMD is smallest in a batch reactor or PFR and is very large in an HCSTR, which is quite contrary to that for free-radical polymerization. This result may be disappointing, since it is, in principle, impossible to produce polymers whose PDI $\overline{M}_w/\overline{M}_n$ is smaller than 2 in step polymerization at sufficiently high conversions. The PDI of polymers produced in a batch reactor is given by $1 + p$, where p is the conversion of the functional group (→ Polymerization Processes, 1. Fundamentals). However, in commercial polymeric materials, polymers with narrower distributions are not always superior to those with broader distributions, since various levels of properties are required at the same time. The use of a cascade of CSTRs and/or PFRs with recycle loops may be one method to obtain a MMD with a PDI larger than two. In practice, however, these methods may have shortcomings because they need a long start-up period and problems may occur with the stability of the reaction system. A method in which additional monomers are fed intermediately to a batch reactor or a PFR was proposed [11], and it was shown that the polydispersity index can be easily controlled over a wide range with values greater than 2.

In a batch reactor, the reverse reactions and the interchange reactions (redistribution reactions) do not change the MMD from the most probable distribution [12–14]. However, these reactions do change the MMD of polymers produced in CSTR, PFR with a recycle loop, and intermediate monomer feed method. Some consideration of these reactions in a CSTR is given in [15]. Qualitatively, these effects lower the polydispersity and make the MMD approach the most probable distribution. This result seems reasonable, because any MMD approaches the most probable distribution with a PDI of two when polymer chains are severed randomly [16–18].

Other than the common reactor types discussed above, other special types of reactor system may be applied. For example, in the polymerization of urethanes, the reaction rates are so high that reaction takes place even when the monomers are being mixed and pumped into molds. In situ polymerization to form the desired articles directly from monomeric liquids is known as reaction injection molding (RIM) [19–21]. A schematic of the RIM process is shown in Figure 7. The RIM processing of polyesters, epoxy resins, polyamides, and dicyclopentadienes has also been introduced, although polyurethanes are the most common product via RIM process. In the RIM process, the reaction is almost complete by the time the material fills the mold, and therefore the mixing and flow equations must be solved simultaneously with those for chemical reactions in a rational model for these complex situations.

In the finishing stage of nylon 6, nylon 66, and PET polymerizations, higher molecular-mass polymers may be obtained by solid-state polymerization in which polymerization occurs by heating chips or flakes of a material below

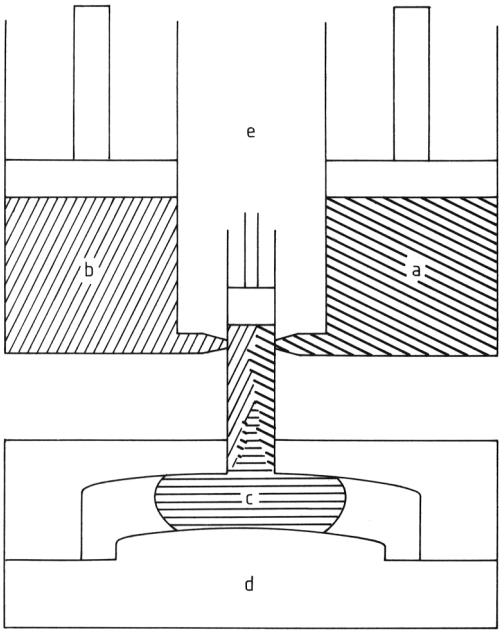


Figure 7. Schematic drawing of the RIM process a) Monomer A; b) Monomer B; c) Polymerizing mixture; d) Mold; e) Mixer

its melting point in a stream of hot gases in a fluidized bed or in a drier operated under vacuum [22–26]. The monomer, condensation products, and various byproducts diffuse out, and further reaction takes place inside the solid. The progress of these types of reaction is affected significantly by the diffusion of the condensation products and the morphology of the solid.

Although step polymerization has a very long history, a systematic kinetic treatment like that available for free-radical polymerization does not exist because of limitations due to system-specific side reactions and the scarcity of reliable kinetic data. However, this synthetic route is becoming more important due to the development of engineering plastics synthesized by step polymerization such as aramides, PPS, PEK, and PES.

3.2. Specific Processes

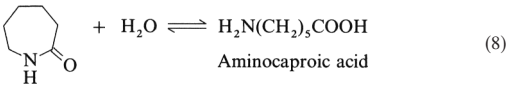
3.2.1. Polyamides (→ Polyamides), (→ Fibers, 4. Polyamide Fibers)

Polyamides are manufactured by two basic routes. One of these is synthesis from cyclic monomers such as lactams. Polymerization of these substances requires ring opening and subsequent chain growth. Another class of synthetic polyamides is formed from diamines and diacids.

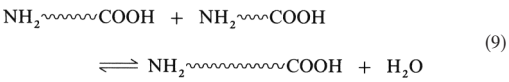
The most common types of polyamides are nylon 6 and nylon 66. The term nylon is often used for synthetic aliphatic polyamides. One number indicates that the product was prepared from a single monomer and represents the number of carbon atoms in the repeating unit. Two numbers refer to the number of carbon atoms in the diamine and that in the diacid, respectively.

Nylon 6 is typically produced by the hydrolytic polymerization of ε-caprolactam [27–33], although polymers with higher molecular mass can be produced by ionic polymerization [27, 28, 34, 35]. The major reactions in the hydrolytic polymerization are:

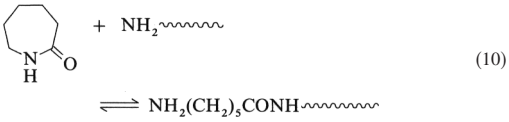
1. Ring opening of ε-caprolactam by water (Eq. 8), which produces aminocaproic acid (ACA)
2. Polycondensation of ACA (Eq. 9)
3. Acid-catalyzed polyaddition (ring-opening polymerization) by nucleophilic attack of the amine nitrogen on the lactam (Eq. 10)



(8)



(9)



(10)

Step polymerization of the amino acid (Eq. 9) accounts for only a few percent of total polymerization of ε-caprolactam. However, step polymerization is important because it usually determines the final degree of polymerization at equilibrium. The MMD is essentially the most probable distribution, except for the presence of monomer and cyclic oligomers. As low molecular mass substances lower the polymer quality, they are usually removed by leaching or vacuum treatment of the polymer melt. The formation of cyclic oligomers is an important side reaction [36, 37].

Various types of polymerization reactors have been proposed both for batch and continuous processes. A commonly used industrial reactor for a continuous process is a tubular reactor such as the conventional VK column (Vereinfacht Kontinuierliches Rohr) [27, 29, 33], which consists of a vertical tube operating at atmospheric pressure. The feed enters the top of the column and is heated to approximately 220–270°C. The simplest model for this type of reactor is a PFR. However, according to impulse response experiments, the flow is approximately laminar rather than plug flow [29, 38], and the reactor could be modeled as a CSTR or a tanks-in-series with recycle streams followed by a tubular reactor when a large quantity of water is used, since a significant convection current and mixing is provided by the evaporating water [39, 40].

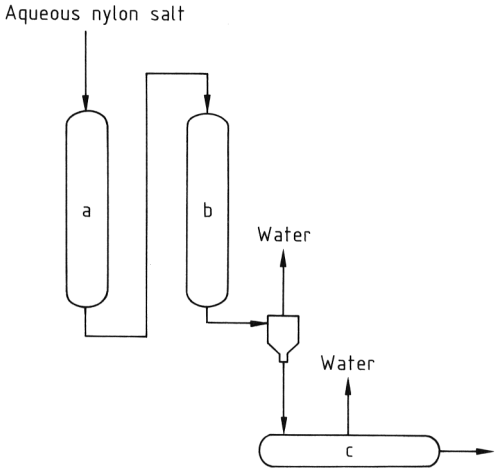
Nylon 66 is manufactured by polycondensation of hexamethylenediamine and adipic acid [39], usually in a multistage process. First, nylon salt (hexamethylenediammonium adipate) is prepared from stoichiometric quantities of hexamethylenediamine and adipic acid in water. The salt can easily be separated by precipitation with methanol.

$$H_2N(CH_2)_6NH_2 + HOOC(CH_2)_4COOH \longrightarrow \begin{bmatrix} {}^{-}O_2C(CH_2)_4CO_2^{-} \\ H_3\overset{+}{N}(CH_2)_6\overset{+}{N}H_3 \end{bmatrix} \quad (11)$$

The use of nylon salt guarantees the presence of equimolar amounts of $-NH_2$ and $-COOH$ groups. Close control of diamine diacid balance is important to control the final polymer molecular mass and reactive end groups.

Nylon 66 is fairly unstable at high temperatures in the presence of oxygen. Not only degradation but also cross-linking may occur. Because of this instability, polymerization was carried out solely in batch processes. However, complete elimination of oxygen has made it possible to carry out continuous polymerization. An example of a continuous melt polymerization process is shown in Figure 8. The aqueous nylon salt solution is heated to above 200°C at >17 bar in an oxygen-free atmosphere. Thereafter, the pressure is reduced to atmospheric and vapor is separated from polymer to promote polymerization to the desired high molecular mass. It is also possible to polymerize molten hexamethylenediamine and adipic acid directly [31, 39]. Polymerization can also be completed in the solid state.

Some examples of the kinetic simulation studies on the synthesis of nylon 66 can be found in [41–44].



	a	b	c
Hold-up time, min	15–30	15–30	60
Temperature, °C	200–235	270–290	270–290
Pressure, 10^5 Pa	17–24	17–24	atmospheric

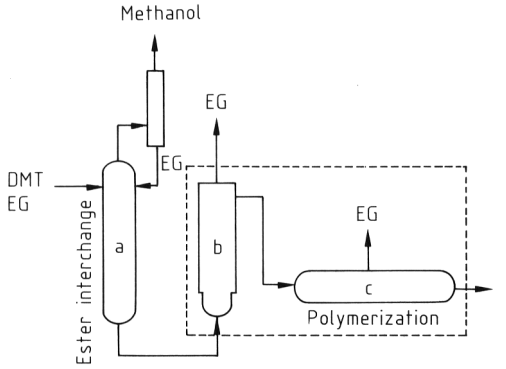
Figure 8. Continuous melt polymerization of nylon 66

3.2.2. Polyesters (→ Polyesters)

The production of high molecular mass polyesters differs somewhat from that of polyamides. In the case of nylons, the chemical equilibrium favors the polyamide under polymerization conditions. With polyester formation, however, the equilibrium is much less favorable. In order to drive the reaction in the forward direction, the condensation product must be removed continuously, usually by application of high vacuum. For polyester reactors, a high vacuum, a high temperature, and a high interfacial area with sufficient surface renewal are required, especially at high conversions.

Both saturated and unsaturated polyesters are produced. Among the saturated polyesters, PET is produced in the largest quantity, and is used for production of fibers, films, molding plastics, and beverage containers. In this section, the engineering aspects of PET formation are illustrated as an example of a polyester production process.

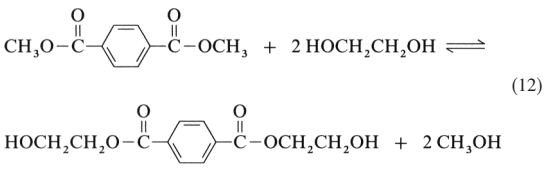
There are two major routes to synthesize PET industrially, although the objective in each case is to obtain an intermediate product, i.e., bis (hydroxyethyl) terephthalate (BHET). Two major routes to synthesize BHET are ester interchange of dimethyl terephthalate (DMT) and direct esterification of terephthalic acid. Figure 9 shows an example of the PET



	a	b	c
Hold-up time, h	4–6	2–3	2–3
Temperature, °C	150–210	265–285	265–285
Pressure, 10^2 Pa	atmospheric	13–133	≪ 6

Figure 9. Continuous polymerization process of PET via ester interchange route

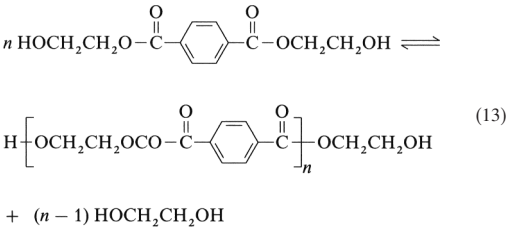
production process via the ester interchange route. The ester interchange reaction



(12)

is operated in the temperature range 150–210°C at atmospheric pressure. The use of a catalyst is common [45, 46]. The methanol and ethylene glycol (EG) emerging from the reactor are passed through a rectifying column and EG is fed back to the reactor. It is very difficult to force the ester interchange reaction to completion, and therefore after a particular conversion (usually 90–95%), the reaction mixture is passed on to the polycondensation stage. The reaction mixture consists of oligomers of various types. Oligomers with degrees of polymerization as high as three may be formed [45, 47, 48]. Several examples of reactor models for both batch and continuous processes can be found in [44–52]. An optimization study showed that the ester interchange reactor should be operated initially at high temperature to obtain high conversion; the temperature should be lowered to reduce side reactions [46, 50].

In the polycondensation stage, the reaction temperature is raised to 265–285°C to keep the reaction mixture molten and polymerization fast.



(13)

For PET production, a dual catalyst system in which one component is specially active for ester interchange and the other for polymerization is often used [53]. The production of high molecular mass polymer requires the complete removal of ethylene glycol due to the unfavorable equilibrium, and therefore a vacuum is applied. Especially in the final stage of the polycondensation reaction, a very high vacuum is required since the reaction system becomes highly viscous. Consideration of the limitations of mass and heat transfer is very important. Various types of reactors such as rotating disc contactors, wiped film reactors, partially filled screw extruders have been developed as finishers for the polycondensation reaction [45, 46, 51]. Details of fluid mechanics, mixing, and mass and heat transfer characteristics are required for a rational analysis and design of such high-viscosity reactors, as was shown in Figure 5. In addition to polycondensation reactions, various side reactions must also be considered since a very high temperature is used.

Melt polycondensation of PET is not generally carried out beyond a particular extent of polymerization, since the degradation reactions dominate the process and the product quality may suffer from various undesirable byproducts. To attain higher molecular masses, the products may be subjected to solid-state polymerization [22–26]. For beverage and food containers, the production processes may prefer to

stop melt polymerization at lower conversion, and solid-state polymerization is applied.

Direct esterification of terephthalic acid (TPA) and ethylene glycol was generally not preferred earlier because of the difficulties in the purification of TPA due to its low solubility and high melting point. However, with improvements in technology, the direct esterification method has been gaining in importance. The process is claimed to give polyesters with superior quality due to their low content of carboxyl end groups and diglycol linkages [53]. In the modeling of this process, aside from the difficulties caused by the various reactions and mass balances involved, it is necessary to take account of the heterogeneity of the reactions due to the low solubility of TPA in EG. Simulation and control of the direct esterification reactors is reported in [46, 51, 54–56]. Figure 10 shows a flow diagram of a continuous process for PET production by direct esterification.

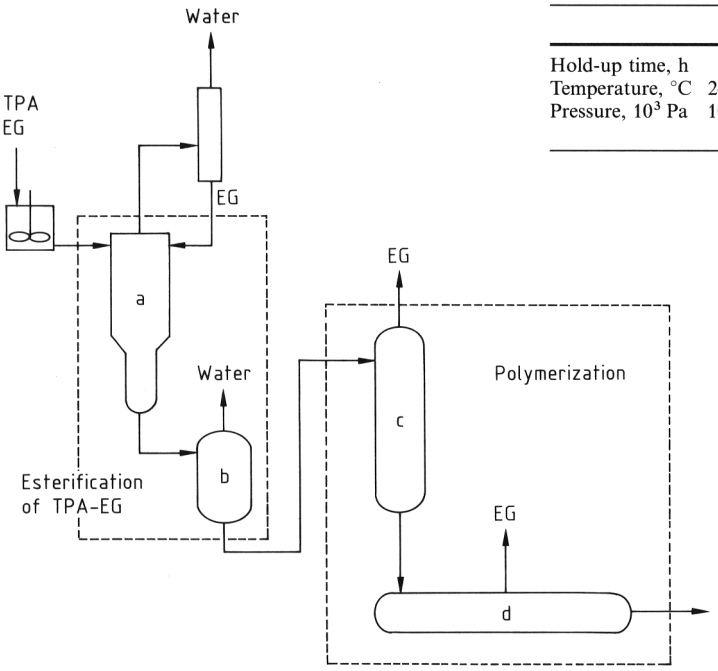
Additional information for the industrial polycondensation processes can be found in [57].

4. Processes and Reactor Modeling for Chain Polymerization

4.1. Introduction to Polymerization Techniques

Four major categories of the industrial polymerization methods used for chain polymerizations are bulk polymerization, solution polymerization, suspension polymerization, and emulsion polymerization. The characteristics of these techniques are summarized in Table 1.

If the final product is a solid polymer, bulk polymerization might be the best method one should aim for, because a highly pure polymer is produced. Major step polymerization processes employ bulk polymerization technique, mainly to prevent side reactions at a high polymerization temperature. Other techniques provide alternatives to overcome the major difficulties of bulk polymerization: mixing and heat removal, except when the product's final form is any one of solution, suspension, or emulsion.



	a	b	c	d
Hold-up time, h	3–5	1–3	2–3	2–3
Temperature, °C	240–260	240–260	265–285	265–285
Pressure, 10^3 Pa	100–300	atmospheric	1–10	≪ 0.6

Figure 10. Continuous polymerization process of PET via direct esterification route

Table 1. Characteristics of major industrial polymerization methods

Method	Advantage	Disadvantage
Bulk polymerization	Minimum contamination of product	High viscosity (mixing, heat removal, pumping, etc.)
	High reactor efficiency	Adhesion to reactor wall and mixing apparatus (fouling)
Solution polymerization	Lower viscosity than bulk	Lower reactor efficiency
	Smaller fouling problems	Separation cost of polymer
	End-usage as a solution form	Inflammability and toxicity of the solvent used
		Side reaction, such as chain transfer
Suspension polymerization	Low viscosity	Lower reactor efficiency
	Good heat transfer	No large-scale continuous processes have been developed
	Higher purity than the emulsion polymers	Waste water treatment
		Adhesion and aggregation (fouling)
Emulsion polymerization	Low viscosity	Lower reactor efficiency
	Good heat transfer	High cost for separation of polymers
	High polymerization rate with large molar mass products in conventional free-radical polymerization	Impurity (emulsifier)
		Adhesion and aggregation (fouling)
	End-usage as a latex form	

4.2. Fundamentals of Material Balance Equations

The following material balance equations apply for multicomponent polymerization, accommodate operation of a well-stirred reactor (no spatial variations in temperature and concentrations), and may be used to simulate different comonomer systems under a variety of operating conditions. Bulk (suspension) and solution polymerizations are considered; extensions required for multiphase systems (emulsion, inverse emulsion, suspension, dispersion, and gas-phase processes) may be found elsewhere [58].

Many bulk, solution, and suspension polymerization systems are characterized by the fact that all of the reactions proceed in a single phase with no spatial variations in temperature and concentration. A model for a reactor carrying out such polymerizations would consist of a set of material balances giving the rates of accumulation, inflow, outflow and a reaction source (sink) term for the various monomers, initiators, chain-transfer agents, and polymer in the reactor. These balance equations are given herein in general form.

Monomer Balances

$$\mathrm{d}N_{\mathrm{M}i}/\mathrm{d}t = F_{\mathrm{M}i}^{\mathrm{in}} - (N_{\mathrm{M}i}/V)v_{\mathrm{out}} - R_{\mathrm{p}i}V \tag{14}$$

where

$N_{\mathrm{M}i}$ = number of moles of monomer i in the reactor
$F_{\mathrm{M}i}^{\mathrm{in}}$ = molar flow rate of monomer i into the reactor
V = reaction volume in the reactor
v_{out} = total volumetric flow rate of all species out of the reactor
$R_{\mathrm{p}i}$ = net rate of disappearance of monomer i by reaction

Reaction Volume. Since the density of a polymer is usually greater than that of its monomer, the reaction volume V decreases with conversion for isothermal polymerization in a batch reactor. This shrinkage must also be taken into account in semibatch and continuous operations. Neglecting volume change on mixing polymer and monomers (thermodynamic data are most often not available and deviation from ideality is often not great) the change in reaction volume may be calculated by using (assuming V is the equilibrium volume):

$$\begin{aligned}\mathrm{d}V/\mathrm{d}t &= v_{\mathrm{in}} - v_{\mathrm{out}} - \text{shrinkage rate} \\ &= v_{\mathrm{s,in}} + \sum_{i=1}^{n} F_{\mathrm{M}i}^{\mathrm{in}} M_{\mathrm{m}i}/\rho_{\mathrm{m}_i} \\ &\quad - \sum_{i=1}^{n} R_{\mathrm{p}i} M_{\mathrm{m}i}\left(\frac{1}{\rho_{\mathrm{m}i}} - \frac{1}{\rho_{\mathrm{p}}}\right)V - v_{\mathrm{out}}\end{aligned} \tag{15}$$

where n is the number of monomer types, $v_{s,in}$ is the volumetric flow rate of inert solvent into the reactor, M_{mi} is the molecular mass of monomer i, ρ_{mi} is the density of monomer i, ρ_p is the density of polymer produced instantaneously.

Polymer Balances. With a batch reactor, where there is no inflow and outflow of polymer from the reactor, the total amount of polymer formed and its composition can be obtained directly from the monomer balances. However, with semibatch and continuous operation, additional balances are required and these follow:

$$dP_i/dt = F_{Pi}^{in} - (P_i/V)v_{out} + R_{pi}V \quad (16)$$

where P_i is the number of moles of monomer i chemically bound in the polymer "in the reactor", F_{Pi}^{in} is the molar flow rate of monomer i bound in the polymer flowing into the reactor.

Additional Ingredient Balances. In order to calculate R_{p_i} for free-radical systems, the total polymer radical concentration and, therefore, initiator concentration are required. In addition, balances for the chain-transfer agent (for molecular mass calculations) and for the solvent in solution polymerizations are required. These balances follow:

$$dN_{Ii}/dt = F_{Ii}^{in} - (N_{Ii}/V)v_{out} - R_{Ii}V \quad (17)$$

$$dV_s/dt = v_{s,in} - (V_s/V)v_{out} \quad (18)$$

$$dN_{CTA}/dt = F_{CTA}^{in} - (N_{CTA}/V)v_{out} - R_{CTA}V \quad (19)$$

where N_{Ii} is the number of moles of initiator of type i in the reactor, F_{Ii}^{in} is the molar flow rate of initiator i into the reactor, R_{Ii} is the consumption rate of initiator i by reaction, V_s is the volume of inert solvent in the reactor, N_{CTA} is the number of moles of chain-transfer agent (CTA) in the reactor, $F_{CTA,\ in}$ is the molar flow rate of CTA into the reactor, and R_{CTA} is the consumption rate of CTA by reaction.

It is convenient to sum the monomer balance equation (Eq. 14) over n, the number of monomer types to give

$$dN_M/dt = F_M^{in} - (N_M/V)v_{out} - R_pV \quad (20)$$

where N_M is the total number of moles of monomer in the reactor, F_M^{in} is the total molar flow rate of monomer to the reactor, R_p is the total molar consumption rate of monomer by reaction.

The equations introduced in this section are solved to determine the time developments of various components, by incorporating with the rate expression introduced in → Polymerization Processes, 1. Fundamentals. For the multicomponent polymerization, the use of pseudokinetic rate constants allows to use the same kinetic rate expression as for homopolymerization. At steady state in an HCSTR, all time derivatives are set to be zero.

4.3. Effect of Reactor Types on Copolymer Composition Distribution

The copolymer composition distribution of polymers formed instantaneously follows the Gaussian distribution [59], which gives the narrowest composition distribution. For the conventional free-radical polymerization, this distribution represents that polymer chains formed instantaneously. On the other hand, for living polymers, the distribution describes the distribution of monomeric units incorporated into various polymer chains instantaneously. The instantaneous copolymer composition can be obtained in an HCSTR at steady state, because the concentrations of all components are kept constant. Note that for the conventional free-radical polymerization, both distributions of molecular mass and composition are the narrowest in an HCSTR.

In a batch or a PFR, a compositional drift occurs, whose trajectory can be calculated by using the equations presented in → Polymerization Processes, 1. Fundamentals. For the conventional free-radical polymerization, the compositional drift occurs among polymer chains formed at different conversion levels, while the drift occurs along a single chain in living polymerization. Obviously, the

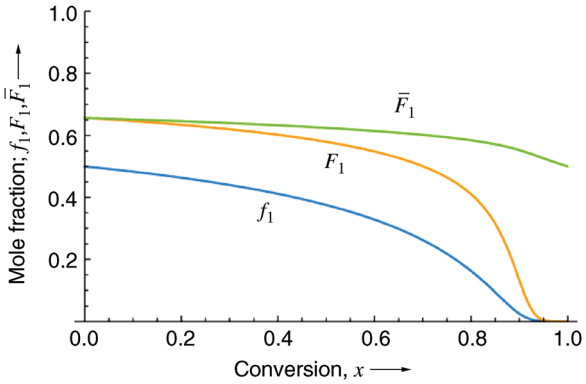


Figure 11. Calculated compositional drift during batch copolymerization of methyl methacrylate (M_1) and acrylonitrile (M_2) reactivity ratio r_1=1.2, r_2=0.15; initial composition monomer $f_1^0 = 0.5$

composition distribution becomes broader than for an HCSTR.

Figure 11 shows an example of compositional drift during batch free-radical copolymerization. The drift of monomer composition f_1, instantaneous copolymer composition F_1, and the accumulated copolymer composition $\overline{F}_1$ are shown. Even when the accumulated copolymer composition $\overline{F}_1$, which is usually measured in experiment, does not change significantly during polymerization, the composition of individual polymer chain (instantaneous composition) may differ significantly, as shown in the figure. Other than using an HCSTR, the compositional drift can be suppressed by using a semibatch operation in which monomers are fed to maintain a constant ratio of monomer concentrations in the reactor [58].

In an SCSTR, the compositional drift occurs within the compartments whose conversion levels are different significantly because of the broad residence time distribution, leading to a broader copolymer composition distribution than that for the batch/PFR [60].

4.4. Effect of Reactor Types on Nonlinear Polymer Formation

Branching/cross-linking reactions in chain polymerization involves reaction with polymer. In a batch polymerization, the polymer concentration increases during polymerization, starting from 0 to the final conversion level. On the other hand, in an HCSTR the polymer concentration is kept constant, and the polymerization proceeds under a high polymer concentration level. Therefore, the branching/cross-linking density is higher for an HCSTR than in a batch reactor at the same conversion level.

The effects of reactor types are considered in detail by taking free-radical polymerization that involves chain transfer to polymer, as an example. Figure 12 shows the process of chain transfer to polymer. Some time after the formation of the primary polymer chain **A**, which already possesses two branch chains, a primary polymer radical **B** attacks **A**, and an internal radical on the backbone chain is formed. At the same time, this internal radical grows to add monomeric units to form a long-branch chain

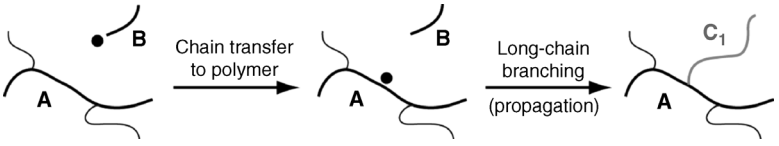


Figure 12. Schematic illustration of the process of chain transfer to polymer, leading to form polymer with long-chain branches

C_1. In free-radical polymerization, each primary polymer molecule is formed within a very small interval, and it is reasonable to consider that all the processes depicted in Figure 12 occur instantaneously.

As any of the monomeric units in polymer can react with a polymer radical, the polymer transfer reaction rate is represented by:

$$R_{fp} = k_{fp}[R^\bullet][M]_0 x \tag{21}$$

where k_{fp} is the rate constant for the polymer transfer reaction, $[R^\bullet]$ is the total polymer radical concentration, $[M]_0$ is the initial (feed) monomer concentration, and x is the monomer conversion to polymer.

The polymerization rate is given by (→ Polymerization Processes, 1. Fundamentals):

$$R_p = k_p[R^\bullet][M]_0(1-x) \tag{22}$$

The branching density, ρ_b is a probability that a monomeric unit in polymer possesses a branch point. In an HCSTR, both the rates of monomer addition (Eq. 22) and branch point formation (Eq. 21) do not change with time, and therefore, the average branching density is given by:

$$\overline{\rho}_{b,HCSTR} = \frac{R_{fp}}{R_p} = C_{fp}\frac{x}{(1-x)} \tag{23}$$

where C_{fp} is the polymer transfer constant ($=k_{fp}/k_p$).

On the other hand, this rate ratio changes with time in a batch reactor. Therefore, the average branching density for a batch reactor is given by:

$$\frac{d(x\overline{\rho}_{b,BR})}{dx} = C_{fp}\frac{x}{(1-x)} \tag{24}$$

which is integrated to give [61]:

$$\overline{\rho}_{b,BR} = C_{fp}\left[\frac{1}{x}\ln\left(\frac{1}{1-x}\right) - 1\right] \tag{25}$$

Figure 13 compares the average branching density, which shows that the use of an HCSTR leads to form larger average branching density than using a batch reactor at the same monomer conversion, x.

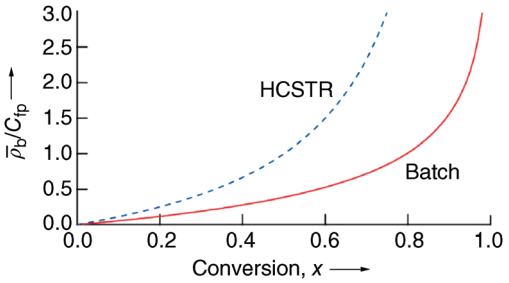


Figure 13. Calculated average branching density for an HCSTR and a batch reactor

The primary polymer chain length distribution in an HCSTR follows the instantaneous distribution, which is the narrowest. On the other hand, branch formation leads to broader distribution, as discussed in → Polymerization Processes, 1. Fundamentals. Normally, branch formation dominates the breadth of the MMD, except for extremely low branching density cases, and a larger average branching density in an HCSTR leads to a larger MM with a broader MMD, compared with a batch reactor at the same conversion level.

As already discussed → Polymerization Processes, 1. Fundamentals, the present reaction system cannot cause gelation without combination termination. Consider the special case where the contribution of combination termination in forming primary chains is negligible, i.e., $R_{tc} \ll R_{td}+R_{fX}+R_{fp}$, where R_{tc} is the rate of termination by combination ($=k_{tc}[R^\bullet]^2$), R_{td} is the rate of termination by disproportionation ($=k_{td}[R^\bullet]^2$), R_{fX} is the rate of chain transfer to small molecule X ($=k_{fX}[R^\bullet][X]$), and R_{fp} is the rate of chain transfer to polymer. In this case, the probability that the head of a primary polymer chain is connected to a backbone chain, P_b is given by:

$$P_b = \frac{R_{fp}}{R_{td}+R_{fX}+R_{fp}} \tag{26}$$

P_b is kept constant for an HCSTR, but it changes with the birth time of the primary polymer molecule in a batch reactor.

In an HCSTR, the head unit of a newly formed primary chain is connected to a backbone chain with probability P_b. Because a larger polymer molecule has a better chance

of being attacked by a polymer radical in the polymer transfer reaction, the probability to connect a newly formed primary chain is proportional to its molecular mass. This type of primary chain connection statistics leads to form an interesting MMD, in which the high MM tail follows the power-low distribution [62], with the relationship, $M(r) \sim r^{-1/P_b}$ [63], where r is the chain length, and $M(r)$ represents the mass fraction distribution. The same primary chain connection statistics operates also in emulsion polymerization during Interval 2, for which the polymer monomer/polymer concentration is kept constant [64, 65].

In a gelling system, the power-low distribution is formed only right at the gel point, with the relationship $W(M) \sim M^{-1.5}$ in the mean-field theory [66, 67], and it is impossible to actually obtain such polymer mixture because the polymerization cannot be stopped right at the gel point. In addition, the power exponent cannot be changed. In the present branched polymer system, the exponent can be controlled by changing the P_b value.

A strange characteristic of the power-law distribution is that the higher order moments always go to infinity, as represented by:

$$Q_i = \sum_{r=1}^{\infty} r^i [P_r] \propto \int_0^{\infty} r^{i-1} M(r) \mathrm{d}r \sim \int_0^{\infty} r^{-(\alpha+1-i)} \mathrm{d}r \tag{27}$$

where Q_i is the ith moment of polymer distribution, r is the chain length (degree of polymerization), and α is the exponent of the power-law distribution, which is $\alpha = 1/P_b$ in the present case. Note that by using the moments, the number-average $\left(\overline{P}_n\right)$ and mass-average $\left(\overline{P}_M\right)$ chain lengths are represented by $\overline{P}_n = Q_1/Q_0$ and $\overline{P}_M = Q_2/Q_1$, respectively.

Equation (27) shows Q_i stays finite for $\alpha > i$, i.e., for $P_b < 1/i$. In other words, Q_i goes to infinity for $P_b \geq 1/i$, meaning that the first moment (number-average) always reaches a steady state, while the second moment (mass-average) goes to infinity for $P_b \geq 1/2$, and the third moment (z average) goes to infinity for $P_b \geq 1/3$. This phenomenon should not be confused with gelation, because it takes an infinite time for the second and higher moments to go to infinity [68]. Gelation is a critical phenomenon, and it involves a critical change in the mass-average MM during polymerization. The present type of strange behavior does not occur in an SCSTR, and the polydispersity index, $\overline{P}_M/\overline{P}_n$ becomes much smaller than HCSTR [69].

Another interesting effect of reactor type is the distribution of branch points among primary chains. Referring to the branching process shown in Figure 12, consider the expected branching density of the primary chain born at $x = \xi$ in a batch polymerization. Suppose the primary chain **A** was born at $x = \xi$. The primary chains formed earlier are subjected to branching reaction for a longer period of time, and the branching density is expected to be larger for these chains rather than the chains formed lately. Let $\rho_b(\xi, x)$ be the expected branching density of the primary chains born at $x = \xi$, when the conversion at the present time is $x\ (> \xi)$. The balance equation for the number of branch points is given by:

$$\rho_b(\xi, x + \Delta x) - \rho_b(\xi, x) = k_{fp}\{1 - \rho_b(\xi, x)\}[R^{\bullet}]\Delta t \cong k_{fp}[R^{\bullet}]\Delta t \tag{28}$$

The final approximation is reasonable, because the branching density for this kind of reaction system is normally much smaller than unity. By using the conversion–time relationship:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_p(1 - x)[R^{\bullet}] \tag{29}$$

One obtains the following differential equation:

$$\frac{\partial \rho_b(\xi, x)}{\partial x} = \frac{C_{fp}}{1 - x} \tag{30}$$

Equation (30) can be integrated to obtain:

$$\rho_b(\xi, \psi) = C_{fp} \int_{\xi}^{\psi} \frac{\mathrm{d}x}{1 - x} = C_{fp} \ln\left(\frac{1 - \xi}{1 - \psi}\right) \tag{31}$$

where ψ is the conversion at the present time.

Figure 14 shows the calculated branching density distribution at the time when the conversion at the present time is $\psi = 0.8$. The primary chains formed at $x = 0$ possess the largest expected branching density because

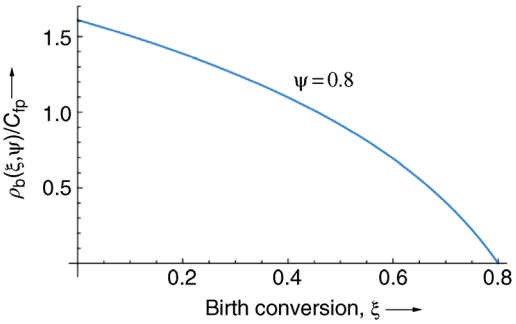


Figure 14. Calculated branching density distribution when the conversion at the present time is $\psi = 0.8$ in a batch polymerization

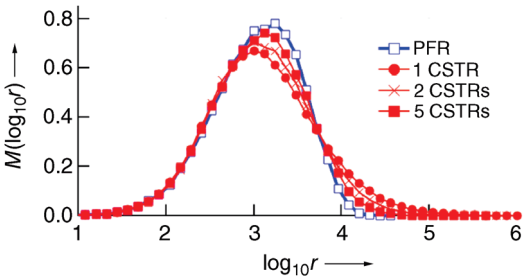


Figure 16. Calculated mass-fraction distribution [71]

they are subjected to branching reaction for the longest period of time in a batch reactor. On the other hand, the primary chains born at $x = 0.8$ do not possess any branching point. The chains formed in later stages of polymerization tend to become branched chains rather than backbone chains.

In the case of HCSTR, the branching reaction rate is kept constant. Therefore, the expected branching density increases linearly with its residence time [70]. The branching density distribution functions for various types of reactors can also be found therein.

Figure 15 shows an example of the calculated branching density distribution, represented as the mass-based probability density distribution $M(\rho_b)$ [71]. In the figure, the area under the curve within a certain branching density interval shows the mass fraction of primary chains possessing such expected branching density values. A PFR is equivalent to a batch reactor. In the figure, the average branching density $\overline{\rho}_b$ is set to be the same for all reactor types. For a PFR (batch reactor), there exists a maximum branching density, represented by the *y*-intercept in Figure 14. For an HCSTR, the branching density distribution is very broad, because of a broad residence time distribution, given by Equation (4) and Figure 3. As the number of tanks increases, the branching density distribution approaches to that for a PFR (batch).

By application of the random sampling technique discussed in → Polymerization Processes, 1. Fundamentals to a Monte Carlo simulation method, it is possible to reconstruct the whole branched polymer molecules, on the basis of the branching density distribution function [71–73]. Figure 16 shows comparison of the full mass-fraction distribution [71]. In the calculation, not only the long-chain branching but random scission reactions are also accounted for, bearing low-density polyethylene (LDPE) synthesis in mind. However, the contribution of scission used for the present calculation is rather minor, so the major effect

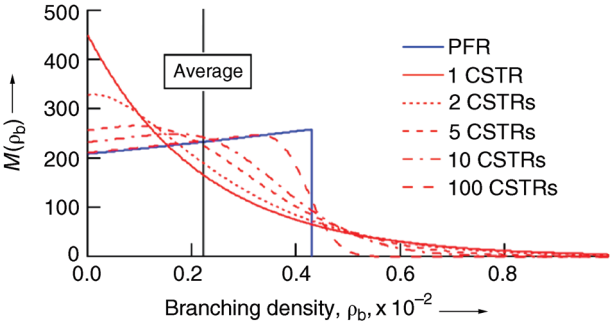


Figure 15. Calculated branching density distribution, represented as the mass-based probability density distribution, for a PFR, an HCSTR, and a tanks-in-series model [71] $\overline{\rho}_b = 2.22 \times 10^{-3}$; average branching density

is through the long-chain formation. Both the average branching density $(\overline{\rho}_b = 2.22 \times 10^{-3})$ and the average scission density $(\overline{\rho}_s = 1.11 \times 10^{-4})$ are set to be the same for all calculation conditions. Even when the average branching density is the same, the MMD is broader for an HCSTR than a batch reactor (PFR). As the number of tanks increases in a tanks-in-series model, the MMD approaches to that for a batch reactor.

In the Monte Carlo simulation, each polymer molecule formed in a reactor can be investigated directly on the computer screen, and therefore, very detailed structural information can be obtained. Figure 17 shows an example of branched polymer structure determined in the Monte Carlo simulation, in which the sphere represented by small dots has a radius that is equal to the radius of gyration of this particular structure. Figure 18 gives the mean-square radii of gyration as a function of chain length for the polymer molecules formed.

Each small dot in Figure 18 shows the mean-square radius of gyration (y axis) and its chain length (x axis) of the polymer molecule formed in a batch/PFR (A) and in an HCSTR (B). In the y axis of Figure 18, U is the number of monomeric units in a random walk segment, and L is the segment length. Here, the radius of gyration

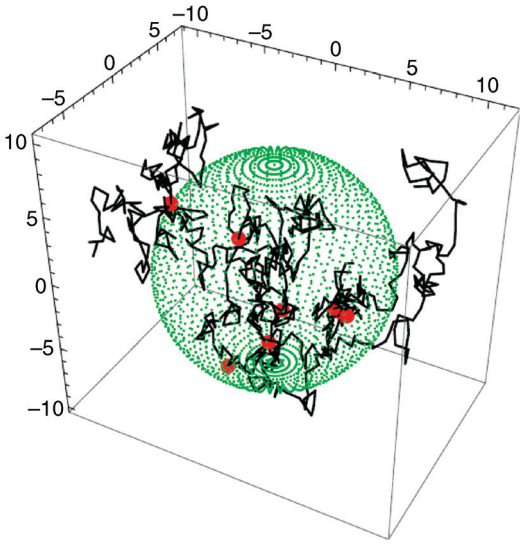


Figure 17. Example of branched polymer structure determined by Monte Carlo simulation [74]

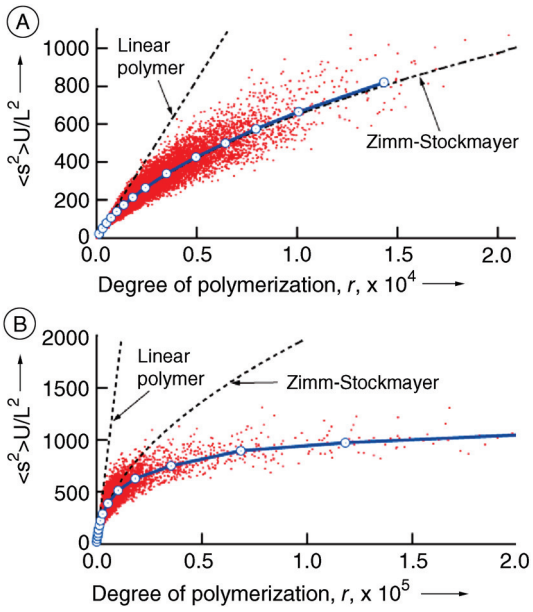


Figure 18. Mean-square radii of gyration as a function of chain length for the polymer molecules formed [74]
A) Batch/PFR; B) HCSTR

was determined by conducting the random walk 100 times, although exact mean-square radius of gyration can be determined by calculating the Wiener index [75], based on the structural information obtained in the Monte Carlo simulation [76]. In the figure, the mean-square radii of gyration for the linear polymers, and those for random branched polymer molecules represented by the Zimm–Stockmayer equation ([77]) are also shown by the broken lines. In the case of batch/PFR, the radii of gyration are close to those for the random branch polymers, although the branched structure is not random, as was shown by the branching density distribution, Figures 14 and 15. As the polymerization proceeds, the curve moves to upward direction and the radii of gyration become slightly larger than the random branched polymers [78, 79].

On the other hand, in an HCSTR, the radii of gyration of large polymers become much smaller than the random branched polymers, as shown in Figure 18B. This is because the primary chains whose residence times are large have large branching density values, as shown in Figure 15. In a highly branched, large-sized polymer molecule, it is expected there are

regions in which many branch points are concentrated, leading to a compact dimension of a polymer. A tanks-in-series model has clarified that as the number of tanks increases, the branched structure becomes closer to that for a PFR [71]. The residence time distribution has a significant effect on the branched polymer structure.

On the basis of the detailed structural information obtained through the MC simulation is now being utilized to estimate the physical properties, such as the viscoelastic properties [80]. The computer-aided polymer design system for complex polymer systems are being developed.

5. Bulk and Solution Polymerization

Bulk polymerization might be the best method to produce pure, solid polymers. To minimize contamination, poly(methyl methacrylate) used for fiber optics, in which high transparency is required, is produced via bulk polymerization. The major operating problem of bulk polymerization is the extremely high viscosity, making it difficult to accomplish good mixing, as well as efficient heat removal. The difference of bulk and solution polymerization is simply the degree of high viscosity when the polymer is miscible to monomer and solvent. In the initial stages of polymerization, monomer acts as the solvent for polymer, and stirred-tank reactor can be used to obtain good mixing. In the later stages of polymerization, however, plug–flow-type reactors with high mechanical strength are often employed.

The standard polymerization kinetics discussed in → Polymerization Processes, 1. Fundamentals are basically valid for bulk and solution polymerization. In the viscous polymer solution, the chain-length-dependent rate constants, resulting from diffusion-controlled reactions are the major problem in the theoretical calculations. Although the chain-length-dependent rate constants are being clarified [81, 82], more research must be done before these topics can be considered standard engineering practice.

One of the most successful classical examples in the modeling work in bulk polymerization is the thermal polymerization of styrene at temperatures > 100°C [83–90]. In this reaction system, the Mayo mechanism for thermal initiation of radicals is valid [91], and the initiation reaction does not become diffusion controlled at monomer conversions as high as 97 % [92]. The polystyrene chains are linear. The Trommsdorff–Norrish effect, although significantly affecting the polymerization rate, has at most a minor effect on molecular-mass development because most of the polymer chains are produced by chain transfer to the Diels–Alder intermediate [91].

Because the ratio of cooling surface area to volume of reacting mixture decreases as the reactor volume increases, the heat removal is one of the major technical problems. When jacket cooling is no longer sufficient to maintain isothermal polymerization, additional modes of heat transfer must be used, as shown in Figure 19. Internal cooling coils

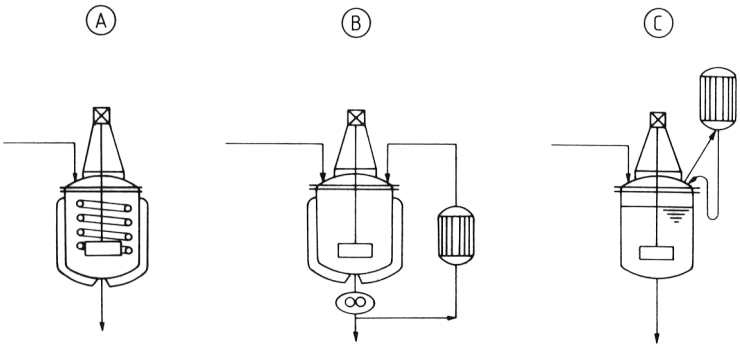


Figure 19. Alternative methods of heat removal for polymerization conducted in a stirred reactor
A) Internal cooling coils; B) External cooler; C) Reflux cooling

are often not practical because they tend to interfere with stirring. External tubular coolers can, in principle, provide a very large heat-transfer area, but they may have very large pumping requirements in the case of highly viscous solutions. Reflux cooling removes the heat of polymerization by evaporation of solvent and/or monomer; the condensed vapor is recycled to the reacting mass. Condensers may be as large as necessary, with the limiting factor usually the amount of vapor that can be treated without causing intense foaming or spattering of the polymer solution. Remixing of the condensed liquid with the more viscous reacting mass may also be difficult.

Another industrially important class of bulk polymerization can be found in photoinitiated cross-linking polymerization [93], applied for coating and printing.

The addition of a solvent in which both monomer and polymer are miscible lowers the viscosity of the reacting mass, thereby improving its flow and heat-transfer characteristics. As a result, and depending upon the nature and concentration of the solvent, the Trommsdorff–Norrish effect can be reduced significantly. Use of solvent can be especially beneficial when evaporative cooling is used. In choosing a solvent, it is important to take into account the possibility of chain transfer to solvent with a concomitant reduction in polymer molecular mass.

5.1. Removal of Solvent and Residual Monomer

Removal of solvent and residual (unreacted) monomer from the highly viscous polymer solution requires very high surface areas to permit rapid devolatilization at the moderate temperatures required to minimize polymerization and degradation of chains during devolatilization to reduce off-spec polymer. Figure 20 illustrates several designs of devolatilizers. One of these, the vacuum degasser, incorporating a type of spray device (A), operates adiabatically, which means that the heat for evaporation is supplied by the solution itself. In contrast, a degasser in series with a tubular heat exchanger causes some of the monomer/solvent to evaporate during passage through the heat exchanger. This evaporation accelerates the flow of product, thereby increasing the heat-transfer rate (B). Twin-screw extruders, as were shown in Figure 5, with one or more vapor outlets that can be connected to a vacuum source are also utilized for the removal of monomer and solvent (C). Intermeshing and self-cleaning screws provide continuous renewal of the evaporating surface. The thin-film evaporators with roatating wiper blades can also be applied (D). More details on devolatilization techniques and their modeling can be found in [94, 95].

Solution polymerization is frequently used in laboratory experiments, but not so often in industry because of the cumbersome solvent

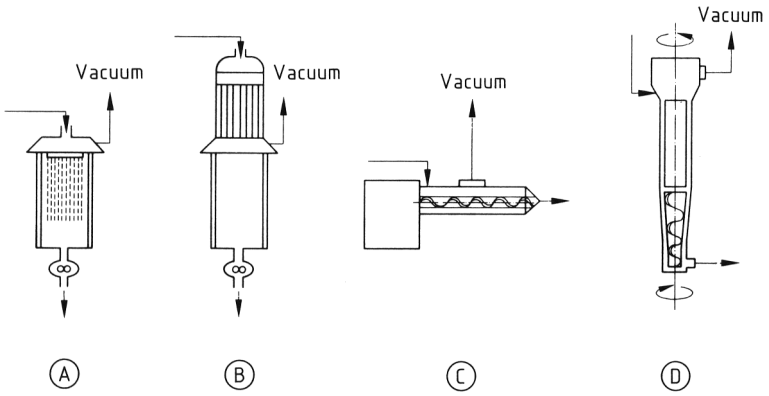


Figure 20. Options for removing residual monomer and solvent
A) Falling strand devolatilizer; B) Tubular evaporator; C) Devolatilizing extruder; D) Thin-film evaporator

recovery process required. On the other hand, to produce well-defined, highly functional polymers through the controlled/living radical polymerization, or reversible-deactivation radical polymerization according to the IUPAC recommendation [96], solution polymerization could be applied.

Recovered monomer/solvent can be recycled to the reactor. However, special attention must be paid to prevent the buildup of impurities (e.g., inhibitors, chain-transfer agents) over time, by using appropriate purge streams.

5.2. Systems with Polymer–Polymer Demixing

Polymer–polymer demixing is important in the production of thermoplastics whose application characteristics are enhanced by the presence of dispersed domains containing an elastomer. Generally, the thermodynamics are unfavorable for complete miscibility between different types of polymers. For a system polymer A–polymer B–solvent, the following generalizations are usually applicable [97]: dilution with solvent and, in most cases, an increase in temperature increases the compatibility; increasing the molecular masses of the polymers has the opposite effect. Except in the case of high dilution, incompatibility in solution is the rule for pairs of polymers, even when the solvent is a good solvent for both polymer types.

Systems such as (polymer A)–(polymer B)–block or graft copolymer AB can be regarded as a polymeric oil-in-oil emulsion in which the copolymer functions as an emulsifying agent. Such systems arise, for example, in the manufacture of high-impact polystyrene (HIPS), or in the preparation of ABS (acrylonitrile–butadiene–styrene) [98]. In the simplest case, ca. 5–10% polybutadiene is dissolved in monomeric styrene to give a homogeneous solution suitable for polymerization. The polystyrene synthesized is incompatible with the polybutadiene present, causing phase separation even at very low monomer conversion and producing a polybutadiene–styrene continuous phase and a polystyrene–styrene disperse phase. Simultaneously, graft polymerization produces polystyrene branches on polybutadiene backbone. The graft copolymer serves as an emulsifier, accumulating at the interface and stabilizing the oil-in-oil emulsion.

With increasing conversion, the volume fraction of the polystyrene phase (which is initially small) increases considerably due to formation of additional polystyrene that absorbs styrene monomer. Finally, often at a phase–volume ratio of about unity, a phase reversal occurs, with the rubber phase now the disperse phase, and the polystyrene phase the continuous phase. Agitation is essential for the completion of phase reversal, since rapid approach to equilibrium with respect to transfer of monomer/polymer must be attained in a highly viscous medium. A common result of inadequate agitation is the interpenetration of two continuous phases.

Phase reversal can lead to a complex morphology; e.g., polystyrene–styrene droplets can be occluded within the rubber particles of the disperse phase, which is often referred to as salami morphology, as shown in Figure 21 [99]. This is actually desirable as it increases the volume fraction of the disperse rubber phase. A reinforcing effect is observed, with the resulting HIPS having higher impact strength for a given mass of rubber in comparison with materials prepared by emulsion grafting, in which occluded polystyrene is not formed [100, 101].

Examples of the modeling and simulation of the bulk HIPS process can be found in [102, 103].

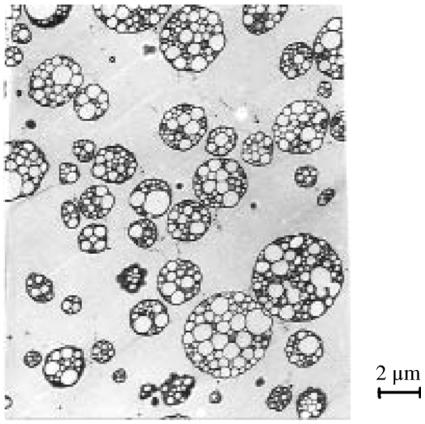


Figure 21. Salami structure of HIPS [99]

6. Precipitation and Dispersion Polymerization

The term precipitation polymerization refers to processes in which the initial ingredients of a recipe are soluble, giving a homogeneous solution, but the synthesized polymer precipitates during the course of polymerization. According to the IUPAC recommendation [104], "polymerization in which monomer(s), initiator(s) and colloid stabilizer(s) are dissolved in a solvent and this continuous phase that is a nonsolvent for the formed polymer beyond a critical molecular mass" is called the precipitation polymerization. The precipitation polymerization that leads to form polymer particles, normally of colloidal dimensions is called dispersion polymerization [104]. Precipitation and dispersion polymerizations were occasionally distinguished by the use of dispersion stabilizer. However, according to the IUPAC recommendation, the precipitation polymerization leading to form colloidal particles can be called a dispersion polymerization. Therefore, the preparation of poly(*N*-isopropylacrylamide) microgels in aqueous medium without using stabilizer, leading to uniform particles [105], can also be called a dispersion polymerization.

6.1. Polymerization without Solvent

A notable example of precipitation polymerizations is a bulk polymerization of vinyl chloride in which polymer is insoluble in its monomer. To ensure convenient handling, the disperse phase must be finely divided, which is achieved by effective agitation. Table 2 shows representative industrial production processes of poly(vinyl chloride). About 80% of worldwide production involves suspension polymerization, in which poly(vinyl chloride) precipitates in the monomer droplets. Bulk polymerization accounts for less than 10%. The final product of bulk and suspension polymerization is made up of primary particles and its agglomerates. The nucleation, growth and aggregation are responsible for the formation internal morphology and associated properties such as porosity, pore size distribution and specific surface area. For details, see also → Poly(Vinyl Chloride).

Polymers derived from halo or pseudohalo-substituted ethylenes such as vinyl bromide, vinylidene chloride, trifluoroethylene, and acrylonitrile are insoluble in their monomer. Polyethylene also falls into this category, at least when produced under moderately high pressure.

The conversion–time curves for the bulk polymerization of such monomer–polymer systems display rate increases with increasing conversion. This phenomenon has been especially thoroughly investigated for the bulk polymerization of vinyl chloride. Its cause may be interpreted as follows: even at very low conversion, poly(vinyl chloride) precipitates, forming a monomer-swollen polymer-rich phase. Initiator is partitioned between the phases, and thus radical generation and polymerization occur in both phases. The bimolecular termination rate is diffusion controlled in the polymer-rich phase and hence the concentration of radicals is higher in this phase. Even though the monomer concentration is lower in the polymer-rich phase, the specific polymerization rate R_p is higher. In addition, the volume of the polymer-rich phase grows at the expense of the monomer-rich phase with increasing monomer conversion. This explains the autoacceleration in rate as monomer conversion increases. Bulk polymerization of vinyl chloride may be a good example to study fundamental aspects of precipitation polymerization, and its mathematical model development can be found in [106–109].

Table 2. Industrial polymerization techniques of poly(vinyl chloride)

Techniques	Initiator	Stabilizer	Particle size, μm	Processing/application
Bulk polymerization	oil soluble	no	100–150	extrusion, injection, calendering
Suspension polymerization	oil soluble	polymeric dispersant	100–150	extrusion, injection, calendering
Emulsion polymerization	water soluble	emulsifier	0.1–2	paste, latex
Microsuspension polymerization	oil soluble	emulsifier	0.1–2	paste, latex
Solution polymerization	oil soluble	no	solution	paint, coating

Precipitation polymerization also encompasses what has been called "gas-phase" polymerization, a process in which polymer particles form within a monomer vapor. Notable commercial application includes gas-phase reactors for low-pressure polymerization of ethylene and propylene. Such polymerization does not actually occur in the gas phase, however, because the catalyst resides either within or on the surface of existing polymer particles, and a significant amount of monomer is dissolved in the polymer. The actual site of polymerization is thus within the polymer particle, to which a continuous supply of monomer flows from the gaseous phase.

Figure 22 shows a classical example called the Unipol process [110] developed by Union Carbide in which polyethylene powder is produced using ethylene as a fluidizing gas in a fluidized-bed reactor. Linear polyethylene, called high-density polyethylene (HDPE), is produced. Copolymerization of ethylene with propene, 1-butene, and 1-hexene gives products with a controlled amount of short-chain branching and lower polymer density, called linear low-density polyethylene (LLDPE). HDPE and LLDPE are produced via coordination polymerization [111], which belongs to the ionic polymerization, not free-radical polymerization. Gas-phase precipitation polymerization and liquid-phase precipitation polymerization mentioned in the next section are the major production methods for HDPE and LLDPE. Note that low-density polyethylene (LDPE) is produced in the high-pressure free-radical polymerization process.

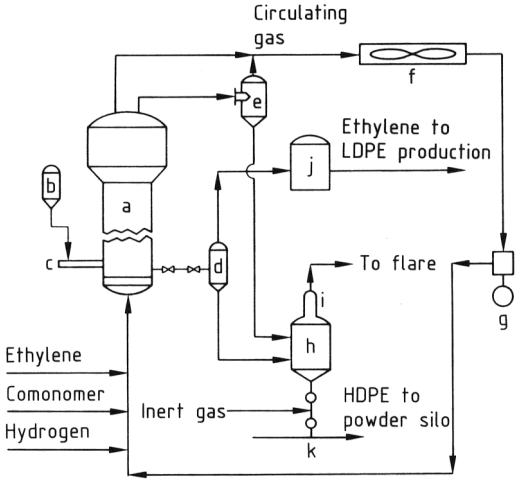


Figure 22. Schematic diagram of the Union Carbide gas-phase process for manufacturing HDPE [110]
a) Fluidized-bed reactor; b) Catalyst transfer tanks; c) Catalyst feeders; d) Product discharge tanks; e) Multiclone dust separator; f) Air coolers; g) Compressor; h) Product degassing tank; i) Filter; j) Ethylene tank; k) Pneumatic transport system

6.2. Polymerization with Solvent

Solvents that can dissolve monomers but precipitates polymers are used for precipitation polymerization. A notable example is the so-called slurry process for manufacture of high-density polyethylene (HDPE), isotactic polypropylene, and their copolymers. Similarly with the gas-phase processes, the polymer is formed around heterogeneous catalyst. The slurry processes use an autoclave-type reactor with agitator or a loop reactor. A loop reactor is a continuous tube or pipe, which connects the outlet of a circulation pump to its inlet, with a cooling jacket outside. The continuous production process using a loop reactor is a variation of a CSTR, and it offers a large heat removal capacity and prevents adhesion through a high-speed circulation of slurry. Two or more reactors can be operated in series to produce polyolefins with more complex microstructures [112, 113].

If the polymer is soluble in its monomer, precipitation polymerization requires the addition of a precipitant that is miscible with the monomer. Polymerization then begins in a solvent – nonsolvent mixture and it ends in a phase consisting only of pure precipitant once conversion of the monomer is complete. Thus, the solubility relationships change during the course of the polymerization, and polymerization may initially occur in a homogeneous manner prior to the onset of precipitation, induced by the enrichment in precipitant that accompanies the consumption of monomer. In precipitation polymerization of this type, it is especially important to ensure that the polymer precipitates in finely divided form. Among other things this ensures that the particles do not overheat during polymerization. The stabilizers can be added to prevent agglomeration.

When the stabilizer (dispersing agent) works effectively in precipitation polymerization, nice uniform spherical particles of micron-sizes can be obtained, which belongs to the dispersion polymerization [114–116]. In this polymerization, the monomers, the initiator, and the stabilizer are dissolved in a solvent. Polymerization starts in a homogeneous phase and polymer precipitates to form unstable nuclei. Nucleation ends when the number of stable polymer particles reaches to the point in which all new nuclei are captured by the existing stable particles. Shorter nucleation period is preferable to obtain uniform particles. The polymerization locus changes from the continuous phase to the dispersed phase.

The key to controlling particle size is the selection of stabilizer type. Among the most effective stabilizers are the so-called amphipathic molecules: block and graft copolymers made up of two polymeric components, only one of which is insoluble in the continuous, diluent-containing phase. Graft copolymers of this type often form during the polymerization as a result of grafting on the dissolved polymer, but it is not absolutely essential that the insoluble portion of the polymeric stabilizer be identical to or soluble in the disperse phase. In many cases its insolubility in the diluent is sufficient to ensure adequate adsorption on the particle surface. These amphipathic dispersing agents act as steric stabilizers [117].

Figure 23A is a schematic representation of the adsorption of di-block, multiple-block, and graft copolymers on the surface of growing polymer particles. Soluble and insoluble portions of the dispersant molecules must be kept carefully in balance. If the insoluble part is too small, or if it interacts too weakly with polymer particles, then adequate adsorption will occur only when the dispersant concentration in the continuous phase is very high. If the soluble portion is too large, the dispersant will be present largely as aggregates or micelles with little tendency to dissociate and be adsorbed on the interface. Figure 23B depicts the equilibrium situation. Finally, it is important to note that multifunctional amphipathic molecules like those shown in Figure 23C can also function as weak flocculating agents.

By selecting appropriate reaction condition, monodisperse polymer particles can be prepared

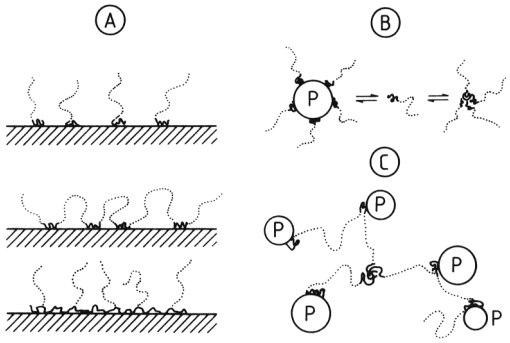


Figure 23. Steric stabilization of precipitating polymer/monomer particles with the aid of amphipathic block and graft copolymers [118]
A) Schematic representation of adsorption of amphipathic molecules on the polymer particles; — insoluble groups, ---- soluble groups; B) Equilibrium established in the course of a precipitation polymerization P = (growing) polymer particle; C) Schematic representation of flocculation due to multifunctional amphipathic molecules

in dispersion polymerization, as shown in Figure 24 [119]. Dispersion polymerization connects nicely the particle size between emulsion polymerization and suspension polymerization. Figure 25 shows approximate particle sizes that can be prepared from various heterogeneous polymerization techniques.

Precipitation/dispersion polymerization can be conducted not only for conventional free-radical polymerization but with reversible-deactivation radical polymerization (RDRP) (or controlled/living radical polymerization) [120, 121]. A problem in conducting RDRP in dispersion polymerization is a longer nucleation period because of slow chain growth in RDRP, which makes the particle size distribution broader. Newer topics in precipitation polymerization include the use of CO_2 as the solvent [122, 123].

7. Suspension Polymerization

7.1. Process Description

The term "suspension polymerization" includes a series of processes, in which polymer is formed in monomer droplets dispersed in a continuous phase that is nonsolvent for both

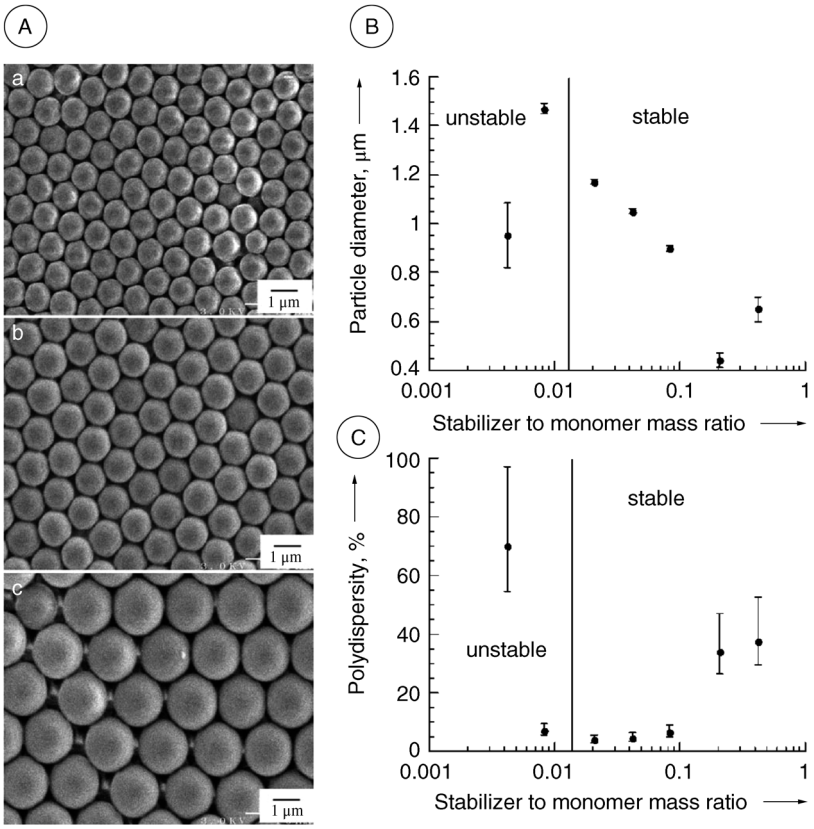


Figure 24. Effect of monomer and stabilizer concentration on monodisperse poly(methacrylate particles prepared by dispersion polymerization in hexane [119]
A) Scanning electron micrographs, a) 15 wt%, b) 26.3 wt%, c) 47.2 wt% monomer concentration; B) Particle diameter as a function of concentration of stabilizer; C) Polydispersity as a function of concentration of stabilizer

monomer and the formed polymer. In suspension polymerization, the initiator is located in the monomer phase. The monomer droplets have diameters usually exceeding 10 µm, which can be considered as miniature bulk polymerization reactors. Although the viscosity inside the droplets increases during polymerization, the effective viscosity of the suspension remains

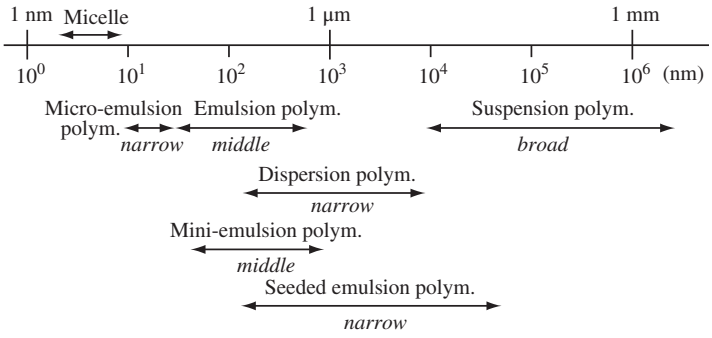


Figure 25. Approximate particle size ranges and distribution width (*narrow*, *broad*, *middle*) that can be prepared from various heterogeneous polymerization techniques

low and effective agitation is possible. Large specific surface area of small droplets and low viscosity of suspension make it possible to have a good heat removal from the reactor. Suspension polymerization is suitable for the preparation of cross-linked polymer particles, such as ion exchange resins and superabsorbent polymers. Cross-linked sodium polyacrylate used for disposable diapers can be produced by the inverse-suspension polymerization in which a hydrophobic organic suspending medium is used.

One of the major disadvantages of heterogeneous polymerization is lower reactor efficiency. The volume ratio monomer/continuous phase in suspension polymerization is usually between 25 : 75 and 50 : 50. Incidentally, the most space-efficient way to pack uniform spheres is in a pyramid shape and the volume fraction of spheres is $\pi/\sqrt{18} \cong 0.74$, which has been known as the Kepler conjecture for more than 400 years and a formal proof was announced completed in 2014 [124].

For the dispersants, water-soluble polymers or insoluble, usually inorganic, particles, the so-called Pickering stabilizers [125] are used. Their function is first to assist in the formation of the initial monomer droplets and then to stabilize the resulting polymer particle suspension. The inorganic stabilizers can be removed easily after polymerization.

In a large-scale commercial suspension polymerization, stirred batch reactors are commonly employed, and huge reactors larger than 100 m^3 are used for the production of poly (vinyl chloride). The continuous suspension polymerization processes are being developed [126, 127]. In the continuous processes, narrower RTD is preferable to prevent coexistence of polymer particles whose monomer conversion is not high enough.

The monomer droplets may experience both breakage and coalescence phenomena. The droplet breakage mainly occurs in the regions of high shear stress, i.e., near the agitator blades, and would be significant at low monomer conversions. After reaching so-called "sticky-stage", the coalescence becomes significant, and the particle size increases. At higher monomer conversions, the particles are sufficiently hard and the coalescence ceases. The particle size distribution remains constant from this point, called the identity point, except for some minor shrinkage due to density difference between monomer and polymer. Increasing the stabilizer concentration (i.e., reducing the size of particles) displaces the identity point towards lower conversion.

The control of the particle size distribution is important in many industrial applications. To control particle sizes, various models and equations were proposed for specific polymerization systems [128], and these empirical approaches are still useful for the industrial applications. To follow the dynamic evolution of the particle size distribution theoretically, the population balance approaches could be used [129–131].

7.2. Polymerization Kinetics

The monomer droplets are large enough to contain a large number of radicals. Assuming that the polymer radical concentration $[R^\bullet] = 1 \times 10^{-7}$ mol/L, a monomer droplet with diameter $d = 100$ μm possesses 3×10^7 polymer radicals. With so many radicals in a polymerization locus, bulk/solution polymerization kinetics is valid. When the polymerization locus becomes so small that radicals are isolated in different particles, one needs to use the emulsion polymerization kinetics that is different from the bulk/solution polymerization kinetics. Each droplet/particle can be considered as a miniature bulk polymerization reactor in suspension polymerization. The statistical variation of the conversion levels among particles is small enough, because each droplet/particle contains a large enough number of monomeric units in it. Assuming a particle with $d = 100$ μm, density 1 g/cm^3, and the molar mass of a monomeric unit 100 g/mol, there are 3×10^{15} monomeric units in it. Therefore, even when droplet/particle breakage and coalescence occur, the concentrations of the various components in the reaction loci are not changed. However, if the effect of residence time distribution cannot be neglected in a continuous production process, one needs to account for the difference in the monomer conversion levels among particles.

The Trommsdorff–Norrish and glass effects must be taken into account, as in the case of

bulk polymerization. The process is sometimes referred to as a water-cooled bulk polymerization. To ensure that conversion is as complete as possible, it is common to employ mixtures of initiator types with different half lives, and to allow the polymerization temperature to increase in the final stages of conversion.

When the polymer formed is soluble in the monomer, nonporous spherical "beads" are formed, hence the term "suspension bead polymerization" is sometimes used. If, however, the polymer precipitates during polymerization, the resulting polymer particles are composed of many smaller primary particles. They are opaque, usually possess an irregular surface, and may have substantial internal porosity. This type of polymerization has been called "suspension powder polymerization". Suspension powder polymerization is the most important commercial process for the manufacture of poly(vinyl chloride). Porous powders with a rough surface are advantageous for rapid incorporation of plasticizers, as well as for a fast removal of residual monomer. The polymer particle morphology development during suspension polymerization of vinyl chloride [132, 133] is an important issue to produce high quality product.

Some of the factors that might be different from bulk/solution polymerizations are: (1) the reflux from condenser may have difficulty in returning to the particles [134], which implies that semibatch operation requires careful attention, and (2) because of the existence of continuous phase, some amount of the components may coexist in the continuous phase. This may change the apparent reactivity ratios when one of the monomers is more soluble in the continuous phase than the others [128].

8. Emulsion Polymerization

8.1. Process Description

Emulsion polymerization involves emulsification of monomers in dispersed phase, normally forming an oil-in-water emulsion, although inverse emulsion polymerization is also possible. The initiator is normally located in water (continuous) phase, but an oil-soluble initiator may also be used for special cases. At the end of emulsion polymerization, a milky fluid called "polymer latex", which is a colloidal dispersion of polymer particles whose diameter is about several tens to a few hundred nanometers, is obtained. In industry, the product latexes contain 40–60 wt% polymer solids, although much smaller solid content latex might be prepared in the laboratory scale experiments. Assuming a 50 wt% latex with the particle diameter $d = 100$ nm and the density of polymer 1 g/cm^3, there are about $N = 1 \times 10^{18}$ polymer particles per liter of latex.

In a batch ab initio emulsion polymerization, the polymerization may be conveniently divided into three intervals, as shown in Figure 26. At the start of polymerization, the monomer droplets whose size is about $d = 1$–$10\,\mu$m and number is about $N = 10^{12}$–10^{14} per liter of latex

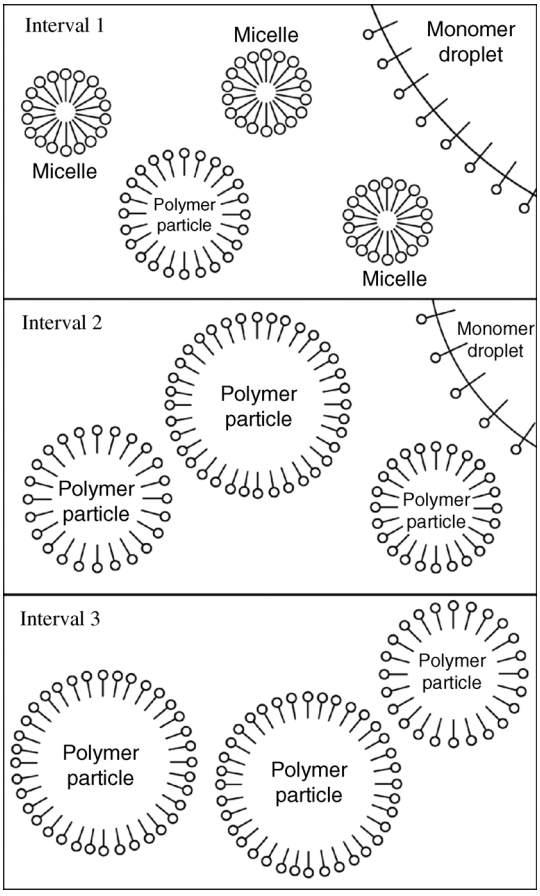


Figure 26. Schematic representation of ab initio emulsion polymerization

are formed, with much larger number of monomer-swollen micelles if the surfactant concentration is higher than the critical micelle concentration (CMC), which is the case for usual emulsion polymerization. The micelles are usually d = 5–10 nm in size, and $N = 10^{19}$–10^{21} in number.

Interval 1 is the nucleation period of polymer particles. As one can guess easily from the size relationship, (micelles) ≪ (final polymer particles) ≪ (monomer droplets), the monomer droplets are not the main loci of polymerization. The initiator decomposes in the water phase to generate primary radicals, which propagate with monomer dissolved in water to form oligomer radicals to obtain sufficient hydrophobicity. The mass transfer coefficient around a spherical particle is given by $2D_w/d$, where D_w is the diffusion coefficient of the oligomer radicals in water phase. Therefore, the total entry frequency of an oligomer radical is given by $(2D_w/d) \times (\pi d^2) \times N = 2\pi D_w N d$. For the $(N \times d)$ value, there is a relationship, (monomer droplets) ≪ (polymer particles) ≪ (micelles). Therefore, the oligomer radicals will have a strong tendency to enter monomer-swollen micelles, and they propagate rapidly with solubilized monomer to form a polymer particle. This is a modern interpretation of the micellar (or heterogeneous) nucleation theory [135–137]. As new polymer particles are formed and grow, the particles absorb monomer from the monomer droplets and the monomer-swollen micelles. At the same time, the polymer particles adsorb surfactant to obtain colloidal stability. Eventually, the micelles are gone and the nucleation of polymer particles ceases. This is the end of Interval 1. Only about one of every 10^2–10^3 micelles are converted to the polymer particles.

The polymer particles formed at the beginning of Interval 1 are expected to be larger than those formed at the end of Interval 1. Therefore, smaller duration of Interval 1 is preferable to obtain a narrower particle size distribution.

At the end of Interval 1, as illustrated in Figure 27, there is a rapid drop in the free surfactant concentration (which throughout Interval 1 is equal to the CMC due to equilibrium with micelles) and the surface tension (head-space gas/latex) rises rapidly from its previously stationary value. Because the fractional coverage of the surface of polymer particles falls after the end of Interval 1, problems with particle stability and coagulation may occur.

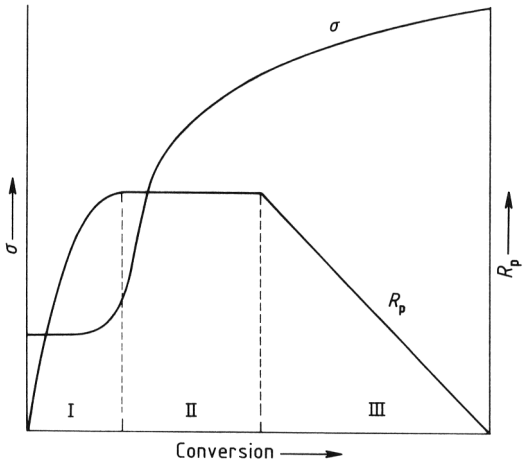


Figure 27. Overall rate of reaction R_p and surface tension σ as a function of conversion during the three intervals of emulsion polymerization (schematic)

As for the polymer particle nucleation, one may heard of the homogeneous nucleation theory [138–140], which assumes that the polymer particles are formed when the oligomer radicals have grown to the critical chain length for precipitation. The precipitated polymer chain is stabilized by the emulsifier and monomer diffuses into this new organic phase, which allows a fast growth of the polymer radical. The homogeneous nucleation would be important when the initial surfactant concentration is below the CMC. In the surfactant-free emulsion polymerization, the ionic initiator fragment (e.g., $SO_4^{\bullet -}$ from persulfate) provides colloidal stability. Nucleation ceases when the number of polymer particles is high enough to capture all oligomer radicals. Regardless of the particle nucleation mechanism, the newly formed polymer particles are very small, and grow rapidly with increasing surface area that needs to be covered by the emulsifier molecules. If the diffusion of emulsifier is not fast enough, the embryo polymer particles may coagulate. The process combining nucleation with subsequent coagulation is referred to as the coagulative nucleation [141].

Interval 2 is known as the polymer particle growth stage, during which the number of particles remains constant (in the absence of coagulation), as does the monomer concentration $[M]_p$ in the latex particles as a result of monomer diffusion from the reservoir of monomer droplets. A constant $[M]_p$ during Interval 2 can be rationalized, at least qualitatively, as follows. Because of the extremely large interfacial areas (polymer particle/water and monomer droplet/water) and associated very rapid mass transfer of monomer, there is an equilibrium with respect to monomer transfer from monomer droplets to polymer particles (the chemical potential of monomer is the same in all three phases, monomer droplet/water/polymer particle). The interfacial energy per unit volume for the small polymer particles contributes significantly to the free energy and is accounted for as follows [142, 143]:

$$\frac{2V_m\sigma}{r_0RT} = -\left\{\ln(1-\phi_p) + \phi_p + \chi\phi_p^2\right\} \tag{32}$$

where V_m is the molar volume of monomer, σ is the interfacial tension (latex particle/aqueous phase), r_0 is the radius of unswollen polymer particle, R is the gas constant, T is the absolute temperature, ϕ_p is the volume fraction of polymer in the latex particle, and χ is the Flory–Huggins polymer–solvent interaction parameter.

For a given set of values, V_m, r_0, T, and χ, one can determine ϕ_p. The saturated monomer concentration in the polymer particle can be calculated from:

$$[M]_p = \frac{1-\phi_p}{V_m} \tag{33}$$

Because σ and r_0 increase simultaneously during Interval 2, $[M]_p$ remains relatively constant [142–144], as long as the monomer droplets are present. Practically, it is more convenient to actually measure the saturated amount of monomer in the polymer particles experimentally. Anyway, the kinetic behavior during Interval 2 could be modeled as a nanosized semibatch reactor for which monomer is fed from the monomer droplets.

Interval 3, known as the depletion or monomer finishing stage, begins with the disappearance of all monomer droplets. The only reservoir of monomer for the polymerization in the latex particles is the aqueous phase. This is hardly sufficient and in Interval 3 the monomer concentration $[M]_p$ falls with time and conversion. For a hydrophobic monomer, the monomer conversion at which Interval 2 ends, x_{c2} is equal to the mass fraction of polymer during Interval 2 that is approximately constant during Interval 2. Therefore, x_{c2} can be estimated by measuring the saturated monomer concentration experimentally.

For more detailed information and realistic problems on emulsion polymerization, one can refer to the review articles and books [145–150].

8.2. Polymerization Kinetics

Emulsion polymerization follows unique polymerization kinetics, and both polymerization rate and molecular mass of the formed polymers can be increased simultaneously, which is difficult to achieve in bulk/solution/suspension polymerization.

Unique characteristics of polymerization kinetics result from the smallness of the polymerization locus, which is the polymer particle, quite often smaller than $d = 100$ nm. In a submicron particle, even a single molecule occupies a sufficient concentration. Table 3 shows the calculated single molecule concentration in a particle with diameter d, i.e., $[\text{Single}]_p = 6/(\pi N_A d^3)$, where N_A is the Avogadro constant. In bulk/solution polymerization, the polymer radical concentration is usually about $[R^\bullet]_{bulk} = \sqrt{R_I/k_t} = \cdot 10^{-8} - 10^{-6}$ mol/L, where R_I is the initiation rate and k_t is the termination rate constant. At least one polymer radical is required to provoke polymerization in

Table 3. Concentration of a single molecule inside a particle with diameter d

Particle diameter d, nm	Concentration of a single molecule, $[\text{Single}]_p$, mol/L
1000 (=1 μm)	3.18×10^{-9}
200	3.97×10^{-7}
150	9.43×10^{-7}
100	3.18×10^{-6}
50	2.55×10^{-5}
25	2.04×10^{-4}

a polymer particle. For the particles with d <100 nm, the radical concentration is significantly larger than in a bulk polymerization. On the other hand, the contribution of a single molecule is negligibly small for $d = 1$ μm, and normally, the bulk polymerization kinetics apply.

In emulsion polymerization, the average time interval between radical entry to a polymer particle $\bar{t}_{entry}$, is normally larger than 10 seconds. During this time interval, a single polymer radical can grow without termination (although it is likely to cause chain transfer reaction in this time interval). When the second radical comes in, the average time required for this radical to cause bimolecular termination is given by $\bar{t}_{term} = 1/(k_t[R^\bullet])$. Assuming $k_t = 1 \times 10^7$ L mol^{-1} s^{-1}, $\bar{t}_{term.} = 8.48 \times 10^{-4}$s for d = 25 nm, $\bar{t}_{term.} = 3.93 \times 10^{-3}$ s for d = 50 nm, and $\bar{t}_{term.} = 3.14 \times 10^{-2}$ s for d = 100 nm. Therefore, the second incoming radical causes bimolecular termination almost instantaneously $\left(\bar{t}_{term.} \ll \bar{t}_{entry}\right)$. Figure 28 shows such behavior in a polymer particle schematically. For a half of the time, it possesses one radical n = 1, and n = 0 for the rest of one half. Statistically, this situation applies to all particles, and the average number of radicals per particle is $\bar{n} = 0.5$. This is so-called zero–one behavior. It is possible to retain a very high average radical concentration, $[R^\bullet]_p = \bar{n} \times [\text{Single}]_p$ by isolating each radical into different polymer particles.

By hypothetically assuming that both a polymer particle and a monomer droplet are the isolated microreactors, the increase rate of local conversion, x, is simply given by that for homogeneous batch polymerization, as follows:

$$\frac{dx}{dt} = k_p(1 - x)[R^\bullet] \tag{34}$$

Because $[R^\bullet]$ is much larger for the polymer particles, the polymer fraction wants to grow much faster in the polymer particles. Therefore, the polymer particles will absorb monomer from the water phase, and the monomer in water phase is supplied from the monomer droplets.

On the other hand, however, in order for the polymer particles to be the main loci of polymerization, the total monomer consumption rate in the polymer particles must be much larger than that in the monomer droplets. Consider the competition of monomer consumption between the polymer particles and the monomer droplets, which is represented by the following ratio, ς.

$$\varsigma = \frac{[R^\bullet]_p[M]_p V_p}{[R^\bullet]_d[M]_d V_d} \tag{35}$$

where the subscripts p and d represent the polymer particle and the monomer droplet, respectively. Note that V represents the total volume, not each particle/droplet.

Suppose that we have polymer particles with diameter 50 nm at conversion 20%. Assuming polymer exists only in the polymer particles and the volume fraction of monomer $\phi_m = 0.5$, then $[M]_p/[M]_d = 0.5$ and $V_p/V_d = 20 \times 2/(100-20 \times 2) = 0.67$, neglecting the density

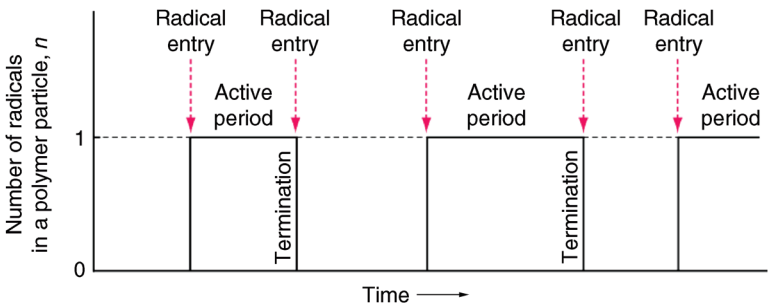


Figure 28. Schematic representation of the time sequence of the number of radicals in a small polymer particle in which bimolecular termination is instantaneous, i.e., so-called zero-one behavior

difference of monomer and polymer. The monomer droplets are large, so the maximum value of $[R^\bullet]_d$ attainable would be the radical concentration in the corresponding bulk polymerization, $[R^\bullet]_{bulk}$. For $\bar{n} = 0.5$ and $[R^\bullet]_{bulk} = 1 \times 10^{-7}$ mol/L, $[R^\bullet]_p/[R^\bullet]_d$ is calculated to be $(0.5)(2.55 \times 10^{-5})/(1 \times 10^{-7})=128$. Therefore, the ς value is $(128)(0.5)(0.67) = 43 \gg 1$. In addition to a larger total radical entry frequency over monomer droplets, as estimated in the previous section, the faster polymerization rate in smaller particles leads to make the polymer particles the dominant loci of polymerization. The emulsion polymerization rate can be represented by the polymerization rate in the polymer particles.

Another explanation as to why the polymer particles win the competition might be given on the basis of a large number of polymer particle combined with the zero-one behavior. At the beginning of Section 8.1, we have estimated that the number of polymer particles is ca. $N_p = 1 \times 10^{18}$ per liter of latex. With the ideal zero-one behavior, one half of polymer particles contain a radical. Therefore, the radical concentration in the latex, meaning within the volume that involves the water phase, is as large as $0.5 \times 10^{18}/N_A = 8.3 \times 10^{-7}$ mol/L, which is already higher than that for usual bulk polymerization.

The main loci of polymerization is the polymer particles, and the emulsion polymerization rate, R_p in mol s^{-1} (L-water)$^{-1}$ is given by:

$$R_p = k_p[M]_p \frac{\bar{n}}{N_A} N_T \tag{36}$$

where k_p is the propagation rate constant, N_T is the number of polymer particles per unit volume of water phase. Normally, the radicals are generated in water phase, and it is convenient to take the water-phase volume as a base unit. Obviously, R_p in mol s^{-1} (L-latex)$^{-1}$ can be obtained simply by changing N_T to N_p.

Equation (36) shows that the polymerization rate can be increased by making the number of particles, N_T larger. Given the radical generation rate in the water phase is kept constant, a larger number of polymer particles makes the average time interval between radical entry larger, leading to larger kinetic chain length. Therefore, both the polymerization rate and molecular mass of polymer can be made larger simultaneously.

By larger polymerization rates in emulsion polymerization it may also be understood that the polymer radicals are segregated into different polymer particles, resulting in the suppression of bimolecular termination reactions. There is nothing wrong with this statement in terms of the radical lifetime, however, notably, the total initiation rate and termination rate within the whole reactor is still balanced, i.e., the total termination rate in the whole reactor is not decreased in emulsion polymerization.

If a chain-transfer reaction occurs during the active period, a small radical formed by chain transfer reaction may exit from the particle. With the exit of small radicals, the active period becomes shorter, while the radical entry frequency may not increase significantly. In such a case, the average number of radical becomes smaller than 0.5 even when the zero–one behavior dominates. Because the chain transfer reaction tend to increase the radical desorption frequency, the addition of chain-transfer agent (CTA) may decrease the polymerization rate by reducing the $\bar{n}$ value [151]. This chain transfer effect in reducing the polymerization rate is a unique characteristic of emulsion polymerization.

On the other hand, as the polymer particle grows, it takes longer time to cause the bimolecular termination reaction. If the third radical comes into the polymer particle before bimolecular termination, the $\bar{n}$ value increases.

Now, let us consider how the polymer radicals are distributed in polymer particles. N_n is considered to be the number of particles containing n radicals per unit volume of water phase. The population balance equation for N_n is given by:

$$\frac{dN_n}{dt} = \left(\frac{\rho_A}{N_T}\right) N_{n-1} + k_f(n+1)N_{n+1} + \frac{k_t}{v_p N_A}{}_{n+2}C_2 N_{n+2} - \left(\frac{\rho_A}{N_T}\right) N_n - k_f n N_n - \frac{k_t}{v_p N_A}{}_n C_2 N_n \tag{37}$$

where

$\left(\frac{\rho_A}{N_T}\right) N_{n-1}$: Generation of N_n through the entry of a radical into the

particle with $n-1$ radicals. Here, ρ_A is the total radical entry rate from the aqueous phase to the polymer particles.

$k_f(n+1)N_{n+1}$: Generation of N_n through the exit of a radical from the particle with $n+1$ radicals. Here, k_f is the desorption rate constant of a radical.

$\frac{k_t}{v_p N_A} {}_{n+2}C_2 N_{n+2}$: Generation of N_n through the bimolecular termination in the polymer particle containing $n+2$ radicals. ${}_{n+2}C_2$ shows the number of possible combination of radicals to cause bimolecular termination reaction. The number of termination events per unit volume is given by $\frac{k_t}{2}\frac{(n+2)(n+1)}{(v_p N_A)^2}$, where v_p is the particle volume. Note that k_t in which the termination rate is represented by $R_t = k_t[R^\bullet]^2$ is used (→ Polymerization Processes, 1. Fundamentals). The number of termination events per particle is given by $\frac{k_t}{2}\frac{(n+2)(n+1)}{(v_p N_A)^2} \times (v_p N_A) = \frac{k_t}{2}\frac{(n+2)(n+1)}{v_p N_A}$.

The 4th to 6th terms in Equation (37) represent consumption of N_n. Note that the bimolecular termination rate constant, k_t might be significantly smaller than that for the bulk polymerization at conversion $x = 0$, because a high mass fraction of polymer exists in the polymer particle from the beginning.

By application of the stationary state hypothesis ($dN_n/dt = 0$), Equation (37) was solved to give the following solutions for $\overline{n}$ and the number fraction of particles containing n radicals, $\Phi_p(n)$ [152, 153].

$$\overline{n} = \frac{a}{4}\frac{I_m(a)}{I_{m-1}(a)} \tag{38}$$

$$\Phi_p(n) = \frac{a^n 2^{(m-1-3n)/2} I_{m-1+n}\left(2^{-0.5}a\right)}{n! I_{m-1}(a)} \tag{39}$$

where $I_m(x)$ is the modified Bessel function of the first kind, $a = (8\alpha)^{0.5}$, $\alpha = 2\rho_A v_p N_A/(k_t N_T)$, and $m = 2k_f v_p N_A/k_t$. The dimensionless variables α and m are the ratios of the radical entry rate ρ_A/N_T and the radical exit rate k_f, with respect to the termination rate of a single pair of radicals divided by 2 and $k_t/(2v_p N_A)$, respectively. (The problem of the division by 2 is caused by the difference in the definition of the termination rate constant, as discussed (→ Polymerization Processes, 1. Fundamentals). Therefore, the α value represents the significance of radical entry, and m shows that of radical exit. The validity of the stationary state hypothesis was confirmed for $m = 0$ by comparing the numerical solution of Equation (37) [154].

Figure 29 shows the calculated results from Equations (38) and (39), for the case of $m = 0$. The comparison was made with the Monte Carlo simulation results that agree perfectly with the calculated results [155]. In Figure 29A, ξ represents the magnitude of bimolecular termination, $\xi = k_t/(k_p[M]_p v_p N_A)$, and faster termination results in $\overline{n} = 0.5$, as expected. When the k_t value is large enough to retain the zero–one behavior, the magnitude of k_t does not affect the $\overline{n}$ value. On the other hand, smaller k_t value (or to be more precise, smaller ξ value) leads to make the $\overline{n}$ value larger. Figure 29B shows that the particles with up to $n = 6$ exist when $\overline{n} \cong 2$.

With the radical desorption ($m > 0$), a radical once exits from the particle and may enter another particle. The ρ_A value in a steady state is given by:

$$\rho_A = k_A[R_w^\bullet]N_T = \rho_w + k_f\overline{n}N_p - k_{tw}[R_w^\bullet]^2 \tag{40}$$

or equivalently,

$$\alpha = \alpha_w + m\overline{n} - Y\alpha^2 \tag{41}$$

where ρ_w is the initiation rate in the water phase, $[R_w^\bullet]$ is the radical concentration in the water phase, k_{tw} is the bimolecular termination rate constant in the water phase, $\alpha_w = 2\rho_w v_p N_A/(k_t N_T)$ and $Y = \frac{k_{tw}k_t}{2k_A^2 v_p N_A N_T}$. The k_{tw} value is expected to be much larger than k_t in the particle, because of low viscosity and oligomeric chain lengths in the water phase. The radical concentration in water phase, $[R_w^\bullet]$ is

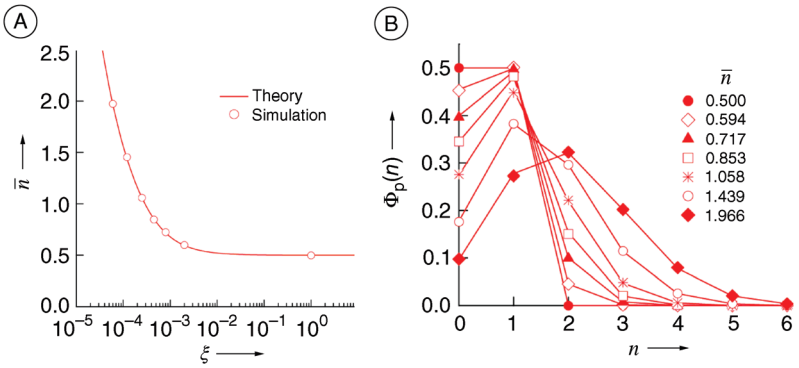


Figure 29. Radical distribution in polymer particles, calculated results [155]
A) Average number of radicals per particle $\bar{n}$; B) number-fraction distribution of the particles containing n radicals
Solid lines: calculation; Symbols: Monte Carlo simulation results

extremely small especially for hydrophobic monomers, and the final term in Equation (41) could possibly be neglected, i.e., $Y \cong 0$.

It is much more convenient if ρ_w is separated from ρ_A in the experimental design, because it is straightforward to control ρ_w, not ρ_A. To do this, Equations (38) and (41) must be solved simultaneously. Because $\bar{n}$ is an implicit function of α_w, a recursive calculation is required. It is not very difficult to do this in the present age of efficient computers. However, for the cases with $Y = 0$, the following approximate equation [147, 156] that is an explicit function of α_w and m is very convenient to use.

$$\bar{n} = \frac{1}{2}\left[\left\{\left(\alpha_w + \frac{\alpha_w}{m}\right)^2 + 2\left(\alpha_w + \frac{\alpha_w}{m}\right)\right\}^{1/2} - \left(\alpha_w + \frac{\alpha_w}{m}\right)\right] + \left(\alpha_w + \frac{\alpha_w}{m}\right)^{1/2} - \frac{1}{2} \quad (42)$$

Figure 30 shows the calculated results for the exact solution of Equations (38) and (41) and the approximation using Equation (42). The maximum deviation of Equation (42) from the exact solution is smaller than 5%. The fully converged lines in the large α_w region is where the pseudo-bulk kinetics are valid, and $\bar{n} \propto \alpha_w^{0.5}$. It seems reasonable that the unique characteristics of emulsion polymerization kinetics are lost for $\bar{n} > 2$. Larger m values mean that the exit of radicals is significant. For hydrophobic monomer such as styrene, the m value is rather small, and a wide region of $\bar{n} = 0.5$ exists. On the other hand, for monomers with higher solubilities in water, such as vinyl acetate and vinyl chloride, the m value is large and close to the linear line with slope 1/2 in Figure 30 prevails. The experimental data of the relationship between $\bar{n}$ and α_w for representative monomers,

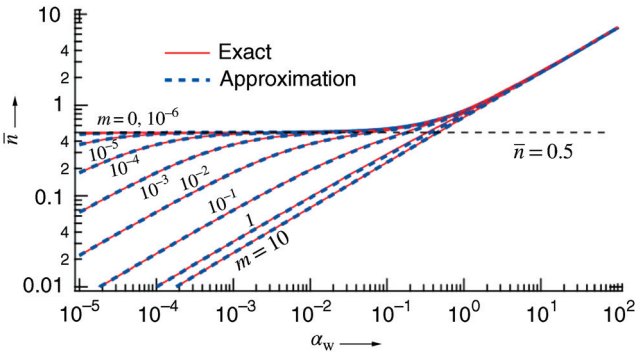


Figure 30. Average number of radicals per particle $\bar{n}$ as predicted from Equations 38 and 41 (Exact), and the approximation from Equation (42) for $Y = 0$

such as styrene, methyl methacrylate, and vinyl chloride, agree reasonably well with the theory presented herein [147].

With the progress of polymerization, the particle volume v_p increases. In addition, k_t may decrease significantly because of the gel effect, especially during Interval 3 where the polymer fraction in the polymer particle increases. Both effects make the α_w value larger, leading to a larger $\bar{n}$ value, as shown in Figure 30. Figure 31 shows an example of the calculated results for the styrene emulsion polymerization [157].

To calculate the polymerization rate by using Equation (36), the number of polymer particles N_T needs to be determined. It is practical to determine the N_T value experimentally. On the other hand, the micellar nucleation theory gives [136]:

$$N_p \propto (\rho_w/\mu)^{0.4}(a_s[S]_0)^{0.6} \propto [I]_0^{0.4}[S]_0^{0.6} \tag{43}$$

where μ is the volumetric growth rate per particle, a_s is the surface area occupied by a unit amount of surfactant, $[S]_0$ is the charged surfactant concentration, and $[I]_0$ is the initial initiator concentration. For a hydrophobic monomer, such as styrene, this agrees with Equation (43).

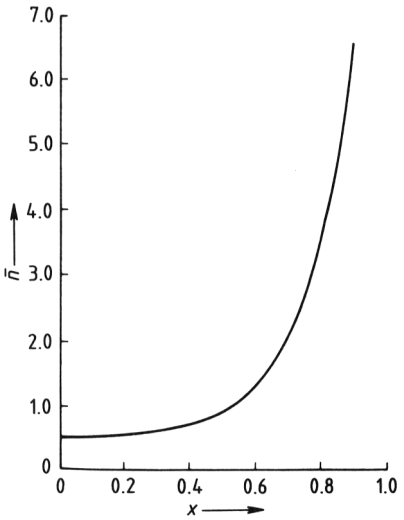


Figure 31. Theoretical course of the average number of radicals $\bar{n}$ per polymer particle with increasing conversion [157]

When the radical desorption is taken into account, Equation (43) can be modified as follows [158–160].

$$N_p \propto (\rho_w/\mu)^{1-z}(a_s[S]_0)^z \propto [I]_0^{1-z}[S]_0^z \tag{44}$$

where $0.6<z<1.0$. The z value increases with the water solubility of monomer, starting from $z = 0.6$ for styrene to $z = 1.0$ for vinyl acetate.

Miniemulsion Polymerization. The polymerization rate expression given by Equation (36) can be applied also for miniemulsion polymerization [161–163], in which all of polymerization can be considered as occurring within the preexisting monomer droplets without the formation of new particles. Initial monomer droplets are small enough (typically, <500 nm), and each monomer droplet could be regarded as an independent microreactor, at least, approximately.

The particle size below which the miniemulsion polymerization rate becomes noticeably larger than the corresponding bulk polymerization can be determined as follows. The effective radical concentration in a particle is given by $\bar{n}[\text{Single}]_p$. If this concentration becomes larger than the corresponding bulk polymerization, the miniemulsion polymerization would win the competition. Therefore, the threshold particle diameter below which the miniemusion polymerization rate becomes larger than the corresponding bulk polymerization, d_c is given by:

$$[R^\bullet]_{bulk} = \bar{n}[\text{Single}]_p = \frac{6\bar{n}}{\pi N_A d_c^3} \tag{45}$$

or

$$d_c = \left(\frac{6\bar{n}}{\pi N_A [R^\bullet]_{bulk}}\right)^{1/3} \tag{46}$$

Figure 32 shows the Monte Carlo simulation results of the miniemulsion polymerization assuming a uniform particle size distribution without the radical exit. In the comparison, the radical generation rate per initial amount of monomer is set to be the same for all calculations, including the bulk polymerization. For the bulk polymerization, $[R^\bullet]_{bulk} = \sqrt{R_I/k_t} = \sqrt{1\times10^{-7}/1\times10^{7}} = 1\times10^{-7}$ mol/L in the present calculation, and therefore, the

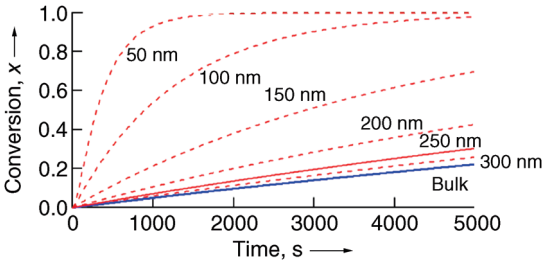


Figure 32. Calculated conversion development for miniemulsion polymerization in which the radical generation rate per unit oil phase is $R_i = 1 \times 10^{-7}$ mol L^{-1} s^{-1} [164] Rate constants: $k_p = 500$ L mol^{-1} s^{-1}, $k_t = 1 \times 10^7$ L mol^{-1} s^{-1}; initial monomer concentration $[M]_0 = 8$ mol/L

threshold diameter is calculated to be $d_c = 252$ nm. As shown in Figure 32, a significant polymerization rate increase is observed for $d < 250$ nm.

8.3. Molecular Mass Distribution

8.3.1. Linear Polymerization

For MMD theory in homogeneous free-radical polymerization, see → Polymerization Processes, 1. Fundamentals. The standard kinetics of conventional free-radical polymerization in homogeneous media leads to form the most probable distribution for the polymer radicals, the mass fraction distribution of which is given by:

$$M^{\bullet}(r) = r(\tau + \beta)^2 \exp[-(\tau + \beta)r] \tag{47}$$

$$\tau = \frac{R_{td} + R_f}{R_p} \tag{48}$$

$$\beta = \frac{R_{tc}}{R_p} \tag{49}$$

where r is the chain length, R_p is the propagation rate, R_{td} is the rate of termination by disproportionation, R_{tc} is the rate of termination by combination, and R_f is the rate of chain transfer reaction.

Chain-Transfer Dominated Systems. When the chain-transfer reaction dominates for the dead polymer chain formation, i.e., for the cases with $R_f \gg R_{tc}+R_{td}$, the instantaneous mass fraction distribution of the dead polymers is simply given by the following most probable distribution:

$$M_{inst.}(r) = r\tau_f^2 \exp(-\tau r) \tag{50}$$

where $\tau_f = R_f/R_p = (k_{fm}[M]_p + k_{fCTA}[CTA]_p/)$ $k_p[M]_p$, and k_{fm} and k_{fCTA} are the rate the constants for chain transfer reaction to monomer and to the chain transfer agent, CTA, respectively.

Notably, Equation (50) is valid, irrespective of the magnitude of $\overline{n}$. The number- and mass average chain lengths are given respectively by (→ Polymerization Processes, 1. Fundamentals):

$$\overline{P}_{n,inst.} = 1/\tau_f \tag{51}$$

$$\overline{P}_{M,inst.} = 2/\tau_f \tag{52}$$

This situation is exactly the same as that for homogeneous free-radical polymerization. In general, the concentrations $[M]_p$ and $[CTA]_p$ changes with the progress of polymerization, although $[M]_p$ may not change significantly during Interval 2 in emulsion polymerization. The accumulated chain length distribution can be obtained by summing up all instantaneous dead polymer chain length distribution. For a batch polymerization, the accumulated mass fraction distribution is given by:

$$M_{accum.}(r) = \frac{1}{x}\int_0^x M_{inst.}(r)\mathrm{d}x \tag{53}$$

MMD of the Zero–One Systems. For the zero–one system, because the second incoming radical will cause bimolecular termination instantaneously, $(R_{tc}+R_{td})/R_p$ is modified to $1/(k_p[M]_p\overline{t}_{entry})$, by referring to the radical entry rate to a polymer particle $\rho_A/N_T = 1/\overline{\tau}_{entry}$. Notably, $k_p[M]_p$ represents the number of monomeric units added to a radical center in 1 s (→ Polymerization Processes, 1. Fundamentals). Therefore, for the zero-one system in

emulsion polymerization, Equation (47) can be used by changing the definition of $\tau+\beta$ to:

$$\tau + \beta = \tau_f + \frac{1}{k_p[M]_p \bar{t}_{entry}} \tag{54}$$

If the dead polymer chain is formed by the chain-transfer reaction, the chain length is the same as that of the polymer radical just before chain stoppage, which is given by Equation (47). When a dead chain is formed by combination termination, an oligomeric radical chain is added to a polymer radical. Because the contribution of the oligimeric chain part is small, the dead polymer chain length is essentially the same as that of the polymer radical just before chain stoppage. Finally, if a dead chain is formed by disproportionation, a dead polymer chain with the same chain length as the polymer radical and an oligomeric dead polymer chain are formed. In summary, if one neglects the oligomeric dead chain formed by disproportionation termination whose mass fraction is negligibly small, the instantaneous dead polymer chain length distribution is essentially the same as that given by Equation (47), with $\tau + \beta$ represented by Equation (54). The effect of oligomeric chains formed by disproportionation termination will be discussed again for the cases where most of the dead polymer chains are formed by termination reactions.

In emulsion polymerization, $\bar{t}_{entry}$ is usually larger than 10 s, and therefore, the dead chain formation is often dominated by chain transfer reaction, whose instantaneous MMD of dead polymer is shown by:

$$M_{inst.}(r) = r\tau_f^2 \exp[-\tau_f r] \tag{55}$$

Without using external CTA and by making $\bar{t}_{entry}$ large enough, it is not difficult to obtain an emulsion polymerization system in which the chain transfer to monomer dominates the dead polymer chain formation. Under such condition, the number fraction distribution of dead polymer chains is given by:

$$N(r) = C_m \exp(-C_m r) \tag{56}$$

where C_m the monomer transfer constant, $C_m = k_{fm}/k_p$.

Notably, when the monomer transfer reaction dominates the dead polymer chain formation, the chain length drift does not occur irrespective of the reactor types used, including the emulsion polymerization. Therefore, from the slope of $\ln[N(r)]$, one can experimentally determine the monomer transfer constant [165–169].

$$\frac{d\ln N(r)}{dr} = -C_m \tag{57}$$

When applying Equations (56) and (57) to emulsion polymerization, (1) the experimental condition must be set to satisfy the condition, $C_m \gg 1/\left(k_p[M]_p \bar{t}_{entry}\right)$, and (2) the surfactant must not cause any reaction with radicals. In addition, (3) the total number of monomeric units polymerized in a particle, u must satisfy $uC_m \gg 1$ [170], because the polymer chain formed during Interval 1 and the final polymer chain that might be stopped abruptly may not follow the distribution given by Equation (56). This requirement implies that the polymerization must not be stopped at very low conversion region, which is a different requirement when using a bulk polymerization for the parameter estimation. Finally, careful attention must be paid to (4) the effect of chain transfer to polymer. The locus of polymerization in emulsion polymerization is the monomer-swollen polymer particle, and the polymer concentration in the polymerization locus is higher than the corresponding bulk polymerization from the beginning. Even for the reaction systems in which the polymer transfer reaction can be neglected in bulk polymerization, the effect of chain transfer to polymer may not be neglected in emulsion polymerization.

Figure 33 shows an example of the MC simulation results that involves the polymer transfer reactions [170]. The C_m value used was 5×10^{-5}, the polymer transfer constant, $C_{fp} = k_{fp}/k_p = 1 \times 10^{-5}$. The MMD shown is at the time when the total number of monomer units bound into polymer in a particle is $u = 1 \times 10^6$. More details on the simulation condition can be found therein [170].

Figure 33A shows the mass-fraction distribution when the independent variable is the logarithm of chain length, which is usually reported in the gel permeation chromatography

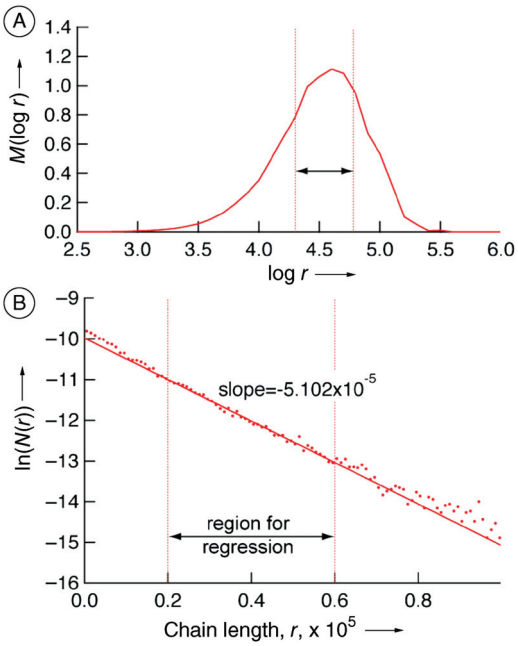


Figure 33. Monte Carlo simulation results for emulsion polymerization with polymer transfer reactions, with constant monomer/polymer ratio in the polymer particles [170]
A) Mass-chain-length distribution as a function of the logarithm of the chain length r; B) Semi-log plot of the number fraction distribution.

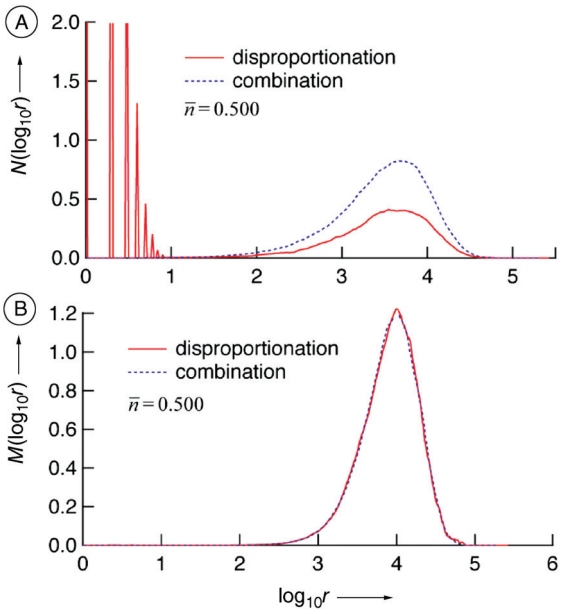


Figure 34. Calculated instantaneous chain length distribution formed in emulsion polymerization with $\overline{n} = 0.5$ and no radical exit [155]
A) Number fraction distribution; B) Mass fraction distribution

(GPC) measurements. Figure 33B shows the semi-log plot of the number fraction distribution $N(r)$, using the same MC simulation data. The distribution deviates from a straight line because of the polymer transfer reaction. However, by using the chain-length data around the peak region in $M(\log r)$, not the high MM tail, one can estimate the C_m value (5×10^{-5}) rather accurately, in spite of the existence of polymer-transfer reactions [170].

Because $\overline{t}_{entry}$ is large in usual emulsion polymerization, the chain-transfer reactions to monomer/CTA tend to be dominant to form dead polymer chains. Even when the polymerization rate is increased due to the gel effect (i.e., decrease in the bimolecular termination rate constant), the MMD still follows Equation (55), as long as most of dead polymer chains are formed by chain transfer reactions. Therefore, when the CTA is used effectively, the MMD is controlled by chain transfer to CTA whose instantaneous MMD is given by Equation (55) with $\tau_f = C_{fCTA}[CTA]_p/[M]_p$.

Theoretically, however, it is important to know the MMD formed by bimolecular termination reactions. Figure 34 shows the MC simulation results of the chain length distribution, assuming all polymer chains are formed by bimolecular termination with $\overline{n} = 0.5$. Figure 34A gives the number fraction distribution $N(\log_{10} r)$. When the bimolecular termination mode is by disproportionation, very large discrete peaks (spikes) appear for $r<10$ (or $\log_{10} r<1$), which correspond to the chains with length $r = 1, 2, 3$, and so on. With disproportionation termination, one half of dead polymer chains in number are oligomers. These oligomers are formed by the newly entered radicals that add a few monomeric units before almost instantaneous termination. Note that a radical can add $k_p[M]_p$ monomeric units in a second, and for example, assuming $k_p[M]_p = 1 \times 10^3$, 5 monomeric units are added in 5×10^{-3} s. As a limit of instantaneous termination, the PDI for the instantaneous MMD formed solely by disproportionation termination is $\overline{P}_{M,inst.}/\overline{P}_{n,inst.} = 4$. On the other hand, if the termination mode is by combination, the

contribution of such oligomeric chain part is negligible in the dead polymer distribution, and the instantaneous MMD basically follows the most probable distribution given by Equation (47) with $\tau = 0$, whose PDI is $\overline{P}_{M,\text{inst.}}/\overline{P}_{\text{n,inst.}} = 2$.

Figure 34B shows the same distribution plotted on a mass basis, $M(\log_{10} r)$. In a GPC measurement, this type of distribution is obtained. The large spikes in the oligomeric range observed for the number fraction distribution disappear, because these spikes are large in number but negligibly small in weight. On the basis of Figure 34B, it is expected that the oligomeric spikes formed by disproportionation termination cannot be detected in the GPC measurement. In terms of the mass fraction distributions $M(\log_{10} r)$, the difference in the termination mode cannot be found, and both types of distribution agree completely. Note however, the agreement simply results from the inability of detecting oligomer chains formed in disproportionation termination.

With disproportionation termination, the oligomeric spikes move toward larger chain lengths as the $\overline{n}$-value increases, and the PDI decreases, as shown in Figure 35. The PDIs approach those for homogeneous polymerization, i.e. $\overline{P}_{M,\text{inst.}}/\overline{P}_{\text{n,inst.}} = 2$ for disproportionation and $\overline{P}_{M,\text{inst.}}/\overline{P}_{\text{n,inst.}} = 1.5$ for combination termination.

The MMD formed at $\overline{n} = 2$ is already very close to that formed in bulk polymerization [155]. As was shown in Figure 30, the M polymerization rate also reduces to that for bulk polymerization for $\overline{n} > 2$. The unique characteristics of emulsion polymerization kinetics are lost for $\overline{n} > 2$, and the pseudo-bulk behavior prevails, for which the simple bulk polymerization kinetics apply.

The deterministic calculation method for the MMD formed in linear emulsion polymerization, on the basis of the population balance equations, can be found in [171–177]. The complexity and uniqueness of emulsion polymerization kinetics result from the fact that the locus of polymerization is very small, often smaller than a few hundred nanometers. On the other hand, this characteristic is a great advantage for an MC simulation method [178]. Suppose the diameter of a particle consisting of polymer chains is $d = 100$ nm, the density of the polymer is 1 g/cm^3, and the molecular mass of monomeric unit in polymer is 100. In this case, the total number of monomeric units in the particle is 3×10^6. Assuming the number-average chain length of polymer molecules is 1×10^4, which is not unusually large in emulsion polymerization, the total number of polymer chains in a particle is only 300. For such a small number of polymer molecules, one can readily simulate the formation processes of all polymer molecules using the MC method with a well-designed simulation algorithm. In fact, some of the figures already shown in this and previous sections are based on the MC simulation results. In addition, it is straightforward to account for any kinetic event in the MC method. Some of the important results shown in the next sections are based on such a direct simulation method.

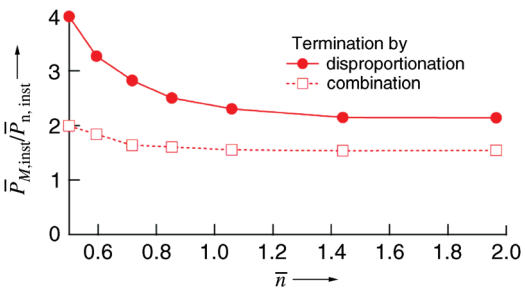


Figure 35. Calculated polydispersity index ($\overline{P}_{M,\text{inst.}}/\overline{P}_{\text{n,inst.}}$) as a function of $\overline{n}$, assuming all polymer chains are formed by bimolecular termination reactions in emulsion polymerization [155]

8.3.2. Nonlinear Polymerization

Nonlinear polymerization, such as with chain transfer to polymer and/or cross-linking reactions, involves reaction with dead polymer molecules. In emulsion polymerization, the polymer concentration is high from the beginning, and therefore, the branching and/or cross-linking density is higher in emulsion polymerization, compared with the corresponding bulk polymerization.

Figure 36 shows an example of the average cross-linking density development. The average cross-linking density is high from the early

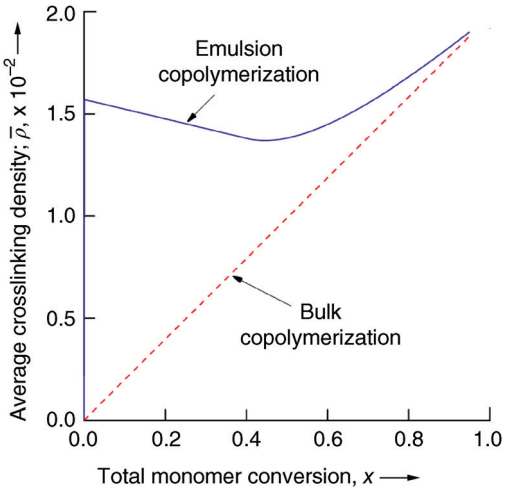


Figure 36. Calculated average cross-linking density development during bulk and emulsion copolymerization of vinyl/divinyl monomer when the reactivities of all double bonds are equal [178]
Initial mole fraction of divinyl monomer: $f_2^0 = 0.01$; monomer conversion at which monomer droplets disappear: $x_{c2} = 0.4$

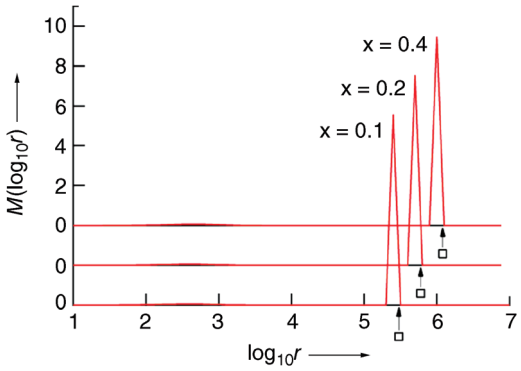


Figure 37. Example of the calculated mass fraction distribution $M(\log\ r)$ formed in emulsion cross-linking copolymerization, with microgels formed from the beginning [180]

stage of emulsion polymerization. A higher cross-linking density may result in unique behavior in emulsion cross-linking polymerization. A microgel may exist from very early stages of emulsion polymerization, and one polymer particle may essentially consist of a single cross-linked polymer molecule. In such a case, a sharp high molecular mass peak that proceeds to larger molecular mass with the progress of polymerization might be found, as the MC simulation shown in Figure 37 predicts. The arrows show the total number of monomeric units bound in polymer, which give the size of a dried polymer particle. For highly cross-linked cases, the MMD is essentially equivalent to the particle size distribution [180, 181]. For more mildly cross-linked systems, bimodal MMD may be formed due to the limitation of the maximum polymer size attainable in a polymer particle [180, 182].

Larger cross-linking density during Interval 1 leads to lower swelling ratio, resulting in a lower monomer concentration. Equation (44) predicts that a lower volumetric growth rate per particle μ results in a larger number of polymer particles N_T, which was reported in the experimental study [183].

For the cases with the polymer-transfer reaction, the branching reaction is enhanced by a larger polymer concentration in emulsion polymerization, similarly as in the case of a CSTR, discussed in Section (4.4). A notable difference of emulsion polymerization is that the size of a reaction locus is very small and there exists the molecular mass limit containable in a particle [178, 184, 185].

To highlight the most fundamental aspects of the limited space effect, consider the case where dead polymer chain formation is dominated by chain transfer to monomer and to polymer. In this case, the primary polymer chain length distribution follows the most probable distribution whose number fraction distribution is given by:

$$N_p(r) = (C_m + C_P)\exp[-(C_m + C_P)r] \tag{58}$$

where $C_P = R_{fp}/R_p$.

Assuming a constant polymer/monomer ratio until the end of Interval 2, C_P is a constant. Therefore, the primary polymer chain length distribution is unchanged until the end of Interval 2. The probability that the chain end of a primary chain is connected, P_b is given by:

$$P_b = \frac{C_P}{C_m + C_P} \tag{59}$$

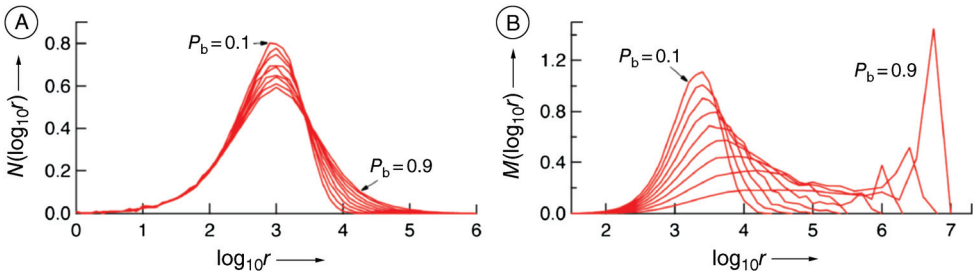


Figure 38. Calculated chain-length distribution for the branched polymer molecules formed in emulsion polymerization with $C_m + C_P = 1 \times 10^{-3}$, which means the number average chain length of the primary chain is $\overline{P}_{np} = 1000$ [185]
A) Number fraction distribution; B) Mass fraction distribution

which is also a constant until the end of Interval 2.

Figure 38 shows the MC simulation results assuming constant values of C_p and P_b. In the figure, the value of P_b is changed from 0.1 to 0.9, with 0.1 increments. These distributions are at the time when the total number of monomeric units bound into polymer in a particle is $n = 1 \times 10^7$. Assuming the molecular mass of the monomeric unit 100 and the density of polymer 1 g/cm^3, $n = 1 \times 10^7$ corresponds to the dried polymer particle with diameter, $d = 147$ nm. The number fraction distribution $N(\log_{10}r)$ shows a smooth, single peak curve, irrespective of the P_b value. On the other hand, the mass fraction distribution $M(\log_{10}r)$, which is normally reported in the GPC analysis, becomes bimodal because of the limitation of the particle size, which corresponds to the maximum chain length, $\log_{10}n$=7. A bimodal $M(\log_{10}r)$ is formed for $P_b > 0.5$.

Similarly with the case for a CSTR discussed in Section 4.4, the power low distribution, $M(r) \sim r^{-\alpha}$ is formed for a constant P_b, with a relationship, $\alpha = 1/P_b$ [185]. Even for the cases with the bimodal distribution in $M(\log_{10}r)$, the power law holds for the chain length region in between two peaks [185]. This feature could be used to determine the polymer transfer constant C_{fp}, on the basis of a well designed emulsion polymerization experiment.

With the MC simulation, one can observe the structure of each polymer molecule directly on a computer screen. An example of 2D structure is shown in Figure 39.

8.4. Effect of Small Reaction Loci in Reversible-Deactivation Radical Polymerization

As discussed in → Polymerization Processes, 1. Fundamentals and also in [164, 186], the reversible-deactivation radical polymerization (RDRP) in the IUPAC recommended name [96], often referred to as controlled/living radical polymerization, the pseudo-livingness is endowed by adding one of the reversible reactions depicted in Figure 40. In SRMP and ATRP, the equilibrium lies to the dormant (P_iX) side and [RGS] $\gg$ [Trap]. In RAFT, not necessarily but often, [RGS] $\ll$ [Trap].

RDRP is a free-radical polymerization, and therefore, the polymerization rate is

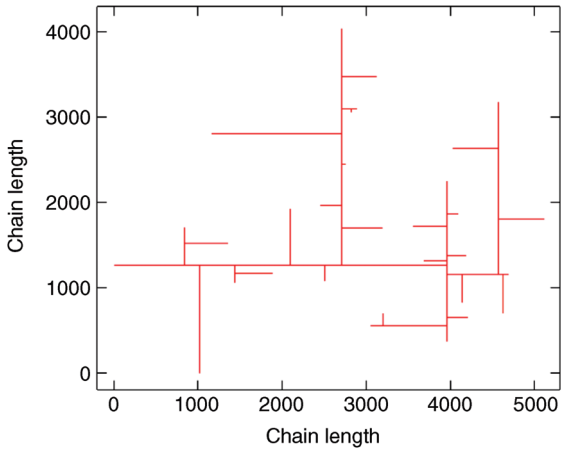


Figure 39. Example of a branched polymer structure formed in a model emulsion polymerization, with P_b = 0.7 and $C_m + C_P = 1 \times 10^{-3}$

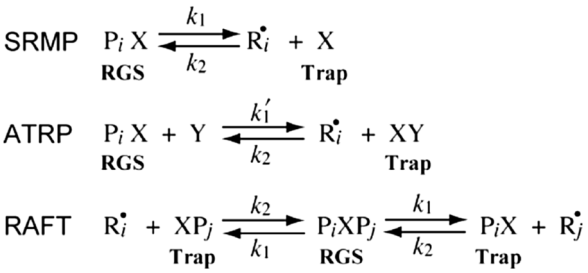


Figure 40. Reversible-deactivation scheme in each type of RDRP
P_iX, XP_i = dormant polymer with chain length $R_i^{\bullet}$ = active polymer radical with chain length i; SRMP = stable-radical-mediated polymerization; ATRP = atom-transfer radical polymerization; RAFT = reversible-addition-fragmentation chain-transfer polymerization; RGS = radical generating species; Trap = trapping agent for the active radical

represented by $R_p = k_p[M][R^{\bullet}]$. In this section, however, the effect of small reaction locus (d smaller than a few hundred nanometers) is rationalized by using the following characteristic polymerization rate expression unique to RDRP (→ Polymerization Processes, 1. Fundamentals).

$$R_p = k_p[M]K\frac{[RGS]}{[Trap]} \tag{60}$$

where $K = k_1/k_2$, with $k_1 = k_1'[Y]$ for ATRP.

Here, we consider an ideal miniemulsion polymerization system with a uniform droplet diameter d_p, and each droplet can be considered as an independent batch reactor. Let us overview an important characteristics for each type of RDRP, based on Equation (60).

8.4.1. Stable Radical-Mediated Polymerization (SRMP) and Atom-Transfer Radical Polymerization (ATRP)

In SRMP and ATRP, [RGS] ≫ [Trap], and therefore, by making the droplet size smaller, the number of trapping agent (Trap) molecules becomes very small, while there still exists a large number of RGS molecules. When the number of Trap molecules in a particle becomes as small as unity, this single molecule concentration could be larger than that in the corresponding bulk polymerization, as was shown in Table 3. Because [Trap] is in the denominator in the polymerization rate expression given by Equation (60), the polymerization rate will become smaller than that for a bulk polymerization. The threshold droplet diameter below which the miniemulsion polymerization rate becomes smaller than the corresponding bulk polymerization, due to a high single-molecule concentration effect, can be estimated as follows.

The concentration of a single molecule in a particle with diameter d_p is given by $1/\{N_A(\pi/6)d_p^3\}$. When this concentration is equal to the trapping agent concentration in the corresponding bulk polymerization, the polymerization rate would be equal to that in bulk polymerization, given all the other conditions are the same. The particle size below which the polymerization rate becomes smaller than in the corresponding bulk polymerization, $d_{p,Trap}^{(1)}$ is given by:

$$d_{p,Trap}^{(1)} = \left(\frac{6}{\pi N_A[Trap]_{bulk}}\right)^{1/3} \tag{61}$$

Note that the trapping agent concentration in the corresponding bulk polymerization $[Trap]_{bulk}$ can be calculated in a straightforward manner by solving the material balance equations. For example, for SRMP,

$$\frac{d[R^{\bullet}]}{dt} = R_I - k_t[R^{\bullet}]^2 + k_1[PX] - k_2[R^{\bullet}][X] \tag{62}$$

$$\frac{d[X]}{dt} = k_1[PX] - k_2[R^{\bullet}][X] \tag{63}$$

are solved with the relationship, $[PX]_0 + [X]_0 = [PX] + [X]$, to determine $[Trap]_{bulk} = [X]$.

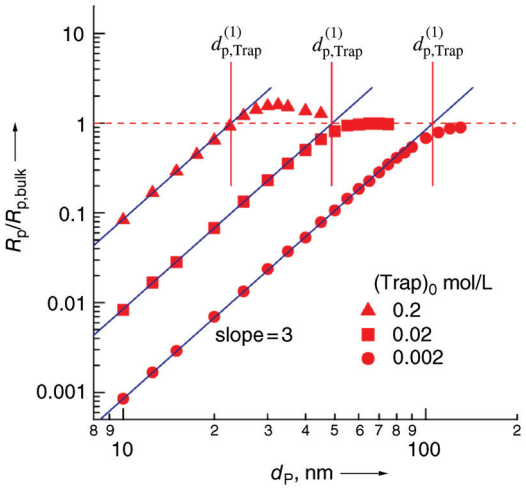


Figure 41. Calculated polymerization rates for the TEMPO-mediated styrene polymerization at 10% conversion with $[PX]_0 = 0.2$ mol/L [187]

The symbols in Figure 41 show the calculated polymerization rate for the 2,2,6,6-tetramethylpiperidyl 1-oxyl (TEMPO)-mediated styrene polymerization at 10 % conversion with $[PX]_0 = 0.2$ mol/L, reported in [187]. The $d^{(1)}_{p,Trap}$ values shown in the figure are calculated by using Equation (61), which predict the onset of significant polymerization rate decrease reasonably well [188].

Equation (60) shows that R_p is proportional to 1/[Trap]. For the particle size region where the high single-molecule concentration effect is significant, [Trap] is given by $[Trap]_p = 1/(N_A v_p)$ and the particle volume $v_p \propto d_p^3$. Therefore, the relationship $R_p \propto 1/[Trap]_p \propto d_p^3$ holds for $d_p < d^{(l)}_{p,Trap}$. This is the reason for the lines with slope = 3 for $d_p < d^{(l)}_{p,Trap}$ in Figure 41. Lower polymerization rates in smaller polymer particles make it difficult to conduct the ab initio emulsion polymerization in SRMP and ATRP.

The decrease in R_p for smaller particles was reported experimentally [189]. Note however, desorption of trapping agents is neglected, which may cause deviation from the fundamental theory discussed herein.

The particle size region for which a slightly larger R_p, compared with $R_{p,bulk}$, is predicted to be formed for $d_p > d^{(1)}_{p,Trap}$. This is due to the statistical variation in the number of trapping agents in a particle [188], although the decreased frequency of termination for a radical due to the segregation of radicals may contribute the rate increase for bad living conditions in which the bimolecular termination is not suppressed well in bulk polymerization [190, 191]. The statistical variation effect is rationalized as follows. Because the number of monomer and RGS in a particle are large enough, the statistical variations of these components are negligible. On the other hand, the statistical variation effects may not be neglected when the average number of the trapping agents becomes smaller than about $\overline{n}_{Trap} = 10$. As an illustrative example, suppose that we have three particles containing 1, 2 and 3 trapping agents, respectively. In this case, the average number of trapping agents is $\overline{n}_{Trap} = 2$, and $[Trap]_{bulk} = \overline{n}_{Trap}/(N_A v_p)$ in the corresponding bulk polymerization, i.e., $R_{p,bulk} \propto 1/[Trap]_{bulk} \propto 1/\overline{n}_{Trap}$. On the other hand, in the miniemulsion polymerization, a strict representation of polymerization rate expression should be $R_p \propto \langle 1/[Trap]_i \rangle \propto \langle 1/n_{Trap,i} \rangle$, where the subscript i indicate the ith particle and $\langle\rangle$ is the appropriate average for all particles. Assuming uniform particles, the above hypothetical example leads to $\langle 1/n_{Trap,i} \rangle = (1 + 1/2 + 1/3)/3 = 0.611 > 0.5 = 1/\overline{n}_{Trap}$. Therefore, the miniemulsion polymerization rate is expected to be 1.22 times faster than the corresponding bulk polymerization. Because the average of the inverse numbers is always larger than the inverse of the average, the miniemulsion polymerization shows a larger polymerization rate than the corresponding bulk polymerization, when the statistical variation of n_{Trap} cannot be neglected. The effect of statistical variation becomes significant when $\overline{n}_{Trap} < 10$ [188], and the threshold particle diameter, below which R_p becomes noticeably larger than the corresponding bulk polymerization, $d^{(sv)}_{p,Trap}$ could be estimated from:

$$d^{(sv)}_{p,Trap} = \left(\frac{60}{\pi N_A [Trap]_{bulk}}\right)^{1/3} \tag{64}$$

Therefore, an acceleration window, $d^{(1)}_{p,Trap} < dp < d^{(sv)}_{p,Trap}$ in which $R_p/R_{p,bulk} > 1$ is predicted for SRMP and ATRP. On the other hand, the effect of the particle size distribution as well as

the exit of trapping agent, which is not accounted for in the present fundamental theory, may need to be considered in the actual miniemulsion polymerization.

8.4.2. Reversible Addition–Fragmentation Chain Transfer (RAFT) Polymerization

In RAFT polymerization, the concentration of RGS (PXP) is smaller than that of Trap (XP or RAFT agent), and therefore, RGS is the candidate that may cause the high single-molecule concentration effect. Because [RGS] is the numerator term in Equation (60), a significant polymerization rate increase is expected for $d_p < d_{p,RGS}^{(1)}$. The threshold particle diameter, $d_{p,RGS}^{(1)}$ can be formulated as follows.

Practically, a significant polymerization rate increase due to the high single-molecule concentration effect occurs only for the systems with zero-one behavior. The zero–one behavior shown in Figure 28 is now modified for RAFT miniemulsion polymerization, as shown in Figure 42. During the active period, the number of propagating radical $n_{R\cdot}$, or equivalently, the number of PXP molecules, n_{PXP} changes between zero and one repeatedly in a complementary manner.

The frequency of radical deactivation is $k_2[R^\bullet][XP]/[R^\bullet] = k_2[XP]\ s^{-1}$. Therefore, the average time for being a radical is $\bar{t}_{R\cdot} = 1/(k_2[XP])$. Similarly, the average time for being an intermediate is $\bar{t}_{PXP} = 1/k_1$. The time fraction of the active radical period during $n = 1$ is given by:

$$\phi_A = \frac{\bar{t}_{R\cdot}}{\bar{t}_{R\cdot} + \bar{t}_{PXP}} = \frac{K}{K + [XP]} \tag{65}$$

where $K = k_1/k_2$.

Therefore, the effective PXP concentration in a zero-one particle is $\bar{n}(1-\phi_A)/\left(N_A v_p\right) = 6\bar{n}(1-\phi_A)/\left(\pi N_A d_p^3\right)$. By equating this concentration with $[PXP]_{bulk}$, the particle size below which the polymerization rate starts to become much larger than in the corresponding bulk polymerization, $d_{p,PXP}^{(1)}$ is given by:

$$d_{p,PXP}^{(1)} = \left(\frac{6\bar{n}(1-\phi_A)}{\pi N_A [PXP]_{bulk}}\right)^{1/3} \tag{66}$$

It is known that the RAFT polymerization rate shows retardation behavior by increasing the concentration of the RAFT agent. To rationalize the retardation, two conflicting models were proposed. One model [192] assumes that the intermediate radical, PXP terminates with the propagation radical $R^\bullet$, which is sometimes referred to as the intermediate termination (IT) model. On the other hand, a slower fragmentation of PXP can also cause retardation [193], which is called the slow fragmentation (SF) model. Both models fit with bulk polymerization data reasonably well, but the estimated k_1 value for the same reaction system could be more than 10^5 times larger for the IT model than the SF model [194]. The large difference in k_1 leads to a significant difference in the PXP concentration, i.e., $[PXP]_{bulk,IT} \ll [PXP]_{bulk,SF}$.

Equation (66) shows that larger $[PXP]_{bulk}$ results in a smaller threshold diameter. Figure 43 shows an example of the calculated threshold diameter change during RAFT polymerization of styrene [186]. In the IT model, a significant polymerization rate increase is predicted for $d_p < 212$ nm. On the other hand, the $d_{p,PXP}^{(1)}$ value is too small to actually conduct the miniemulsion polymerization.

Figure 44 shows the MC simulation results for the conversion development during

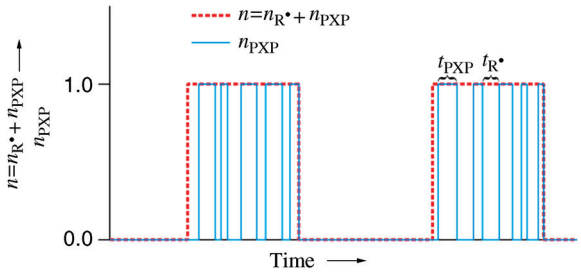


Figure 42. Schematic representation of the zero–one behavior in RAFT miniemulsion polymerization

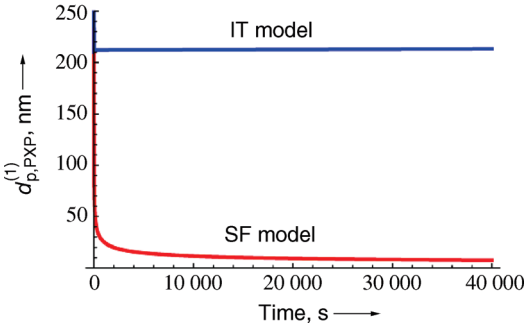


Figure 43. Calculated threshold diameter, using representative parameters for the styrene RAFT polymerization [186]

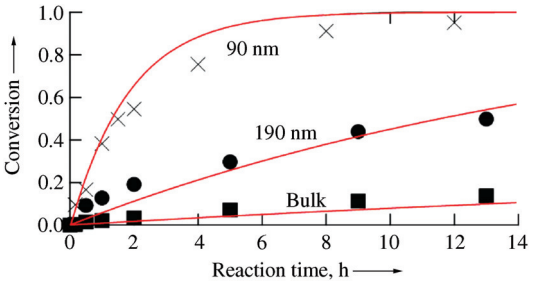


Figure 45. Conversion development during polystyryl dithiobenzoate mediated styrene miniemulsion polymerization at different particle sizes at 60°C [195]
Solid lines: MC simulation results using the IT model; symbols: experimental data

miniemulsion polymerization, by using the same set of parameters as in Figure 43. In the IT model (Figure 44A), the miniemulsion polymerization shows significant polymerization rate increase for $d_p < 212$ nm, as predicted by Equation (66) and shown in Figure 43. In the case of SF model (Figure 44B), the $d^{(1)}_{p,PXP}$ value is too small, and the polymerization rate is not changed by the particle size.

This characteristic can be used for the model discrimination. The symbols in Figure 45 show the experimental results of the polystyryl dithiobenzoate mediated styrene miniemulsion polymerization at 60°C, conducted by changing the particle size. Because a significant polymerization rate increase is observed in miniemulsion polymerization, it can be considered that the IT model applies to this reaction system [195]. The curves are the MC simulation results, using the IT model parameters. This conclusion agrees with the electron paramagnetic resonance (EPR) measurement results [196].

Various aspects of RDRP in emulsified systems are discussed in [120, 197–199].

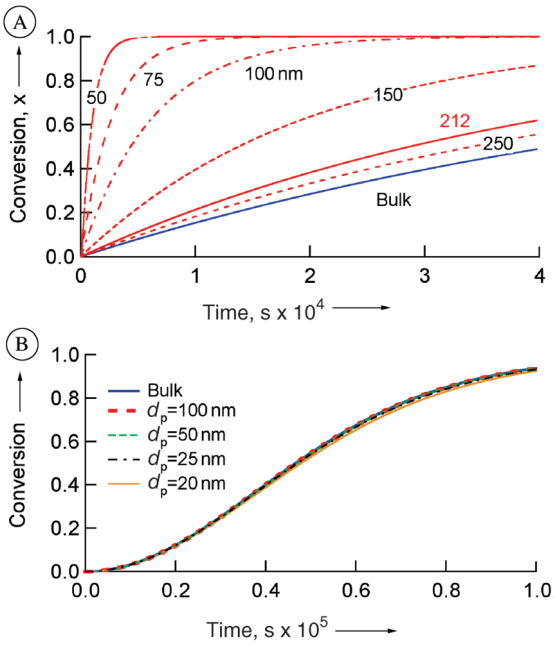


Figure 44. Monte Carlo simulation results for IT and SF model, with the same parameters as in Figure 43, showing the particle-size (d_p) effect on the miniemulsion polymerization rate A) IT model; B) SF model

List of Symbols

a	parameter for the calculation of the $\bar{n}$ value, $a = (8\alpha)^{0.5}$
a_s	surface area occupied by a unit amount of surfactant
ABS	acrylonitrile–butadiene–styrene rubber modified coplymer
ACA	aminocaproic acid
ATRP	atom-transfer radical polymerization
BHET	bis(hydroxyethyl)terephthalate
BR	batch reactor
CCD	chemical composition distribution
C_{fp}	polymer transfer constant ($=k_{fp}/k_p$)
C_m	monomer transfer constant ($=k_m/k_p$)
C_M	monomer concentration

CMC critical micelle concentration
C_P rate ratio between chain transfer to polymer and propagation, $C_P = R_{fp}/R_p$
CSTR continuous stirred tank reactor
CTA chain-transfer agent
d diameter
d_c threshold particle diameter below which the miniemulsion polymerization rate starts to become larger than the corresponding bulk polymerization
d_p diameter of polymer particle
$d^{(1)}_{p,Trap}$ threshold particle diameter below which the miniemulsion polymerization rate of RDRP starts to become *smaller* than the corresponding bulk polymerization due to a high *single-molecule concentration effect* of Trap
$d^{(sv)}_{p,Trap}$ threshold particle diameter below which the miniemulsion polymerization rate of RDRP starts to become *larger* than the corresponding bulk polymerization due to the *statistical variation effect* of Trap
$d^{(1)}_{p,PXP}$ threshold particle diameter below which the miniemulsion polymerization rate of RAFT starts to become *larger* than the corresponding bulk polymerization due to a high *single-molecule concentration effect* of PXP
$d^{(1)}_{p,RGS}$ threshold particle diameter below which the miniemulsion polymerization rate of RDRP starts to become *larger* than the corresponding bulk polymerization due to a high *single-molecule concentration effect* of RGS
DMT dimethyl terephthalate
D_w diffusion coefficient of oligomer radicals in water phase
EG ethylene glycol
$E(\theta)$ residence time distribution function
f_1 mole fraction of monomer 1 in copolymerization
f_1^0 initial mole fraction of monomer 1 in copolymerization
F_1 mole fraction of monomer 1 bound in polymer produced instantaneously in copolymerization
$\overline{F}_1$ mole fraction of monomer 1 bound in accumulated copolymer
F_M molar flow rate of monomer
GPC gel permeation chromatography
HCSTR homogeneous continuous stirred tank reactor
HDPE high-density polyethylene
I initiator
$[I]_0$ Initial initiator concentration
$I_m(x)$ modified Bessel function of the first kind
IT intermediate termination in RAFT polymerization
k_1 activation rate constant in RDRP
k_2 deactivation rate constant in RDRP
k_A entry rate coefficient for the radicals from the water phase to the polymer particles
k_f desorption rate constant of a radical
k_{fCTA} rate constant for chain transfer to CTA
k_{fm} rate constant for chain transfer to monomer
k_{fp} rate constant for chain transfer to polymer
k_{fX} rate constant for chain transfer to small molecule, X
k_p propagation rate constant
k_t rate constant for bimolecular termination ($=k_{tc}+k_{td}$)
k_{tc} rate constant for bimolecular termination by combination
k_{td} rate constant for bimolecular termination by disproportionation
k_{tw} rate constant for bimolecular termination in the water phase
L reactor length
L segment length
LDPE low-density polyethylene
LLDPE linear low-density polyethylene
m dimensionless rate ratio, between radical exit and termination, $m = 2k_f v_p N_A/k_t$
M monomer
[M] monomer concentration
$[M]_0$ initial monomer concentration

MC	Monte Carlo
$[M]_d$	monomer concentration in monomer droplets
$\overline{M}_n$	number-average molecular mass
M_m	molecular mass of monomer
$[M]_p$	monomer concentration in polymer particles
MMD	molecular-mass distribution
$\overline{M}_M$	mass-average molecular mass
$M(r)$	mass chain length distribution
$M_{accum.}(r)$	mass chain length distribution of accumulated polymer
$M_{inst.}(r)$	"instantaneous" mass chain length distribution
$M^{\bullet}(r)$	mass chain length distribution of polymer radicals
$M(\rho_b)$	mass fraction of monomeric units in polymer whose expected branching density is ρ_b
n	number of monomer types in multicomponent polymerization
n	number of radicals in a particle, or the sum of $R^{\bullet}$ and PXP in the case of RAFT miniemulsion polymerization
$\overline{n}$	average number of radicals in a polymer particle
n_{PXP}	number of PXP molecules in a particle for RAFT miniemulsion polymerization
$n_{R^{\bullet}}$	number of active radicals in a particle for RAFT miniemulsion polymerization
N	number of tanks in the tanks-in-series model
N	number of particles per liter of latex
N_A	Avogadro constant
N_M	number of moles of monomer molecules
N_n	number of particles containing n radicals per unit volume of water-phase
N_p	number of polymer particles per liter of latex
$N(r)$	number chain length distribution (number-fraction of polymer molecules of length r)
N_T	number of polymer particles per liter of water-phase
p	conversion of functional group in step polymerization
P_b	probability that the head of a primary chain is connected to a backbone chain
PEK	polyetherketone
PES	polyethersulfone
PET	poly(ethylene telephthalate)
PFR	plug flow reactor
P_i	number of moles of monomer i chemically bound in the polymer
$\overline{P}_n$	number-average chain length (degree of polymerization)
$\overline{P}_{n,inst.}$	number-average chain length of dead polymer chains formed instantaneously
PPS	poly(phenylene sulfide)
P_r	polymer with chain length, r
$\overline{P}_M$	mass-average chain length (degree of polymerization)
$\overline{P}_{M,inst.}$	mass-average chain length of dead polymer chains formed instantaneously
PXP	intermediate adduct radical formed in RAFT polymerization
$[PXP]_{bulk}$	PXP concentration in bulk RAFT polymerization
Q_i	i-th moment of polymer distribution
r	polymer chain length (degree of polymerization)
r_0	radius of unswollen polymer particle
r_1, r_2	reactivity ratios
R	gas constant
$R^{\bullet}$	active polymer radical
$[R^{\bullet}]$	radical concentration
$[R^{\bullet}]_{bulk}$	radical concentration in the case of bulk polymerization
$[R^{\bullet}_w]$	radical concentration in the water phase
RAFT	reversible-addition-fragmentation chain-transfer
RDRP	reversible-deactivation radical polymerization
R_f	rate of chain transfer
R_{fX}	rate of chain transfer to small molecule X
RGS	radical generating species in RDRP
R_I	initiation rate
RIM	reaction injection molding
R_p	polymerization rate

R_t termination rate ($=R_{tc}+R_{td}$)
R_{tc} rate of termination by combination
R_{td} rate of termination by disproportionation
RTD residence time distribution
$<s^2>$ mean-square radius of gyration
$[S]_0$ charged surfactant concentration
SCSTR segregated continuous stirred tank reactor
SF slow fragmentation in RAFT polymerization
$[Single]_p$ concentration of a single molecule in a polymer particle
SRMP stable radical-mediated polymerization
t time
$\overline{t}$ mean residence time
$\overline{t}_{entry}$ average time interval between radical entry
T temperature
TPA terephthalic acid
Trap trapping agent in RDRP
$[Trap]_{bulk}$ concentration of trapping agent in bulk RDRP polymerization
v volumetric flow rate
v_p volume of a polymer particle
u total number of monomeric units polymerized in a particle
U number of monomeric units in a random walk segment
V reactor volume
V_d total volume of monomer droplets in the reactor
V_m molar volume of monomer in polymer particle
V_p total volume of polymer particles in the reactor
x monomer conversion
x_{c2} monomer conversion at which Interval 2 ends in ab initio emulsion polymerization
X small molecule that causes chain-transfer reaction
Y parameter indicating the significance of termination with respect to radical entry, defined by $Y = \frac{k_{tw}k_t}{2k_A^2 v_p N_A N_T}$
z spatial coodinate
α power exponent for the power-law distribution
α dimensionless rate ratio, between radical entry and termination in a particle, $\alpha = 2\rho_A v_p N_A/(k_t N_T)$
α_w dimensionless rate ratio, between initiation in the water phase and termination in a particle, $\alpha_w = 2\rho_w v_p N_A/(k_t N_T)$
β kinetic dimensionless parameter ($=R_{tc}/R_p$)
θ dimensionless residence time $= t/\overline{t}$
μ volumetric growth rate per particle
ξ conversion at which given primary chain was born
ξ dimensionless rate ratio, between termination and propagation in a particle, $\xi = k_t/\left(k_p[M]_p v_p N_A\right)$
ρ_A total radical entry rate from the aqueous phase to the polymer particles
ρ_b branching density
$\rho_b(\xi, \psi)$ expected branching density of the primary chain formed at $x = \xi$, when the conversion at the present time is ψ
$\overline{\rho}_b$ average branching density
ρ_m density of monomer
ρ_p density of polymer
$\overline{\rho}_s$ average scission density
ρ_w initiation rate in the water phase
σ interfacial tension
τ kinetic dimensionless parameter $[=(R_{td}+R_f)/R_p]$
τ_f kinetic dimensionless parameter $[=R_f/R_p]$
ϕ_A time fraction of the active radical period in RAFT polymerization
ϕ_p volume fraction of polymer in polymer particle
$\Phi_p(n)$ number fraction of particles containing n radicals
χ Flory–Huggins polymer-solvent interaction parameter
ψ conversion at the present time

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Plastics Processing, 1. Processing of Thermoplastics

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This article considers the processing of thermoplastics to semifinished and finished products, as well as the processing stages that occur prior to the final manufacturing step. The complexity and diversity of the subject limit the depth of the discussion here to the more fundamental aspects.

1. Introduction

Thermoplastics consist of macromolecules that are formed by addition polymerization [e.g., poly(vinyl)chloride], polycondensation (e.g., polycarbonate), polyaddition (e.g., polyurethane), or polymer transformation [e.g., transformation of poly(vinyl acetate) to poly(vinyl alcohol)]. The macromolecules can be linear or branched and are entangled. Additionally, they are held together by van der Waals forces. These can be classified according to their origin as dispersive, dipole, or induction forces and hydrogen bonds. Depending on their molecular structure, thermoplastics can be amorphous or semicrystalline. The thermal and rheological behavior is decisive for processing and application characteristics. Below the softening temperature (glass transition temperature), thermoplastics are rigid and brittle. The intramolecular forces decrease with increasing temperature, which results in an increase in the mobility of the molecular chains. Above the glass transition temperature, amorphous polymers exhibit elastic behavior caused by chain entanglements. With semicrystalline materials, dimensional stability is maintained by the unmelted crystalline regions; the simultaneously existing "melted" amorphous regions give high impact strength. With increasing temperature, the chain entanglements loosen even more due to increased thermal motion; with semicrystalline materials this occurs even in crystalline zones at temperatures above the crystalline melting point. The result is the plastic melt required for processing. The transition from solid to melt is reversible; on cooling, the processes described above occur in the reverse order. A characteristic of the melt is that the material still possesses elastic properties due to the residual chain

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entanglements. Additionally, flowing of the melt leads to alignment of the molecules. The degree of orientation in a preferential direction depends on the temperature and the length of the molecular chains. When the material is cooled, this orientation is to some extent frozen in, a situation that may be desirable. For example, this leads to an increase in the mechanical properties in the direction of orientation. However, internal stresses are also frozen in, which relax when the temperature is increased and can lead to distortion of the finished product. To suppress this phenomenon, during molding, the melt must be held at the maximum temperature possible for a long residence time, to allow relaxation to occur. This is not always possible, because thermal damage can result.

The rheological properties of polymer melts are of considerable importance for processing. The strong dependence of viscosity on both temperature and shear velocity plays a significant role in the selection and design of processing machines and molds, as well as the choice of operating parameters. During processing a rapid input of energy is desirable to give a processible melt with sufficiently low viscosity as quickly as possible. Because of the poor thermal conductivity of polymers, conductive heating is unsuitable since it is too slow, and large temperature gradients could result. Convection also plays a minor role because high-molecular melts exhibit laminar flow at extremely low Reynolds numbers. Hence in most cases, the polymer is melted by internal friction (dissipation), generated by the introduction of mechanical energy and the resulting friction and shearing forces to which the molecules are exposed. Polar polymers can also be heated in a high-frequency electromagnetic field. Radiation heating, generally employing IR radiation, is typically used to warm surfaces and planar articles. However, the most important method is melting by dissipation in screw machines, combined with conductive heating via the contact surfaces.

Removal of heat from the melt is more difficult because the only mechanism available is thermal conduction. This can lead to major problems, especially with thick-walled moldings. Hence, the low thermal conductivity of polymers, and the resulting problems regarding heating and cooling, are decisive in the selection of processing technology and have a significant influence on process economics.

2. Compounding Processes

Compounding includes all the processing stages between the manufacture of the crude polymer and the molding step. The transition from compounding to processing can be a gradual change. Thus, storage, transportation, metering, mixing, plastication and granulation are regarded as compounding.

Compounding is necessary because either as-polymerized plastics cannot be processed directly or their properties are inadequate. Consequently, additives must be introduced to the crude polymer to allow the production of articles on an industrial scale.

Heat stabilizing additives enable the polymer to withstand processing temperatures without thermal degradation. Additionally, processing aids are employed which, for example, reduce melting time, influence melt viscosity, or decrease the material's residence time in the processing machine by preventing adhesion of the polymer to metallic machine components.

By using plasticizers, rigid and brittle polymers can be rendered flexible and ductile, opening up new applications.

Similarly, optical properties can also be varied by employing additives. By using pigments, polymer products can be manufactured in all colors imaginable, and gloss can be specifically influenced.

Fillers are increasing in importance not only because of their volume-enlarging effects but also because of their influence on processing and properties.

Another significant aspect of compounding is that many polymers are produced in a form unsuitable for further processing (e.g., as a fine powder). In such cases the material must be reshaped in an intermediate processing step known as pelletizing, which, for example, improves the feeding behavior in processing equipment.

Generally, polymer compounding is carried out by the polymer manufacturer, so the processor can purchase a compound that is ready for use. On an industrial scale, the only thermoplastic compounded by the processor is poly(vinyl chloride).

2.1. Mixing

The production of a homogeneous mixture of polymer and additives places high demands on machine and process. The objective of mixing is to distribute the additive throughout the crude polymer as evenly as possible without excessively stressing the polymer itself. The two basic processes are cold mixing at room temperature, in which the components are simply mixed, and hot mixing, during which absorption and diffusion occur.

Examples of cold mixers are the tumble mixer, in which mixing occurs simply under the action of gravitational forces, and the ribbon mixer, which mixes the materials with a spiral in a horizontal barrel.

Hot mixers are classified according to the method of introducing heat. The polymer can be heated by contact with heated metal components, by irradiation, by convection (e.g., in a plowshare mixer), or by dissipation of mechanical work in the product in the form of heat of friction. Because this form of energy introduction requires high mixer revolutions, these mixers are known as high-speed or turbo mixers. This type of mixing allows rapid heating of the materials and is therefore widely used throughout the plastics processing industry. It is described in more detail below, by using poly(vinyl chloride) (PVC) compounding as an example.

PVC is compounded in mixing vessels equipped with ring- or propeller-shaped mixing elements (Fig. 1). The vessel is usually double walled to allow better temperature control. The peripheral velocity of the mixing elements is generally 20 – 50 m/s. These simultaneously mix and heat the components by throwing them against the container walls and causing them to rise. This results in a whirling motion, with the material being circulated between the center of the container and the base of the vessel. The powder is heated by friction between particles and by particle collisions.

During the initial phase of mixing, the components are merely distributed homogeneously. Actual hot mixing begins above 50 °C. On further heating, during which the plastication temperature of PVC (ca. 150 °C) must not be exceeded, the additives are ground together, and meltable additives are melted. The PVC powder, which is not ground in this process, absorb

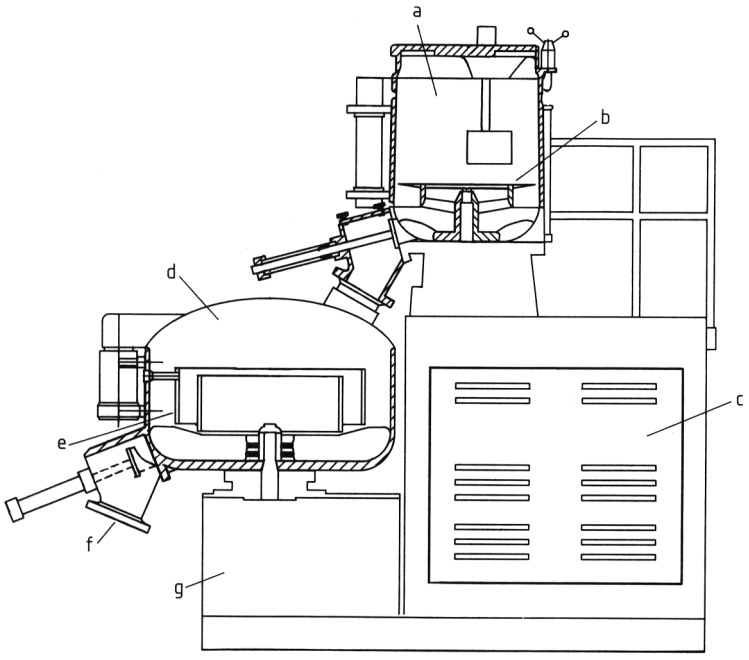


Figure 1. Heating/cooling mixer combination for compounding PVC
a) Heating mixer; b) Mixing element (propeller); c) High-speed drive; d) Cooling mixer; e) Stirrer; f) Outlet; g) Low-speed drive

the molten additives so that at the end of hot mixing a dry powder, the so-called dry blend, results. This material has a final temperature between 110 and 130 °C, and must be cooled in a cool mixer before it can be stored. It is allowed to fall into a water-cooled mixer situated beneath the hot mixer, where it is cooled to ca. 40 °C with constant, slow stirring to prevent fusion of the pellets.

The dry blend produced in this way can be processed without further compounding steps, as is typical for rigid PVC by use of twin screw extruders, or it can be pelletized, as is normal for plasticized PVC.

2.2. Rolling and Kneading

Thermoplastics are often plastified prior to processing. The material is compacted, melted, degassed (if necessary), homogenized, and modified with additives. The oldest process is *rolling*, which involves passing the plastic between two counterrotating, heated rolls where it is plastified and pressed to a thin layer. The plastic is heated by contact with the rolls and by friction in the buildup of material before the roll gap and during passage through the narrow gap between rolls. The major advantage of this system is that it is an open process which, in addition to facilitating addition of additives, also allows scrap material such as edge trimmings to be reintroduced without any difficulty. Because of the high surface-to-volume ratio, the material temperature can be controlled precisely. This is of considerable significance with thermally sensitive materials such as PVC. Furthermore, cleaning the machines is straightforward, and the process can be monitored visually.

A disadvantage is that rolling is a batch process and difficult to automate. More recently, a roll unit has been developed which can be operated in a continuous mode thanks to spiral-shaped grooves that are worked into the roll surfaces. The polymer is fed to one side of the rolls and, passing through the roll gap several times, is driven by the spiral grooves to the other side where it is taken off.

Internal mixers also process polymers batchwise. The material is kneaded between blades rotating in a double barrel and discharged when plastication is complete.

In continuous kneaders, the kneading blades are in the form of rotors with multiple screw channels on the feed side that transport the polymer to the actual kneading elements. The kneading zone is followed by a pump zone, which ejects the plasticated material.

The planetary roller extruder is based on the principle of a single-screw extruder, where the screw is designed as a spindle around which several planetary spindles rotate (Fig. 2 A). This design enables intensive shearing and mixing of the material due to repeated renewal of the material surface. Because of the thin layers of material and the large surfaces of the central and planetary spindles, precise temperature control is possible.

In the *plasticator* a feed screw transports the polymer to a conical rotor in a conical cylinder housing (Fig. 2 B). The conical gap can be adjusted by moving the cone relative to the housing. The excellent homogeneity of the plasticated product can be attributed to the fact that the powdered material is initially sintered and subsequently plastified. The material is spread out by the cone and repeatedly separated and relayered by spiral grooves or threads. Excellent temperature control is possible due to the large surface area. The plasticated material finally passes to further processing units via a discharge screw.

Additionally, a range of other compounding equipment is available, including cokneaders and co- or counterrotating twin-screw extruders. All possess various advantages and drawbacks; hence their selection is not necessarily a question of material-specific or process aspects alone. Plant conditions and economics also play major roles.

2.3. Pelletizing

Pelletizing is the manufacture of pellets (granules) of equal shape and size, to give optimum feed behavior on the processing equipment. The material to be granulated is melted in a single- or twin-screw extruder and fed to a pelletizer. Both hot and cold pelletizing processes are used. Depending on the manufacturing procedure, bead, cylinder, or cube granulate is obtained.

In cold pelletizing, strands, ribbons, or sheets are formed by a pelletizing die; after

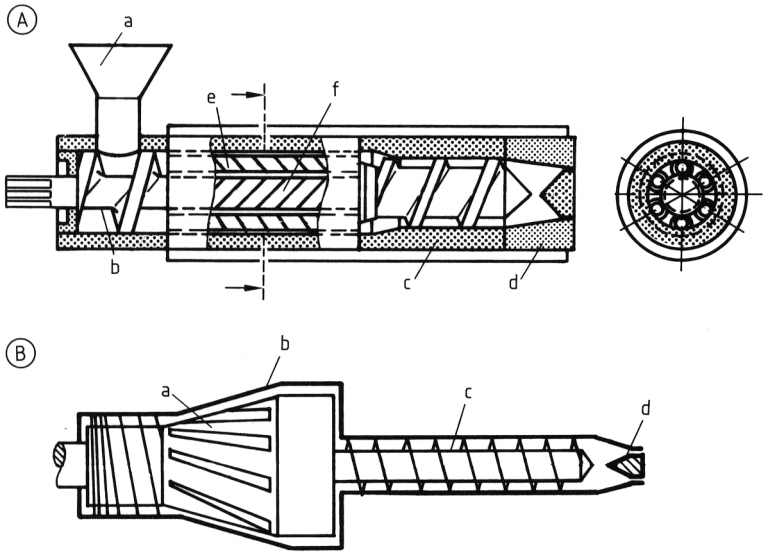


Figure 2. A) Planetary screw extruder: a) Hopper; b) Feeding screw; c) Housing; d) Die; e) Planetary spindle; f) Central spindle
B) Plasticator: a) Rotor; b) Housing; c) Discharge screw; d) Die

solidification, they are chopped to the desired shape by using rotating knives.

In hot pelletizing, the plasticated material is pressed through a die, and the exiting strand is chopped by a blade that rotates on the surface of the die plate. Cooling of the melt occurs after pelletizing, either with air (dry pelletizing) or water (wet pelletizing), although in the latter case, the water must be subsequently removed. With materials of very low viscosity and materials that tend to adhere, the melt passes through the die plate directly into a water bath (underwater pelletizing) where it is cut by blades rotating under the water surface. The resulting pellets must then be dried.

2.4. Shredding and Grinding

During the processing of thermoplastics, a variety of off-specification semifinished and finished products are generated, such as pipes, profiles, injection moldings, and hollow articles, along with scrap such as flash, die leakages, cutting die residues, and film and sheet edge trimmings. For reasons of economy and ecology, these materials are fed to reclaim systems (recycling of single-product manufacturing scrap).

These materials must be cut to produce a pellet form suitable for processing (chip granulate). In doing so however, a range of particle sizes is always obtained.

Cutting mills are generally employed for regranulating. Scrap material is added through a feed system: original-length pipes and profiles are fed horizontally; grinders for film edge trimmings can be incorporated directly in suction pipes. The rotor revolves with high momentum and is equipped with multiple cutting heads that operate against one or more stationary cutting edges mounted in the housing.

In some models, to increase efficiency the rotating cutting heads are divided and displaced with respect to each other. The feed material is cut in the cross direction and — with repeated reorientation — further chopped in subsequent cutting operations. When the desired particle size is reached, the material is ejected through a sieve whose pores determine the particle size. Heat generated in the cutting process can be removed by water cooling of the housing and rotor.

For processing larger plastic articles, a two-stage grinding process has proved effective. The first stage involves coarse chopping with a guillotine (for film rolls and start-up chunks, i.e., material formed before melt calibration

commences) or by a preliminary cutting rotor (for bulky materials). The second stage normally involves the cutting mills described above.

To process thermoplastics in pressureless processes (see Chapter 3), they must generally be available as a flowable, finely divided powder. In many cases, they are not produced in this form during polymer syntheses, or compounding with additives in a mixing and granulation process may be necessary. Sinter powders are therefore often produced by grinding granular materials.

In the impact disk mill, the product passes from the feed hopper over a vibration-metering rim. A rotating wheel catapults the material with high velocity against a ribbed conical disk rotating in the opposite direction. The adjustable gap between the rotating rear disk and the conical front cover determines the fineness of the ground material. Powerful suction equipment then removes the powder from below. Heating of the plastic is prevented by the high air throughput and by water cooling the housing. The discharged powder is classified in a cyclone and then sieved. Coarse material is returned to the grinding mill.

2.5. Storage and Transportation

Automatic equipment has become well established in the polymer processing industry for storing and transporting base polymers and intermediate products. Compared to manual operations, these provide improved working conditions, reduction in material losses, lower workplace and machine contamination levels, and a reduction of accident risks.

For the storage of polymers, generally in powder or pellet form, large external silos are suitable. These can be freighted by road or rail. The outlet cone of the silo is generally fitted with a discharge mechanism. The formation of granule bridges is prevented by ventilation of the silo base or by using vibrating frames, bunker cushions, slotted shelves, or similar techniques.

Reserve materials or smaller charges and additives are shipped in bulk containers, drums, or sacks. These are emptied by special discharge equipment, tipper mechanisms, or sack shakers. Within a plant, small intermediate silos, (homogenizing) vessels, and containers are used to store raw materials and prepare polymer mixtures. Containers are preferred when frequent material changes are involved because they are portable and can be stacked. When fitted with a sliding floor, they can also be used as feeding vessels for the hoppers on processing equipment.

Powders and pellets are generally conveyed with pneumatic equipment. High-pressure conveyors (operating pressure 0.2 – 0.4 MPa) are used for high outputs when filling storage silos from pressure-resistant rail or truck tanks. Medium-pressure conveyors operating at ca. 0.15 MPa are generally used for transport from the storage silos to day or intermediate containers. Low-pressure conveyors with radial blowers are used for short transport distances. Suction conveyors, operating at ca. 50 KPa are most suitable for feeding machine hoppers and gravimetric equipment. The transport interval can be controlled by using fill-level sensors, and air filters are automatically cleaned by back flushing. Mechanical conveyors include screw conveyors (also available as flexible versions) or oscillation conveyors in the form of tubes, channels, and spirals with electromagnetic vibrators or motor drives.

Oscillating displacement pumps, particularly piston, membrane, and bellows pumps, are used for metering liquids such as plasticizers and other additives for compounding. Solids are volumetrically metered by using single- or twin-screw equipment, vibration channels, rotating plates, or cellular wheel sluices. Gravimetric metering equipment can be used for all types of solids, regardless of particle size, homogeneity, flow properties, or adhesion. Weighing vessels, as used in batch processes, are also applicable for continuous metering by discharging with a screw mechanism whose rate of revolution is adjusted to match the weight of material required in a given time. With metering belts, either the belt speed or the rate of revolution of the feeding mechanism is adjusted.

The material flow in a processing plant, including compounding equipment, is shown schematically in Figure 3.

Some thermoplastics, such as polycarbonate (PC), polyamide (PA), and poly(methyl methacrylate) (PMMA), must be dried prior to processing; otherwise the mechanical or optical properties of the resulting products would be considerably impaired. Drying is carried out by heating for several hours in an oven at 80 to 120 °C, depending upon the material concerned.

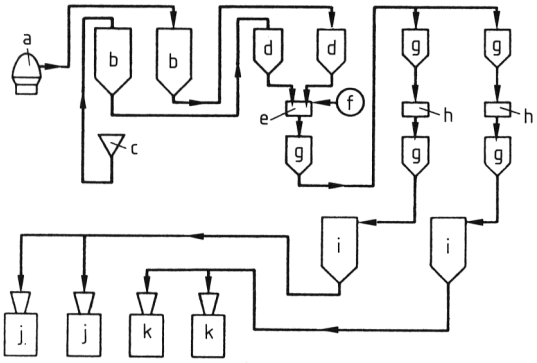


Figure 3. Schematic of a processing plant
a) Rail or truck container; b) Storage silo; c) Sack chute; d) Intermediate silo; e) Weighing; f) Additives; g) Interim storage; h) Mixer; i) Silo for one day's supply; j) Granulator; k) Processing machine

3. Pressureless Processing Techniques

Pressureless proceses are used for starting materials that flow and can be formed under the action of gravity without application of external forces. These include monomers, polymer solutions and dispersions, heat-gelable PVC – plasticizer mixture (pastes), low-viscosity melts, and finely divided, meltable powders. The solid end product is formed by reaction, evaporation of the solvent or dispersant, or cooling.

3.1. Casting

Monomer Casting. Thick-walled articles, embeddings, sheets, blocks, and rods, preferentially of polystyrene, polyamides, and poly (methyl methacrylate), can be produced by polymerization of monomers in molds. Control of the heat of reaction necessitates prolonged reaction times. Adequate temperature regulation is required to avoid thermal stresses. The choice of mold material depends on the extent of use and the desired surface quality of the molding. Apart from metal molds with cooling channels, it is often possible to use simpler molds made of sheet metal, wood, ceramic, or glass. To guarantee ease of release and ensure smooth molding surfaces, even with porous materials, those components of the mold that come in contact with the monomers must be sealed by coating or impregnating.

Film Casting. Filtered polymer solutions, dispersions, or melts are cast onto a substrate (e.g., paper, textiles), directly onto a metal drum or rotating belt, or in the case of cellulose films, from a slot die into a precipitation bath.

The solvents are recovered by evaporation in heating and separation stages. The only major application of this process today is manufacture of cellulose acetate films, mainly for the photographic industry.

Slush Molding. Hollow articles made from PVC pastes are manufactured in a pressureless process using two-part metal molds. The molds are heated to the gelation temperature and filled with paste. The paste gels at the outermost edges to form a skin, whose thickness depends on the temperature and the composition of the paste. After excess paste is poured off, the layer remaining in the mold is completely gelled in an oven. After cooling, the hollow molding is removed from the mold.

Rotational Casting. A further development of slush molding is the manufacture of hollow articles from plasticized PVC by rotational casting of PVC pastes or powders. The method is also applicable to other thermoplastics or liquid monomers containing activators and polymerization catalysts.

In this case, only the amount of paste required for the manufacture of the article is metered to the mold, so that removal of excess paste and postgelation are not necessary. During the heating stage, the mold is rotated about two perpendicular axes (Fig. 4), causing uniform wetting of the cavity surface. To achieve optimum distribution of mold contents, the two axes

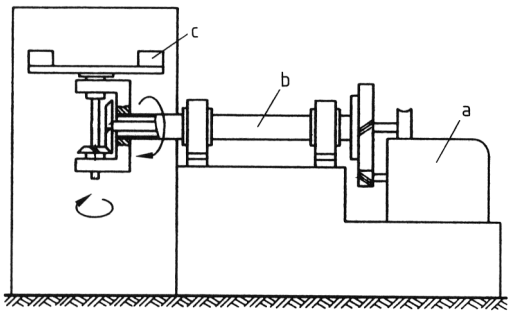


Figure 4. Rotational casting machine
a) Motor; b) Drive shaft; c) Molds

are rotated at (usually adjustable) different speeds (max. 30 rpm). The individual process steps (filling and closing the mold, rotating in an oven, cooling, and removal of the molding) are performed at separate stations. Either the molding is transported to the appropriate station on rails, or the heating oven or cooling air system can be brought to the rotational casting machine.

Numerous modifications of the process that permit shorter cycle times are known. In modern equipment, an oven is no longer used; instead the double-walled aluminum molds are heated with a circulating heat-transfer fluid. The direct-contact heating allows higher production rates. The gelation temperatures are 180 – 220 °C. Filling levels and cycle times are determined in pretests.

Advantages of this process include the low investment costs and the ability to manufacture moldings of various dimensions without pinch or weld seams, virtually free of stresses and with constant wall thicknesses.

Centrifugal casting is used in the manufacture of thick-walled, rotationally symmetrical moldings (e.g., pipes, sockets). In a variation of monomer casting — in this case, mainly limited to polyamide — polymerization occurs in the partially filled mold during rapid rotation about the central axis. The material in the mold is pressed outward and compacted by centrifugal forces. High-quality internal coatings (e.g., for pipes) can be applied directly by centrifugal casting, preferably using meltable powders (see Section 3.4).

3.2. Dipping

A mold or article may be dipped into solutions, dispersions, PVC pastes, melts, or meltable powders; after its removal, the material adhering to the surface is brought to its end-use state by heating or solidification.

Paste Dipping. For the manufacture of articles in which one side remains open (gloves, boots, etc.), a positive model is immersed and the coating is gelled. The process was adapted from the rubber industry; procedures and equipment are practically the same. The positive models are made of metal, glass, or porcelain.

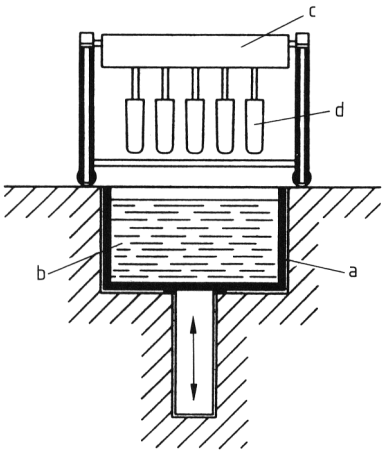


Figure 5. Dipping unit
a) Vessel; b) PVC paste; c) Dipping frame; d) Molds

For mass production, series of identical molds mounted on dipping frames are used (Fig. 5). Degassed PVC paste is placed in a vessel that is raised and lowered during the dipping process. In some cases, the vessel is stationary and the dipping frame is moved. The immersion and removal stages must be carried out relatively slowly to prevent the introduction of air into the paste and to allow it to flow homogeneously from the mold. The vessel or dipping frame must be moved smoothly without vibration to avoid imperfections or marks on the molded article. This is normally accomplished by using hydraulic drives.

During gelation by warming, the pastes temporarily become fluid. To prevent loss of material due to increased flow, it is necessary to heat by using a thermal shock, with rotation, or in an oil bath. Gelation is normally completed in a circulating air oven. The molds carrying the gelled coating are subsequently cooled to ca. 50 °C by immersion in water. At this temperature, even harder moldings can be removed easily from the molds, which are generally treated with talc before use.

Other items (usually made of metal, e.g., grids or handles for tools) can similarly be coated by using a dipping process. Cables and wires can be continually coated in this way. Thicker coatings can be obtained by repeatedly coating a form or object after gelation of the previous layer.

Powder Immersion (Fluidized-Bed Sintering). The dipping of articles directly into polymer melts has not gained major significance. In contrast, immersion of preheated and degreased (metallic) objects in plastic powders is widely used in the manufacture of plastic coatings. In the simplest case, the heated articles are immersed directly in the powder; a continuous coating is formed as a result of melting on the surface.

A more elegant and economical process, which is also applicable for large, irregularly shaped articles, is powder immersion using the fluidized-bed sinter technique. In this case, an immersion bath with fluidized powder is employed (Fig. 6). The upper floor of the immersion vessel has many small holes; a porous ceramic plate is usually employed.

The layer of powder at the base of the vessel is agitated by introducing a gas stream, usually an inert gas (e.g., nitrogen) to avoid oxidation reactions, filling the vessel with a fluidized powder. The preheated articles are immersed in the open bath. Thicker coatings can be obtained by repeating the heating and immersion stages. The powder must have good flow properties and give melts of low viscosity. To ensure pore-free coatings, the articles must usually be subjected to posttreatment, either in an oven or with a naked flame. This process is employed in the production of anticorrosion polyolefin or polyamide coatings. Today, fluidized-bed sintering is carried out both manually on individual articles or small production runs and on a fully automated, mass production scale.

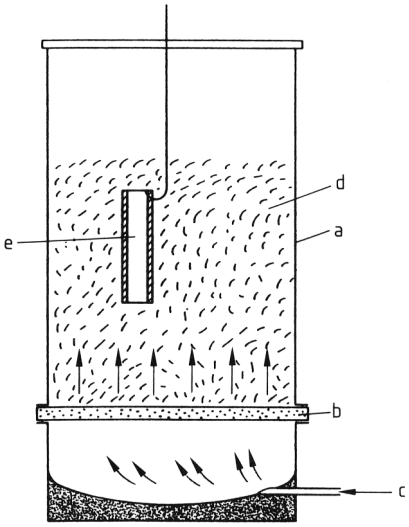


Figure 6. Fluidized-bed sintering unit
a) Immersion bath; b) Filter plate; c) Air inlet; d) Fluidized powder; e) Heated article

3.3. Coating

The coating process is used to coat sheet materials such as paper and textiles and, in combination with release papers, in the production of self-supporting films. All products that can be cast maybe used for coating, such as polymer solutions, dispersions, and melts. PVC pastes, which are used in the production of coatings, floor tiles, and imitation leathers, are the most important.

Equipment. A coating machine consists of an unwinding station, an expander, coating head, gelling channel, cooling system, and a rewind station (Fig. 7). The unwind station is slowed by using disk brakes, whereas the rewind station is driven so that the product is held under tension but stretched as little as possible when running through the system. The expanders provide a smooth crease-free sheet. The PVC paste is applied to the moving sheet manually or mechanically by the coating head and then spread to the required thickness by a doctor blade.

The doctor blades are housed in a revolving holder so that they can easily be changed and adjusted in height and inclination. For thick coatings, doctor blades with a wide base (5 – 20 mm) are employed. These are designed with a sharp back edge and an undercut; any rising paste gathers here and can be removed periodically so that it does not drip onto the coating (Fig. 8). For thinner coatings, doctor blades with rounded edges 1 – 2 mm wide are used so that the paste is not forced too deeply into the fabric.

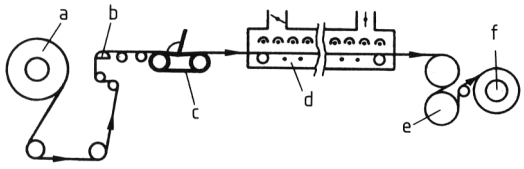


Figure 7. Coating unit
a) Unwinding station; b) Expander; c) Coating head; d) Gelling tunnel; e) Cooling roll; f) Rewind station

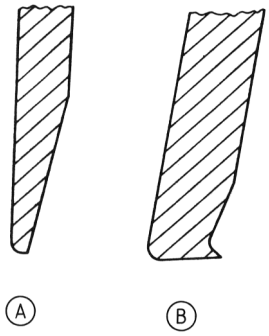


Figure 8. Doctor blades
A) Narrow base with rounded edges; B) Wide base with undercut

Various doctor blade systems are employed, depending on the composition of the paste, the coating material, and the intended use of the product (Fig. 9). With an air knife, the web runs freely between two rollers or metal bars; air knives are generally used with low-viscosity pastes. For many fabrics the knife-on-blanket doctor, in which the fabric lies on an endless rubber belt driven by two rollers, is suitable. This system requires intensive maintenance because of the ease of contamination and the high likelihood of swelling of the rubber belt caused by the plasticizers in the coating. With knife roll coaters, the sheet is supported by a revolving roller, which results in an exactly defined contact area. With steel rolls, complications caused by loose and irregular fabrics can occur, particularly with thin coatings (punctures, disturbances in the coating process); this can be prevented by coating the rollers with soft rubber. The reverse roll coater is employed for coated articles for technical applications in which a defined coating thickness and high operating speeds are important. Two rolls are positioned above a single lower roll (typically steel) over which the web is transported. These two rolls distribute the escaping paste and form it into a film. The separation between the rolls is adjustable and the rotation speeds can be regulated.

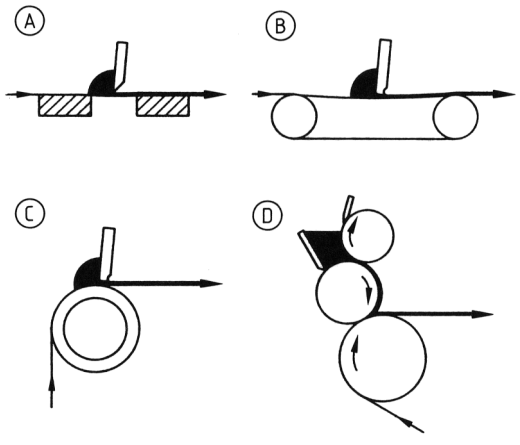


Figure 9. Doctor blade systems
A) Air knife; B) Knife-on-blanket doctor; C) Knife roll coater; D) Reverse roll coater

The length of the gelling tunnel depends on the required operating speed; it can be as long as 20 m. The heat required for gelation of the paste is supplied by either hot air or infrared dryers. With circulating air heat, the air is warmed by steam or oil heating or in heat exchangers using oil burners. Alternatively, the tunnel can be heated by the combustion gases of an oil heater. In modern equipment, air is directed at an oblique angle toward the web through nozzles arranged in the direction counter to the machine direction. With infrared heating the elements are combined in groups that can be slid into position and individually activated. In this way, heating — one of the more expensive aspects in a large-scale operation — can be adapted to suit the process in question. In some cases, circulating air heating is combined with infrared heaters.

The cooling system generally consists of two water-cooled, corrosion-resistant hollow drums. The cooling effect must be high enough that no adhesion between individual layers occurs during winding, nor is any subsequent material deformation (impression from the substrate web) possible. Continuous winding is performed with multistation winders.

Process. In a coating process, depending on the article being manufactured, various thicknesses can be applied in a single- or multiple-step system. Loosely woven fabrics are first smoothed on a textile calender (steel against paper rolls) at 80 – 120 °C. The coating weight of the paste depends on its composition, the water content of the filler system, and the heating system used in the gelling tunnel. With coating weights >500 g/m^2, the danger of blister formation during gelation exists; hence, the desired coating thickness must be applied in several layers.

The primer layer must have excellent adhesion to the fabric; in general, compositions with high plasticizer content and low filler content are used. After gelation of the primer at ca. 130 °C, the filler or intermediate coating can be applied, in one or more stages. Pastes with high filter content or expanded pastes are often used. Each coating stage is followed by a preliminary gelation stage; if insufficient heating capacity is available in the gelling tunnel, thicker coatings must be exposed to an intermediate full gelation stage. The topcoat has the function of providing the product with an appropriately dry and durable surface. For particularly dry surfaces (e.g., necessary for upholstery) a finishing methacrylic coating is applied to seal the surface. This is usually carried out in a roll coating system with an immersion roll (Fig. 10). A mat-steel roll is immersed in a bath, and excess coating is removed by using a doctor blade. The sheet takes up the coating from the steel roll under pressure exerted by the rubber roll mounted above.

When required, a structured surface (e.g., grained) can also be generated in an embossing stage. The product is transported from an unwinding station and passed over a teflon-coated heating drum. After additional heating with infrared radiation, the sheet is embossed at 150 – 160 °C by a patterned rubber roll. The rubber roll is cooled constantly by spraying with water, which is subsequently removed by a nip roll. Before rewinding, the web is cooled by passing it over a series of cooling drums. Because the coating process normally involves multiple layers and generally higher working speeds (30 m/min), the surface is usually embossed in a separate process (embossing speed 1 – 5 m/min), particularly when frequent design changes are commonplace.

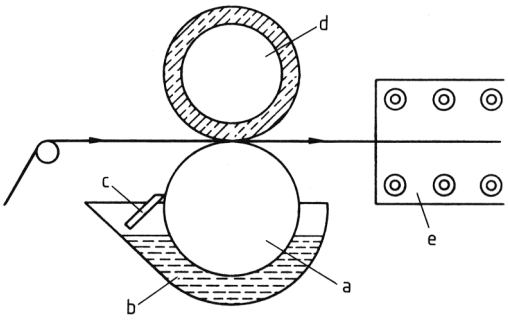


Figure 10. Immersion roll coater
a) Steel roll; b) Trough; c) Doctor blade; d) Rubber roll; e) Drying oven

Foamed products can be produced by adding blowing agents or by employing mechanically foamed pastes (whipped foam; air is emulsified by rapid mixing). To attain specific foaming characteristics, precise temperature control and residence time in the gelling tunnel are required. For the manufacture of unsupported foamed sheets, or when light fabrics or nonwoven materials are being coated, indirect coating methods (transfer or countercoat techniques) are used. Either the coatings are applied in reverse order (topcoat first) onto endless metal or sieve belts, or carrier fabrics or release papers are employed as transport substrates; after being passed over the cooling drums, they are removed and wound individually.

3.4. Foaming (see also → Foamed Plastics)

In principle, all polymers can be foamed. To date however, only a limited number of materials have been employed in the manufacture of foams. These include the thermoplastics polystyrene, poly(vinyl chloride), and low-density polyethylene (LDPE), as well as phenolic and polyurethane resins.

Foams are generated by adding physical (gases and low-boiling compounds) or chemical blowing agents (gas-releasing compounds) to the polymer.

A basic requirement for foaming plastics is that the foaming process begin while the polymer is in a flowable form that allows bubbles to develop. Once the bubbles have reached the optimum size for the desired material properties, this condition must be fixed.

The flowability of the polymer to be foamed can be achieved in several ways. With thermoplastics, the polymer can be melted or used as a solution. With thermosets, flowability is obtained by using an incompletely cross-linked polymerization mixture or prepolymer.

The required bubbles can also be generated in various ways. With chemical blowing agents, the gas is evolved either as a byproduct of the polymerization reaction (polycondensation), as

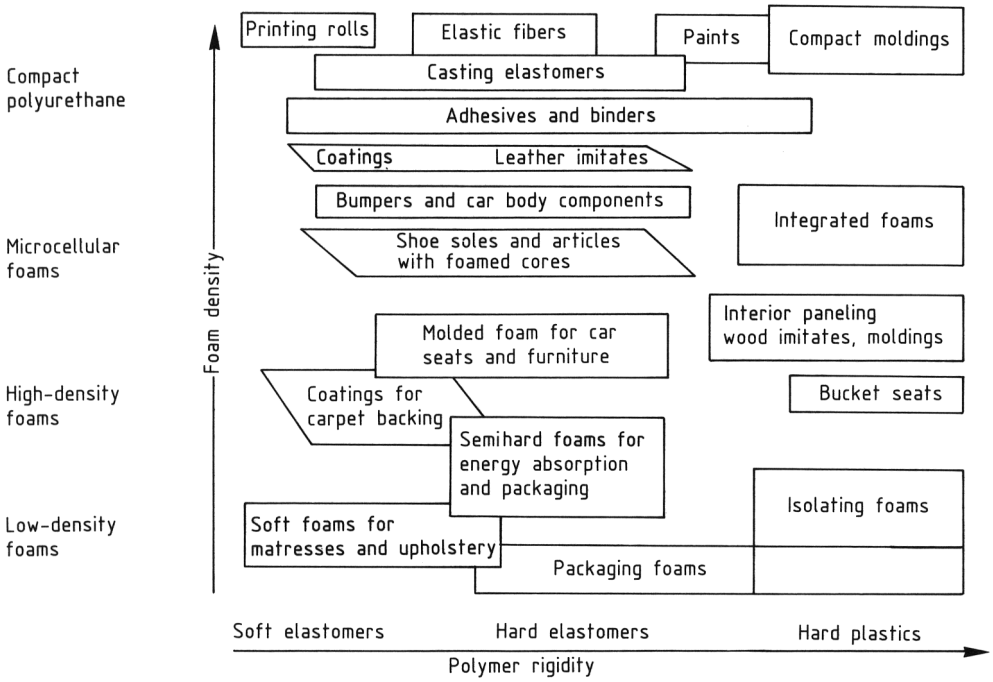


Figure 11. Overview of polyurethane applications

a product of a reaction between the polymer and the blowing agent, or as a result of chemical decomposition of the blowing agent.

Physical blowing agents include the mechanical whipping in of air or other gases and the evaporation of low-boiling liquids.

Polyurethane Foam (see also → Polyurethanes). Polyurethanes manufactured by reaction injection molding (RIM) techniques are processed exclusively by using the so-called one-shot process, which involves direct reaction of the starting materials to form the polymer; (i. e., the reaction begins immediately after mixing of individual components). The starting materials permit wide variations in density and hardness to be achieved. By modifying the chemical composition, soft, flexible, or hard articles can be produced. Accordingly, the range of applications for products made from polyurethane is broad and includes, for example,

1. Soft foams for matresses and upholstery
2. Hard foams for thermal insulation (construction industry, refrigerators)
3. Integral foams for automobile body components, where a variation in density over the cross section is required
4. Microcellular (compact) RIM components (e.g., computer housings)

Figure 11 illustrates various applications as a function of material density and stiffness. The incorporation of fabrics, long and short fibers, and fillers opens up additional areas of application.

Thermoplastic Foams . To foam a thermoplastic melt, a component must be added that is gaseous at predetermined temperature and pressure. Nitrogen is added directly to the melt by special gassing units; low-boiling hydrocarbon compounds can be added to the melt or during polymer synthesis. Chemical propellants are usually powdered substances that decompose at a certain temperature, generally releasing nitrogen.

The advantage of chemical blowing agents over direct gassing is that structural foam components can be manufactured on conventional injection molding equipment, and also that the

raw material can be prepared simply by mixing the blowing agent with the granulate.

To guarantee optimum foaming of the melt, the gas formation reaction must go to completion within the prescrew zone. The reaction must not begin in the area around the feed opening of the plastication unit, however, because this would allow part of the gas to escape. To set the barrel temperature and obtain conditions that meet these requirements, the decomposition temperature must be known.

In conventional thermoplastic foam casting processes, the mold cavity is only partially filled, and complete filling is obtained as a result of the foaming reaction.

4. Processing under Pressure

This section considers processes in which solid thermoplastic materials are melted, molded to shape, and subsequently cooled. Because of the extremely high melt viscosities that can be involved, the molding process may require high pressure; for example, several tens of megapascals for extrusion and >100 MPa for injection molding.

4.1. Compression Molding

Compression molding of polymers to semi-finished or finished products dates back to the onset of polymer processing but has meanwhile been almost totally displaced by injection molding thermoplastics. Compression molding is now used only in the manufacture of thick-walled components and components made of materials that can not be plastified in extruders [e.g., ultra-high molecular mass polyethylene (PE)]. However, compression molding still plays a significant role in the processing of elastomers and thermosets.

In its simplest form, a press consists of fixed and moving platens. The plunger and cavity components of the compression mold are mounted on these plates, with the parting plane horizontal. Closing and exertion of pressure are usually carried out hydraulically. In compression molding, the cold plastic is placed in the cavity and melted by heating the mold under slight pressure (compression). After melting, the mold is closed and pressure is applied. The molding cools via the mold surface, during which time the pressure is increased further to prevent void formation. Once the ejection temperature has been reached the press is released and the molding removed. The drawback of this process is the long cycle time, which is due to the material being heated and cooled by conduction via the mold surface. For this reason, compression molding is highly uneconomical.

One method of improving the economics is to employ multiplaten presses. In this case, multiple (up to 20) plane-parallel heatable and coolable press tables are loaded simultaneously with plastic, lying on press platens, by using special handling equipment and then pressed simultaneously.

In transfer molding, the starting materials are melted in a cylinder prior to injection into the mold cavity. The mold need only be cooled in this technique. Transfer molding is thus an intermediate between injection molding and compression molding.

4.2. Rolling and Calendering

Rolling mills consisting of only two rolls are employed exclusively in the compounding of thermoplastics. These so-called roll mills are used for additive compounding, plastication, and homogenization (see Section 2.2). The resulting product is a sheet that can be either granulated after cooling or fed in plasticated form directly to processing equipment. The main application is processing of PVC and rubber, typically in a batch process.

If a polymer is to be shaped by using rolls, then more than two rolls are necessary. Such machines are known as calenders and can be equipped with up to seven rolls, but more commonly come with four. Depending on the arrangement of the rolls, they are referred to as I, F, L, or Z calenders (Fig. 12). The rolls are generally made of highly polished cast iron and are individually driven and heated. Oil or water can be used as heating medium. A calender is generally operated with increasing temperature and speed from one roll to the next. The roll nips can be individually adjusted. Because of the high pressure in the nips, as well as the weight of the roll itself, large rolls tend to sag and hence

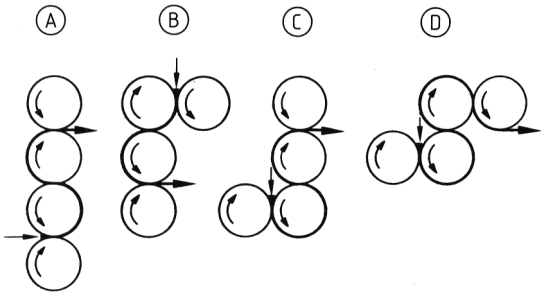


Figure 12. Configuration of calender rolls in four-roll calenders
A) I type; B) F type; C) L type; D) Z type

give an irregular thickness distribution across the width of the final product. This is counteracted by using convex-ground rolls, by roll bending using additional bearings, or by offsetting the roll axes with respect to each other. The roll mill itself must be extremely rigid and stable to withstand the forces to which it is exposed. For this reason, calenders are among the most expensive types of polymer processing equipment. Since they can be economically operated only under conditions of extremely high throughput, they are used for a few special products such as floor coverings and films made of plasticized PVC. Typical calenders have roll lengths (i.e., machine widths) of ca. 1.5 m, but calenders with widths exceeding 3 m are also used. Sheet thicknesses that can be manufactured range from 0.1 to 1 mm. Thinner gauges can be obtained by drawing down using faster speeds for the takeoff rolls. Takeoff speeds are typically 40 – 100 m/min, with throughputs up to several tonnes per hour.

Figure 13 illustrates a calendering line with a four-roll F calender. The roll arrangement shown is employed for processing plasticized PVC, since in this configuration plasticizer vapor that escapes can be removed easily by suction and thus prevented from condensing on the other rolls. The first roll nip is fed continuously from an extruder and conveyor belt. In the first nip a kneading stock is built up from material that is forced back by pressure in the nip. Figure 14

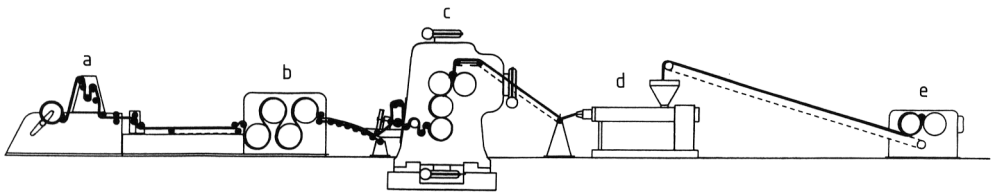


Figure 13. Calendering line
a) Winder and edge cutter; b) Cooling rolls; c) Four-roll calender, F type; d) Extruder; e) Mixing roll mill

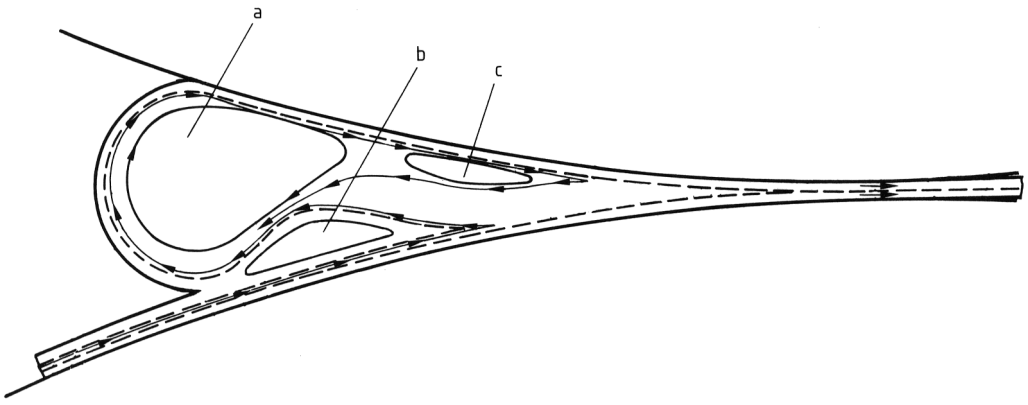


Figure 14. Flow relations in the roll gap
a) Kneading current; b) Feeding current; c) Outlet current

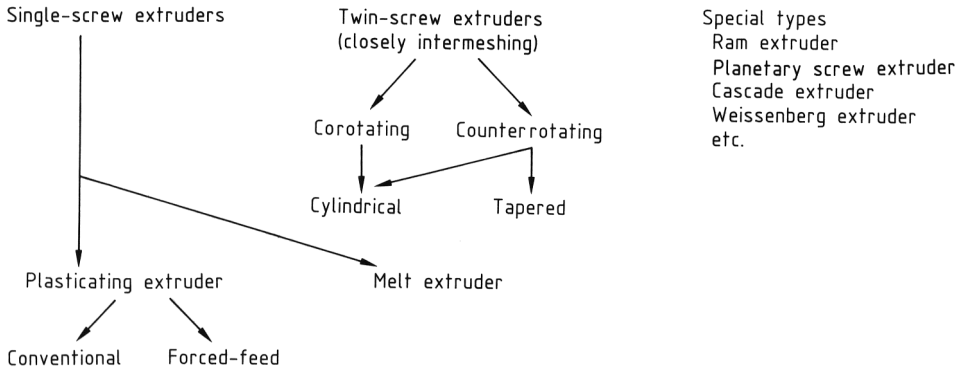


Figure 15. Classification of extruders

shows a cross section through this stock, illustrating the various currents that are formed. Whereas the lower part of the sheet can pass through the nip essentially unaffected, the remaining material is subject to the currents, which lead to continuous creation of new surfaces and increasing homogenization of the melt. Thus the formation of this kneading stock is of considerable significance for product quality. After preforming in the first nip, final shaping takes place at the next two nips, and the surface quality is established.

A process related to calendering is the roll melting process. In this case, cold polymer is fed to the initial roll nip from a hopper, or is preplasticated in an additional pair of rolls or an extruder. In this case the first roll nip must complete melting of the polymer. The material is then rolled and drawn to the desired thickness in subsequent roll nips. In the manufacture of coatings and laminates, preheated substrate is fed to the last roll nip so that the bond is formed under pressure. After this, both materials are removed simultaneously. Surface effects can be included by embossing with additional rolls.

4.3. Extrusion

Extrusion is the term used to describe the continuous manufacture of a semifinished plastic product (film, sheet, pipe, profile). An extrusion line consists of the following:

1. Extruder
2. Mold or die
3. Calibration and cooling
4. Takeoff
5. Finishing

Extruders. The extruder is the heart of every extrusion line; its task is to feed a homogeneous melt of predetermined temperature and pressure into the mold or die. Figure 15 provides an overview of the various types of extruder. An extruder normally consists of:

1. Machine frame
2. Drive (motor, gears, back pressure bearing)
3. Plasticating unit [screw(s), barrel, heating system]
4. Control panel (regulation, control mechanisms, electrical supplies)

Three types of plasticating extruder are most widely used:

1. Single-screw extruders with smooth feed bushes and three-zone screws
2. Single-screw extruders with grooved feed bushes and screws with mixing and sometimes shear zones
3. Twin-screw extruders with closely intermeshing, co- or counterrotating screws

Single-Screw Extruders. A distinction is drawn between melt and plasticating extruders. The basic concepts of both types are essentially identical. The different feed materials — melt extruders are fed with molten plastics, and plasticating extruders with free-flowing solid particles — require specific screw geometries.

Function		Characteristics of the process technology	Engineering solution
Transport	Solid	Low bulk density Low drag forces	High flight depth Grooved feed zone
	Melt	Higher melt density, usually barrel wall adhering	Lower flight depth
Plastication		Solid–melt mixture with low thermal conductivity and increasing density	Decreasing flight depth Shear elements
Homogenization		Inhomogeneous material and temperature distribution	Shallow-flighted mixing zone Mixing elements

Figure 16. The functions of a plasticating extruder

The functions of a melt extruder are limited to melt transportation and homogenization. For this reason, additional details of this type of extruder are not considered here. All further discussions refer to plasticating extruders. An extruder is normally classified by its screw diameter and effective screw length, which is given as a multiple of the screw diameter D (e.g., 50 mm/25 D).

The functions of a plasticating extruder are summarized in Figure 16. Transportation of the material in the extruder results from adhesion of the melt to the barrel and the screw, which move relative to one another. This mechanism is known as drag transportation. The resulting drag flow is superimposed by the pressure flow, whose magnitude and direction depend on the pressure drop along the length of the screw.

A third flow component is leakage flow, which is the flow that exists between the screw flight and the barrel wall. Because of the narrow gap width, the material is exposed to particularly high shear forces in this region.

Extruder Screws. The screw is the most important element of an extruder. Because of the multitude of demands (feeding, transportation, plastication, homogenization), the geometry varies along the screw length. Figure 17 shows typical screw geometries. The three-zone screw is the most widely used; it is made up of the following sections:

1. The feed zone, which draws the solid plastic from the hopper into the extruder and transports it
2. The compression zone, which compresses and plasticates material from the feed zone
3. The metering zone, which homogenizes the melt and heats it to the required temperature

Most thermoplastics can be processed with three-zone screws, although some polymers require additional shear and mixing zones.

Nevertheless, other screws have become established for special applications. The short-compression-zone is used for semicrystalline thermoplastics. The short-compression-zone results from the decrease in channel depth from the deep-flighted feed zone to the shallow-flighted metering zone.

The long-compression-zone screw, which is used for PVC, has a constantly increasing root diameter toward the tip (see Fig. 17 C). Extruders or screws designed for specific applications can be regarded as technically suitable when they fulfill the following conditions:

1. Constant, pulsation-free transport
2. Thermally and materially homogeneous melt
3. Ability to remain within the thermal, mechanical, and chemical material degradation limits

These demands must be met in all cases; additionally, for economic reasons, they must be

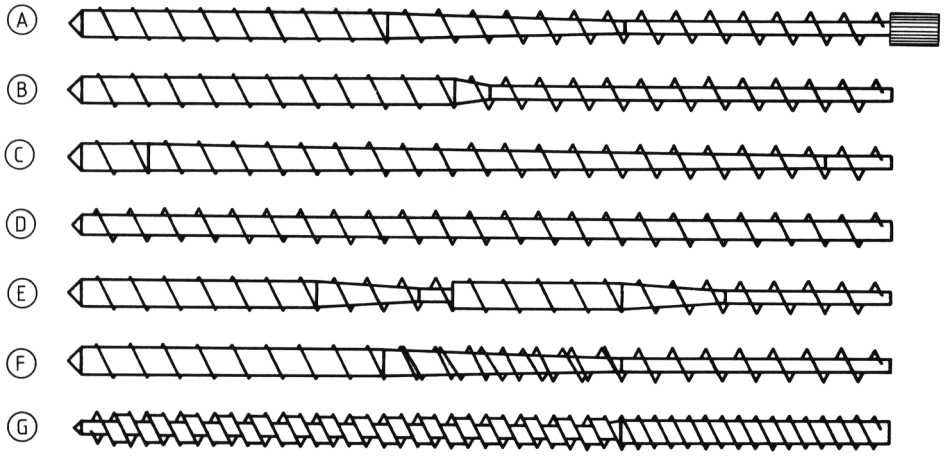


Figure 17. Plasticating screws in common use
A) Three-zone screw; B) Short-compression-zone screw; C) Long-compression-zone screw; D) Conveying screw (only in combination with grooved bushes); E) Degassing screw; F) Maillefer screw; G) Double-flighted wave screw (rarely used)

combined with high mass throughputs and low specific operating costs.

Modern extruders have screw diameters D ranging from 19 mm (laboratory extruder) to special designs of 300 mm. The length has increased from the 6 D of melt extruders for rubber processing to ca. 25 D for typical industrial plastication extruders. Plastication extruders with lengths up to 30 D are also available, and degassing extruders have lengths >35 D.

In addition to diameter and length, screws are classified according to the distribution of the functional zones and the compression ratio. The latter is defined as the ratio of the channel depth of the metering zone h_2 to that of the feed zone h_1. To ensure complete filling of the screw, the compression ratio must at least equal the ratio of the bulk density of the solid in the feed zone to the density of the melt in the metering zone.

The screws described here are employed in two different extruder concepts, which differ in the shape of the extruder barrel in the feed zone, the so-called feed bushes.

Conventional single-screw extruders have a smooth barrel surface in the feed zone; the metering zone is regarded as decisive for output. Molten material from the previous zones is homogenized in the metering zone and subsequently forced through the attached extrusion die under pressure.

In this design, the metering zone acts as a pressure generator. The pressure along the length of the screw depends not only on screw geometry, but also on the die back pressure.

Transport of the solid plastic is governed by coulombic friction between the barrel walls and the granules and between the granules themselves.

The result is that a strong correlation exists between the throughput behavior of the extruder and other operational parameters (temperature, back pressure, etc.). In particular, the temperature of the feed zone plays an important role. For this reason, the feed zone is generally cooled.

Fixed Transport Single-Screw Extruder. Feed bushes with axial grooves were developed to attain large, back-pressure-independent throughputs. The so-called forced-feed bush is part of the cylinder which forms the feeding zone; it is usually removable. The interruptions in the otherwise smooth barrel wall caused by the regularly spaced axial grooves prevent the cold feed polymer from rotating with the screw. Thus they increase the coefficient of friction of the barrel wall. This leads to increased throughput and generation in the feed zone of the pressure required for flow through the following zones.

The feed bush zone must be cooled to prevent melting of the plastic. Figure 18 shows a typical grooved bushing with conically formed

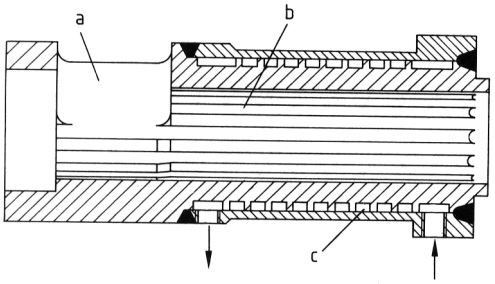


Figure 18. Forced-feed bush
a) Feed opening; b) Axial grooves; c) Cooling channels

grooves. This eliminates the possibility of mixing due to back flow caused by the back pressure. Pressure flow, drag flow, and leakage flow contributions are oriented in the same direction. For this reason, mixing zones must be used to obtain satisfactory melt homogeneity.

Plastication Process . The heat required to melt the plastic is introduced by dissipation and by heat-transfer mechanisms. This includes heating by conduction from the heated barrel to the cold material and the generation of heat by internal and external friction (dissipation) in and between the material.

Twin-Screw Extruders. Twin-screw extruders exist in co- and counterrotating versions; the latter are also available with conically tapered screws. The screws are non-intermeshing or closely intermeshing.

Corotating extruders are used in compounding, whereas counterrotating, intermeshing systems with cylindrical or tapered screws are employed for processing rigid PVC (dry blend).

Corotating Twin-Screw Extruders. With corotating twin-screw extruders, the melt contained in one screw channel is transferred to the other channel with each rotation. The transport mechanism (drag forces) is comparable to that of a single-screw extruder. The melt however is exposed to a greater shear stress due to the increased path length through the extruder.

This type of construction enables integration of closely intermeshing kneading and shear elements into the screw without any problem. Such extruders are almost exclusively employed for compounding.

Counterrotating Twin-Screw Extruders. The most widespread equipment for the extrusion of rigid PVC profiles and pipes consists of closely intermeshing, counterrotating twin-screw extruders. This type of extruder has a different transport mechanism. Each screw segment forms a sealed chamber, which means that during transport, virtually no exchange of material between neighboring chambers occurs over the full length of the screw from hopper to screw tip. Drag forces are not required for this forced conveying; hence, dissipation heating occurs to a considerably lesser extent.

Material heating occurs essentially by barrel heating, which can be controlled precisely and allows a mild treatment of sensitive products. The closely intermeshing screws form C-shaped chambers that are sealed by the screw flights. The C-shaped chamber is formed because the flight of one screw runs in the channel of the other and thus seals it (Fig. 19).

Generally, the counterrotating twin-screw extruder is operated with partially filled screw chambers. This is necessary to ensure a constant flux of material and an optimum balance of extruder, material, and mold. If the extruder were operated with full chambers, the volume of the individual chambers would have to be matched to the volume of polymer, which varies during heating and melting. Otherwise, very high pressures would be generated which lead to increased wear of the cylinder and screws.

The material being transported melts extremely slowly. Only in the final screw channels before the die does sintering occur, caused by the pressure buildup, and material is forced through the chamber gaps (leakage flow). This portion of material melts spontaneously under the short-term shear stress.

Although this transportation and melt mechanism guarantees well-controlled, mild treatment of the plastic, the product is often nonhomogeneous and insufficiently plastified.

The twin-screw extruder is a relatively expensive piece equipment due to the following factors:

1. Expensive bearings that are difficult to house

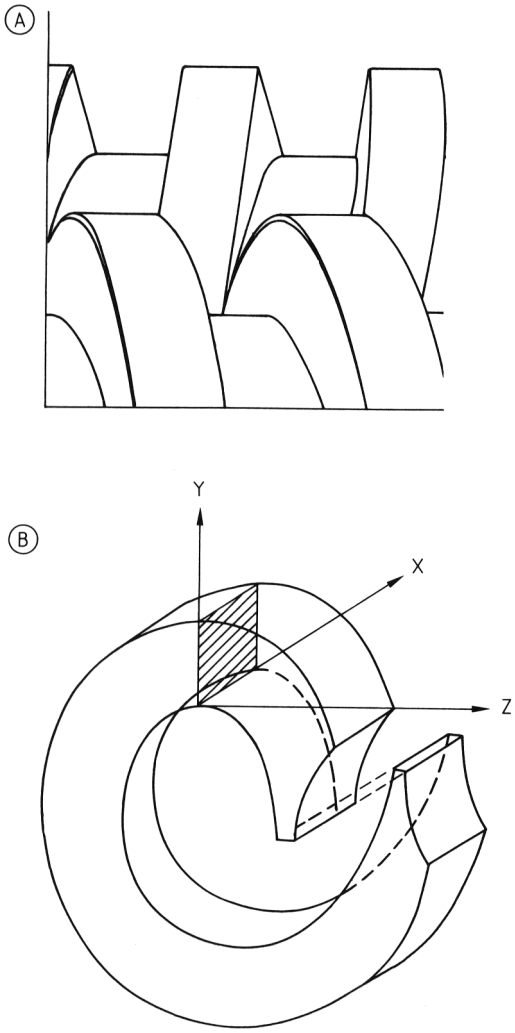


Figure 19. A) Intermeshing counterrotating twin screw; B) Strip of melt removed from one of the C-shaped chambers

2. Complex drives
3. Barrel with a figure-eight bore

The intermeshing of the screws and the pressure buildup in the last screw channels lead to extensive wear of screw and barrel. Extruders with diameters up to 160 mm are commonly employed.

Degassing Extruders. During the melting process, volatile components, such as moisture, decomposition products, and residual monomers, may degas. Since this can lead to defects in the extrudate, these gases must be removed from the system. This is carried out with degassing screws in which, after the compression zone, the channel depth is increased (decompression) so that the pressure drops to ambient levels. A degassing opening in the barrel is incorporated at this position, through which the material is degassed by vacuum. Ideally, at this point in the extruder the material should not be fully melted and should have as large a surface area as possible. The degassing zone is followed by further compression and metering zones (Fig. 17 E). A degassing screw can thus be regarded as a series connection for two screws, whereby the balance between the two is of importance in preventing the melt from leaking out of the degassing orifice.

Degassing extruders can be of both single- and twin-screw types. With counterrotating twin-screw extruders for PVC processing purposes, a degassing zone is standard.

Special Extruders. Apart from the extruders mentioned above, a range of extruders (Fig. 15) exist for special applications, all of which have individual advantages and drawbacks. The most significant of these are the cascade extruders in which two separate extruders are operated in series so as to divide the feeding and melting stages of the extrusion process from the homogenization and output stages, allowing better control and regulation of the process.

Ram extruders are piston plastication units employed in the processing of materials that are not suitable for processing with screws (ultra-high-molecular weight polyethylene, polytetrafluoroethylene).

Extruder Temperature Control. An extruder is heated by barrel heaters. Several heating zones are used to establish a temperature gradient along the barrel.

Commonly employed heating systems include the following:

1. Electrical heating with band heaters
2. Aluminum jackets with cast in heating wires and cooling pipes or ribs
3. Heating and cooling with a heat-transfer medium (oil, steam, pressurized water) that is in direct contact with the barrel walls (double-walled barrel with spiral ribs in the cavity)

The first two methods are sometimes combined with electric cooling fans. The third method is seldom used.

A thermocouple is located in the barrel wall of each heating zone, from which a temperature-dependent electrical signal is input to a control unit.

Additionally, during the processing of thermally sensitive materials such as PVC, the temperature of the screw is regulated with a heat-transfer oil.

Extrusion dies mounted on the extruder give the melt, the desired cross-sectional form. These forms include

1. Solid strand profiles (ribbon, quadratic, etc.)
2. Hollow profiles (shutters, window profiles, etc.)
3. Open profiles (U-shaped, etc.)
4. Pipes
5. Films
6. Sheets
7. Fibers

Furthermore, sheathing dies exist for cables, as well as a range of other constructions. The dies are heated, usually electrically.

All the dies contain a flow channel — the so-called runner system (melt distributor) through which the cylindrical melt strand leaving the extruder must flow. The following melt distributors are of importance.

The *spider* or *displacer* (*torpedo*) is the simplest runner system. It has a streamlined torpedo-shaped mandrel connected to the outer wall of the flow channel by so-called spider legs. The side facing the extruder is conical, but this changes to the desired outlet cross-sectional form as it approaches the die outlet (Fig. 20).

Applications: pipes, profiles, etc.

The *coat hanger distributor* (Fig. 21) spreads the melt over a required width. Melt enters the feed manifold, where the cross section tapers according to the decrease in mass flow, and flows over the so-called island region. This area contains choking elements (restrictor bars, adjustable lips), which can be used to correct irregular melt outputs across the die width.

A variation of the coat hanger distributor is the fishtail distributor in which the feed manifold has a geometrically simplified form.

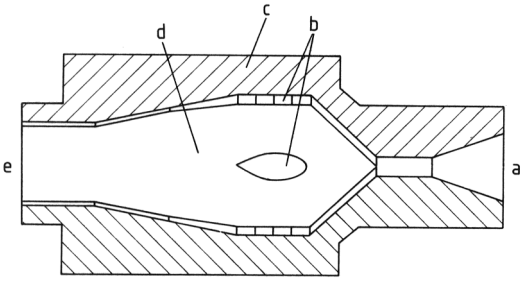


Figure 20. Spider-type manifold
a) Inlet; b) Spider legs; c) Die ring; d) Torpedo; e) Outlet

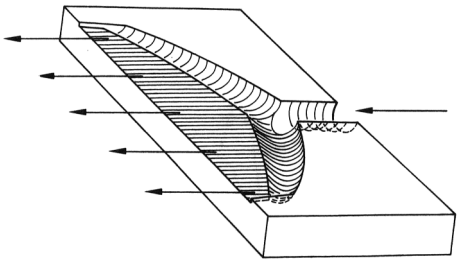


Figure 21. Coat hanger distributor

Applications: films, sheets, etc.

The *pinole* (side-fed die) is a cylindrical or conical coat hanger distributor (Fig. 22), which forms a tubular melt. What is characteristic,

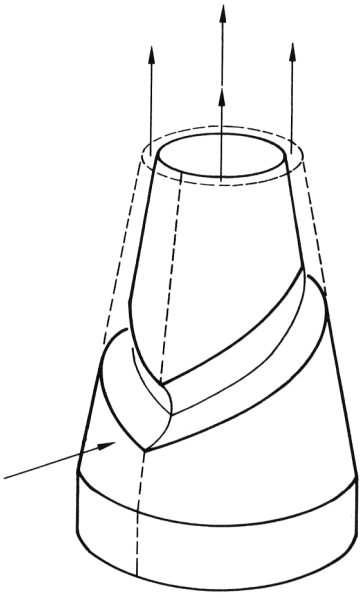


Figure 22. Pinole

however, is that the incoming flow direction is not parallel to the outgoing cylinder, but perpendicular to it.

Applications: pipes, tubular film, cable sheathing, etc.

The *spiral mandrel distributor* is a core with multiple spiral-flow channels of progressively decreasing depth in the direction of the die outlet (Fig. 23). This causes separation of the melt flow into axial and circumferential components. The result is a melt that is homogeneously distributed around the complete circumference and is free from the flow lines and seams that can occur, for example, at flow junctions following the spider legs and with pinole dies.

Application: blown films (tubes).

Subsequent Equipment. The melt leaving the extrusion die must be fixed in shape and dimension; this occurs in the calibration stage. The extrudate is pressed against the walls of the calibrator by compressed air or a vacuum and is cooled. After leaving the calibrator, it must be sufficiently solidified that during subsequent cooling stages no further distortion can occur and the dimensions are fully retained. Thus the length of the calibration zone must be adapted to the throughput and the geometry of the extrudate.

Transport of the extrudate through the calibrator requires high takeoff tensions due to the friction between the extrudate and the surface of the calibrator. Doing this without deformation by using only the cooling capacity of the calibrator is rarely possible, and it is usual to include a subsequent cooling zone.

For profiles, pipes, cables, and similar products, water baths through which the respective extrudate is passed are also employed. Flat extrudates are cooled with rolls. It is also possible to employ water sprays and air cooling mechanisms.

The cooling zone is followed by the takeoff unit whose objective is to remove the extrudate from the die (via calibrator and cooling zone) at a constant speed. Various takeoff systems are available such as band, roll, or caterpillar takeoffs. Elastic extrudates such as cables, fibers, films, and tubes are wound on reels following the takeoff. Rigid extrudates (pipes, sheets, profiles, etc.) are cut to length by saws or guillotines and then stacked.

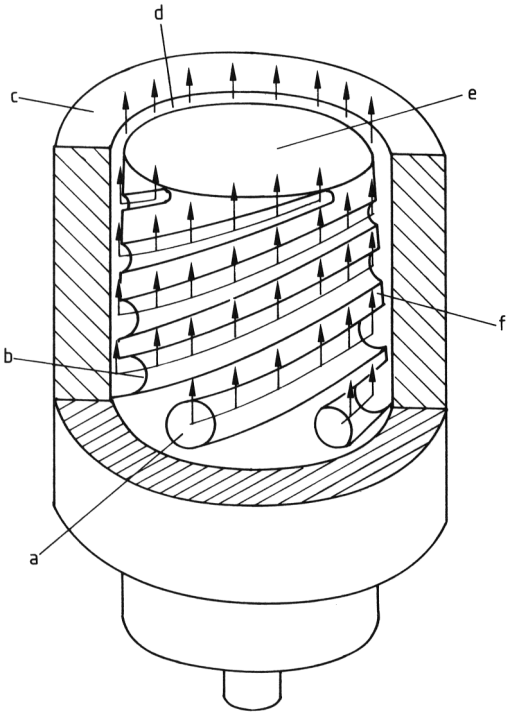


Figure 23. Spiral mandrel distributor
a) Feeding; b) Spiral channel; c) Casing; d) Annular gap; e) Mandrel; f) Steps

Examples of Equipment. *Profile Extrusion Line.* Figure 24 shows a typical profile extrusion line. It consists of an extruder and a die followed by calibration, cooling, caterpillar takeoff, and cutting.

Flat film (sheet) extrusion lines (Fig. 25) consist of an extruder and a coat hanger die. These are followed by a roll mill, normally with three rolls, which calibrate and cool the film (sheet). Subsequent to this is a roller conveyor, which allows air cooling of the sheet and the takeoff roll. Finally, the film is wound, or the sheet is cut and stacked.

Blown film lines are employed to manufacture very wide films (Fig. 26). They consist of an extruder with a blown film head normally equipped with a spiral distributor. The vertically extruded tubular film is passed through a cooling ring where it is cooled by air. The tube is inflated to the desired circumference by blowing air into it. At the upper part of the tower, the tube is folded together on a collapsing board and the air is removed by nip rolls. Finally, the film is wound

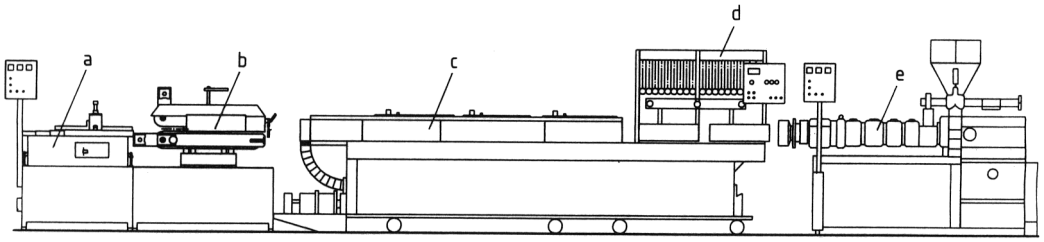


Figure 24. Profile extrusion line
a) Saw; b) Takeoff unit; c) Cooling system; d) Calibrator; e) Extruder

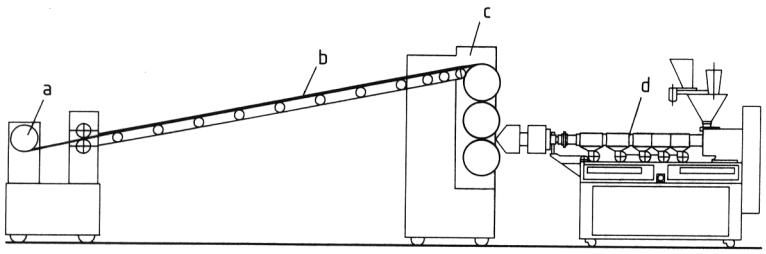


Figure 25. Flat film extrusion line
a) Winder; b) Roller belt; c) Roll mill; d) Extruder

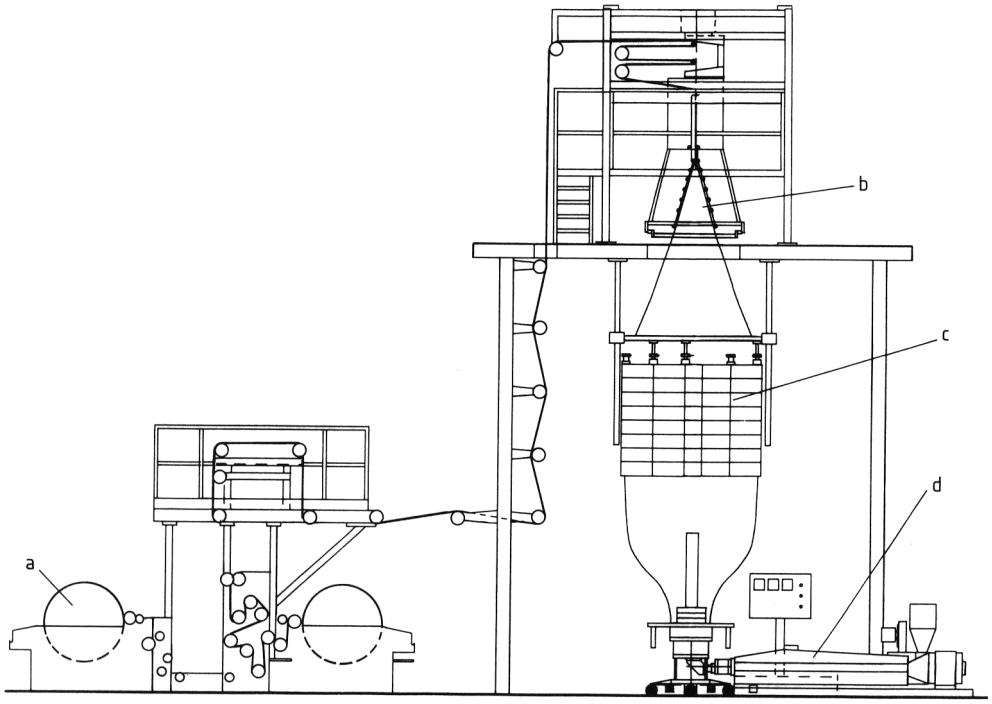


Figure 26. Blown film line
a) Twin winder; b) Guide rolls and collapsing boards; c) Calibrating basket; d) Extruder

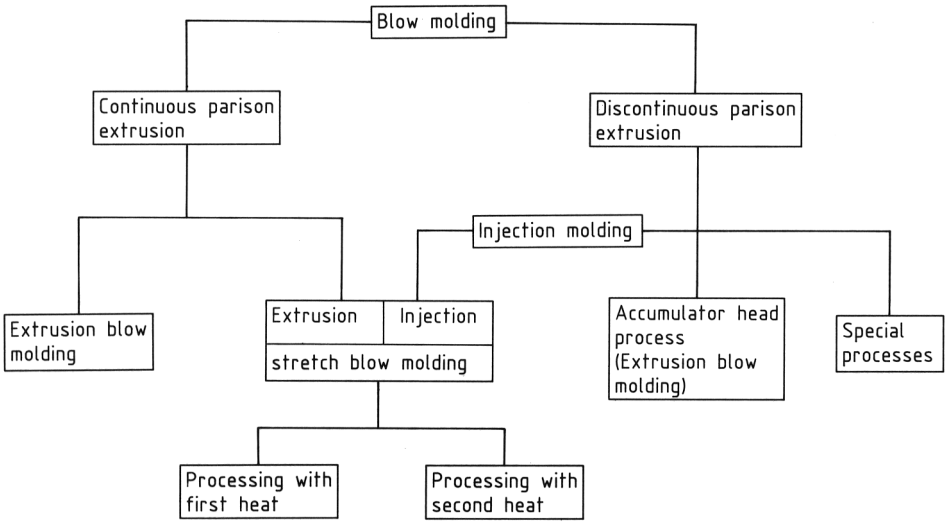


Figure 27. Blow molding processes

on reels. A calibration unit to maintain constant film bubble width can be mounted between the cooling ring and the collapsing board.

Coextrusion. The multitude of demands placed on modern extruded products can sometimes not be met by a single material. A solution to this problem is coextrusion, in which two or more molten materials are combined in a die under pressure. In adaptor coextrusion dies, the individual melt streams are combined in a so-called adaptor and subsequently shaped together in the melt distributor. In multiple manifold dies, each melt stream is individually shaped prior to being combined. Possible adhesion problems between various materials are addressed by incorporating coupling agents.

Well-known examples of the use of coextrusion include cable insulation and packaging films, where composite films with up to seven layers are used.

With coextrusion lines, the individual extruders and subsequent units are essentially identical to the corresponding units in the conventional lines.

4.4. Blow Molding

The most commonly employed techniques for manufacturing hollow articles from thermoplastic materials are extrusion blow molding and related processes such as stretch blow molding. Figure 27 gives an overview.

Blow-molded articles include simple products such as bottles and more complex components such as ventilation ducts, surfboards, suit cases, roof racks, or fuel tanks for automobiles. The volume of such articles can vary from a few milliliters (packaging for medical products) to ca. 13 000 L (tanks for heating oil).

Extrusion blow molding is made up of two parallel processes:

1. Continuous extrusion of a preform (parison)
2. Batchwise shaping of the preform in a mold by using compressed air

The individual steps of the process are shown in Figure 28. The first step begins when the extruded tube (parison) has reached the required length. The mold closes around the parison, which is then cut by a blade. The mold is then conveyed to the blowing station, the blow mandrel is inserted into the mold, and the actual blow process is carried out. After cooling, the mold is opened and the finished molding removed. The open mold then returns to the position below the extrusion die so that it can accept a new parison. Large and heavy molds are not moved; instead, the parison is cut by a gripper that transports it to the mold.

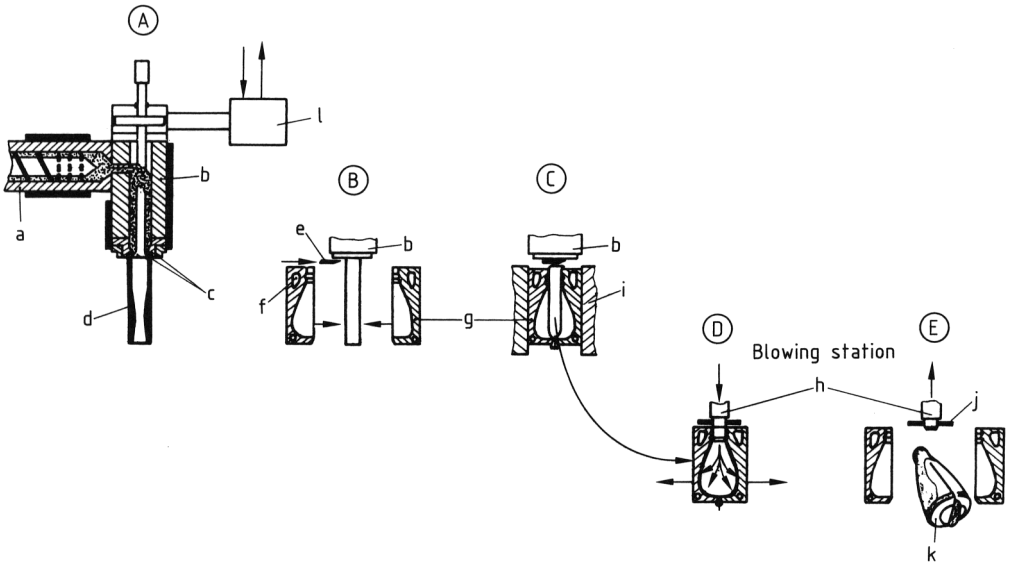


Figure 28. Extrusion blow molding process
A) Parison extrusion; B) Positioning of blow mold; C) Collecting and cutting of parison; D) Shaping and cooling; E) Demolding and flash trimming
a) Extruder; b) Crosshead die; c) Nozzle and mandrel; d) Parison; e) Cutter; f) Cooling channel; g) Blow mold; h) Blow mandrel; i) Closing unit; j) Stripper ring; k) Molding; l) Servohydraulic

An extrusion blow molding machine has four major components (Fig. 29):

1. Machine frame with closing mechanism and blowing station
2. Mold
3. Extruder
4. Crosshead and die

The machine frame is the basic framework of the machine and contains the closing mechanism as an integral component. The latter has the task of opening and closing the mold halves (similar to an injection molding machine), as well as transporting the mold between the die and the blowing station. The closing unit is normally of lighter construction than the counterparts

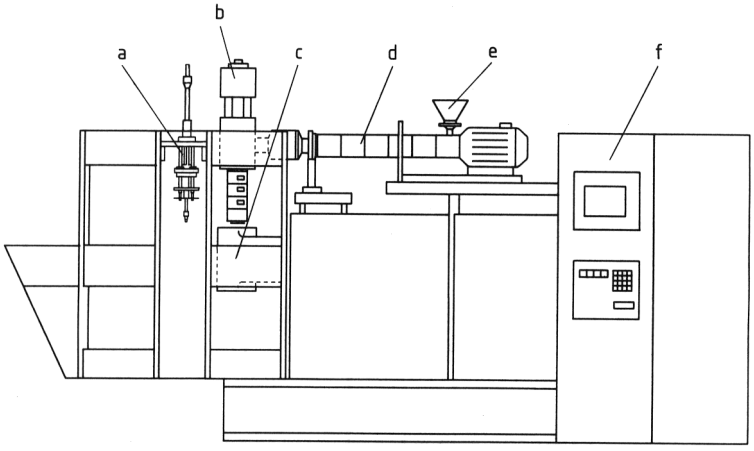


Figure 29. Extrusion blow molding machine (Krupp – Kautex type)
a) Blowing station; b) Blowing head; c) Mold; d) Extruder; e) Metering station; f) Control unit

involved in injection molding since the mold closing forces are relatively low because of the low mold internal pressure (ca. 0.8 MPa). The closing mechanism is driven hydraulically.

The blowing station is that part of the equipment in which the mold is located when the blowing mandrel is inserted and the actual blow process occurs.

The blowing mandrel introduces inflating air and shapes and calibrates the neck of the finished article. Figure 30 shows a closed mold containing a parison and the inserted blow mandrel.

The mold consists in general of two halves in which the negative contours of the molding have been incorporated. This has the function of shaping the parison, cooling the molding, and forming the welds. The latter are necessary because the parison is a portion of an extruded tube, which can only be blow molded when the ends have been sealed, preventing the escape of compressed air. In the case shown in Figure 30, one of the ends is sealed by the blow mandrel. At the other end, the tube is compressed during the closing motion by the pinch-off edges of the mold, and the molten material is welded together. These weld seams are a telltale characteristic of extrusion blow molded products. Thus, materials for blow molding must be weldable.

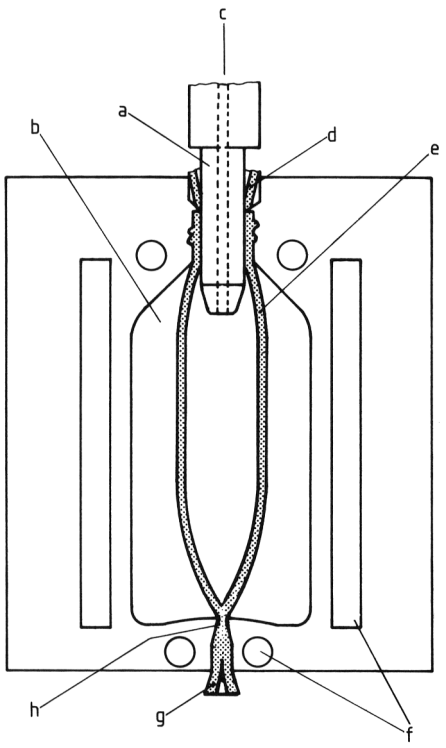


Figure 30. Blow mold
a) Blow mandrel; b) Mold cavity; c) Blowing air inlet; d) Top flash; e) Parison; f) Cooling channels; g) Bottom flash; h) Pinch-off blade

Cooling is possible on only one surface of the molding — the outer surface — by a water-cooled mold. Hence, cooling times are longer than those associated with injection molding, in which heat can also be removed through the core of the mold. This problem is counteracted by incorporating an exhaust air bore in the blowing mandrel. Compressed air flows through this and over a throttle (to maintain the required pressure); hence a circulating exchange of air takes place within the blow section, which also has some heat-transport effects (purging air technique).

Cooling times can be reduced further by using highly cooled nitrogen (N_2 process) as a blowing medium or adding liquid carbon dioxide (CO_2 process) to the compressed air.

Because compressed air seldom has a pressure greater than 0.4 – 0.6 MPa, no great demands are placed on the mechanical design of the mold. Due to its good thermal conductivity and workability, aluminum is widely used.

Like other processing techniques, the extruder must provide a thermally homogeneous melt stream of predetermined flow rate and pressure. For blow molding, single-screw extruders with a screw length of 20 – 25 D are generally used. A grooved and cooled feed zone is also used for some plastics (see Section 4.3).

In general, the screws are equipped with mixing zones to attain adequate melt homogeneity.

The so-called crosshead or parison die is flanged onto the extruder. This has the task of changing the melt flow direction from horizontal to vertical and forming a tube.

Near the outlet region, the flow channel is generally conical, and either the inner or the outer cone is movable, allowing continuous adjustment of parison wall thickness during extrusion. In this way, uneven blow ratios, which can occur with articles of complex geometry, can be accommodated and products with almost constant wall thicknesses can be manufactured (Fig. 31). This technique is referred to as wall thickness programming.

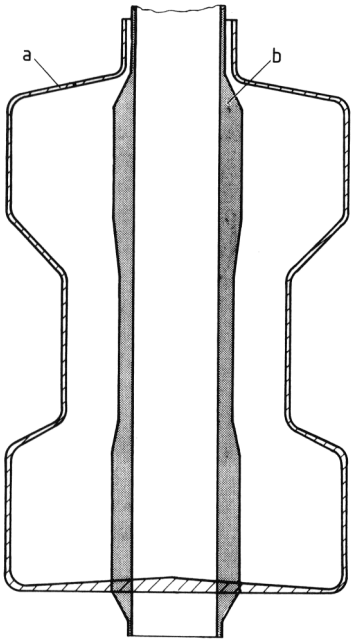


Figure 31. Wall-thickness profiled parison
a) Blown product; b) Parison

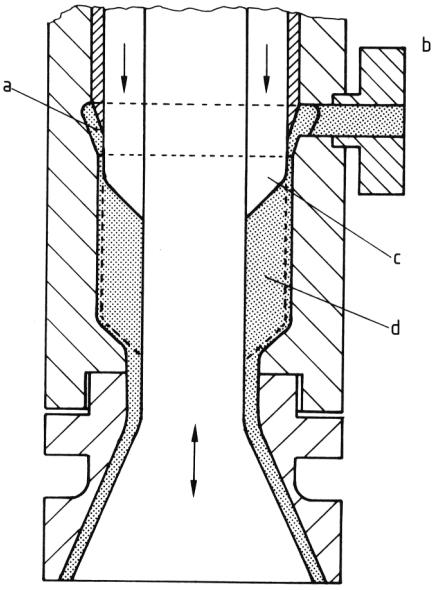


Figure 32. Accumulator head
a) Ring channel; b) Extruder; c) Annular piston; d) Accumulator chamber

A distinction is made between blow heads that function in a continuous mode and so-called accumulator heads. In the former, a continuously extruded tube is cut and passed to the blow mold in a cyclic operation. With large articles (i.e., molding volume greater than ca. 30 L), the parison itself is so heavy that it may deform under its own weight during extrusion. In such cases, accumulator heads are employed in which the melt is collected in a storage chamber and rapidly ejected by a piston to form the parison (Fig. 32). Modern storage heads are equipped with ring-shaped storage chambers, which are continuously fed with melt by one or more extruders according to the FIFO (first-in, first-out) principle.

Use of parison wall thickness regulators is also possible with storage heads.

Stretch blow molding is a special form of blow molding. The process exploits the fact that high degrees of orientation can be introduced in plastics by drawing at temperatures near the glass transition temperature or crystalline melting point. Mechanical properties are considerably improved in this way. In this process, the preform is drawn not only in the circumferential direction (as with extrusion blow molding) but also in the machine direction. The longitudinal drawing is brought about mechanically by using a ram. Because of the relatively low temperature at which this process is carried out, high deformation forces are required (air pressure up to 2 MPa).

Figure 33 illustrates the principal steps involved in stretch blow molding, beginning with an injection molded preform.

Preferred materials for use with this process are PVC, polypropylene (PP), and poly(ethylene terephthalate) (PETP).

The preforms for stretch blown moldings are prepared mostly by injection molding and are subsequently either oriented immediately in an injection stretch blow molding machine or first cooled and then fed to a separate stretch blow molding machine.

Preforms made of PVC for example, which are not suited for manufacture by injection molding, are prepared in an extrusion blow molding process and then processed on extrusion blow molding equipment.

Injection-molded preforms have the advantage of exact wall thickness distributions and a

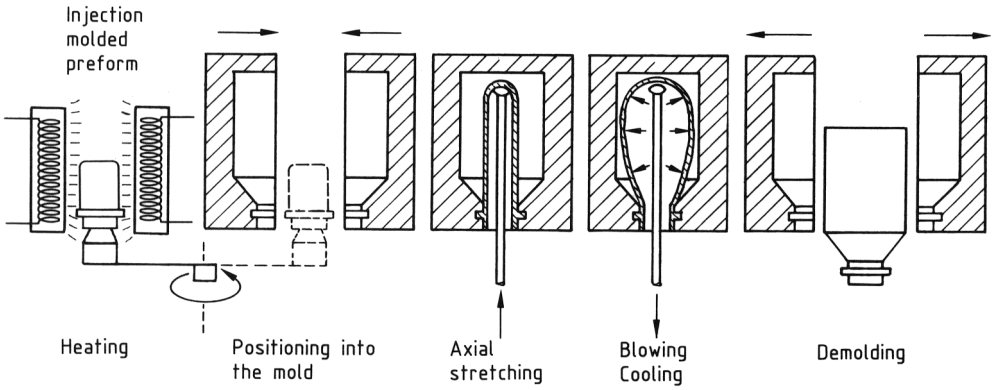


Figure 33. Stretch blow molding process

precisely calibrated neck. Additionally, they are free of weld seams.

4.5. Injection Molding

Injection molding is the most important process for producing moldings from thermoplastics, elastomers, and thermosets. The significance of injection molding is due to its ability to manufacture complex molding geometries in a single stage with high levels of reproducibility. A finishing operation (removing the runner, deflashing) is seldom necessary. Because of the high degree of automation possible, this molding process is also suitable for mass production operations.

Apart from its use for commodity articles, this technique is increasingly being used to produce technical moldings (e.g., compact discs, automobile bumpers).

The size of the molding can vary from a few tenths of a gram to several kilograms.

Injection molding machines consist of several individual units (Fig. 34). The most important components are the plastication unit for melting the plastic pellets, the clamping unit for holding and closing the injection mold, the control unit for coordinating the process, and a temperature control unit for cooling or heating the mold.

Injection molding is a discontinuous process in which plastic pellets, granules or powder is melted and injected under pressure into the cavity of a mold, where it is solidified by cooling or thermally cross-linked.

Process Stages. Production of an injection molding involves the following steps, which make up the injection molding cycle (Fig. 35):

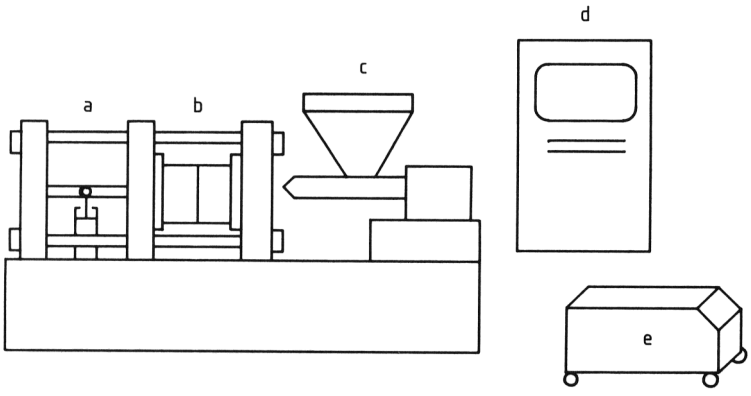


Figure 34. Schematic of an injection molding machine
a) Clamping unit; b) Mold; c) Plasticating unit; d) Control unit; e) Temperature control unit

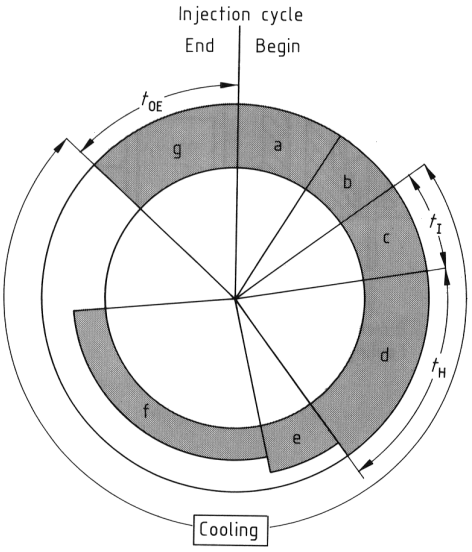


Figure 35. Injection molding cycle
a) Closing the mold; b) Moving the plasticating unit forwards; c) Injection; d) Holding pressure phase; e) Moving the plasticating unit backward; f) Metering; g) Opening the mold and ejection of molding

1. Closing the mold
2. Injection
3. Holding pressure stage
4. Cooling stage
5. Metering
6. Opening the mold
7. Ejection/removal of the molding

This cycle is repeated for each molding.

The cycle begins by closing the mold after ejection of the molding from the previous cycle (Fig. 36). The hot melt prepared in the front part of the injection cylinder is injected into the mold cavity through the runner system. Because of the increasing length of the flow path and the cooling of the melt in the mold, the pressure required to move the cylinder and polymer melt increases. Toward the end of the filling stage, the maximum injection pressure must be exerted. Depending on the material, molding, and process control, this can vary from several bar to 2000 bar. Injection times vary from several hundredths of a second to minutes.

The holding pressure phase begins at the end of the injection phase. Its objective is to counteract volume losses caused by cooling of the melt in

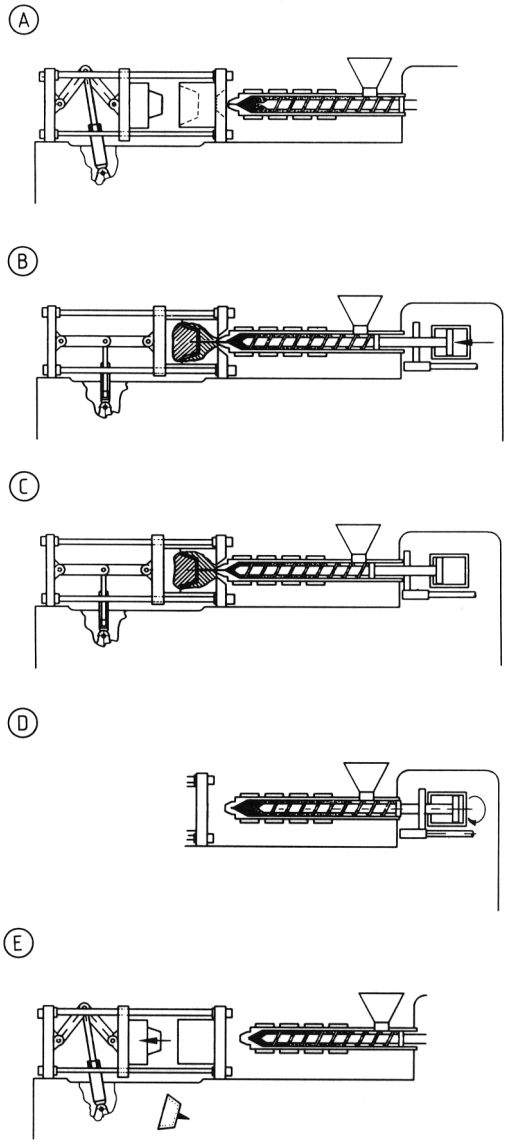


Figure 36. Machine status in various stages of injection molding cycle
A) Closing the mold; B) Injection; C) Holding pressure and cooling stage; D) Metering; E) Mold opening and ejection of molding

the mold and hence avoid sink marks and voids in the molding. At the beginning of the injection process, the melt, which is at 200 – 300 °C, begins to cool in the mold. After the holding pressure stage, the molding must be cooled until its dimensional stability is sufficient for ejection. The cooling time thus extends from the beginning of injection until the mold is opened.

At the end of the holding pressure phase, the plastication unit begins to prepare the plastic for the next cycle by rotating the screw. The screw moves helically backward in the plastication cylinder against a back pressure and thus transports melt to the area in front of the screw.

After the cooling stage, the mold is opened and the molding is removed mechanically, pneumatically, or by handling equipment.

The total cycle time depends on the maximum wall thickness and the geometrical complexity of the molding. With simple, thin-walled moldings, cycle times of ca. 1 s are possible, whereas with bulky, thick-walled moldings, cycle times of several minutes may be necessary. The process itself is coordinated by a control unit and is fully automated.

Machine Components. *Plastication Unit.* The plastication unit of an injection molding machine plastifies, meters, stores, and injects the plastic.

To meet these requirements, general-purpose screws are used (Fig. 37).

With these so-called reciprocating screws, the polymer is plasticated by the rotary motion of the screw as in an extruder (see Section 4.3) (Fig. 38). Simultaneously with the turning movement, the screw moves backward from the forward end position against a back pressure. This translatory motion results from transport of the melt into the area in front of the screw.

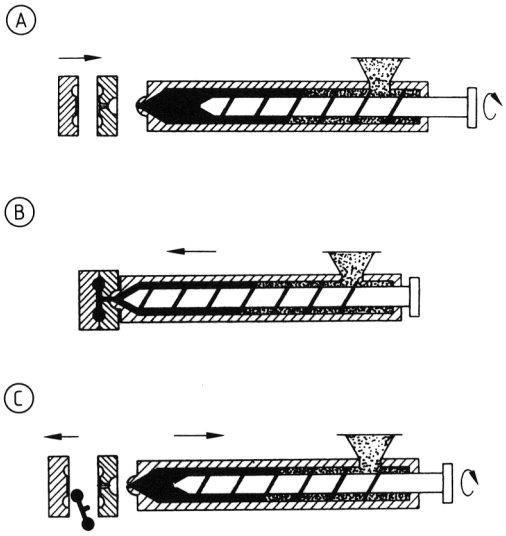


Figure 38. Reciprocating screw injection molding machine
A) Melt in front of the screw; B) Injection by screw stroke; C) Demolding and plasticating by screw rotation

At the end of the metering step, material is injected into the mold by a purely axial motion of the screw. Today, both the rotational and the translational movements of the screw are generally carried out hydraulically. However, using electric drives for the rotational motion is becoming more common, because they consume less energy than hydraulic systems.

The injection pressure for axial displacement of the screw is provided by a hydraulic cylinder.

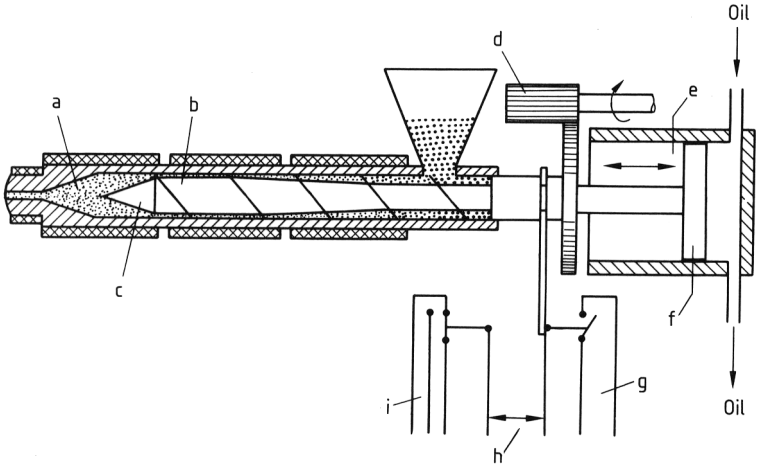


Figure 37. Conventional plasticating unit
a) Shot chamber; b) Screw; c) Screw tip; d) Screw drive; e) Hydraulic cylinder; f) Hydraulic piston; g) Back limit switch (stops rotation of screw); h) Injection stroke; i) Front limit switch (switching from injection pressure to holding pressure)

The general-purpose screw has three zones: (1) feed zone, (2) compression zone, and (3) metering zone.

The feed zone draws the polymer granules from a hopper into the screw. To achieve high mass throughputs, despite the low bulk density, the channel depth of the screw is relatively high.

In the compression zone, material transported from the feed zone is compressed.

In the output or metering zone, the melt is homogenized and heated to processing temperature.

Screw diameters range from 14 to 200 mm, and screw lengths, between 18 D and 24 D. To adapt the injection volume to the volume of the molding, usually the stroke of the screw (i.e., the distance between the front position after injection and the back position after plastication) is varied. The screw stroke cannot be increased to an unlimited extent by varying the back position, because when the screw is moved back the remaining screw length decreases. Therefore the effective length of the screw for melting and homogenizing the plastic is decreased, which results in a lower temperature for the plasticated material.

It is also possible to exchange the plastication unit and, therefore, the screw diameter and maximum stroke on a given machine.

During plastication, the machine nozzle that joins with the mold is sealed either by the runner of the molding or by a shutoff nozzle (Fig. 39) to prevent leakage of the melt caused by the pressure under which the plasticated material is held.

To prevent back flow of the melt during injection, a nonreturn valve is sometimes mounted at the tip of the screw (Fig. 40). The locking ring is pushed forward during plastication, which allows the melt to advance; during injection, the ring is pushed back, sealing the area in front of the screw.

Besides the general-purpose screw, screw geometries also exist that are specially adapted to suit the polymer to be processed. These include thermoset screws, rubber screws, and special screws. With degassing screws (Fig. 41), any moisture or residual monomer present in the melt is removed through an opening in the cylinder wall.

The most significant advantages of the reciprocating screw system include the mild plastication that allows the processing of thermally sensitive products, the lower cycle time, and compact construction compared to ram plasticators. Apart from the horizontal construction illustrated in Figure 34, the plastication unit can also be mounted vertically.

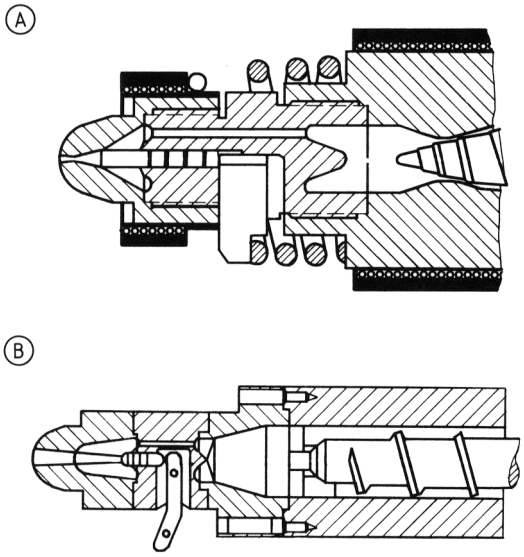


Figure 39. Shutoff nozzles
A) Needle valve nozzle (spring loaded); B) Needle valve nozzle (separately controlled)

Although such reciprocating screws are most frequently employed, specialty constructions also exist, for example ram extruders with screw preplastication units (Fig. 42). The polymer is plasticated in an extruder, and the resulting melt flows through a nonreturn valve into the reservoir chamber in front of the injection ram. Such systems are used only in special cases.

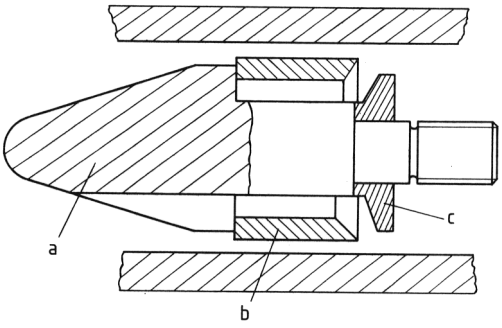


Figure 40. Nonreturn valve with a mobile locking ring
a) Screw tip; b) Sliding ring; c) Thrust ring

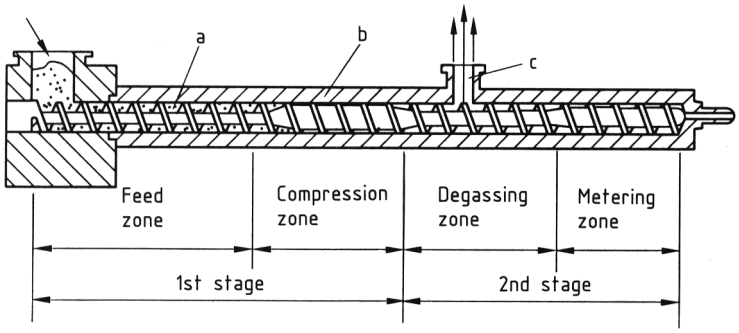


Figure 41. The degassing – plasticating unit of an injection molding machine
a) Melting; b) Cylinder; c) Degassing outlet

Clamping Unit. The clamping unit contains the halves of the mold, that are mounted on platens, and opens and closes the mold. Additionally, in most cases, mechanisms for ejecting the molding (e.g., cylinders for activating ejector pins) are also housed in the clamping unit.

During opening or closing of the mold, only one platen is moved. The platen on the side nearest the plastication unit is fixed to the machine frame and, hence, is immobile. The movement of the closing-side platen is guided by four tie rods (Fig. 43).

After closing, the full clamping force is exerted to prevent the mold from opening as a result of internal pressure during the injection and holding pressure phases. Otherwise, melt leaks in the parting surface (two mold halves) and which leads to formation of flash and possibly damage to the mold.

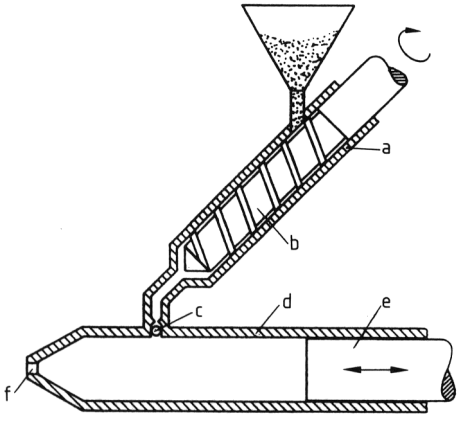


Figure 42. Injection molding with screw preplastication
a) Extruder barrel; b) Screw; c) Nonreturn valve; d) Injection cyclinder; e) Piston; f) Nozzle

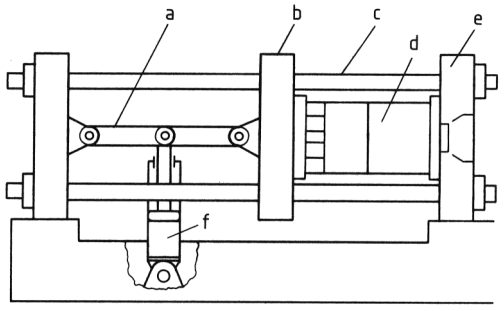


Figure 43. Toggle clamping unit
a) Toggle system; b) Moving platen; c) Tie rod; d) Mold; e) Fixed platen; f) Driving cylinder

Clamping forces of injection molding equipment range from 0.1 to 100 MN. Two main types of clamping mechanism are used:

1. Toggle clamping units (Fig. 43)
2. Fully hydraulic clamping units (Fig. 44)

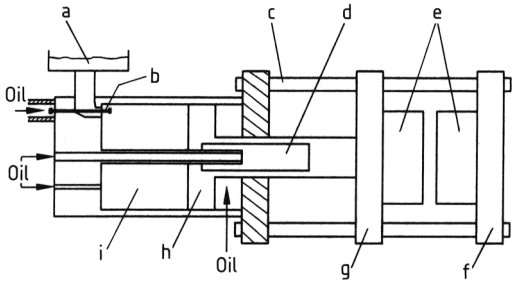


Figure 44. Hydraulic clamping unit
a) Oil tank; b) Suction valve; c) Tie rods; d) High-speed injection cylinder; e) Mold; f) Fixed platen; g) Moving platen; h) Main piston; i) Main cylinder

In the toggle clamping unit, the closing force is generated by extending a toggle driven by a hydraulic cylinder. The advantage of the toggle clamping unit is the favorable force – speed characteristic. High manufacturing costs are the main drawback.

With a fully hydraulic clamping unit, the clamping force is applied by a hydraulic cylinder alone. The advantage of this system is cheaper design; its disadvantage is the generally slower opening and closing motion.

Injection Molds. The central component in the injection molding process is the mold itself (Fig. 45). The injection mold does not form part of the machine, but must be constructed or modified for each molding. The number of design variations corresponds to the multitude of different injection-molded components. All molds, however, fulfill the following basic tasks. From a technological point of view, the mold must

1. Distribute the melt
2. Shape the melt to the desired molding geometry
3. Cool the melt (thermoplastics) or heat the contents of the mold (elastomers, thermosets)
4. Eject the molding

Additionally, the mold must meet design objectives, such as

1. Accomodate all forces
2. Transfer all motion
3. Guide mold components

To allow ejection of the molding, the mold consists of at least two parts. The front half, which contains the gate system and possibly also the flow channels, is mounted on the fixed, machine platen; the other half including the ejector mechanism is mounted on the moving platen of the clamping unit. Centering devices are used for precise adjustment.

In some cases, the molds have exchangeable inserts, which allow a basic unit to manufacture various moldings.

The mold is joined to the nozzle of the injection unit by the runner channel. The radius of the sprue bushing must always be greater than the radius of the nozzle, and similarly, the diameter of the sprue bushing bore must be larger than the nozzle bore. With voluminous moldings, a conical sprue gate is often used (Fig. 46). When the mold is opened, this is broken off at the

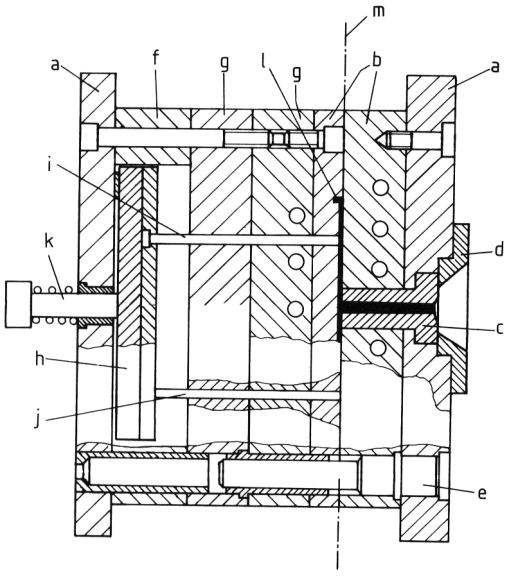


Figure 45. Injection mold
a) Base plate; b) Mold plate; c) Sprue bush; d) Locating ring; e) Guide pin; f) Supporting strip; g) Support plate; h) Ejector plate; i) Ejector pin; j) Ejector plate return pin; k) Ejector bolt; l) Molding; m) Parting line

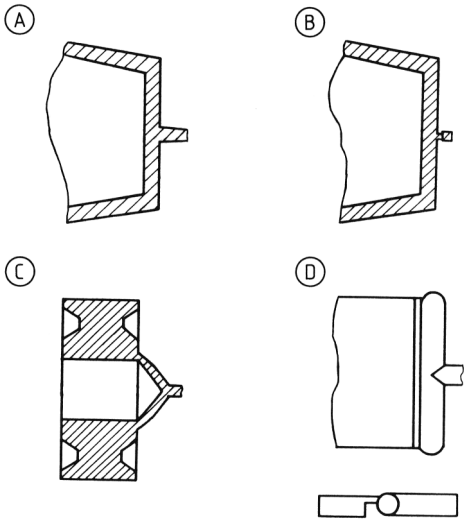


Figure 46. Gate types
A) Sprue gate; B) Pin gate; C) Disk gate; D) Film gate

nozzle. It remains as a stalk on the molding and must subsequently be removed. With a pin gate, the melt is injected through short, narrow holes into the mold cavity. During demolding, the gate breaks at the junction with the molding; no finishing process is required. Disk and film gates are used, for example, in the production of gear wheels or cartridges to avoid weld lines during filling. The film gate is advantageous with flat moldings because,in such cases,the linear filling avoids warpage and distortion of the molding.

Multicavity molds, which are used for simultaneous production of several moldings, are equipped with mold cavities connected to the gate channel by the manifold system. As with multiple gates on an individual mold, the gate and the runner system (hot runner mold) can be heated to reduce material requirements. Material in the hot runner system remains molten and is thus available for use in the next filling stage.

The runner system should be designed so that the melt fills each cavity uniformly and simultaneously at the same temperature and pressure. The position of the gate is chosen so as to avoid as much as possible the formation of weld lines that result when melt substreams combine. The position of the gate also determines the flow direction and hence the orientation on which mechanical strength, shrinkage, and distortion of the molding depend.

Special Processes. In addition to the classical injection molding process described above, several variations exist.

Injection – Compression Molding. With thin-walled, large-area moldings (i.e., when long flow lengths are involved), mold resistance is often so large that extremely high injection pressures must be exerted to fill the mold. With injection – compression molding, the mold is filled at only partial clamping pressure, causing the mold halves to open slightly (Fig. 47). To complete filling, the full clamping pressure is applied, whereby the clamping unit essentially operates as a press. The holding pressure exerted by the injection unit prevents the flow of the melt out of the mold cavity. Due to the homogeneous pressure over the complete injection area, moldings without warpage are obtained.

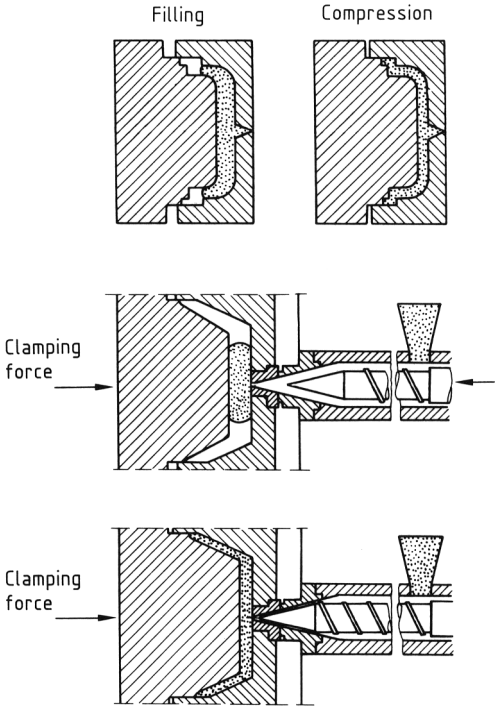


Figure 47. Injection – compression molding process

Intrusion Injection Molding. With thick-walled moldings, the injection pressure required for mold filling is usually so low that the pumping pressure from the rotating screw is sufficient. In the flow molding process (intrusion), the screw near the front end position plasticates the material and pumps the melt relatively slowly into the mold cavity under extrusion pressure alone. The holding pressure that counters shrinkage of the cooling molded component is applied by means of a short translational movement of the screw after the filling stage is completed. This process is used in the manufacture of thick-walled containers made of polyethylene and of PVC fittings whose volume exceeds the injection volume of the equipment by a factor of three to five.

Two-Component Injection Molding. The principal steps involved in two-component injection molding are shown in Figure 48.

The mold is first partially filled with material A. After the changeover point has been reached, complete filling takes place by injection of component B. During this stage, material A is

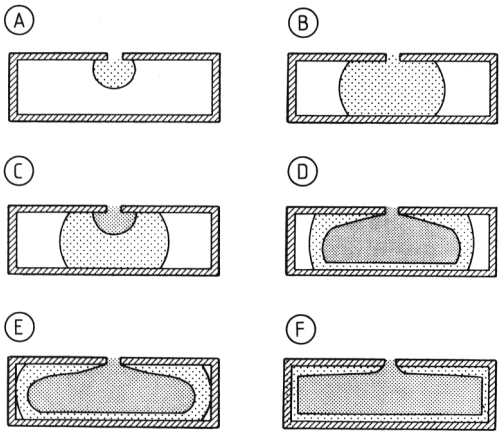


Figure 48. Two-component injection molding

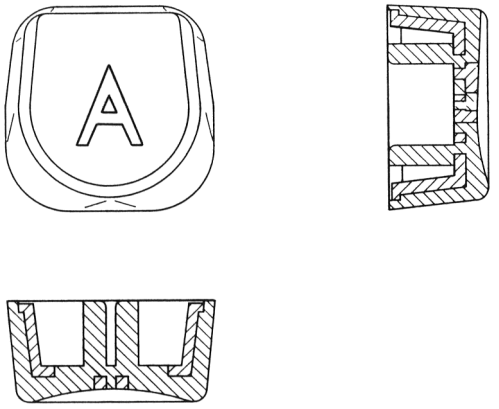


Figure 49. Two-color injection molding of a typewriter key

displaced by material B and forced against the walls of the mold. A multilayer molding is obtained in which the surface component A completely encloses the core component B. The external appearance of the molding and other surface properties are hence determined exclusively by material A.

The possible combinations of surface and core material are essentially unlimited, if adhesion between the two components is adequate and both materials exhibit similar shrinkage behavior. Two-component injection molding also offers economical and environmental advantages. The use of polymer waste and regranulate as the core material allows the molding to be manufactured at lower cost.

A second plastication cylinder is required for two-component injection molding.

Multicolor Injection Molding. In contrast to the two-component process, a sandwich-structured molding does not result with multicolor injection molding. In this case, all of the components form an integral part of the molding surface. This is illustrated in Figure 49 by using a typewriter key as an example. Another application is in the covers of automobile taillights; these are also injection molded with several colors.

Such combinations of different colors are achieved by rotating one-half of the mold (Fig. 50). First, one component is injected into a defined part of the mold cavity, while those regions of the cavity intended for components of another color are sealed. By rotating one-half of the mold, these regions are made available for filling with additional components.

Thermoplastic Foam Casting. Structured foam moldings are manufactured from thermoplastics (usually polystyrene, polystyrene copolymers,

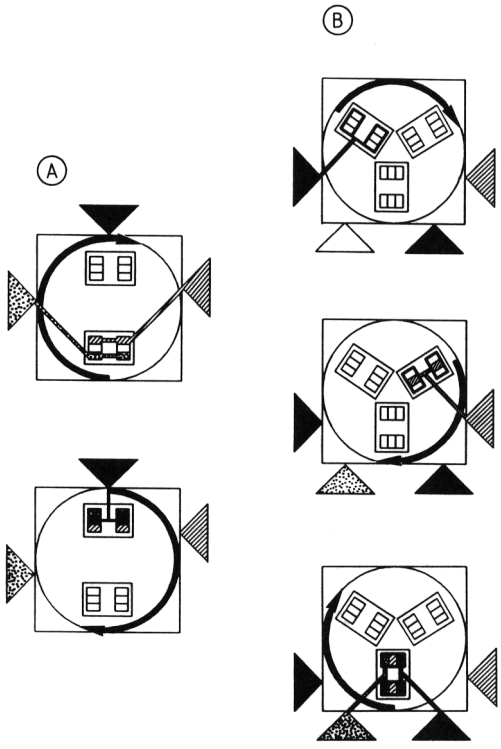


Figure 50. Multicolor injection molding
A) Three-color injection molding; B) Four-color injection molding

and polyolefins) containing a blowing agent. Moldings with a compact surface and a foamed core are obtained, which are employed mainly in the audio and furniture industries, as well as technical applications. Ram injection molding machines with screw preplastication units are generally used. The process requires lower injection pressures and closing forces than conventional injection molding techniques. The mold is only partially filled (50 – 80 %). Complete filling of the mold results subsequently from the foaming process. A holding pressure phase is hence unnecessary.

5. Forming Processes

The term forming refers to processes in which semifinished plastic products are heated and shaped under the influence of external forces. Apart from modifying the shape of an article, an objective of the process is often to increase material strength by introducing molecular orientation.

5.1. Drawing

To obtain an anisotropic material behavior in thermoplastics (usually an increase in mechanical stiffness and strength), the molecular chains must be oriented and the orientation frozen in. One way of achieving this is by stretching or drawing. The original semifinished product is heated to the drawing temperature and then mono- or biaxially drawn, followed by fixing the oriented state by cooling while the final shape is maintained. With amorphous thermoplastics, drawing is normally done at or around the glass transition temperature, and with semicrystalline materials, slightly below the crystalline melting temperature. When a drawn product is reheated, the forming process is reversed due to elastic deformations frozen into the article. If the draw ratio is not too high, the article may even revert to its original form. This ability to return to the original form can be desirable in some cases (e.g., shrink wrapping films). Generally, however, the product must be tempered (heat set) after drawing to relax any frozen-in elastic stresses.

The drawing of monofilaments and films is of major industrial importance.

Monofilaments are drawn in so-called godets (driven draw rolls). The fibers are fed through a preheating zone (oven or tempering bath) and taken off at high speed. The draw ratio is determined by the adjustable speed difference between individual godets. Typical draw ratios range from 1 : 3 to 1 : 12. Finally, drawn fibers pass through a tempering zone in which elastic deformations can relax while the orientation that has been introduced is retained. To compensate for shrinkage, the draw rolls run at slightly reduced speeds in this area. The whole process takes place simultaneously on many fibers, which are subsequently wound individually on spools. At this stage, a constant filament tension must be maintained. With multifilament machines, several hundred filaments are drawn simultaneously. Cold drawing is in principle a similar process, in which preheating is omitted. The fibers are heated by the internal shear to which the material is exposed on constriction.

Films are also drawn to increase their mechanical strength. Another reason, however, can be to reduce thickness. The film is heated by heated rolls and then passed over two pairs of rolls, with the second pair rotating at a higher speed than the first. This leads to monoaxial orientation in the machine direction. During this step, the film necks. If the film is to be biaxially oriented, it is held at both edges by a series of clips mounted on a chain that draw the web in the transverse direction (Fig. 51). This process can be carried out simultaneously with longitudinal drawing or separately in a second process step. Once the drawing process has been completed, the film is cooled and wound in a roll. As with calenders and fiber spinning equipment, biaxial drawing units

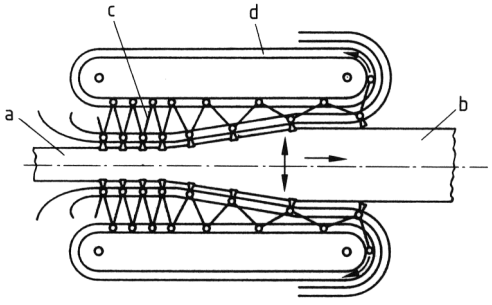


Figure 51. Biaxial simultaneous drawing
a) Initial sheet; b) Drawn sheet; c) Tenter chain; d) Guide frame

with integrated film extrusion are expensive. The most important oriented films include polyethylene, polypropylene, polystyrene, and polyester. Major products include films for magnetic tapes and for capacitors.

5.2. Thermoforming

The manufacture of three-dimensional moldings from flat plastic preforms such as films or sheets, under the influence of heat and pressure or vacuum, is a process referred to as thermoforming. In principle, the process can be carried out by a variety of techniques. Industrially, the most important method is the molding of a heated preform using a vacuum or compressed air, as well as mechanical stretching. Forming is carried out in the rubber-elastic temperature range, although in contrast to drawing , the introduction and freezing-in of orientation must be avoided as much as possible. For this reason, forming temperatures as high as possible are selected, which are essentially limited only by the onset of flow of the material, so that sufficient opportunity to relax is available. Depending on the material and temperature, geometric draw ratios of several hundred percent can be attained in thermoforming.

The range of products that can be manufactured by this process varies from packaging containers (up to 100 000 articles per hour) to bulky moldings such as swimming pools 8 m×4 m×1.5 m (1.5 articles per hour). Furthermore, this is also an important process for the production of automobile components such as dashboards and passenger compartment panels.

The preferred materials for processing include amorphous thermoplastics [PVC, polystyrene (PS), acrylonitrile – butadiene – styrene (ABS), styrene – acrylonitrile (SAN), cellulose acetate butyrate (CAB), PMMA, and PC], as well as semicrystalline materials (PP, PE, PETP) and special laminates that economically combine the favorable properties of several polymers in one film.

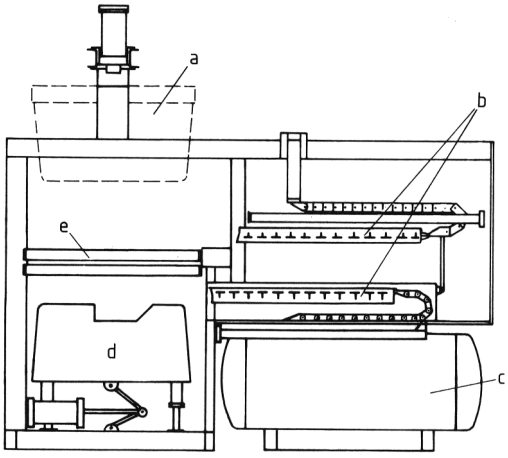


Figure 52. Single-station thermoforming machine
a) Top mold; b) Movable heaters; c) Vacuum tank; d) Bottom mold; e) Molding station

Thermoforming is a purely stretching technique that is carried out as a continuous process. The article to be formed is secured at the edges, and the geometric increase in area is thus accompanied by a reduction in thickness.

Two types of industrial thermoforming machines have become established:

1. Single-station machines
2. Multistation machines

With *single-station machines* (Fig. 52) the heating and forming steps take place in the same station. The heating system is generally conveyed to and from the article; occasionally, however, the secured preform is transported to the heating zone. With multistation machines (Fig. 53), heating and forming take place in separate stations.

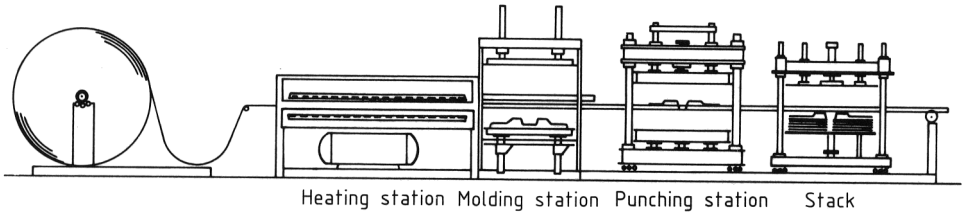


Figure 53. Multistation thermoforming machine

The technique of thermoforming polymers can be broken down into three basic process steps:

1. Heating
2. The transfer and forming process
3. Cooling

Heating, the first stage in all thermoforming techniques, is of decisive importance for the final quality of the molding. The process involves heating the sheet from its original temperature to the forming temperature.

Because films and sheets in thicknesses ranging from ca. 0.1 to 12 mm are thermoformed, a variety of preheating methods have evolved:

1. Convection heating
2. Contact heating
3. Heating with infrared radiation

In all the techniques, heating can be either single or double sided. With the exception of extremely thin films, two-sided heating is generally employed.

Heating with infrared radiation is used most widely today. Its major advantage is that because a portion of the energy penetrates directly into the bulk of material, high heat flow densities can be used to decrease the heating time without causing thermal damage to the polymer surface. Ceramic and quartz elements are the primary sources of radiation. The heating stations in modern thermoforming equipment consist of numerous, individually controlled radiator elements in a modular structure. In all thermoforming processes the heated preform is rapidly drawn biaxially. This generally takes place in half a second and thus can be assumed to be isothermal as long as it is a free draw (i.e., without contact to the mold). On contact with the walls of the mold, however, the material cools immediately. Particularly with semicrystalline thermoplastics, which are formed at or slightly below the crystalline melting point, this leads to a spontaneous increase in the resistance to deformation. To exert the necessary force, mechanical drawing mechanisms, compressed air, and vacuum are utilized.

With thermoforming, a distinction is drawn between male and female forming processes (Fig. 54). The decision to employ a male or a female process depends primarily on which side of the molding is to be replicated exactly. Only

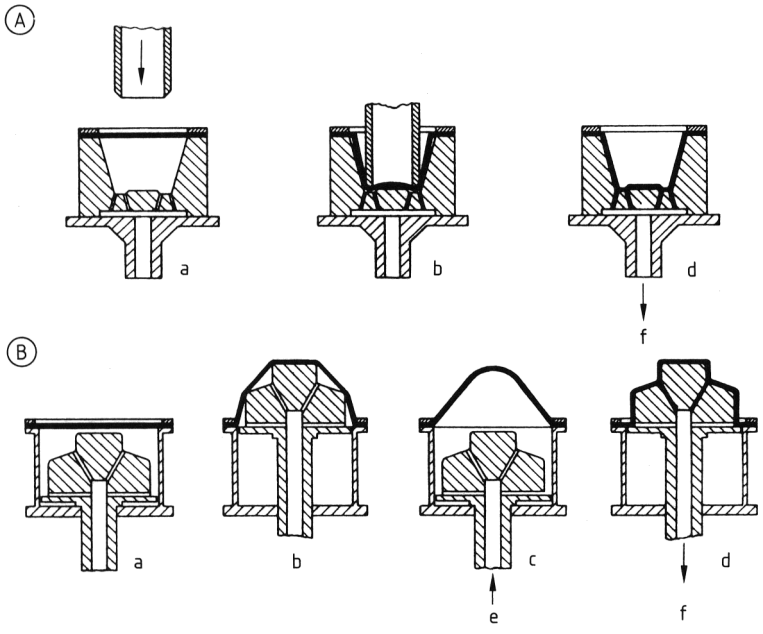


Figure 54. Vacuum forming
A) Female forming; B) Male forming
a) Original state; b) Mechanical prestretching; c) Pneumatic prestretching; d) End state; e) Compressed air; f) Vacuum

the surface in contact with the mold is dimensionally precise, whereas the other surface exhibits its inherent inaccuracies, particularly in the unavoidable rounding of corners. The cooling process begins, by definition, once the film comes in contact with the mold and ends at the onset of the unmolding step.

For mass production purposes, the mold is equipped with temperature regulation. Mold temperatures vary from approximately 10 °C (PP packaging materials), to 70 °C [polystyrene (PS) inner panels for refrigerators], up to 100 °C [high-density polyethylene (HDPE) moldings]. Depending on the numbers of articles to be manufactured, the machines are fitted with single- or multicavity molds.

In most cases, one side of the material is cooled by contact with the mold, and the other surface is cooled by convection. Convective cooling occurs either via ambient air (free convection) or by use of a ventilator (forced convection). To intensify the cooling effect, atomized moisture is also added to the ventilated air (spray nozzle cooling).

The main advantages of thermoforming compared to alternative manufacturing techniques are the low mold costs, the short processing times, and when multicavity molds are used, the high throughputs. Additionally, reduced wall thicknesses are possible compared to injection molding. Thermoformed articles generally have about half the weight of equivalent injection-molded products.

In contrast to injection molding processes in which pressure acts only on the surface perpendicular to the flow direction during molding, in thermoforming the total mold surface is used. This is the reason thermoforming pressures are 20 – 30 times lower, and also the reason large moldings can be manufactured with lighter equipment, lower forming pressure, and lower energy consumption.

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Plastics, Processing, 2. Processing of Thermosets

ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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1. Vinyl Ester Resins, and Phenol – Formaldehyde Resins

In curable polymers, the liquid or meltable resins as received from the supplier are rendered solid, insoluble, and unmeltable during processing by addition of a curing agent. This reaction can occur independently or be initiated by heat or ultraviolet radiation.

This two-phase formation of the resin has the following advantages: a multitude of processing and design possibilities are available when starting materials that are liquid or that can be melted are employed. The resins can be dyed and processed with or without filters. By embedding reinforcing fibers, composite materials are obtained whose mechanical properties can be modified to suit the demands placed on the completed product simply by selecting the type, amount, and orientation of the fibers introduced, along with the processing technique employed. The properties of the finished article are governed not only by the choice of material, but also by the processing technology and the curing method.

Various processing techniques differ mainly in the complexity of the equipment used to provide the shape and to impregnate the reinforcing fibers. Customized moldings, small series, and bulky molding, as well as paneling and protective layers, can be manufactured manually with simple equipment. For large-scale operations, mechanized processes with a low manual cost contribution but correspondingly complex plants are available.

Table 1 gives an overview of the processing techniques for glass-fiber-reinforced composites. The use of more sophisticated processing machinery leads to improved reproducibility of properties, greater dimensional precision, and savings in terms of finishing operations. When selecting a process, one should consider the fact that the strength of the finished product depends strongly on fiber content. This is influenced, among other things, by the starting material and the processing pressure.

Table 2 lists a selection of mechanical characteristics of glass-fiber-reinforced unsaturated polyester (UP) resins with various types of

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Table 1. Applications and characteristics of different processing methods for fiber – plastic composites*

	Manual processing	Fiber spray-up process	Vacuum bag process	Resin transfer molding	Cold liquid resin press molding	Hot liquid resin press molding	Press molding of molding compounds	Filament winding	Rotation molding	Pultrusion	Continuous lamination	Autoclave process
Application	single pieces, small series, large-area pieces	small to medium series, large-area pieces, linings	small series, large composite material	medium series	medium series	large series	large series	wound articles	rotationally symmetrical hollow moldings	solid and hollow profile	smooth and curved plates	high loaded components small series
Resins used	UP, EP	UP	UP, EP	UP	UP, EP	UP, EP	UP, EP, PF	UP, EP, VE	UP, EP, VE	UP, (EP)	UP	EP
Suitable reinforcing materials (glass content, wt%)	mat (20–30) fabric (35–50) rovings (50–70)	chopped strands (20–30)	mat (20–35) fabric (40–60)	mat (20–25) fabric (40–60)	mat (25–40) preform (25–40) fabric (50–60)	mat (25–45) preform (25–45) fabric (50–60)	mat (20–40) chopped strands (20–40)	rovings fabric (40–70) mat	mat (20–35) chopped strands (20–35) fabric (30–40)	rovings fabric (50–70)	mat (20–25)	fabric
Labor costs	high	high	high	medium	medium to high	medium	low	low medium to high	low	low	low	high
Investment	low	medium	low	medium	medium to high	high	high	high	high	high	very high	medium
Molds	open, one or multipart mold made of wood, metal, glass-fiber-reinforced plastic	open, one or multipart mold, made of wood, metal, glass-fiber-reinforced plastic	one part or with rigid counter-mold, made of wood, glass-fiber-reinforced plastic	closed, split mold made of glass-fiber-reinforced plastic	closed, split mold made of glass-fiber-reinforced plastic	closed, split mold made of steel	closed, split or multipart mold made of steel	one or multipart, steel mold core	one or multipart, rotor made of steel, aluminum	profile mold, sometimes with steel core		open, one part with vacuum bag
Economically feasible molding size, m^2			0.5–30	0.5–20	0.3–5	0.3–5	0.05–3	0.1–100	1–100		width ≤5 m any length	
Cycle time	30 min to several days	30 min to several days	30 min to several hours	30 min to several hours	5–30 min	2–10 min	2–5 min	depends on molding size	10 min to several hours			several hours
Processing temperature, °C	room temperature	room temperature	room temperature	room temperature	20–60	80–120	120–160	room temperature	room temperature	≤160	room temperature and higher	80–200
Pressure, MPa			≤1	≤4	≤10	10–30	2–50	filament tension	centrifugal force			≤2

Wall thickness, mm	2–10 usual	2–10 usual	1–5 usual	1–5	1.5–5	1–5	1–10	1–10	3–10	3–20	1–3	0.5–10
Wall thickness tolerances, %	mat ≤50 fabric ≤10	≤50 unavoidable	≤20	≤20	≤20	≤20	≤10	depends on reinforcement ≤20	≤20	≤10	≤10	≤5
Different wall thickness	possible	possible	limitedly possible	possible	barely possible	not possible	possible	possible	possible	usual in pulling direction	not possible	possible
Undercuts	possible with multipart mold	possible with multipart mold	limitedly possible	possible with multipart mold	not possible	not possible	possible	not possible	not possible	perpendicular to the pulling direction possible	perpendicular to the pulling direction possible	possible with multipart mold
Stiffening layers	possible	possible	possible	possible	limitedly possible	limitedly possible	possible	possible	not possible	possible	not possible	not usual
Gel coat	usual one side	usual one side	one-sided; with rigid countermold both sides possible	both sides possible	limitedly possible	not possible	not possible	possible	possible	not possible	possible	not usual
Surface	one side smooth	one side smooth	one side smooth; with rigid countermold both sides smooth	both sides smooth possible	both sides smooth, minor fiber structure	both sides smooth, minor fiber structure	both sides smooth	one side smooth	both sides smooth	all sides smooth	both sides smooth	one side smooth
Aftertreatment	edge trimming	edge trimming	edge trimming	deflashing, edge trimming	edge trimming	deflashing	deflashing	separate	separate	separate	separate, edge trimming	edge trimming

* UP = unsaturated polyester; EP = ethylene–propylene; PF = phenol–formaldehyde; VE = vinyl ester.

Table 2. Dependence of the properties of glass-fiber-reinforced UP moldings on reinforcing material and glass content

Property	Glass matss		Woven glass fabric		Glass rovings
Glass content					
wt %	20 – 30	40 – 50	40 – 50	50 – 60	70 – 80
vol %	11 – 17	25 – 32	25 – 32	32 – 42	53 – 66
Density, g/cm^3	1.3 – 1.5	1.5 – 1.75	1.5 – 1.75	1.6 – 1.85	1.9 – 2.1
Thermal expansion coefficient, 10^{-6} K^{-1}	40 – 30	24 – 20	22 – 18	18 – 16	14 – 12
Thermal conductivity, W K^{-1} m^{-1}	0.14 – 0.19	0.23 – 0.31	0.19 – 0.25	0.35 – 0.31	0.37 – 0.41
Tensile strength, N/mm^2	65 – 90	130 – 170	200 – 240	240 – 275	700 – 800
Breaking elongation, %	2	2	2	2	2
Modulus of elasticity (tensile), N/mm^2	5000 – 7000	9000 – 10 000	10 000 – 14 000	14 000 – 17 500	21 000 – 26 000
Bending strength, N/mm^2	115 – 145	180 – 220	220 – 260	260 – 300	400 – 500
Modulus of elasticity (bending), N/mm^2	5000 – 7000	9000 – 11 000	10 000 – 14 000	14 000 – 17 500	
Compressive strength, N/mm^2	110 – 135	165 – 200	150 – 180	180 – 200	
Shear modulus, N/mm^2	2000 – 3000	4000 – 5000	2000 – 3000	3000 – 4000	
Impact strength, kJ/m^2	25 – 55	75 – 105	130 – 160	160 – 190	

reinforcing material and fiber content. Figure 1 shows the market development for glass-fiber-reinforced polymers from 1986 to 1988.

Table 3 lists the main areas of application, and Table 4 the processing techniques that are employed.

1.1. Raw Materials

Selection. The most widely used reinforcing fibers are glass fibers (→ Fibers 5. Synthetic Inorganic, Section 2.1.) in the form of rovings, nonwoven fiber matting, and glass fabrics.

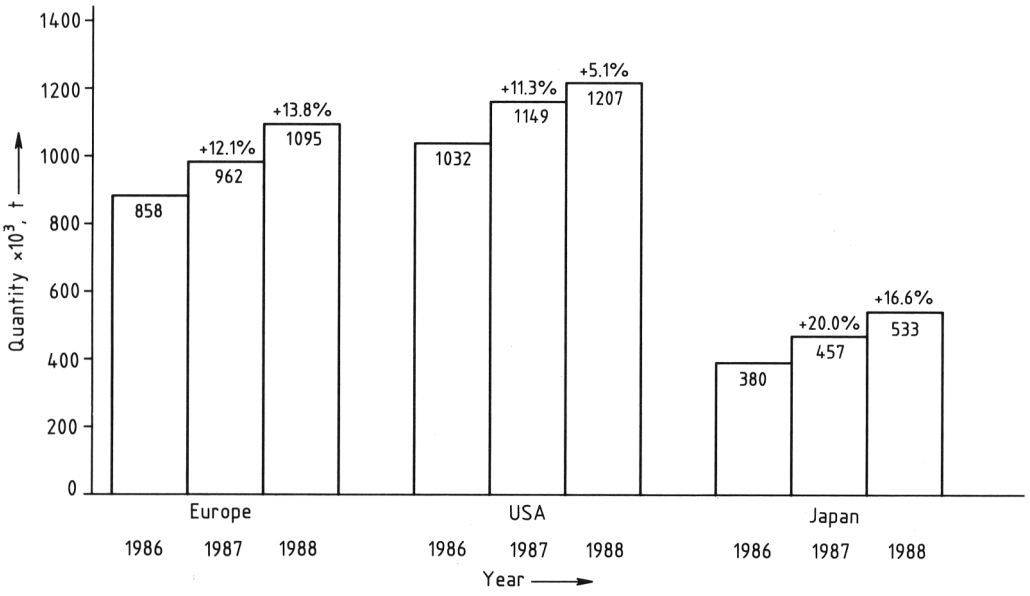


Figure 1. Development of glass-fiber-reinforced plastics market

Table 3. European glass-fiber-reinforced plastics market in 1988 according to end use

End use	Consumption, %
Construction	14.2
Sports and leisure	7.3
Industry and agriculture	18.0
Transportation	25.8
Electricity and electronics	18.1
Consumer goods	8.6
Military and other uses	8.0

Table 4. European glass-fiber-reinforced plastics market in 1988 divided according to process

Process	Use, %
Manual lamination	20.4
Fiber spraying	7.4
Press molding	29.2
Granulation (thermoplastic)	23.9
Injection molding (thermosets)	2.7
Continuous lamination	6.8
Pultrusion	1.5
Filament and rotational processes	4.5
Others	3.6

Carbon and aramid fibers, which were initially applied in aviation and space, are increasingly being used in industrial applications. Their significantly higher price compared with glass fibers is often justified by their much higher stiffness and strength and their more favorable thermal expansion behavior. All reinforcing fibers must be coated with a coupling agent to achieve satisfactory adhesion to the polymer matrix. Additionally, the coupling agents protect the fibers from abrasion during processing.

The resins are selected primarily for their final properties, corresponding to the demands placed on the finished product. With few exceptions, unsaturated polyester (UP), epoxy (EP), and vinyl ester (VE) resins can be processed by using all the techniques described below, although differing processing properties must be considered in selecting the resin. This applies particularly for phenol – formaldehyde (PF) resins, which cure via a condensation reaction and hence can be processed only under pressure.

The advantages of *EP resins* are air-drying cure; high filler levels possible; wide variation due to different combinations of resin and hardener; low volume shrinkage during curing (2 – 3 %), which begins before gelation and hence results in extremely good retention of dimensions and freedom from stress in the end product; no deformation during curing; high adhesive strength (i.e., good adhesion to the substrate and the fibers) and hence high mechanical strength of fiber-reinforced components, especially during dynamic loading.

In the latter case, the favorable mechanical properties of EP resins, including high fracture strain and tensile strength, also play an important role. High application temperatures may necessitate the use of EP resins. Certain types permit long-term service temperatures exceeding 200 °C.

Disadvantages of EP resins include high price; long curing times and hence higher processing costs; extreme care needed to meter resin and hardener; high viscosity, which makes degassing the resin and impregnating glass fibers difficult; sometimes difficulty in demolding as a result of low shrinkage.

The advantages of *UP resins* are low price; low curing times (i.e., rapid demolding is possible); easy handling due to low viscosity; low susceptibility to erroneous mixing of the final formulation.

Disadvantages of UP resins are higher volume shrinkage on curing (6 – 8 %), which makes it difficult to manufacture stress-free components and leads to a tendency to deform. In addition, during selection of the type of resin, attention must be paid to the reactivity. Low-reactivity resins cure with relatively low stresses, and the end products have good elasticity but generally exhibit poor resistance to corrosion and aging. High-reactivity products can be cured easily without heating, but removal of the heat of reaction must be effective to minimize stresses in the end product, shrinkage, and separation of the resin from the fibers, as well as possible thermal damage to the material itself. The long-term service temperature of components made from UP and VE resins is limited to 70 – 120 °C.

The advantages of *VE resins* compared to the chemically related UP resins include improved mechanical properties and, particularly, greater chemical stability, especially toward acidic media. Their disadvantage is the high price.

The PF resins represent one of the oldest and cheapest classes of polymer. Their advantages include very low manufacturing costs, excellent chemical and thermal stability, favorable

combustion behavior, and low toxicity of combustion products. This has led to considerable importance in applications where safety is a prime consideration (aircraft inner paneling, transportation). The drawbacks of PF resins are poor mechanical properties (low fracture strain) along with problematic processing. Because the latter can be carried out only under pressure, techniques involving open molds cannot be employed. Only processes involving presses and autoclaves are of any importance.

Because of their high price, EP resins are employed where higher material costs are justified by improved adhesion to the substrate or improved mechanical properties (e.g., for surface protection and coatings).

Because they are easy to process, UP resins are employed preferentially for glass-fiber-reinforced products, with the exception of components that must withstand high dynamic loads, such as helicopter rotor blades; components for aircraft, rockets, and spacecraft; and skis.

Where corrosion problems are likely to be encountered, resins are selected according to their resistance to chemical attack.

Transportation, Storage, and Safety. The inflammability of resin systems depends on their chemical composition. During storage, transport, and processing, the regulations and safety information provided by the supplier must be followed.

Reactive resins must be stored below 20 °C, with the exclusion of atmospheric moisture and light. Resins supplied as a final mixture ready for direct reaction and including the curing agent — as is the case, for example, with preimpregnated fiber materials known as prepregs — must be stored under refrigerated conditions at −18 °C.

During handling and processing of UP and VE resins, the skin and respiratory irritations that can result from the styrene component must be considered (MAK 20 ppm), along with the strong skin irritations that can be caused by several cross-linking agents. Particular care is necessary when dealing with peroxides, which are often used as hardeners (explosion hazard).

During the processing of EP and PF resins, safety gloves, clothes and glasses must be worn.

Several cross-linking agents for EP resins (e.g., amines) are strong skin irritants or can lead to allergic reactions. With PF resins, adequate ventilation must be ensured to remove reaction products.

1.2. Mold Materials

The choice of mold material depends on the processing technique and the number of articles to be manufactured. For casting, molds can be manufactured from flexible materials such as plasticized PVC or silicone rubber. These allow the production of moldings with undercuts. The number of castings is limited by the low solvent resistance.

Wood and plaster are used for making molding patterns; wood is also employed in manufacturing single-component molds for individual moldings or small production runs using pressureless processing techniques. The surface must be sealed with a paint that is resistant to aromatic compounds.

For the manufacture of glass-fiber-reinforced moldings in pressureless processes and the production of small series by cold press molding, a processor generally prepares his own molds from glass-fiber-reinforced UP or EP. The EP resins have the advantage of greater dimensional stability, but they must be coated to protect them from aromatic compounds. By casting a supporting substrate of polymer concrete or concrete on reverse surface, the molds can be made rigid.

For large production runs, metallic molds are most suitable. For hot press molding, heated molds made of tempered steel are employed. The sealing edges of molds for liquid resin press molding are formed as nip, shear, or pinch ridges. Molds for processing molding compounds and sheet molding compounds are described in Section 2.5.

To ensure faultless demolding, mold surfaces are treated with a release agent [wax, silicone grease, poly(vinyl alcohol)]. Prior to application of the release agent, the remains of any previous molding processes must be removed thoroughly.

1.3. Preparation of Resins

The resin components are either premixed by the supplier (e.g., prepregs) or metered and mixed by the processor. This is performed by automated mixers fitted directly to the processing machine (e.g., injection techniques such as resin transfer molding) or by hand mixing.

In all cases, the equipment (mixing vessels, stirrers, metering units, etc.) must be clean, dry, and free of residual deposits from previous batches. All components, including glass fibers must be thoroughly dried and, if necessary, warmed to room temperature before use. Mixing is best performed with a high-speed stirrer. The speed should be adjustable to avoid the inclusion of air bubbles. Highly viscous batches (e.g., EP resins) are prepared and held under vacuum until completely degassed.

The components are added in the following order: resin; styrene (with UP resins); plasticizer and diluent (with EP resins); hardener; additives such as stabilizers, lubricants, dyes, film formers, conductivity additives, thickeners, thixotropic agents, flame retardants, fillers, and accelerators. For properties and applications of additives, see → Plastics, Additives.

Materials that are difficult to disperse or additives that are not divided finely enough are made into a slurry before mixing by using small amounts of UP resin or EP thinner.

With UP resins, the curing reaction begins with addition of the second reactive component; initially the resin gels and then solidifies rapidly. Processing of the resin mixture must therefore be completed within the narrowly limited pot life dictated by formulation and processing temperature (i.e., before the onset of gelation). With resins that already contain an accelerator, the hardener is therefore always added as the final component. To avoid exceeding the pot life of UP resins prior to processing, the following procedure can be followed: all of the additives are mixed into the resin and the resulting batch is divided into two equal volumes. The hardener is added to one half, and the accelerator to the other. Immediately before processing, equal volumes of the two batches are mixed together.

With EP resins, the rate of hardening decreases with increasing viscosity. The pot life therefore does not end so sharply with the onset of gelation as with UP resins.

1.4. Pressureless Processing without Fiber Reinforcement

Casting and Embedding. Because of their light colors and low viscosity, UP resins are particularly suitable for casting figures and embedding specimens. The resin mixture can be adequately degassed by allowing it to stand for a short period prior to casting. For embedding two or more layers are usually cast. After the first layer has begun to cure, the item being embedded is laid on the surface and covered with further resin mixture. Because of shrinkage during curing, the casting must generally be finished by grinding and polishing.

EP resins are preferred for casting and embedding technical articles, where the slightly darker color is unimportant but high demands are placed on dimensional stability (e.g., for models) as well as embedding of electronic components. Figure 2 shows a schematic of a casting plant for EP resins. Resin and hardener are firstly melted or heated to lower the viscosity. Fillers and additives are then added. To degas the viscous resin mixture completely, mixing and casting must generally be done under vacuum.

When embedding electronic components, penetration of the resin mixture into joints and

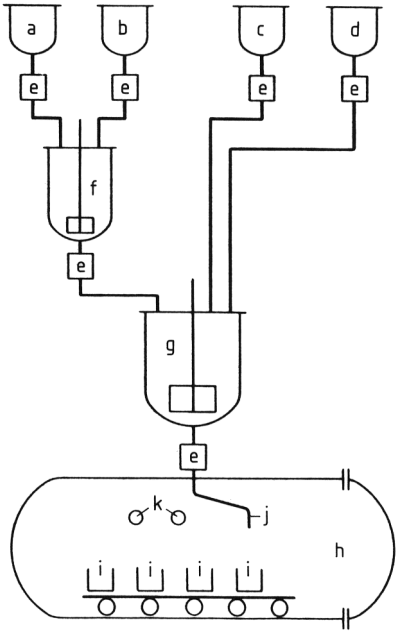


Figure 2. Schematic of a casting plant for epoxy resins
a) Heated storage tank for resin; b) Storage tank for fillers; c) Heated storage tank for hardener; d) Storage tank for other additives; e) Metering units; f) Heated, evacuable mixer; g) Heated and evacuated mixer for final mixing; h) Evacuable casting vessel; i) Casting mold; j) Swivel arm; k) Sight glasses

voids can be promoted by removing the vacuum once the casting stage has been completed.

In dipping processes, components are immersed in the resin mixture while under vacuum and exposed to atmospheric pressure after their removal.

In the drip process, the cold resin mixture drips onto a rotating, preheated substrate. During this process, the viscosity decreases and the resin penetrates any voids. This process is used among other things to bond axially parallel windings of wound articles (see Section 1.8).

Coating. Another important area for which EP resins are particularly well suited due to their excellent adhesion properties is in surface coatings. Coating is carried out with a liquid, low-viscosity resin – hardener system or with solid components dissolved in a solvent. Resin powders can be applied by fluidized-bed sintering, flame spraying, or electrostatic coating.

These processes and the continuous coating of printed paper or fabric webs with UP resins are described in → Plastics Processing, 1. Processing of Thermoplastics, Chapter 3.

Polymer Concrete. Both EP and UP resins are used in the manufacture of polymer plaster, mortar, and concrete. Because of their extremely low shrinkage and low viscosity, resins based on poly(methyl methacrylate) are also employed. These resins replace the conventional cement and water binder used for concrete. Gravel, pebbles, sand, and ground stone are used as additives. Polymer concretes have much shorter setting times and can be subjected to loading after about one day. Preparation and processing correspond with the techniques already in use with cement-based concrete.

The mechanical strength of polymer concrete is higher than that of cement concrete, and polymer concrete adheres well to set concrete. It is thus widely used to cast joints, for repair purposes, and above all as a coating for concrete surfaces when increased resistance toward acid, alkali, and salt solutions is required.

Another important application is the manufacture of bases for machines or machine housings. The advantage over the more common gray cast iron or cast alloy construction is the vibrational damping exhibited by polymer concrete.

The choice of resin depends mainly on the required thermal stability and chemical resistance, as well as the maximum allowable shrinkage.

For outdoor use, the sensitivity of the hardening reaction to water (soil moisture, rain) and temperature must be considered.

Foamed polymer concrete with low density, good mechanical properties, and low thermal conductivity can be produced by adding blowing agents to the resin mixture.

1.5. Pressureless Processing with Glass-Fiber Reinforcement

Gel Coating. The appearance of moldings made from glass-fiber-reinforced plastics (GRP) can be impaired by the presence of glass-fiber on the surface. Gel coatings are used to cover the glass fibers, giving a smoother surface and improving the resistance to weathering and chemicals. Such layers adhere better to the composite surface than subsequently applied paint coatings because they are anchored by chemical bonds. The gel coating process can be combined with most processing techniques.

To produce a gel coating, a layer of fiber-free resin is sprayed or painted onto the surface of the mold in a thickness of 300 – 600 μm. The coating can be dyed or filled to improve abrasion resistance. Before the following composite layer can be applied, the gel coating must be cured sufficiently so it is not swelled by styrene or solvents and cannot be penetrated by glass fibers during subsequent processing stages. The curing reaction must, however, not be so complete that bonding to the composite layer is reduced.

Manual Production of GRP Components. The manual process (Fig. 3) is the simplest method of producing GRP moldings and requires only

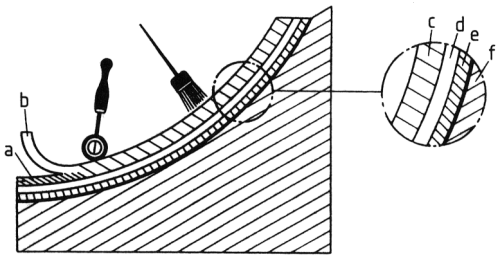


Figure 3. Manual production of GRP moldings
a) Resin; b) Fiber reinforcement; c) Laminate layer; d) Gel coat; e) Release agent; f) Mold

basic equipment. It is also the oldest processing technique. Production of GRP moldings began in the 1940s in the United States and, despite the development of machine processes, has retained a considerable portion of the market. The manual process is especially suitable for manufacturing large-area moldings; for small series using single-part, light-construction molds; and for reinforcing components made of thermoplastics. The moldings can be designed freely and are not subject to constraints regarding size.

A gel coat is first applied to the mold whose surfaces have been coated with a release agent. After initial curing, the first resin layer is applied and a layer of glass fibers, nonwoven glass-fiber matting, or glass fabric is applied by using a brush or fleece roll and a structured roll. Any air bubbles that form between the fine layer and the laminate must be removed. This primary composite layer is first cured slightly to prevent the ingress of air bubbles and movement of the layer during further processing. After this, additional composite layers are quickly applied wet-in-wet. The number of reinforcing layers depends on the strength required of the finished molding. The embedding of subcomponents made from other materials, such as stiffening ribs and screw thread sockets, is also possible. If required, a finishing surface coating, similar to the gel coating can be applied to cover the glass fibers on the surface. A film former (paraffin dissolved in styrene) is usually added to the topcoat when UP resins are used, to protect the surface of the composite from atmospheric oxygen. This also gives a tack-free surface even on curing at room temperature.

Before the molding is removed the curing reaction must be so far advanced that the article is not damaged by tearing or by separation of the resin and fibers (stress whitening). Subsequently, the product is stored in simple support equipment until curing is complete to avoid deformation, because upon hardening, all deformations become fixed. Moldings that are manufactured in single-part molds have a smooth surface only on the side that was in contact with the mold.

Attainable glass contents with glass matting range between 20 and 30 wt %, and with glass fabrics between 40 and 50 wt %. Suitable matrix materials include UP, VE, and EP resins.

Fiber Spray-up Process. The fiber spray-up process is a partially mechanized manual process. It is particularly useful for linings and in the manufacture of complex moldings. Only UP resins are used in this process.

After application of a gel coating, which for linings also serves to seal any pores, the resin mixture and chopped glass fibers are sprayed simultaneously onto the mold and then, in a manner similar to the fully manual process, are compressed with a roller and degassed with a structured roll. The fiber spray-up equipment illustrated in Figure 4 operates with two resin feeds, one of which contains the hardener, and the other the accelerator. The two components are fed to a double pistol and sprayed with compressed air. They are mixed immediately prior to contact with the mold. The glass rovings are fed to a chopping unit located between the two nozzles, where they are chopped to staple fibers and accelerated along with the two streams of resin onto the mold. With high-pressure spray equipment, accelerator-containing resin and hardener are pumped from storage tanks to the spray pistol via a mixing and metering unit.

With the fiber spray-up process, the layering of glass fibers and the glass content are comparable to those of manual processes. Maintaining constant wall thickness, however, requires skill and experience in spraying, compacting, and degassing the fibers, which initially lie very loosely. An advantage over the manual process is that large batches of resin with prolonged pot life can be processed, while very rapid curing times are also tolerated. Furthermore, the labor-intensive cutting of the glass matting to size is avoided, along with losses incurred during

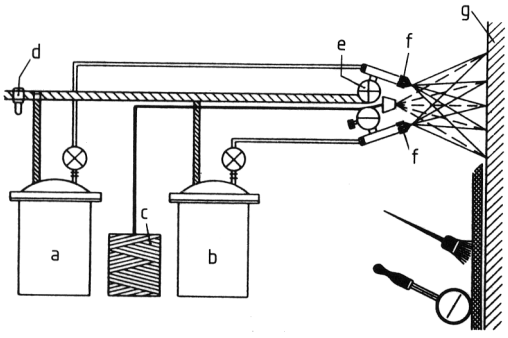


Figure 4. Fiber spray-up process
a) Resin with hardener; b) Resin with accelerator; c) Roving reel; d) Compressed air inlet; e) Fiber cutting device; f) Spray gun; g) Mold

trimming. Start-up and cleaning procedures for fiber spray equipment require considerable time. Usage is thus recommended only when extended production times without long interruptions can be expected.

1.6. Low-Pressure Processes

Low-pressure processes allow the production of articles of large surface area in small to medium production runs. Manufacturing times are usually shorter than with manual processes but longer than with compression molding. Low-pressure processes can be used to improve laminates manufactured with pressureless techniques (vacuum film process) and permit direct impregnation of fiber materials in a closed mold.

Vacuum bag process:

1. With single-component rigid mold and elastic sheet as countermold (Fig. 5): The resin mixture is applied to the mold; the glass-fiber reinforcement is added and, after an airtight seal is generated, impregnated with the resin by applying a vacuum.
2. Molding with two elastic sheets: A laminate that has been impregnated and degassed by hand is deep drawn by vacuum between two elastic films. This technique is suitable for the manufacture of domes.
3. Form and counter form are rigid: After the form has been coated with resin mixture, the fiber reinforcement and, when appropriate, the core material are applied, and the counterform, which is also coated with resin mixture, is used to form an airtight seal. The necessary compression is generated by applying a vacuum. Two-sided topcoats are possible. This process is suitable for items of large surface area and is used primarily to coat plywood sheets and rigid foam cores for refrigerated trucks and containers.

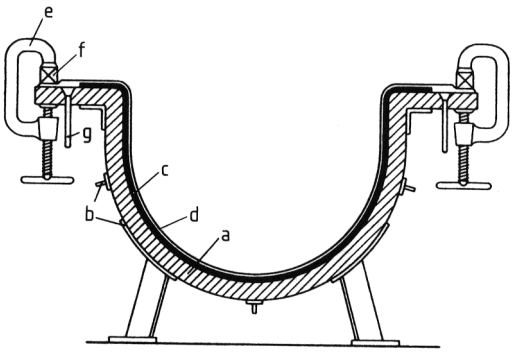


Figure 5. Vacuum bag molding
a) Mold; b) Reinforcing profiles; c) Laminate; d) Flexible sheet as countermold; e) Clamp; f) Sealing frame; g) Suction vents

Autoclave Processes. The low-pressure autoclave process is a variation of the vacuum bag technique. It is used mostly for the manufacture of high-quality components for the aviation and aerospace industries. The costs are high due to the use of a heated, pressurized autoclave and high-quality prepregs. Furthermore, the structure of the laminate is complex, containing release films and fabrics, suction, pressure distribution, and surface layers (Fig. 6). Cycle times can be several hours.

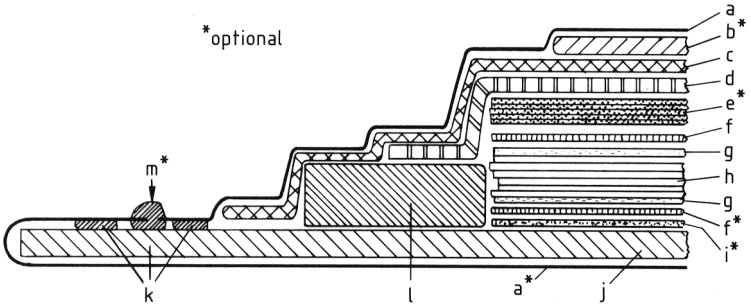


Figure 6. Structure of a laminate produced in the autoclave process
a) Vacuum bag; b) Compression plate; c) Pressure-distribution layer; d) Release film, perforated; e) Absorbent material; f) Release film or fabric; g) Peeling film; h) Fiber composite laminate; i) Release film; j) Mold; k) Sealing compound; l) Mold boundary; m) Double gasket

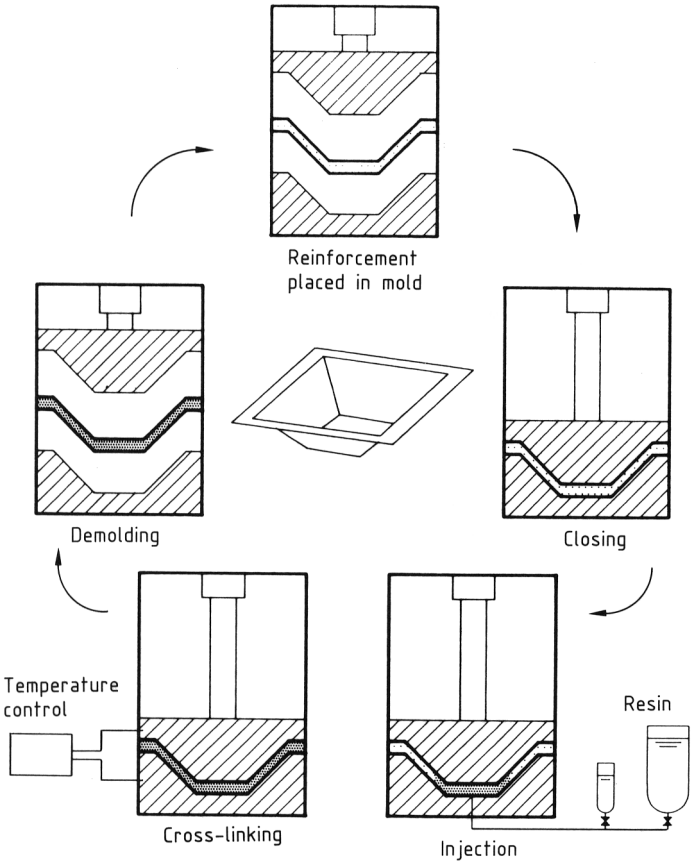


Figure 7. Resin transfer molding process

Resin Transfer Molding. In the resin transfer molding (RTM) process (Fig. 7), two-component or multicomponent rigid molds made from metal or GRP are employed, which are opened and closed by hydraulic mechanisms. The fiber reinforcement is cut to shape and placed in the mold. The mold is closed, and the resin mixture is injected from the bottom under pressure. Air release valves allow control of the resin flow. Application of a vacuum assists the impregnation stage. Large-surface moldings with topcoat matts on both surfaces can be manufactured with this technique.

Apart from moldings made from preshaped glass-fiber matting and UP resins (fiber content 20 – 40 vol %), which can withstand moderate loadings, the RTM process is equally suited for producing high-quality components from fiber fabrics and EP resins (fiber content up to 65 vol %). The injected resin must be of low viscosity and highly reactive. However, for modern resins, these requirements are associated with low softening temperatures and hence low use temperatures of the final molding.

1.7. Press Molding

Press molding allows the production of medium to large series of GRP moldings with smooth surfaces on both sides, good dimensional stability, and high glass content. The presses are generally hydraulic; two- or multipart molds are used. Labor costs are considerably lower than with pressureless processing.

Liquid Resin Press Molding. In liquid resin press molding the glass-fiber reinforcement is placed in the mold, and the resin mixture is poured into the center so that the flow paths to all sides of the mold are equally long. When the

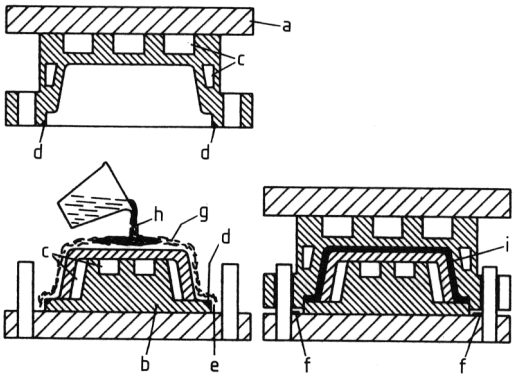


Figure 8. Liquid resin press molding
a) Female mold; b) Male mold; c) Heating channels; d) Cutting edges; e) Overflow; f) Excess; g) Fiber reinforcement; h) Resin; i) Molding

press is closed, the resin mixture is distributed evenly throughout the reinforcing material, and any air remaining in the mold is forced out of the cavity by the flow front (Fig. 8). The mold closing speed must be reduced significantly over the final 5 – 10 mm of the closing movement to avoid shifting or tearing of the fiber insert due to rapid flow of the resin and to prevent entrapment of air pockets.

Generally, glass matting is used as fiber reinforcement; glass fabrics or preforms are also used. In the production of preforms, glass fibers cut to a length of 20 – 50 mm are drawn onto a punched screen that exactly matches the shape of the item to be pressed. The fibers are bonded by spraying with a binder; after the binder has been dried, the preform can be processed. With moldings containing severe bends this process avoids the complex cutting and laying of glass matting, and overlap areas are avoided.

Topcoats can also be incorporated with liquid resin molding. However, this requires an extendable press table with two interchangeable lower mold halves to achieve acceptable cycle times. To obtain smooth surfaces a polymer or glass-fiber nonwoven fabric is best used as the first and last fiber layer. After being demolded, the pressed molding must be stored on support equipment to prevent distortions.

Generally UP resins are used; EP resins are less suited for liquid resin molding because of their long curing times. Filler contents up to 40 – 60 parts per 100 parts resin improve the surface quality by suppressing the fiber structure. Articles with varying wall thickness cannot be manufactured with wet pressing techniques because a constant glass content cannot be achieved at the junctions. The use of ejectors to assist in removing the molding is not recommended because of the possibility of malfunction caused by ingressing resin. They are usually not necessary because the mold must be slightly conical to avoid shifting or tearing of the glass-fiber reinforcement on closing.

Cold liquid resin press molding uses highly reactive UP resins containing hardener and accelerator. Pressing temperatures range from 20 to 60 °C. The amount of resin mixture is adjusted so that the resin begins to gel a few seconds after the mold closes. The mold surfaces are warmed by the heat of reaction. Additional heating of the mold is thus not necessary but does help to maintain a constant cycle time, particularly for the initial six to eight press cycles at the beginning of a shift or following a machine stoppage until the molds have reached their final temperature. Typical press pressures range from 0.1 to 1 MPa. When textile glass matting or preforms are used, glass contents of 25 – 35 wt % can be achieved.

Low pressures permit the use of molds made of GRP, supported by a polymer concrete or concrete backfilling for rigidity (Fig. 9). These molds are considerably cheaper than steel molds. Their lifetime is shorter; however, they are well suited for small- to medium-sized runs in which the required cycle times of 5 – 15 min are acceptable. The mold seal forms a nipping edge. By reducing the pressing layer thickness around this nipping edge to approximately one-third of the original thickness, the glass fibers are so compressed that they prevent leakage of the resin and permit the necessary pressure buildup.

Hot liquid resin press molding is suitable for the mass production of moldings. The presses and molds are described in → Plastics Processing, 1. Processing of Thermoplastics, Section 4.1. When processing UP resins, the cavity plate and core plate should be heated individually; temperature differences of 5 – 10 °C assist demolding, and the quality of the surface in contact with the warmer plate is improved.

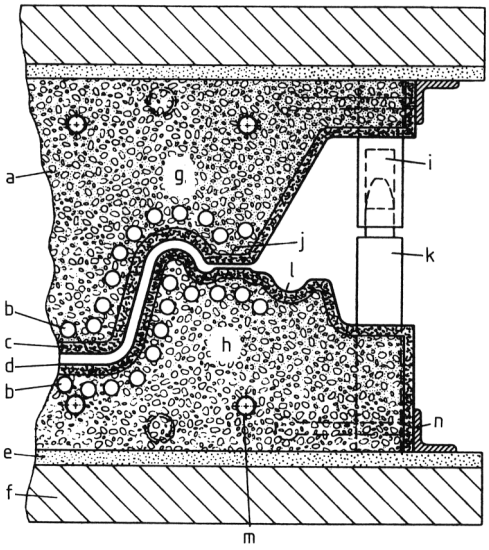


Figure 9. Compression mold made from glass-fiber-reinforced plastic with pinch-off edges for cold press molding
a) Backfilling of polymer concrete or cement concrete; b) Heating tube; c) Mold surface of glass-fiber-reinforced plastic; d) Gel coat; e) Rubber plate; f) Press table; g) Male mold; h) Female mold; i) Guide sleeve; j) Pinch-off edge; k) Guide pin; l) Overflow channel; m) Reinforcement of back filling; n) Frame for fixing mold

Liquid heating of the molds is preferable to electric heating because it allows removal of the heat of reaction. Press pressures of 0.5 – 5 MPa and temperatures of 80 – 120 °C are used.

In hot press molding, curing is initiated by external heat. UP resins can thus be used without the addition of accelerators. The pot life of the resin mixture ranges from several days to weeks at room temperature. The required press time is ca. 1 min per millimeter of wall thickness. Since the curing reaction begins shortly after the resin comes in contact with the mold surface, the filling and closing phases must be carried out rapidly. The mold seals form shear or immersion edges (Fig. 10).

Press Molding of Preimpregnated Fiber Articles. Preimpregnated textile fibers (prepregs) contain all the necessary components for manufacturing a pressed molding. The mixing of resins and the combining of resins with reinforcing material, which are necessary with wet pressing, are avoided during such processing.

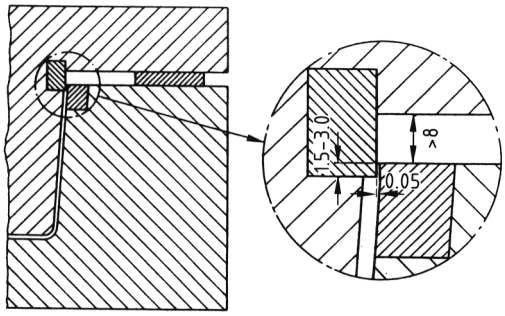


Figure 10. Shear edges on a steel compression mold

A distinction is made among preimpregnated fabrics, preimpregnated rovings, sheet molding compounds (DIN 16 913), and fiber-containing molding compounds (DIN 16 911 and 16 912). The processor can prepare these molding mixtures or purchase them ready for use. See → Plastics Processing, 1. Processing of Thermoplastics, Section 4.1 for processing molds and presses.

Prepregs in the form of fabrics or parallel glass, carbon, or aramid fibers are manufactured by impregnating the fibers with epoxy or phenolic resin. The resin is essentially solid, but still reactive and slightly tacky, and must be dissolved in a solvent or melted to penetrate the fibers completely. The resulting prepreg must be cut to fit the mold exactly because it cannot flow. Prepregs are employed mainly for highly loaded, thin-walled components (e.g., in aircraft). Besides press molding, processing with autoclave techniques is also common (see Section 1.6).

Sheet molding compounds are manufactured exclusively from UP resins. The resin mixture is composed of approximately equal weights of resin and filler (chalk, talc, clay), sometimes with addition of a lubricant. Curing agents with high initiation temperatures are used to give long pot lives at room temperature. To increase viscosity, thickening agents such as magnesium oxide are added, which cause a sudden thickening of the liquid to give a dry, leathery consistency. The thickening process takes from several hours to several days.

Impregnation is carried out immediately after the resin is mixed. Either glass is treated on equipment operating in a continuous process, or the resin mixture is applied on a film, cut glass

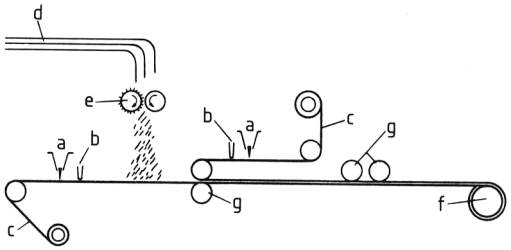


Figure 11. Production of sheet molding compounds
a) Feed tank for resin; b) Doctor blade; c) Cover sheet; d) Roving strands; e) Fiber cutting device; f) Winding of sheet molding compound; g) Impregnation of fibers with resin

fibers are added, and another film coated with resin is applied as a cover. After processing the fiber – resin mixture between several pairs of rolls, the sheet including the protective films is wound in a roll (Fig. 11). Because the thickening reaction continues during storage, the pot life is limited.

When working with sheet molding compounds preparation of the resin mixture is no longer necessary, and processing does not require the use of exactly cut sections. Because of the high viscosity, all components flow at the same rate under the molding pressure at the mold temperature. Thus, moldings with varying wall thickness can be manufactured, although in such cases, higher pressures are required than with liquid resin press molding.

To avoid the surface subsidence of areas with thick walls caused by the volume shrinkage of UP resins, low-shrinkage resin systems [low-profile (LP) resins] have been developed. These contain solutions of thermoplastics dissolved in styrene. On curing, part of the styrene contained in the thermoplastic particles evaporates prior to polymerization and causes foaming of the resin mixture, which in turn compensates for shrinkage.

Fiber-containing molding compounds are obtained by kneading chopped fibers into the resin mixture or by cutting continuous, impregnated roving strands to the desired length. These molding compounds can also be processed by injection press molding and injection molding (see → Plastics Processing, 1. Processing of Thermoplastics, Section 4.5). However, abrasion of metallic components by the hard glass fibers is a problem.

1.8. Semicontinuous Processing Techniques

Filament winding is a highly reproducible process for the manufacture of hollow articles with high mechanical strength. The equipment and the manufacturing technology are complex. Resins are selected according to their mechanical, thermal, and chemical loading; UP, EP, and VE resins are generally used. The fiber content of the product depends on the laminate structure, the process parameters, and the viscosity of the resin. Normal values range between 50 and 60 %.

The so-called lathe system is used for winding containers, container jackets, and pipes (Fig. 12). The winding equipment consists of a rotating winding mandrel and an oscillating fiber guide, the drives of which can both be regulated. Rovings are generally used for reinforcement, although woven tapes can also be employed. The rovings are fed through a resin impregnation bath, which is frequently combined with the fiber guide system to form a single unit. The impregnated fibers are then wound onto the core under constant tension and with an exact geometrical pattern governed by the ratio of the rotation speed of the core to the feeding speed of the fiber guide.

Modern winding equipment has up to six axes or degrees of freedom for the fiber guides and is usually computer controlled. This control system calculates data for the motion of individual axes, corresponding to the geometry of the winding mandrel and the desired winding pattern.

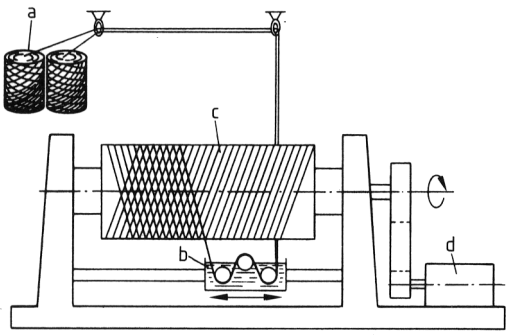


Figure 12. Filament winding (lathe system)
a) Roving reels; b) Support with impregnating bath and fiber guide; c) Winding mandrel with laminate; d) Drive

In parallel winding, individual roving strands are wound side by side without a gap, at a winding angle of almost 90°. To obtain sufficient strength in the axial direction, either warp-knitted fabrics are incorporated between the individually wound layers, or dry or impregnated glass fibers are sprayed between the winding layers.

With diagonal or cross winding, a winding angle of 30 – 70° is employed. The strength of the wound article can be adapted to the expected loading in the axial and radial directions by varying the winding angle.

Depending on the size of the molding, cold or hot curing resin systems are used for winding. Smaller moldings a few meters in length, which fit into hardening ovens or whose mandrels can be heated, are cured thermally to obtain superior material properties and extended resin pot lives. In contrast, large containers and pipes — diameters up to 12 m can be manufactured at present — must be cured in the cold or by using ultraviolet radiation.

Because the wound molding shrinks on the mandrel during curing, retractable winding mandrels are used to facilitate removal. Container bases, flanges, and supports are manufactured batchwise and are bonded to the container jacket or pipe by adhesion or lamination.

Feed silos; containers for drinks, chemicals, and heating oil; and pipes for the chemical industry (e.g., pipes for acid, wastewater, and exhaust air) are manufactured via winding processes. Mechanically loaded components including drive shafts and centrifuge drums can also be wound.

For the manufacture of highly stressed pressure vessels for the aerospace industry, equipment is used in which the winding mandrel rotates about two axes, or the fiber feed and the mandrel both rotate. Single fibers are used and wound in complex patterns.

A continuously operating winder has been designed for the mass production of pipes or container jackets in which an endless steel band is employed as the winding mandrel. This band runs spirally around a support using transport rolls, and is unwound at the outlet of machine and fed back through the inside of the core. The continually wound laminate comprising radially oriented rovings and axial fabric or matting reinforcement is cured by passage through a heated section after winding.

Rotation Molding. Cylindrical hollow articles with smooth internal and external surfaces can be manufactured by rotation molding. Glass matting or chopped glass fibers, sometimes in combination with textile fabrics, are employed as reinforcing materials. The choice of resin depends on the anticipated exposure to corrosive influences. The rotation equipment consists of a balanced cylindrical steel drum of adjustable rotation speed. With small-diameter pipes, the reinforcing matting or fabric is rolled in the stationary drum. On rotating, the strands are unrolled and pressed smoothly against the wall of the drum. The resin mixture is then distributed evenly across the complete length by use of a metering device. Due to the influence of centrifugal force, the reinforcing material is pressed against the wall and the resin mixture impregnates the fiber layers and displaces the air. Finishing coats can also be applied in this way. Pipes with smooth inner surfaces can be obtained by using a slight excess of resin. Generally, cold curing resin systems are employed. However, heating of the drum is advantageous, particularly with EP resins.

Larger vessels with diameters of several meters can be manufactured from UP resins by combining the rotation process with a modified fiber-spraying technique (Fig. 13). The mold is an aluminum rotor strengthened by external ribs and mounted on driven rolls. The feed vessel for the resin mixture and the fiber cutter are mounted in the head of a telescopic arm that is driven back and forth during coating in the rotating rotor. The glass fibers leaving the cutter are oriented by air blowing so

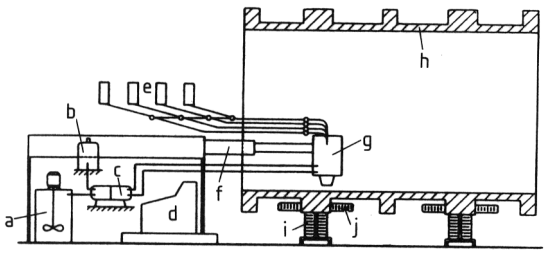


Figure 13. Centrifugal casting plant for large vessels
a) Vessel for resin and accelerator; b) Vessel for hardener; c) Mixing and metering pump; d) Control unit; e) Roving reels; f) Telescopic arm; g) Application unit with cutting device, compressed air inlet, and resin feed; h) Rotor; i) Driving rolls; j) Guide rolls

that the ratio of longitudinal to transverse orientation matches the expected mechanical loading of the container. Vertical containers, feed silos, and similar articles can be made with progressively increasing wall thickness from top to bottom. The roof of the container is placed in the rotor prior to rotation and is immediately bonded onto the container wall. The attainable glass content is 25 – 30 wt %.

1.9. Continuous Processes

Pultrusion. The pultrusion process is particularly suitable for mass production of uniaxially loaded solid and hollow profiles of any length. Labor costs are low, and equipment costs depend on the profile cross section. Glass rovings are used as reinforcement.

Figure 14 shows a vertical pultrusion machine. The rovings are wet with the resin compound in an immersion bath and then drawn into a heated profile mold. An inlet nozzle at the entrance of the mold retains any excess resin and entrapped air. The reactivity of the resin, curing temperature, temperature of the mold, and takeoff speed must be matched so that the resin mixture is dimensionally stable when it leaves the profile mold. Premature gelation causes adhesion to the mold, and delayed gelation can lead to deformation of the profile cross section. The solidified profile subsequently passes through a heating channel and is cured completely. The profile is then cut to length by a flying saw. Attainable glass contents vary between 50 and 75 wt %. The profiles can withstand high tensile forces in the fiber direction, but the strength in the transverse direction corresponds to that of the resin alone. This can be improved by employing textile tapes or looped rovings.

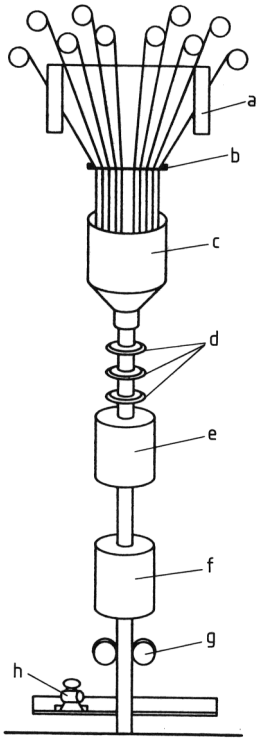


Figure 14. Pultrusion
a) Roving frame; b) Roving guide; c) Impregnating bath; d) Inlet nozzles; e) Profile mold; f) Heating channel; g) Takeoff unit; h) Cutting device

Continuous lamination is used for the manufacture of plane and longitudinally or laterally corrugated endless sheets of constant thickness. Glass matting or chopped glass fibers are used for reinforcement. Lightly colored, light-stabilized UP resins are employed. The production of corrugated sheets was the first large-scale processing technique for UP resins. It requires careful matching of resin – hardener system, curing temperature, and production speed to obtain an economical throughput via rapid curing times and to avoid a sudden curing reaction. This could lead to shrinkage of the resin from the fibers, which results in loss of transparency and embrittlement. Two processes have been developed for the production of corrugated sheets, which differ in the method of shaping. Figure 15 shows a machine for the production of

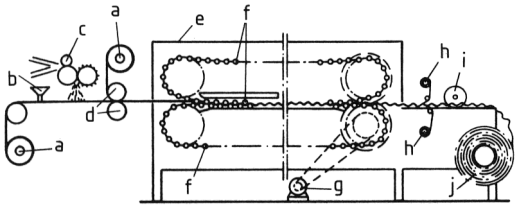


Figure 15. Continuous lamination of transversely corrugated sheets
a) Release film; b) Application of the resin; c) Fiber cutting device; d) Calibrating rolls; e) Hardening oven; f) Forming roller; g) Drive; h) Removal of release films; i) Trimming; j) Windup

transversely corrugated sheets. The resin is cast onto a cellulose or polyester release film and spread homogeneously by a doctor blade. The glass matting is then added, or glass fibers are distributed from a cutter unit fed with rovings positioned above the substrate. An open zone follows in which the resin is allowed to impregnate the fibers and air is forced out. Subsequently, a second release film is added from above, and a pair of calibrating rolls presses excess resin and air bubbles out of the laminate. The forming unit consists of a forming roller with displaced upper and lower rolls. The sheet passes between the shaping rolls in the curing oven, which consists of gelation and curing zones. The release films are then removed, the edges are trimmed, and the completed corrugated sheet is wound.

With longitudinal corrugating equipment, the impregnated laminate layer, calibrated between two films, is first shaped on a special forming element to a narrower-profile band and then passed through the curing oven on a longitudinally profiled slide system.

A significant improvement of the continuous process can be achieved by use of UV-curing UP resins because the hardening process is easier to control.

2. Curable Molding Compounds and Laminates

Moldings are manufactured from curable compounds under pressure and heat in closed molds; the molding compound is melted (or softened), shaped, and cured.

Terminology. Molding compounds are unshaped products that can be permanently molded to articles or semifinished products under pressure and temperature. Curable (thermoset) and uncurable (thermoplastic) molding compounds are available. Curable molding compounds always contain ca. 50 – 60 % filler and reinforcing materials. Press compounds are molding compounds that are suitable for press molding, injection press molding, or extrusion. Injection molding compounds are used for injection molding. The processing of curable molding compounds and the manufacture of laminates are described below; for low-pressure processes, see Section 1.6.

2.1. Processing Techniques

2.1.1. Processing Curable Molding Compounds

Curable molding compounds are formed and cured under the influences of temperature and pressure. On heating, the curable resin (which is present in the mass as a binder) softens, and the molding compound flows, filling the mold cavity. At the same time the cross-linking reaction begins, in which the binding agent and hence the molding compound harden. From this moment the material can no longer be melted; the curing (cross-linking) is irreversible. The molding is removed while still hot.

Flow – Cure Behavior. Figure 16 illustrates the flow – cure behavior of curable molding compounds. Figure 16 A shows how the molding

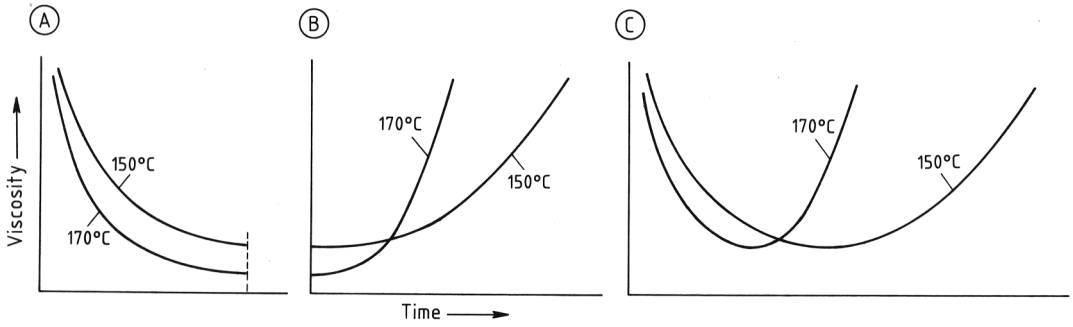


Figure 16. Flow – cure behavior of curable molding compounds
A) Molding compound without hardener, heated in the mold; B) Molding compound with hardener, heated immediately to mold temperature; C) Actual behavior of curable molding compound in press molding

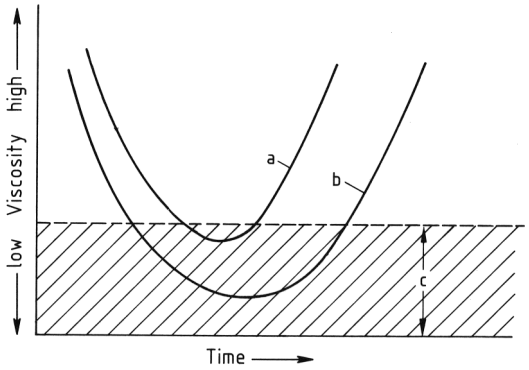


Figure 17. Flow – cure behavior for hard and soft flow
a) Hard flow; b) Soft flow; c) Possible processing range

compound is warmed and softens in the heated compression mold when no curing reaction takes place (this can be brought about by omitting the curing agent during preparation of the molding compound, which then behaves like a thermoplastic). Figure 16 B shows how the viscosity of the molding mass increases and the mass hardens if the curing agent is added suddenly and the mold is heated to 150 – 170 °C. Figure 16 C, the superposition of Figures 16 A and 70 B, shows the changes in viscosity observed when the mold is heated to 150 or 170 °C, filled with cold molding compound, and closed. Figure 17 shows the difference in behavior between hard and soft flow molding compounds. A hard-flowing compound generally cures faster than a similar compound with soft flow. The required viscosity of the molding compound depends on the design of the molding, the processing method, and the available forming pressure. In all cases, it must lie within the shaded zone in Figure 17; otherwise, the compound is too hard and the mold cavity will not be correctly filled.

Preparation Stages. Curable molding compounds are prepared by the manufacturers to be processed without further additives; the molding compound supplied to the processor contains all the necessary fillers, curing agents, stabilizers, lubricants, colorants, and flame retardants. The processor adds other materials only in exceptional cases. Occasionally, small amounts of lubricant can be added (e.g., 0.1 – 0.2 % zinc stearate) when particular processing conditions make this necessary. Molding compounds for screw injection molding machines can be colored by the processor, although it is difficult to manufacture uniformly colored molding in this way and the technique is seldomly used.

Release agents prevent adhesion of the cured resin to the surfaces of the mold that come in contact with the molding compound (mold cavity, gate, runner system, and all parts that could lead to the formation of flash). Waxes, metal soaps, fats, oils, and silicones, which are applied as solutions, sprays, or aqueous emulsions, or are melted and spread with a brush or compressed air, are available.

In the production of moldings that are to be painted, only release agents that do not impair adhesion of the paint should be used; otherwise, the molding would have to be degreased in an extra process stage.

Metering of the molding compound in a preliminary step is necessary for press molding, injection press molding, and pelletizing. Injection molding machines meter the material themselves (in the compressed state), as do plastication units of all types.

Automatic metering systems require satisfactory flow properties of the molding compound. Finely powdered compounds or those with high dust content require special accessories to permit automatic metering. Fibrous or doughy compounds can be metered only — if at all — by using special units.

Molding compounds are cut to the desired length and reweighed after the release film is removed. Exact cutting is not usually necessary.

Pelletizing of the molding mass is usually carried out for the following reasons:

1. Because the mold cavity is too small for the molding compound
2. To rationalize the feeding process
3. To permit high-frequency prewarming

Automated pelletizing machines operate with either constant pellet height or constant pelletizing force. Typical pelletizing pressures are 100 MPa and above. Circular pellets are generally used, with heights amounting to 20 – 60 % of the diameter. In special cases, square, rectangular, or ring-shaped pellets are produced.

Prewarming the molding compound simplifies processing in the case of press molding and

injection press molding. Prewarmed compounds flow better and hence require lower press pressures and shorter closing times for press molding, as well as reduced injection pressure and shorter injection times for injection press molding; furthermore, the curing time is also reduced, particularly with press molding.

Phenolic and aminoplastic molding compounds evolve moisture and other volatile components during prewarming, which has a favorable effect on the properties of moldings. They exhibit reduced shrinkage, better electrical insulation, improved surface gloss, and reduced moisture absorption.

Polyester molding compounds incorporating styrene as a curing agent should be prewarmed only slightly or not at all.

Widely used prewarming processes are

1. High-frequency prewarming
2. Screw plastication
3. Oven warming (only applicable to phenolic and aminoplastic molding compounds, usually to remove moisture and other volatile components)
4. Infrared prewarming, where a thin layer of the compound is exposed to radiation

Molding compounds can be prewarmed quickly and homogeneously in a high-frequency field; pelletized materials are best suited. A prerequisite for a homogeneous temperature is constant thickness of the molding compound or constant pellet height and density. Typical prewarming times range between 0.5 and 2 min; temperatures of 100 – 140 °C are used.

Press Molding. A metered amount of the molding mass — either loose or in pellet form; as-received, prewarmed, or plasticated — is fed into the open mold, which has already been heated to curing temperature (Fig. 18). When the mold is closed, the mass softens as a result of heat flux from the mold walls and flows into the mold contours. Curing then takes place while the mold is closed. The hot molding is removed when sufficient curing has occurred and is then deflashed. Advantages of the process are the simplicity of the molds and presses; the low levels of filler orientation in the molding and, therefore, the almost isotropic properties; and the low molding shrinkage. Disadvantages include long curing times (especially when prewarming or preplastication is not employed), pronounced flash formation because the mold is closed only when the compound has begun to flow out of the mold (displacement of air), and the large deviations in mold-independent dimensions (see DIN 16 901).

Large, high-quality moldings (e.g., for automobile bodies) can be manufactured by press molding of molding compounds. Such moldings are processed by using computer-controlled, parallel-regulated hydraulic presses. The investment costs are high.

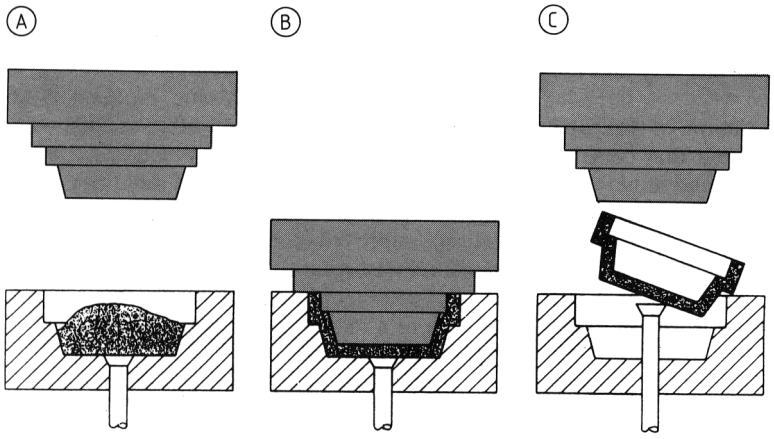


Figure 18. Press molding
A) Filling; B) Pressing; C) Ejection

The following stages are involved in press molding:

1. Filling the mold with the molding compound
2. Closing the press until the mass is squeezed out of the mold
3. Opening the press briefly ("breathing", optional)
4. Closing the press until curing is complete
5. Opening the press
6. Removal of the molding
7. Cleaning (blowing out) the mold

When metallic inserts are to be incorporated in the molding, they are placed in the mold prior to filling with the molding compound.

Injection Press Molding. In injection press molding (Fig. 19) a metered quantity of the molding compound, usually pelletized and prewarmed or preplasticated, is introduced into the injection cylinder of the mold. After the mold is closed, the compound is compressed by a piston, further plasticated, and injected through the gate into the mold cavities. The internal friction that results from this action leads to further heating, which accelerates the curing reaction. After curing, the molding and gate are either simultaneously or separately ejected from the open mold.

The advantage of injection press molding over press molding result from the fact that the mass is injected into the closed mold while hot and, hence, of relatively low viscosity:

1. Less flash is formed
2. The mold-independent dimensions are more exact
3. The manufacture of complicated contours and variable wall thicknesses is possible
4. Embedding of sensitive metallic components is possible
5. Curing times are reduced, particularly with thick-walled moldings

The disadvantages include the high consumption of molding compound since the material that remains in front of the injector piston and in the runner system also cures and cannot be reused. Additionally, depending on the gate geometry, variations in filler orientation can result, which in turn can lead to anisotropy of the strength and dimensional stability.

Injection Molding. In injection molding of curable molding compounds, the material is metered, plasticated, and injected into the heated mold by the screw of the injection cylinder (→ Plastics Processing, 1. Processing of Thermoplastics, Section 4.5). The cylinder is heated moderately, while the mold is heated to the final curing temperature. Due to shear heating of the compound (dissipation) during plastication in the cylinder and passage through the

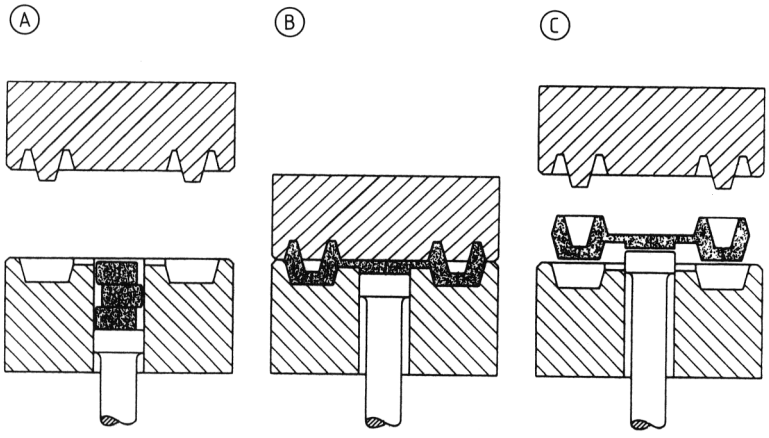


Figure 19. Injection press molding
A) Filling; B) Injection and pressing; C) Ejection

nozzle and gate, it is well plasticated and prewarmed. This leads to shorter curing times in the mold because only small amounts of heat need to be supplied conductively. The cycle times are short. More information on injection molding equipment is given in → Plastics Processing, 1. Processing of Thermoplastics, Section 4.5.

The advantages and disadvantages of injection molding compared to press molding are similar to those for injection press molding. The process cycle is generally shorter than with injection press molding, and pelletizing and high-frequency warming stages are not required. Additionally, a higher degree of automation is possible with injection molding.

Injection – compression molding (Fig. 20) is an adaptation of injection molding. With injection – compression molding, the mold is initially closed without pressure, and the plasticated molding mass is injected, whereby the mold opens up a few millimeters. The mold is then closed under pressure, and the compound is formed (see also → Plastics Processing, 1. Processing of Thermoplastics, Section 4.5).

Injection – compression molding offers the following advantages:

1. Filler orientation similar to that of press molding, which improves with increasing flow of the compound during pressing (the favorable filler orientation leads to more isotropic strength and improved dimensional precision)

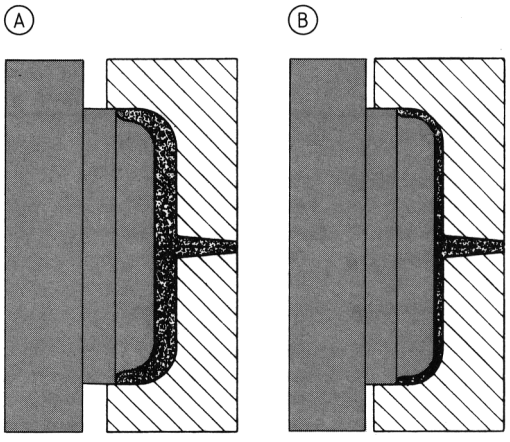


Figure 20. Injection – compression molding
A) Injection; B) Compression

2. Relatively low closing force required for pressing
3. Relatively low injection pressure and therefore lower back pressure at the screw and higher shot volume
4. Higher injection speeds, which can partially compensate for time losses caused by pressing
5. Disappearance of the gate during embossing (given appropriate mold construction)
6. Improved degassing
7. More uniform molding surface characteristics

Posttreatment. The molding is generally subjected to posttreatment after removal from the mold.

Setting. In certain cases, particularly when high dimensional precision is required, thermoset moldings are placed in a cooling template after being demolded.

Deflashing. Moldings produced by press, injection press, and injection molding have varying amounts of flash that must be removed. For reasons of economy, flash should be removed as quickly and simply as possible. For this, the flash must be as thin as feasible. Flash formation depends on the molding compound, processing technique, processing conditions, and above all on the quality of the mold. The finer the filler in the molding compound, the better the molding can be deflashed. Automatic deflashing is not possible with long-fiber fillers. Several of the more common deflashing processes are compared in Table 5.

Air-jet deflashing is the technically most developed and economical technique. With particle-jet deflashing, particles should be softer than the material from which the flash is to be removed. Organic materials are typically employed for jet particles (e.g., ground apricot stones or polyamide granules). The minimum particle diameter is ca. 0.5 mm; otherwise, the intensity of the collision is too low. Modern deflashing equipment has multiple nozzles, along with dust removal units and feed mechanisms for antistatic agents.

Polishing. If the mold has perfect surface quality, the resulting molding will have a smooth, glossy surface. This applies only to a limited

Table 5. Deflashing of thermoset moldings

Deflashing	Application	Performance (number of articles per unit time)	Deflashing quality	Dust formation	Influence on surface quality
Mechanical treatment (drilling, filing)	flash thickness >0.4 mm or fiber-filled molding	low	high	low[b]	none
Abrasive belt treatment	flash in one or two planes (max.)	low	high	low[b]	damage possible
Drum deflashing	only with loose flash; no brittle parts and no sensitive metal inserts	high	moderate to good[a]	low[c]	low, not recommended for larger moldings with high surface quality
Air jet	flash thickness: 0.1 mm (max.)	high (several nozzles)	sufficient to good[a]	low[b]	none
Particle jet	flash thickness: 0.1 – 0.4 mm	high	good	low[b]	none

[a]Depending on the shape of the molding.
[b]With additional aids such as wet sawdust.
[c]Removal by suction is recommended.

extent to compounds with coarse fillers. The surface can be further improved by grinding and polishing.

Small moldings that are deflashed in drums can be simultaneously polished by addition of polishing agents.

Annealing. Postcuring is not usually necessary for thermoset moldings. However, heat treatment of the molding is often advantageous if it is to be thermally loaded during use. With polycondensation resins, annealing results in the slow discharge of volatile components, which in turn results in the advanced removal of postshrinkage, improved electrical properties, and increased application temperature.

General statements regarding duration and temperature of annealing are not possible; they depend on the case in question and must be determined experimentally. An extended treatment at lower temperature is always better for the material than a short period of annealing at higher temperature, even though the shrinkage is identical in both cases. This is particularly true for thermally sensitive aminoplastic materials.

2.1.2. Manufacture of Laminated Plates

Laminated plates are semifinished products manufactured from layered resin substrates with curable resins as binders. Phenolic, aminoplastic, unsaturated polyester, epoxy, and silicone resins are used as binders. Suitable resin substrates include paper (for paper-base laminate); cotton and glass fabrics (for fabric-based laminates); glass matting (for glass-mat-based laminates); and wood veneers (for synthetic resin laminated wood).

In the manufacture of laminated sheets, webs of the resin substrate are coated or impregnated with resin, dried (when necessary), cut, layered, and pressed between plane parallel plates. Phenolic and aminoplastic laminated papers and fabrics are usually pressed in multiplate presses at ca. 160 °C and 10 – 13 MPa (with synthetic resin laminated board at 25 MPa or higher).

Additionally, twin-belt presses are increasingly being employed because of their ability to function in a continuous process.

Laminates based on other resins are often pressed at considerably lower pressure (several bar).

Depending on binder, temperature, and laminate thickness, curing times vary from a few minutes to several hours. For some applications, laminated sheets are coated on one or both sides with special surface layers, for example:

1. With copper foil (laminated paper or fabric laminated to copper foil) for the production of printed circuits
2. Fine wood veneers for laminated board
3. With colored or printed, aminoplastic resin-impregnated papers for decorative laminated boards (e.g., for the furniture industry)

Aminoplastic-impregnated, decorative paper laminates can also be laminated directly to wood sheets (e.g., chip board).

Laminate moldings can also be pressed by using closed press molds once they have been appropriately cut and layered. Examples of this include pressed plywood moldings (for chairs) and pressed moldings made of polyester mat-based laminates.

2.2. Processing Properties

The processibility of a curable molding compound depends on structure, flow characteristics, and curing behavior.

The *structure* plays an important roll in automatic metering; consistent, rounded particles with good flow properties are preferred. The dust content should be low. Molding compounds containing fibrous reinforcing materials (e.g., cellulose, glass fibers) are granulated in many cases; glass-fiber compounds are also available in rod form. Impact-resistant molding compounds are employed in randomly oriented fiber structures; however, in such cases, the molding compound must be weighed and added by hand, and the mold must have a sufficiently large cavity.

Flow characteristics are adjusted by the manufacturer of the molding compound. With condensation resin molding compounds this is carried out by varying the extent of condensation of the binder during production. The flow level of a molding compound is selected according to the processing technique and the complexity of the molding. It also exerts an influence on the quality of the molding. Hard-flowing compounds generally give lower molding shrinkage, better surface gloss, and improved electrical insulation. However, they require higher processing pressure, often cannot be injected, and often cure more quickly.

The *curing behavior* of a molding compound can also be varied by the manufacture within certain limits. As a rule, a processor desires high curing speeds to attain high production throughputs. The higher the processing temperature, the faster is the curing reaction. However, the temperature can be increased only to a level at which the mold can still be filled without difficulty.

2.3. Processing Conditions

Processing guidelines can be established and described only for individual cases; they differ according to molding compound, processing technique, mold, and molding. Furthermore, processing difficulties or molding faults that may arise can be dealt with only as individual cases. The causes may lie in the molding compound, the processing equipment, or processing conditions so that a knowledge of all possible circumstances is necessary to make any evaluation or correction.

Table 6 gives an overview of processing conditions for the most commonly employed curable molding compounds.

Phenolic resin molding compounds are the thermosets that are easiest to process, regardless of whether press molding, injection press molding, or injection molding is used. This applies particularly to the standard compound of phenolic resin with sawdust (DIN 7708, type 3), but also to most other phenolic molding compounds.

Some fiber and macerate compounds, because of their structure, cannot be processed automatically (or only by using special equipment).

The most important operating conditions in press molding processes include temperature, pressing force, and curing time. When pressing phenolic molding compounds, the mold temperature is typically 160 – 170 °C. Higher temperature leads to quicker curing; hence the highest temperature possible is always used. The upper temperature limit is

1. For compounds containing sawdust, ca. 180 °C
2. For compounds with organic fibers or fabric cuttings, ca. 170 °C
3. For compounds with inorganic resin substrates, ca. 190 °C

In all cases, care must be taken to ensure that the temperature is not so high as to partially cure the material while the mold is closing and thus lead to faulty moldings.

The harder the flow characteristics, the larger the resin substrate, or the less intense the preheating, the higher is the pressing force required. Additionally, design, wall thickness, and height all play a role in determining the required pressure.

With *press molding*, curing time depends on the thickness of the pressed component, the mold temperature, the curing characteristics of the molding compound, and the prewarming.

Table 6. Processing conditions for curable molding compounds*

Process	Phenolic resin molding compound	Urethane resin molding compound	Melamine resin molding compound	Melamine –phenol resin molding compound	Polyester resin molding compound
Press molding					
Mold temperature, °C	160 – 190	130 – 160	150 – 170	150 – 170	130 – 190
Molding pressure, MPa	15 – 80	15 – 80	15 – 80	15 – 80	10 – 40
Approximate hardening time per millimeter of wall thickness, s	30 – 60	20 – 40	20 – 40	20 – 40	10 – 20
Injection press molding					
Mold temperature, °C	160 – 190	130 – 160	150 – 170	150 – 170	140 – 190
Outer injection pressure, MPa	50 – 200	50 – 200	50 – 200	50 – 200	30 – 80
Hardening time, s	40 – 120	30 – 120	30 – 120	30 – 120	10 – 60
Injection molding					
Temperature, °C					
Cylinder (feed zone)	65 – 85	70 – 80	65 – 80	65 – 80	40 – 60
Nozzle	85 – 120	95 – 125	90 – 120	90 – 110	60 – 90
Screw	65 – 85	70 – 80	65 – 120	65 – 80	40 – 60
Mold	110 – 140	120 – 140	130 – 140	125 – 135	80 – 110
Compound	170 – 190	140 – 160	160 – 180	160 – 180	150 – 190
Outer injection pressure, MPa	80 – 250	100 – 250	100 – 250	100 – 250	30 – 100
Hardening time**, s	20 – 80	15 – 80	15 – 80	15 – 80	10 – 60

* Optimal conditions for individual cases must be determined experimentally. Some cases require conditions that do not lie in the range described here.

** Independent of wall thickness for thickness up to 20 mm.

For phenolic resins without prewarming, a mold temperature of 160 °C, and a molding thickness of 2 – 6 mm, a curing time of 30 – 60 s is estimated per millimeter of wall thickness, whereby the thickest part of the molding must be considered. Curing time can be decreased by increasing the mold temperature and particularly by pre-heating. In this way, the curing time even of thick-walled moldings can be reduced to 1 – 2 min.

Additionally, the curing time can be shortened by ventilation (i.e., temporary opening of the mold shortly after the initial closing stage, which allows any built-up gases to escape).

With *injection press molding*, the most important operating conditions are mold temperature, injection pressure, closing pressure, and curing time. The same applies in this case regarding mold temperature as reported above for pressing techniques.

In practice, injection pressures up to ca. 200 MPa, and in certain cases even higher, are employed. Often independent adjustment of the injection velocity and the injection force is desirable; too high an injection velocity can cause local scorching of the molding due to adiabatic overheating if air present in the mold cannot escape quickly enough.

The required injection pressure depends on the mold (molding design, gating), the molding compound (flow properties, resin substrate), and preheating. The curing time is generally only slightly dependent on wall thickness in injection press molding. When the gate is correctly dimensioned, the molding compound enters the cavity at the full mold temperature, and after the injection phase, only curing takes place. In practice, curing times in the injection press molding of phenolic compounds lie in the range of 0.7 – 2 min.

With *injection molding*, preparation stages (pelletizing, prewarming) are not required. However, several specific operating conditions in addition to those for injection press molding must be considered: the temperature of the plastication and injection units, screw rotation speed during plastication, back pressure during plastication, holding pressure, plastication time, and cycle time. In many cases, the mold temperature exceeds that used in press or injection press molding.

The injection cylinder is generally cooled in the feed zone. The next zone, the metering zone, is generally heated to 65 – 85 °C. The temperature of the front zone of the cylinder and the nozzle should be 85 – 120 °C. Up to a diameter

of ca. 50 mm, control of the temperature of the screw is not normally necessary.

Fluid heating systems give good temperature consistency and permit removal of the excess heat of friction that can be generated under certain circumstances during plastication.

The temperature of the compound, measured on the plasticated material injected through the nozzle, is often considerably higher (20 – 40 K) than the temperature of the cylinder. Hotter molding compound can be injected more easily and hardens faster, but the risk of operational interruption is also greater.

Adjustment of the back pressure to counter the reverse movement of the screw during plastication allows control of the plastication stage. At low back pressure (3 – 5 MPa) plastication is still possible while the injection unit is withdrawn; high back pressure (8 – 15 MPa) leads to high compound temperature. Computer control of the back pressure opens up new possibilities for decreasing curing time.

The injection pressure in injection molding corresponds roughly with that of injection press molding with thoroughly preheated compounds. Depending on the flow rating and resin substrate of the molding compound, as well as the complexity of the mold, the injection pressure typically lies in the range 80 – 200 MPa, with an injection time of 3 – 10 s. After injection, a holding pressure is applied. The holding pressure should be 50 – 80 % of the injection pressure and be maintained until the material in the gate has hardened.

The curing time is generally lower with injection molding than with injection press molding. If the layout of the mold (gate) is correct, the curing times for phenolic molding compounds range from 0.3 to 1 min. They are independent of molding thickness over a wide range of values.

The cycle times are determined mainly by the curing time. Only in cases of very long plastication times or very short curing times does the cycle depend on plastication time rather than curing time. Whenever possible, the plastication time in such cases is reduced by processing with a faster screw.

Aminoplastic molding compounds (i.e., molding compounds with urea, melamine, or melamine – phenol resins) have similar processing characteristics to phenolic molding compounds. Hence, the processing information provided above for phenolic compounds is largely valid for aminoplastics. Deviations exist only for the processing temperature and curing time (see Table 6).

Urea resin molding compounds are particularly sensitive to overcuring, which can occur with standard curing times at 170 °C mold temperature, or with prolonged curing times at 160 °C. Melamine and melamine – phenolic resin molding compounds are less sensitive to overcuring, although excessive mold temperatures are not recommended.

With thin-walled moldings, the temperature can be increased to the upper limits of the regions mentioned above; with thick-walled components, however, lower temperatures are used. When press and injection press processes are employed, extensive high-frequency preheating is normal.

The curing time of aminoplastic molding compounds is usually 30 – 50 % shorter than that of corresponding phenolic compounds, given identical processing techniques, although mold temperatures with urea resin molding masses are as a rule 10 K lower.

Polyester resin molding compounds behave differently from phenolic and aminoplastic resins, the latter being condensation products that cure relatively mildly. In contrast, the polymerization reaction involved in curing polyester resins is usually strongly exothermic.

The mold temperature influences flow properties. If the mold is too hot, the resin cures before the mold cavity is completely filled; hence, the mold temperature has an upper limit. At the lower temperature limit the molding sticks in the mold. Between these two extremes, sufficient room for maneuverability exists to allow for malfunction-free operation. Additionally, the working temperature range is determined by the composition of the molding compound, particularly by the type of curing catalyst employed.

Except at low temperature, curing time is usually relatively short; in some cases, a few seconds suffice.

Air that is entrapped in the mold and unable to escape can easily lead to faults in the molding, particularly with injection press molding

injection molding. This involves not only scorching but also insufficiently cured areas because atmospheric oxgen can disturb the curing reaction.

Contamination of the molding mass by traces of phenolic resins can impair curing; processing of phenoplastic and polyester resin molding masses should be done separately.

In mold construction, undercuts must be avoided for polyester resin molding masses, since moldings with undercuts cannot be demolded.

Ventilation of the mold is generally not recommended for processing polyester resin molding compounds, because the resulting decrease in the mold temperature is undesirable.

Polyester resin molding compounds are available as granules, long fibers (premix), and resin matting (sheet molding compounds). Granules are used for press, injection press, and injection molding.

Processing conditions are listed in Table 6.

Polyester resin molding compounds with randomly distributed long glass fibers — usually with styrene as cross-linking agent and moist doughy to semidry, strawlike consistency — can be processed at relatively low pressure (ca. 10 MPa for press molding and $\geq$30 MPa for injection press molding) and also injection molded by using special equipment. Additionally, polyester resin premix is frequently processed with low-pressure press molding techniques (see Section 1.6).

Styrene-free, dry polyester molding compounds are also available; they usually contain diallyl phthalate as cross-linking agent. These are also supplied as rods (chopped strands with parallel glass fibers) that require higher processing pressures.

Polyester resin sheet molding compounds are usually processed by press molding to give large-area moldings. Similarly, polyester sheet molding compounds are often processed by low-pressure press molding techniques (see Section 1.6).

2.4. Influence of Processing on Molding Properties

The properties of a plastic molding are determined not simply by material properties, but also determined by other factors, particularly the shape of the molding and the processing itself. For this reason, tabulated values determined on standard samples are valid only for those samples and cannot be transposed to any arbitrarily designed molding. The most important factors from a processing viewpoint are degree of curing and filler orientation.

The *degree of curing* depends on the original state of the molding compound and the processing procedure, in particular the variation of temperature with time and the length of the curing process. The degree of curing may not be constant throughout the molding. A thick-walled press molding, for instance, may be fully cured in the outer layers but still uncured in the center. With moldings made from urea resin compounds overcured, undercured, and well-cured regions may be found within one and the same article.

Overcuring can be recognized by the lack of surface gloss. In addition, bubbles can occur, and the molding may adhere to the steel walls of the mold. Overcuring of aminoplastics can lead to bubbles and, in some cases, cracks.

Variations in curing conditions can lead to internal stresses that might prove to be a drawback if the molding gives the appearance of being correctly cured. Undercuring of the complete molding is naturally a more significant problem; with aminoplastics this is also true of overcuring. Many properties depend on the degree of curing for phenolics and aminoplastics, these include surface gloss, stiffness, dimensions, water uptake, and electrical insulation properties.

With all processing techniques, *filler orientation* depends strongly on the flow process involved. Since, when processing thermosetting molding compounds, the tensile deformations exceed the shear deformations, the filler and reinforcing additives are oriented mainly perpendicular to the flow direction.

Filler orientation particularly determines the dimensional stability and strength of the molding. In injection press molding and injection molding, orientation can be influenced mainly by the gate position and less so by processing conditions. With press molding, the flow and hence the orientation can be influenced by the type of feeding, (e.g., concentrating the material in one position). Orientation has a greater effect

with long-fiber reinforcement than with, for example, sawdust.

Molding shrinkage is defined as the difference between the dimensions of the mold and the corresponding dimensions of the molding. It is influenced significantly by the molding compound and the filler orientation, and additionally by the processing conditions, in particular the mold temperature and the pressure in the mold cavity. The influence of filler orientation on shrinkage arises because shrinkage is impeded in the direction parallel to the reinforcing fibers but not in the direction perpendicular to them.

The following applies to the relationship between shrinkage and processing conditions:

1. The higher the mold temperature, the greater is the molding shrinkage
2. The higher the pressure on the molding, the smaller is the process shrinkage
3. Low curing leads to increased molding shrinkage

Distortions arising from local differences in shrinkage are also influenced by filler orientation. The higher the content of inorganic components in a resin substrate, the less pronounced is the tendency to distort. In contrast, the longer the fibers in impact-resistant compounds, the greater is the distortion to be expected. Distortion can also result from local differences in the curing reaction (mold temperatures) or from inhomogeneous cooling of the molding.

The molding shrinkage can be reduced or even completely compensated by adding suitable fillers (e.g., thermoplastic powders), especially in the case of polyester resin molding compounds (low-profile systems).

Mechanical properties are often influenced strongly by filler orientation. With long-fiber reinforcement (glass fibers) and pronounced orientation, the strength in the direction of highest orientation can be several times greater than that in the least oriented direction. Materials containing short-fiber fillers such as sawdust exhibit similar differences in strength in the flow direction and perpendicular to it; however, these differences are small (typically 10 – 30 %). In contrast, curing conditions play only a secondary role in mechanical strength, if the molding has not been strongly over- or undercured.

The electrical insulation properties of phenolics and aminoplastics depend on the degree of curing. Undercuring has a negative effect, particularly on surface resistance.

To attain the best possible insulation characteristics:

1. As hard flowing a molding mass as possible should be used
2. The molding mass should be dried in an oven prior to processing
3. The molding must be perfectly cured

With aminoplastics, overcuring can be as detrimental as undercuring. Phenolic resins are less sensitive to overcuring.

For polyester molding masses, the relationship between degree of curing and electrical properties has minor practical significance. Undercured polyester moldings can be recognized visually and are not suitable for use even though the electrical characteristics are adequate.

2.5. Molds

The quality of the mold has a considerable influence on the manufacturing costs of the molding. With small production runs, the mold should be as simple as possible even if this necessitates use of a finishing process. For mass production, use of a more precise and possibly more complex mold is worthwhile if it avoids finishing.

Most molds for curable molding compounds are manufactured by machining or spark erosion of steel blocks. High-quality steels are employed, particularly for mold cavities. The forming surfaces are polished, hardened, and generally hard chromed to protect them against corrosion and wear. When cavities are manufactured by spark erosion, completely hardened steel is used. Nitriding is rarely employed in molds for processing thermosets. Mold components that are subject to the greatest wear should be easily replaceable or made from hard metals (e.g., gate inserts). With multicavity molds, the cavities themselves are often produced by hollowing with a stamp. Several systems of standard mold units are available with which mold manufacture can be rationalized. They include mold plates made of high-quality steel out of

which the mold cavities can be cut, platens, guiding elements, and ejector systems that can be combined in a modular fashion.

Approximately 30 – 40 W/kg is sufficient to heat molds weighing 50 kg or more. Smaller molds and flat molds require up to ca. 80 W/kg. At least 20 mm of steel should separate the heating element from the mold cavity. The temperature sensor should be located between the heating element and the cavity. During operation, the mold temperature should not vary by more than 5 K. Ideally, each component of the mold should be equipped with its own heating and temperature control unit. Especially with small molds, insulation against heat loss is advantageous. Insulation by a thermal insulation sheet attached to the mounting platens is recommended in all cases to reduce heat losses.

In its simplest form, a *press mold* consists of a punch and a cavity (Fig. 18), generally electrically heated and mounted on the moving and fixed tables of a press. If required, an ejector system is built into the punch, cavity, or both, which releases the molding after the mold has been opened. The ejector pins are so distributed that the molding is ejected without indentation or deformation; the pressing surfaces are sufficiently large that they do not penetrate the molding even when it is still hot.

The formation of the flash surface plays a major role in a press mold (Fig. 21). One version or another is preferred, depending on whether a vertical or horizontal flash is desired (a function of the preferred deflashing method), the available molding pressure, how exact the metering is, whether much air or molding mass is driven out via the flash, and the degree of precision demanded for the thickness of the base.

For press moldings with undercuts, side openings, screw threads, metal implants, and other specialties, multicomponent molds, split molds, and molds with movable inserts, side slides, or supplements are employed. Multicavity molds have several identical or different cavities, with separate or common filling volumes.

Injection press molds usually consist of a top part, a bottom part with injection cylinder, and an injection plunger activated by the weaker plunger of the injection press (transfer press, two-plunger press) (Fig. 19). Channels lead from the free end of the injection cylinder to the mold cavities, which are located in the parting surface between the upper and lower parts of the mold. The narrowest part of the channel, the gate, is located at the junction with the mold cavity.

In another type of injection press mold (Fig. 22), the injection cylinder is incorporated in the top part of the mold, and the molding compound is injected through a gate in the top part into the mold cavity. These molds are used on single-plunger presses. Other mold constructions are also available that are suitable for injection pressing on single-plunger presses.

For *injection molding*, mold constructions typical for the injection molding of thermoplastics

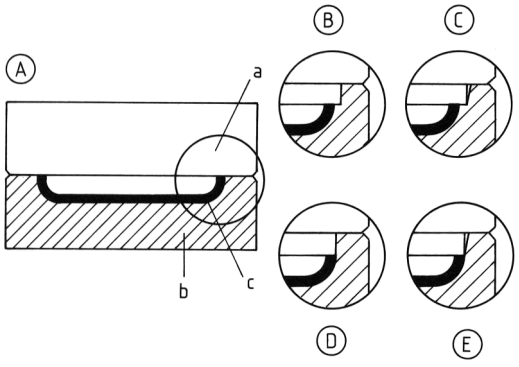


Figure 21. Shaping of the flash
A) Flash mold; B) Flash mold with charge cavity; C) Flash mold, charge cavity with inclined wall; D) Positive mold; E) Positive mold with inclined wall
a) Plunger; b) Punch; c) Mold

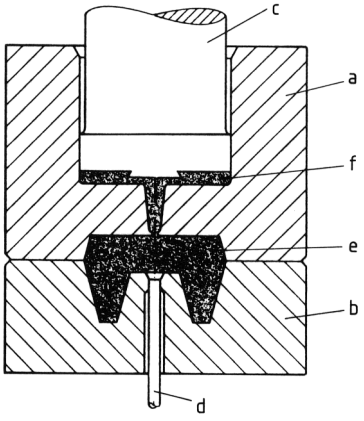


Figure 22. Injection press mold for single-plunger press
a) Top part of mold with injection cylinder; b) Bottom part of mold; c) Injection plunger; d) Ejector pin; e) Mold; f) Injection mass with gate

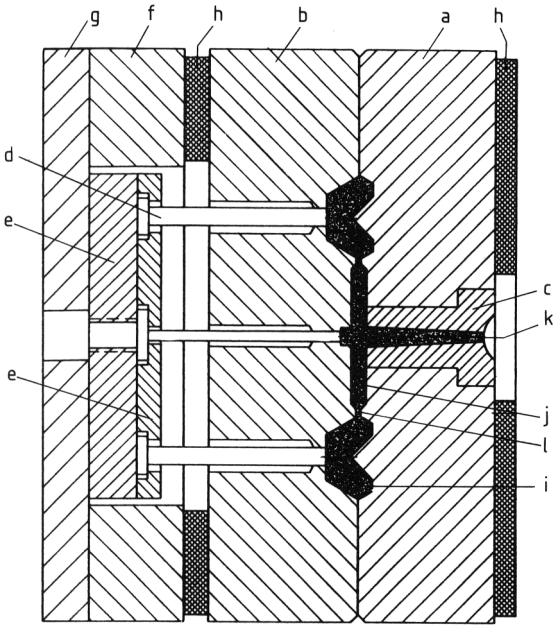


Figure 23. Injection mold
a), b) Mold plates; c) Sprue bush; d) Ejector pin; e) Ejector plates; f) Spacer; g) Adapter plate; h) Heat insulating plate; i) Mold; j) Runner; k) Sprue; l) Gate

are generally preferred; such molds (Fig. 23) have two mold plates, one containing the sprue bush and the other the ejector system.

The cavities and runner systems are incorporated in the parting surface between the two plates.

Molds for injection press molding and injection molding are also available as multicomponent molds, split molds, molds with side slides, or screw thread inserts, etc. Molds for injection press and injection molding require venting channels if air contained in the cavity cannot escape quickly enough via leakages in the parting surface or ejector system during injection of the molding compound into the cavity. The channels are generally best positioned opposite the gate and should be approximately 0.1 – 0.2 mm deep and 2 – 8 mm wide. Alternatively, the closed mold can be evacuated prior to injection of the molding compound.

In molds for injection press and injection molding the gate is the narrowest point in the injection channel and lies directly in front of the junction with the mold cavity. The gate determines the flow of the molding compound during injection into the mold cavity and thus also the filler orientation and structure of the cured material.

With optimum dimensioning of the gate, the molding compound is subject to further heating as it passes through this final constriction so that it enters the mold cavity at a temperature just slightly below the mold temperature. If the gate is too narrow, the mold cavity is not completely filled; if it is too wide, the compound enters the cavity at too low a temperature and takes too long to cure. However, in injection press and injection molding, the conditions do not depend only on the gate, but also on the flow and curing properties of the molding compound along with the pressure and temperature.

As a rule of thumb for dimensioning the gate, with curable molding masses, for each cubic centimeter of cavity volume V, a gate cross section F of 1 mm^2 should be allowed: $F/mm^2 = V/cm^3 \pm 50\,\%$

The margin of $\pm$ 50 % permits special cases to be taken into account. Molding compounds with coarse and fibrous reinforcing materials require larger gates than those containing sawdust; furthermore, the flow properties of the compound, injection pressure, temperature, and design of the molding must also be considered.

The above rule is valid primarily for sheet or film gates (i.e., for rectangular cross sections with height-to-width ratios ranging from 1 : 10 to 1 : 200). Cylindrical pin gates can be made considerably narrower than estimated by the formula. Large amounts of material can generally pass through a pin gate without difficulty; cases are known in which the throughput is greater than 20 cm^3/mm^2. The pin gate is also easier to machine; it can be removed more easily from the molding and normally does not require finishing. It does, however, cause pronounced filler orientation in the immediate vicinity of the gate.

The most homogeneous orientation is achieved with a film gate over the complete width or length of the molding. The film gate should not be thinner than 0.2 mm, and with larger moldings or with impact-resistant masses, no thinner than ca. 0.4 mm.

The runner system should have a much larger cross section, and thus offer less resistance to flow than the gate; depending on the gate type and the position of the runner system, the latter should be three to ten times larger in cross

section than the gate. It should approach the mold cavity with as full a cross section as possible so that the actual gate is short.

2.6. Machines

Presses and Injection Presses. Motor-driven *toggle presses* permit pressing forces up to ca. 1 MN. The toggle is so designed that the press initially closes rapidly and with little force, but toward the end of the motion becomes slower and reaches full force only over the final few millimeters. Overloading is prevented by incorporating a slip clutch between the drive and the toggle. The movement and the development of force of the toggle press are in most cases well suited for the conventional processing of curable molding compounds by press molding, however they are unsuitable when the full molding pressure is required over a displacement of several centimeters (e.g., the motion of an injection plunger in injection press molding).

Hydraulic presses dominate for press forces >1 MN; they are widely employed, however, in laboratory presses down to 100 kN and are available up to ca. 100 MN. Depending on construction, distinctions are made between frame presses and column presses; downstroke presses (lower press table fixed, upper table moved by a piston) and upstroke presses; and presses with single drives (usually oil) or with group drives (usually water).

For high-quality moldings, electronically parallel controlled presses are often used. In addition to the main cylinders that activate the closing and pressing mechanism, additional cylinders are present to ensure the parallelism of the press table even under asymmetrical loading.

Two-piston presses, which are often employed in injection press molding, are usually equipped with a powerful upper piston to close the mold and a weaker lower piston to operate an injection cylinder or an ejector. Figure 24 is a schematic of a two-piston press (column form). The force ratio between the pistons of a two-piston press is generally between 2 : 1 and 8 : 1. Apart from those mentioned above, alternative constructions are available (e.g., with injection cylinders positioned above).

Large-surface presses, with pressing forces that are relatively small compared to the area of the plate, are used primarily for processing

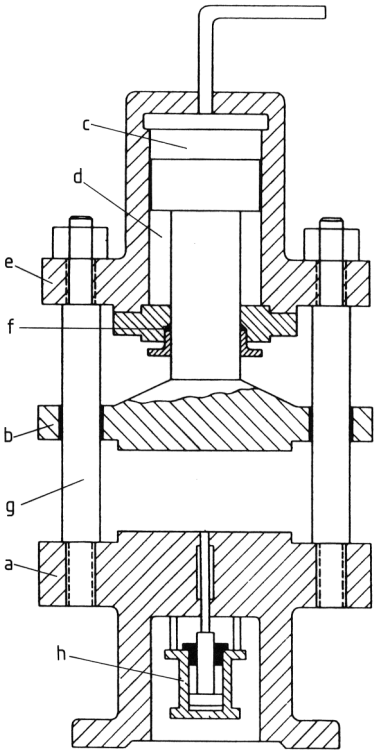


Figure 24. Hydraulic downstroke column press with hydraulic ejector mechanism
a) Fixed lower table; b) Movable upper table with differential piston for drawback; c) Pressure chamber for molding; d) Pressure chamber for drawback; e) Main cylinder; f) Concentric gasket; g) Pillars; h) Hydraulic ejector

resins with glass-fiber reinforcement, and also for low-viscosity polyester resin molding compounds with long glass fibers [e.g., DIN 16 911, type 801 (premix) or DIN 16 913, type 830].

Multiplaten presses with 2 – 20 parallel press platens are used to simultaneously press several identical items. Multiplaten presses, usually with steam-heated and, when required, water-cooled platens are used to press laminates (see Section 2.1.2). The platen size is up to 10 m^2, and the press force up to ca. 100 MN.

Semi- or fully automatic operation of all the press types outlined above is possible. In semi-automatic operation the process stages decisive for processing consistency — closing the press, controlling the curing time, opening the press, the injection stage in injection press molding, and ejection — are automated. The remaining steps — feeding the mold, removing the molding after

completion of the program, and cleaning the mold — are carried out manually. With fully automatic plants, manual operations are limited to filling the molding compound hopper and transporting the completed moldings.

Injection Molding Equipment. Injection molding equipment for curable molding compounds (see → Plastics Processing, 1. Processing of Thermoplastics, Section 4.5) is similar to the screw injection molding machines used for processing thermoplastics. The major components are the clamping unit and the injection unit.

The clamping unit is a toggle or hydraulic press that closes and opens the mold and often activates the ejectors.

The injector unit, which consists of a cylinder (with cylinder head and nozzle), preferably fluid-heated, and a screw, meters and plasticates the molding compound and injects it into the mold. For transportation, metering, and plastication, the screw rotates, usually driven by an electric or hydraulic motor. For injection, it moves longitudinally (normally without rotation); in this case the drive is almost always hydraulic. The injection unit can be moved in the longitudinal direction so that the nozzle can either contact the mold sprue bush or be removed from it.

With the majority of machines, the closing and injection units are positioned horizontally one after the other. However, other constructions also exist, for instance, where the closing and injection unit can be rotated into place when needed.

Injection molding of curable molding compounds requires higher injection pressure than for thermoplastics (at least 150 MPa, or better still, 200 – 250 MPa). Many thermoplastic injection molding machines can be modified for use with curable molding compounds.

Injection molding machines for curable molding compounds generally have a capacity of ca. 50 – 1000 cm^3 and a closing force of 5 MN; larger machines are, however, also in operation.

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Plastics Processing, 3. Machining, Bonding, Surface Treatment

ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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1. Machining

1.1. Estimating Machinability

The special properties and low cost of thermoformed plastics have led to their widespread use in the construction of machines and other equipment. Machining of components from plastics is significant because of the increasing number of design variations of manufactured components; the demand for greater stength and for cheap production of samples, individual articles, and small series; and the fabrication of thermoformed components (e.g., holes in PVC window frames for hinges). An important prerequisite for economical machining is the selection of optimum cutting conditions. This requires knowledge of the machinability of polymers and the wear resistance of the tools. A prerequisite for the economical utilization of machining techniques is a knowledge of the parameters that influence the machinability of the material. Experience from the metalworking industry cannot be applied directly to polymers. Even a comparison between the physical properties of metals and those of polymers shows that certain factors exerting a large influence on the machinability of metals are only slightly or

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not at all significant for plastics. Furthermore other factors can arise in polymer processing, such as the generation of dust, evolution of gaseous compounds, and melting of the component or of the shavings removed from it, that do not occur with metals.

The following criteria, which are also used in the metal industry, are used for judging machinability:

1. Effective machining forces
2. Resulting machining temperatures
3. Attainable surface quality, shaving formation, and wear of machining tools

1.2. Shaving Formation

With thermoplastics, shaving formation influences the attainable surface quality and the static and dynamic process controlling the cutting action and advancing force. The tendency to form long, ribbonlike shavings often hinders machining, and the poor thermal conductivity causes welding of the shavings, as well as distortion, leveling, melting, and smearing of the surface.

In turning polyamides, depending on machine conditions and material properties, three basic types of shaving may result, which can generally be broken down into continuous and discontinuous forms (Fig. 1). This figure shows that the shape of the shaving is a result of the type of shaving, which depends on water content, cutting geometry, and cutting speed, and its cross section.

The shape of the shaving is assessed by using the so-called shaving volume number, which is the ratio of the volume required by an amount of disordered shavings to the volume of material from which they were produced. It is most favorable for discontinuous shavings.

Drilling low-density polyethylene (LDPE), polyacetal, and polyamides with spiral drills gives similar shaving shapes, with three characteristic types (folded shavings, helical shavings, lamellar shavings) [4]. Milling of polyamides gives shaving typical of those obtained from machining metals (ribbon shavings, snarl shavings, spiral shavings, helical shavings, crumble shavings, needle shavings, and melted shavings).

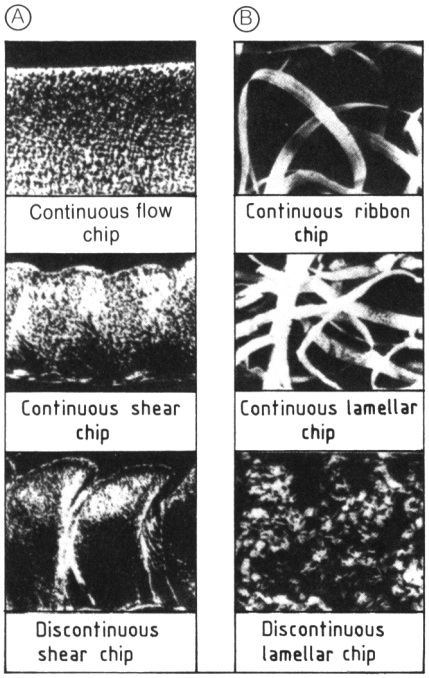


Figure 1. Classification of shaving types (A) and forms (B)

1.3. Surface Quality

In the qualitative evaluation of the turned surfaces of thermoplastic polymers, depending on shaving conditions, three different characteristic surface structures can arise (Fig. 2): (1) a groove profile, (2) a smeared groove profile, and (3) a groove profile with breakouts. The occurrence of surface breakouts under certain machining conditions during turning was first reported by Spur and Zug [6–8] for polyamides and polyacetal, and for poly(vinyl chloride) and polyacetal resins by Ferichmann [9]. With several materials, the tendency to form surface breakouts is particularly pronounced (e.g., rigid PVC and bulk-polymerized polyamide [9], [10]).

As with metals, the surface roughness value T_t as defined by DIN 4760 can be used for a quantitative characterization of surface quality. It is the maximum vertical separation between the highest and the lowest points of a surface structure. Experimental determinations during turning of polyamide illustrate that the maximum roughness increases with increasing feed, whereby water-containing materials exhibit higher roughnesses than dry materials [6],

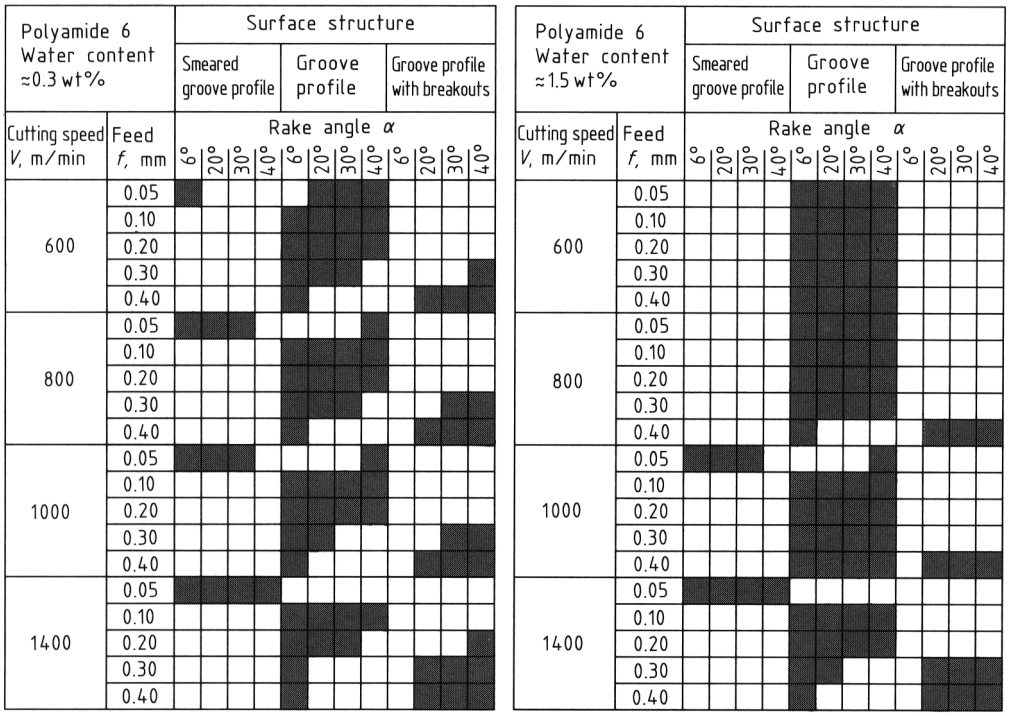


Figure 2. Occurrence of certain surface structures as a function of cutting speed, effective cutting angle, feed, and water content of Ultramid KR 1337

particularly under conditions of large feed. The surface roughness decreases with increasing cutting angle. For polyamide 6 containing 15 wt % glass fiber and polyamide 6 with 5 wt % graphite, increasing machining time causes an increase in surface roughness, whereas with the extruded materials polyamide 6 and polyamide 6 containing 1 wt % MoS_2, the surface roughness remains unchanged. The time dependence of the surface roughness with glass- and graphitefilled polyamides results from increased tool wear caused by the fillers.

In milling and grinding polyamides, surface melting generally occurs with tooth feeds $f < 0.1$ mm. For $f > 0.02$ mm, the surface roughness increases with increasing feed, whereby the best surface quality is attained with a rake angle of $\alpha = -6°$ to $+6°$. With short machining times of <30 s and cutting speeds V<500 m/min, the best surface quality is obtained with a small clearance angle (γ<5°). Longer cutting times and higher cutting speeds (V>500 m/min) require larger clearance angles due to increased warming of the cutting tool, particularly with small tooth feeds. Large stressed cross sections can lead to increased *breakouts* from the surface, proportional to the cutting speed. Surface *breakouts* occur more frequently with greater depth of cut and positive rake angle.

As a consequence of restricted shaving removal and the continuously changing cutting geometry of spiral drills, large surface roughness values result from drilling. The surface quality is influenced mainly by the heat generated during the machining process.

Drilling of polyamide and polyacetal showed that with high levels of feed, lamellar shavings occur that are accompanied by surface breakouts [10]. In contrast, in drilling LDPE, no lamellar shavings occur even at greater feeds, and the surface remains free of breakouts. With bulk-polymerized polyamide 6, polyamide 6 containg 0.5 wt % MoS_2, polyamide 6 containing 25 wt % glass fibers, polyamide 6 containing 35 wt % glass fibers, polyamide 66 containing 25 wt % glass fibers, polyamide 66 containing 35 wt % MoS_2 and polyacetal, the surface roughness increases once a threshold feed value

has been exceeded ($f = 0.4$ mm; with polyacetal, $f = 0.8$ mm). An exception to this tendency is polyamide 6 containing 5 wt % MoS_2 at a cutting speed V of 40 m/min, and also LDPE. With polyamide the surface roughness decreases with increasing feed, whereas for LDPE the surface roughness is almost independent of feed. Since surface quality is reduced by melting of the bore wall, particularly at small feeds and high cutting speeds, it can be improved by cooling. Although external application of a drilling oil emulsion causes little or no improvement in surface quality, surface roughness can be reduced, especially at high cutting speeds, by cooling with compressed air via a series of internal cooling channels. The best surface quality is obtained at feeds of $f<0.8$ mm by circulating drilling oil through internal cooling channels.

1.4. Cutting Forces

The effective cutting and feed forces involved in machining thermoplastics are generally far lower than those required for metals. The cutting forces that occur on turning polyamides increase almost linearly with increasing feed and depth of cut, if shaving shape is constant. Another significant factor affecting cutting force is the machining angle. Thus, for the same shaving cross section, the cutting force during turning of polyamide at a rake angle of 50° can be 50 % lower than at a rake angle of 0°. This applies only when the moisture content is constant [6]. The correlation is particularly significant for the widely used polyamides (PA 66, PA 6) because the high moisture absorption of these materials leads to considerable changes in mechanical properties. In turning polyamides, the cutting forces are approximately 30 % lower for a material with a moisture content of 3.5 wt % than for a dry sample.

When drilling polycarbonate, polyethylene, poly(vinyl chloride), poly(methyl methacrylate), polystyrene, acrylonitrile – butadiene – styrene (ABS) polymers, polytetrafluoroethylene, polyacetal, polypropylene, and polyamide, the torque and feed force increase linearly or slightly degressively with increasing feed. The speed of the spiral drill has little influence on shaving force [11]. Hoffmann investigated the influence of cooling lubricants on feed force and torque in drilling bulk-polymerized polyamide 6 and showed that when cooling lubricants are employed, the advancement force increases slightly because the strength of the polymer is extremely temperature dependent [4]. Whereas the torque increases significantly when internal compressed air cooling is employed, the lubricating effect that occurs when drilling oils are used causes it to increase to a considerably lesser extent due to the reduction of the fiber friction at the bore walls. The lowest values are obtained without cooling by using drills equipped with internal cooling channels.

1.5. Cutting Temperature and Tool Wear

The temperatures that arise during the machining of unfilled thermoplastics are so low that they do not influence the lifetime of the machining tools. Measurements carried out during drilling and turning have shown that the lowest temperatures occur in the machining of polyethylene, and the highest with polyamide. Under certain machining conditions, temperatures can exceed the melting point of the material being processed. However, due to the low thermal conductivity of polymers, this affects only the surface areas. The cutting temperature is particularly critical when gaseous decomposition products can form, which is especially applicable to nitrogen-containing polymers, phenol – formaldehyde resins, and fluoropolymers [12].

Tool wear is considerably lower in the machining of unfilled polymers than it is with metals [13]. In machining filled polymers, a significantly greater amount of wear occurs compared to unfilled plastics. This is especially true for graphite-filled materials, although glass-fiber-filled materials also cause increased tool wear [4, 6, 14, 15].

1.6. Guidelines for Machining Polymers

Tables 1–3 list guidelines for turning, milling, and drilling thermoplastics and thermosets with hard metal tools. Standardized tools are used for machining polymers, with cutting edges made

Table 1. Guidelines for turning plastics

Material	Type of turning	Depth of cut, mm	Cutting speed, m/min	Feed, mm	Cutting geometry, degrees		Attainable surface quality, μm
					Clearance angle γ	Rake angle α	
Thermoplastics							
Polyolefins	rough	3 – 5	250 – 400	0.5 – 1	5 – 15	≦0	6 – 10
	smooth	1 – 3	350 – 600	0.1 – 0.6			
Polystyrene	rough	1.5 – 4	80 – 120	0.1 – 0.2	8 – 12	≦0	3 – 6
	smooth	0.5 – 1.5	100 – 200	0.02 – 0.08			
PVC, rigid	rough	2 – 6	100 – 250	0.4 – 0.5	12 – 18	−5 to 0	3 – 10
	smooth	0.5 – 1	250 – 350	0.1 – 0.2			
Poly(methyl methacrylate)	rough	1.5 – 3	100 – 150	0.1 – 0.2	10 – 15	0 – 5	6 – 10
	smooth	0.5 – 1.5	200 – 350	0.05 – 0.1			
Polyamide	rough	2 – 4	100 – 200	0.2 – 0.5	5 – 15	35 – 45	3 – 6
	smooth	1 – 2	200 – 250	0.1 – 0.2			
Polyacetal	rough	2 – 5	120 – 200	0.2 – 0.3	10 – 15	−5 to 5	6 – 10
	smooth	0.4 – 2	180 – 300	0.1 – 0.25			
Thermosets							
Phenolics	rough	2 – 4	200 – 300	0.2 – 0.3	5 – 10	20 – 25	10 – 20
	smooth	0.5 – 1.5	350 – 450	0.08 – 0.15			
Aminoplastics	rough	1.5 – 3.0	200 – 350	0.1 – 0.15	5 – 10	20 – 25	10 – 20
	smooth	0.5 – 1.0	400 – 500	0.05 – 0.1			
Paper- and fabric-based laminate	rough	2	100 – 180	0.3 – 0.5	12 – 18	15 – 25	6 – 20
	smooth	0.5 – 2	200 – 250	0.1 – 0.2			
UP – GF*	rough	1.5 – 3	90 – 120	0.1 – 0.2	8 – 10	−5 to −2	10 – 20
	smooth	0.5 – 1.5	120 – 150	0.05 – 0.1			

* UP – GF = glass-fiber-reinforced unsaturated polyester resin.

of high-speed steel, hard metal, or ceramic. For the production of small series, bits with cutting edges made of high-speed steel can be used, whereas for mass production, hard metal is preferred because less wear occurs.

1.7. Processing of Fiber-Reinforced Plastics

The processing of fiber-reinforced plastics (see → Plastics, Processing, 2. Processing of

Table 2. Guidelines for milling plastics

Material	Depth of cut, mm	Cutting speed		Feed per tooth		Cutting geometry, degrees		Attainable surface quality, μm
		Rough, m/min	Smooth, m/min	Rough, mm	Smooth, mm	Clearance angle γ	Rake angle α	
Thermoplastics								
Polyolefins	1 – 5	250 – 350	300 – 500	0.2 – 0.3	0.05 – 0.2	15 – 20	−5 to 0	6 – 10
Polystyrene	1 – 5	150 – 200	250 – 400	0.3 – 0.5	0.04 – 0.1	20 – 25	10 – 20	6 – 20
PVC, rigid	3 – 8	250 – 350	350 – 550	0.4 – 0.6	0.05 – 0.3	25 – 30	20 – 25	6 – 20
Poly(methyl methacrylate)	1 – 5	130 – 150	180 – 300	0.1 – 0.2	0.03 – 0.1	25 – 30	20 – 25	4 – 8
Polyamides	1 – 5	100 – 140	150 – 180	0.2 – 0.5	0.05 – 0.1	25 – 30	20 – 25	6 – 10
Polyacetals	1 – 4	120 – 160	150 – 200	0.1 – 0.3	0.03 – 0.1	6 – 14	0 – 8	6 – 10
Thermosets								
Phenolics	3 – 7	150 – 250	200 – 300	0.3 – 0.6	0.08 – 0.4	20 – 30	20 – 25	6 – 10
Aminoplastics	3 – 7	150 – 250	200 – 300	0.4 – 0.8	0.08 – 0.3	20 – 30	20 – 25	6 – 10
Paper- and fabric-based laminate	1 – 4	80 – 150	150 – 250	0.2 – 0.4	0.08 – 0.1	20 – 25	20 – 30	6 – 10
UP – GF*	1 – 5	50 – 150	200 – 600	0.1 – 0.2	0.05 – 0.1	10 – 15	5 – 10	10 – 20

* UP – GF = glass-fiber-reinforced unsaturated polyester resin.

Table 3. Guidelines of drilling plastics [35]

Material	Average drill speed for a given drill diameter, min^{-1}			Feed, mm	Clearance angle γ, degrees	Rake angle α, degrees	Point angle σ, degrees	Recommended drill oversize, mm	Coolant
	4 mm	10 mm	20 mm						
Thermoplastics									
Polyolefins	4000	1800	1100	0.1 – 0.5	10 – 20	0 – 10	110 – 120	0.15 – 0.2	none
Polystyrene	800	550	180	0.1 – 0.3	6 – 10	5 – 8	49 – 90	0.05 – 0.08	water
PVC, hard	2000	950	630	0.2 – 0.6	10 – 30	0 – 5	110 – 130	0.06 – 0.09	compressed air
Poly(methyl methacrylate)	1000	600	300	0.2 – 0.3	8 – 12	10 – 15	60 – 90	0.05 – 0.08	water
Polyamides	7500	2500	1000	0.1 – 0.4	10 – 12	8 – 10	100 – 120	0.08 – 0.12	compressed air
Polyacetal	4800	2200	1300	0.1 – 0.25	10 – 15		60 – 100	0.08 – 0.10	none
Thermosets									
Phenolics	4000	1600	800	0.1 – 0.3	6 – 8	12 – 24	60 – 100	0.02 – 0.05	compressed air
Aminoplastics	4800	2000	850	0.05 – 0.15	5 – 10	10 – 15	60 – 120	0.06 – 0.08	compressed air
Paper- and fabric-based laminate	3500	1200	650	0.2 – 0.4	15 – 20	10 – 15	90 – 110	0.05 – 0.08	compressed air
UP – GF [*]	9000	5400	2800	0.05 – 0.1	10 – 12	14 – 16	140 – 150	0.03 – 0.05	water

[*] UP – GF = glass-fiber-reinforced unsaturated polyester resin.

Thermosets, Section 1.5) leads to more problems than the processing of unreinforced or filled polymers.

During the manufacture of a fiber composite component, several processing operations are generally required, in which the properties of the fiber material must be taken into account. Figure 3 gives an overview of the relevant properties and the fracture behavior of glass, carbon, and aramid fibers. The brittle fracture behavior of glass and carbon fibers contrasts with the ductile failure of aramid fibers, which tend to split in the fiber direction because of their molecular structure. In addition to the physical properties of individual fibers, the laminate structure, fiber orientation, fiber length, and fiber content of the product also influence processing characteristics. In general, machining operations are required at the beginning and the end of the manufacturing sequence: to cut the semifinished product to size and to produce the desired final contours. Continuous fiber sheet molding compounds are a widely used starting material. Trimming is generally performed manually with knives, scissors, or special equipment. Even this processing stage exhibits a range of problems and requires the use of tools adapted to suit the type of fiber employed. Difficulties also arise from adhesion of resin and fiber fragments to the equipment, which prevents a clean cut. Frequently, fibers are pulled out of the matrix, and ragged cut edges result. Prepreg trimming can be improved by using ultrasonically vibrating blades.

After shaping and curing, a finishing operation is generally necessary. This can involve edge trimming and deflashing, as well as generation of dimensionally precise functional surfaces. Finishing can be carried out by classical techniques such as milling, turning, and drilling, or by newer methods such as laser, water-jet, or abrasive water-jet cutting. None of these methods is suitable for all finishing operations. For example, laser and water-jet cutting are not well suited for generating high-quality functional surfaces, but have advantages in edge trimming and deflashing or in introducing *cutouts*.

Figure 4 shows the topography of cut surfaces generated by laser cutting, water-jet cutting, and milling of a sheet molding compound (SMC) material. The condensation of decomposed material and melt residues on surfaces cut by laser are typical of this method. The porous, relatively smooth surface is characteristic. Cracking of the surface indicates that the sample has suffered some thermal damage. Cracks are also apparent in the surface cut by a water jet. These are caused by local mechanical overloading of the fiber – matrix composite as a result of pressure buildup in the sample. Damage occurs

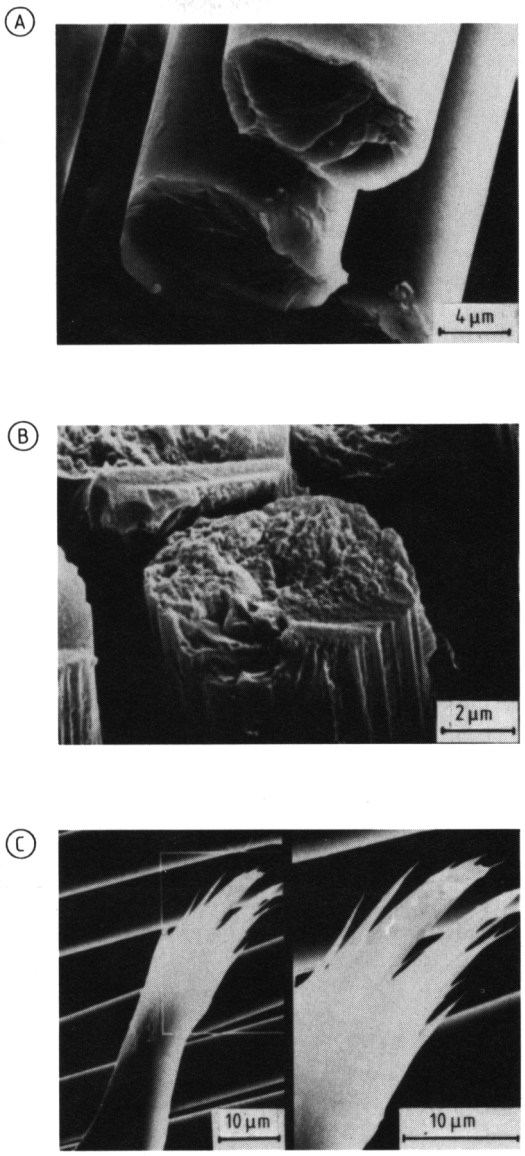


Figure 3. Properties and fracture characteristics of glass (A), carbon (B), and aramid (C) fibers

mainly to areas in the vicinity of the jet outlet because, in this position, support by underlying material is either partially or totally absent. Characteristic surface features include the almost parallel ridges oriented against the direction of advancement, whose course and size can be influenced over a wide range by the choice of process parameters. The best optical appearance is given by the milled surface. In this case, only slight unevenness is apparent, and the surface is macroscopically free from machining damage. Milling also permits the highest advancement speed. The brittle fracture characteristic of glass fibers is an advantage for mechanical methods such as water-jet cutting or milling, and the large difference between the melting points and decomposition temperatures of the fiber and matrix materials causes problems with processing by use of thermal energy.

Additionally, the high abrasiveness of glass and carbon fibers also causes problems. Milling thus necessitates the use of hard metal tools. Often polycrystalline diamond (PCD) cutting edges are preferred. Despite the considerably higher cost compared to hard metal tools, the use of PCD is often justified by improved processing quality and reduced machine down time due to longer lifetime of the tool.

In processing aramid-reinforced materials, the abrasive effects do not cause as many problems as the high toughness of the fibers and hence the ragged appearance of the cut edge. For this reason, opposing screw formed ground hard metal bits are preferentially employed to grind aramid composites in contrast to one- or two-bit heads to grind GRP and carbon-reinforced plastic (CRP) (Fig. 5).

A comparison of the various methods for finishing fiber-reinforced plastics is given in Table 4.

Apart from technological and economic aspects, environmetal aspects of the processes will become more important in the future, including the emission of pollutants and noise.

2. Bonding

Bonding processes for polymers can be categorized into three groups:

1. Welding
2. Adhesion
3. Mechanical bonding

A designer employing polymers has a limited choice of bonding process because fully cross-linked polymers cannot be welded, and several non-cross-linked polymers can be adhered to only with extreme difficulty or to a certain degree. All polymers can be mechanically

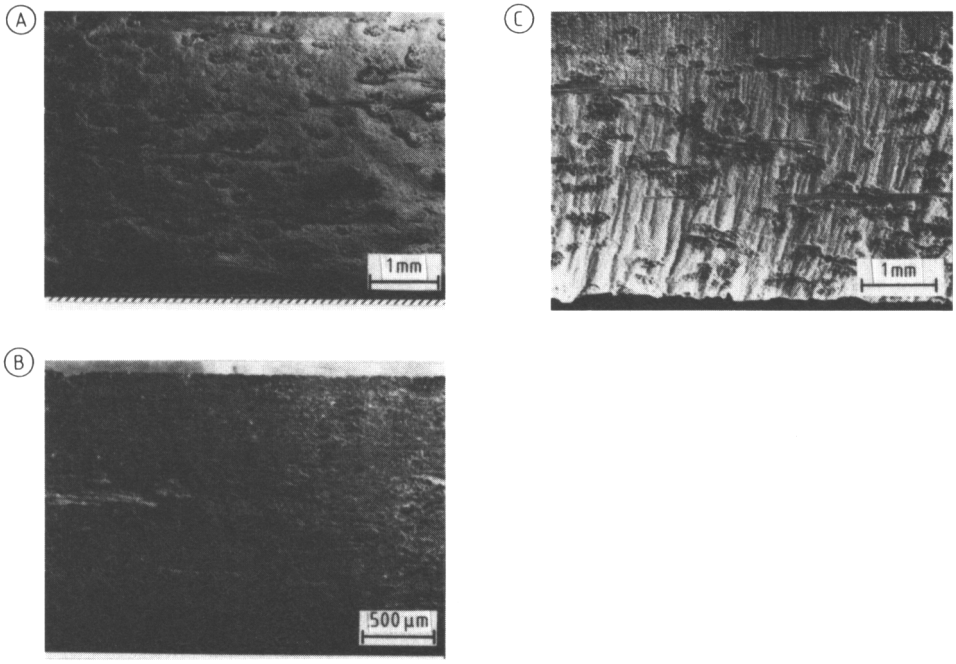


Figure 4. Cut surface of a polyester – glass fiber SMC component after laser cutting (A), milling (B), and water jet cutting (C)

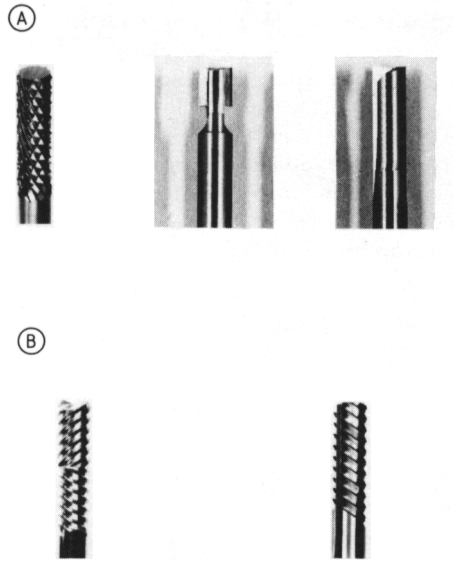


Figure 5. Milling cutters for glass and carbon-fiber-reinforced plastics (A) and aramid-fiber-reinforced plastics (B)

bonded to each other or to other materials, (e.g., by riveting, bolting, or clips). However, with fiber-reinforced polymers, because of anisotropy, clip and plug bonds are problematic, and the sensitivity to notch effects places constraints upon riveting and bolting.

Welding and adhesion yield permanent bonds; this also applies to riveting. All other mechanical bonds can be regarded as reversible. The choice of bonding technique is determined by processing factors, particularly bonding time. Welding and mechanical bonding require little time, whereas adhesion necessitates longer periods to allow for surface pretreatment and hardening of the adhesive.

2.1. Welding

Only polymers that can be softened or melted by heating can be welded (i.e., non-cross-linked polymers) [16, 17]. Exceptions to this include poly tetrafluoroethylene, heat-resistant polyaromatics such as polyimides and polybenzimidazoles, and ultrahigh-molecular-mass thermoplastics (e.g.,

Table 4. Criteria for evaluating the processing of fiber-reinforced plastics

	Process			
Criterion	Water-jet cutting	Abrasive water-jet cutting	Laser cutting	Contour milling
Mechanical stress	low	low	very low	medium
Thermal stress	very low	very low	very high	low – medium
Pollution	none	none	very high	high (dust)
Noise	high	high	medium	very high
Width of cut	low	medium	low	tool diameter
Shape of cut	slightly conical	conical	slightly conical	any
Minimum radius, mm	0.5 – 1.0	1.5 – 2.0	0.2 – 0.5	tool diameter
Symmetry of cut edge	parallel to jet direction	parallel to jet direction	parallel to jet direction	perpendicular to tool axis
Tool wear	low	medium – high	very low	medium – high
Acessibility of the workpiece	both sides	both sides	both sides	one side

UHMW-PE and cast PMMA), whose softening or melting temperature lies above their thermal decomposition temperature.

During welding, the polymers are heated in the region surrounding the weld seam until they pass into the plastic state. They can then be joined under pressure, whereby macromolecules of the two substrates undergo mutual diffusion processes.

Apart from possible thermal chain degradation, chemical reactions do not take place during polymer welding. To obtain an acceptable, materially intact joint, the material flow process in the plane of the seam must take place at a temperature comparable to that of the original forming process (injection molding, extrusion, etc.).

Various welding techniques are generally classified according to the way in which energy is introduced:

1. Thermal conduction
2. Convection
3. Radiation
4. Friction
5. Induction

The following welding techniques are commonly used today (the energy source involved is given in parentheses):

1. Heated-tool (HT) welding (thermal conduction)
   a. Direct heating of seam area
   HT butt welding
   Heated wedge welding
   Welding by bending
   HT socket welding
   Electric socket welding
   b. Indirect heating of seam area
   Thermal sealing
   Heat impulse welding
2. Hot-gas (HG) welding (convection)
   HG area welding *
   Draw welding *
   HG extrusion welding *
3. Radiation welding (thermal radiation)
   HT radiation welding
   Laser welding
   Laser extrusion welding *
4. Friction welding processes (friction)
   a. Heating via internal friction within the material
   High-frequency welding
   Ultrasonic welding
   b. Heating via external friction
   Rotation friction welding
   Vibration welding
5. Induction or electromagnetic welding (induction) *

(Asterisked processes require the use of welding rods)

2.1.1. Heated-Tool Welding

In HT techniques the welding zone is heated conductively by electrically heated metallic elements. In direct HT welding, heat flows directly from the heating element to the weld zone; with indirect HT welding, heat transport proceeds from an external source through the welding substrate to the welding zone. Because of the poor thermal conductivity of polymers, indirect

HT welding is used only for thin materials (films).

In *direct HT welding*, both welding partners are heated by the same heating element. For this, the components are mounted in their respective welding positions on two mechanisms that can be closed against each other. The heating element is introduced between the welding substrates, and the sections to be heated are pressed against the front and back surfaces.

Once the desired temperature has been reached, both welding partners are lifted briefly from the heating element, which is then removed, and the welding process is completed by contacting the welding partners under pressure. In all HT welding processes, the following parameters influence the quality of the weld seam:

1. Melt length (reduction in dimensions of the welding substrate during heating phase)
2. Heating time
3. Time required to remove heating element
4. Seam pressure
5. Holding time

Heated-tool butt welding is simple to automate, which is essential for reproducible welding seam quality. It requires short cycle times and is particularly suitable for welding partners with large weld seam areas (solid preforms, pipes, window frame profiles, transport pallets) and also for fine welds (e.g., taillights for automobiles). Due to melting of the bonding partners, a so-called weld bead is usually formed, which in some cases must be removed in a separate step. In the most favorable cases, the strength of the weld can reach the strength of the bonded materials.

Heated-wedge welding is a continuous bonding process for polymer films and plastic-coated fabrics (Fig. 6 A). In the manual process, the heated metal wedge and the pressure roll are operated by hand. In the mechanized version, the heated wedge and the transport and pressure roll are fixed, and sheets to be welded are drawn over the wedge. The thickness of overlapping films can reach 0.4 mm. Welding speeds up to 15 m/min can be reached.

Welding by bending is a manual technique used for sheets and plates (Fig. 6 B). The wedge-

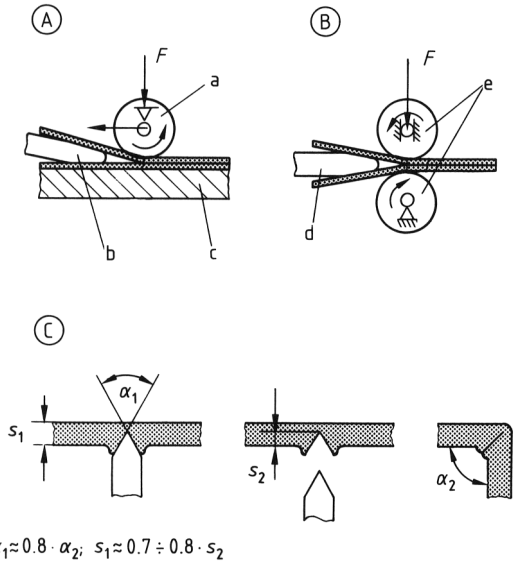


Figure 6. Manual (A) and mechanized (B) heated wedge welding, and welding by bending (C)
a) Pressure roll (manually operated); b) Heated wedge (movable); c) Support; d) Heated wedge (fixed); e) Transport and pressure rolls

shaped tip of the heated tool is inserted three-quarters of the way into the welding substrate and is removed after a period of heating (essentially pressureless). The sheets are welded together by bending. To ensure that sufficient welding pressure can be introduced, the angle at the tip of the heating tool should be approximately 20 % smaller than that at the opposing end. To reduce the heating period for thick sheets, a wedge-shaped groove can be milled into the sheet.

Heated-tool socket welding is a process for bonding pipes with sockets by means of an overlapping weld seam (Fig. 7 A).

The heating element has the inner contours of the socket on one side and the outer contours of the pipe on the other. The dimensions of the heating element, pipe, and fitting are such that after heating, removal of the heating element, and repositioning, pressure is built up at the weld seam during welding. The technique is employed almost exclusively for pipes made of PE and PP.

Electric socket welding is another technique for bonding pipes. The injection-molded socket has electrical heating coils incorporated in the inner surface, which, after positioning at the end

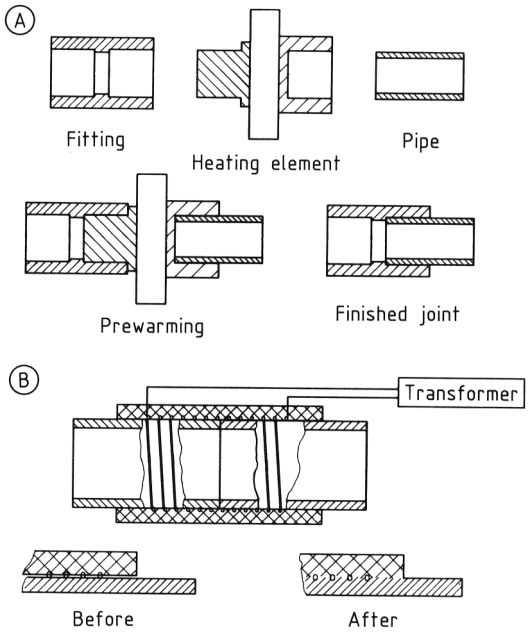


Figure 7. Heated-tool socket welding (A) and electric socket welding (B)

of the pipe, are connected to a welding transformer (Fig. 7 B). The inner surface of the sleeve and the outer surface of the pipe are plasticated. Because the sleeves are generally injection molded with intrinsic orientation, shrinkage occurs on heating, which generates the radial pressure required for welding. The coils remain within the bond.

An *indirect heated-tool* welding technique is thermal contact welding, which finds widespread application for moldings and films of low wall thickness (<1 mm) (Fig. 8). The surface of the continually heated element can be structured to permit combination of the welding process with embossing. Areas of application include packaging technology (heat sealing, welding on lids, closing plastic sacks, etc.). With heat impulse welding, the heating element is not heated continually (Fig. 8 B). At the onset of each welding phase, thin metal rods coated with an antiadhesive layer [generally polytetrafluoroethylene (PTFE)] are subjected to a short but powerful current impulse and are thus heated. The heat passes through the film to the weld zone by conduction. In the two-sided process, the temperature profile in the weld zone is symmetrical because of the arrangement of the heating bars, but it is asymmetrical in the one-side process. The main application is in packaging technology, although this technique is not suitable for welding large areas because of the heaters used (narrow bus bars). Because the welds cool via the ram and counterram, cycle times are shorter than in heat contact welding.

In all indirect HT welding techniques, a temperature profile across the thickness of the weld seam is formed during heating, with the highest temperature on the surface nearest the heating element. The welding parameters (HT temperature and heating time) must therefore be

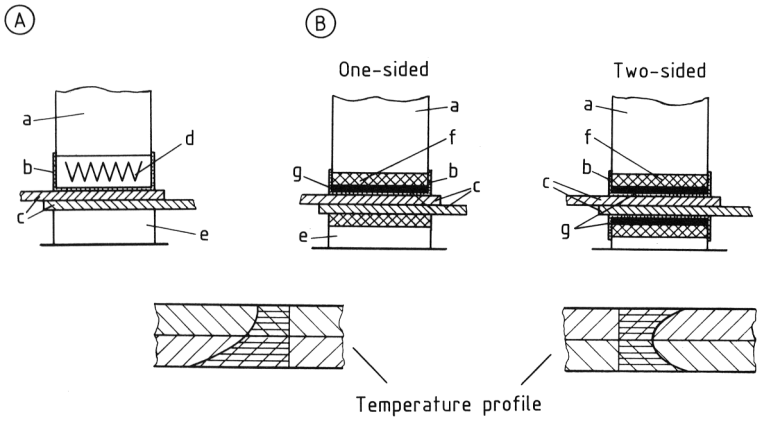


Figure 8. Thermal sealing (A) and heat impulse welding (B)
a) Ram; b) Antiadhesive coating; c) Films; d) Heating element, continuously heated; e) Counterram; f) Thermal insulation; g) Impulse heating bar, discontinuously heated

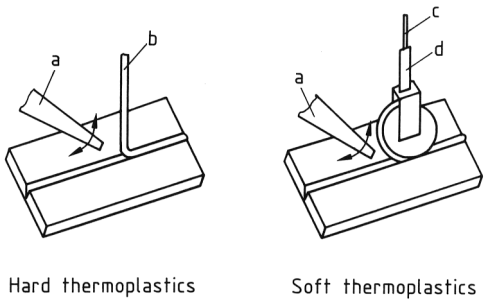


Figure 9. Hot-gas welding
a) Hot gas; b) Welding rod (manually guided); c) Welding rod; d) Pressure roll (manually guided)

adjusted so that a sufficiently high temperature is reached in the welding plane, without overheating the polymer on the surface.

2.1.2. Hot-Gas Welding

Hot-gas welding is usually carried out manually.

The heat-transfer medium is generally hot, clean compressed air; for oxidation-sensitive materials, inert gases such as nitrogen or carbon dioxide are also used. The surfaces to be joined are heated via the hot gas stream and welded under pressure, usually with welding rods (Fig. 9). This method is particularly suitable for assembly and repair, as well as machine and container construction. Use of hot-gas welding is recommended when access to the weld seams is difficult or when the materials concerned are difficult to weld.

The most important requirements for high weld quality are constant welding pressure, gas temperature, and gas flow rate, as well as precise guiding of the gas nozzle and welding rod.

Three variations of hot-gas welding exist.

In swirl welding, the welding substrate and welding rod are heated by a swirling motion of the circular hot-gas die. The welding rod (a few millimeters in diameter) is fed perpendicular to the surface to be welded (Fig. 9). With soft weld rods, a pressure roll is used to avoid folding of the welding rod.

In draw welding, the welding rod is warmed separately in a specially formed hot-gas nozzle. The metal housing removes heat from the gas stream and transfers it to the welding rod by conduction. The welding rod leaves the die in a

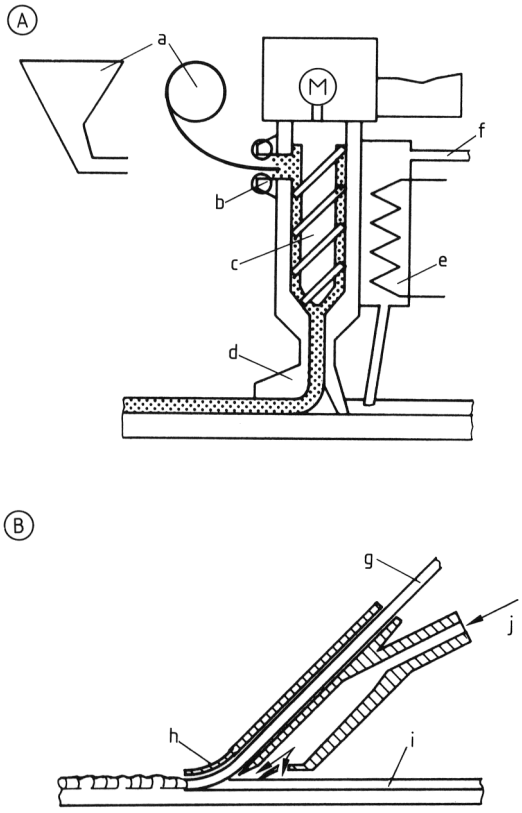


Figure 10. Extrusion (A) and draw (B) welding
a) Pellet hopper or wire reel; b) Wire feed; c) Extruder; d) Welding shoe; e) Heater; f) Air supply; g) Welding rod; h) Pressure lip; i) Part to be welded; j) Hot air

plasticated state and is pressed onto the basic material by a pressure lip (Fig. 10 B). Higher welding speeds are possible than with swirl welding.

Extrusion welding is mainly employed to bond thick-walled moldings because deep weld grooves can be filled in a single operation. The substrate is warmed with hot gas during which time the welding rod is fed as a plasticated ribbon directly from an extruder and pressed into the groove by a welding lip (Fig. 10 A).

2.1.3. Radiation Welding

Radiation welding techniques can generally be classified into two groups: those in which the thermal radiation from a heating element is utilized and those that employ lasers.

With HT radiation welding, the welding surfaces are not brought in contact with the heating element. Instead, heat transport from the heating element to the weld region takes place across a 0.5 – 1 mm air gap, mainly by radiation and partly by convection. The process is particularly advantageous for polymers that tend to adhere to the heating element and be drawn into fibers. To accelerate the heating process, radiation heating elements are generally operated at higher temperature than those employed in conductive methods. Care must be taken not to overheat the surfaces to be welded.

In laser welding, heating of nontransparent polymers is performed with a laser. This process is employed only in special cases for films and in winding fiber-reinforced polymer components with a thermoplastic matrix.

In laser extrusion welding, the substrate is heated by a laser instead of the hot gas used in conventional extrusion welding.

2.1.4. Friction Welding

Friction welding utilizes the heat of friction to plasticate the welding surface. A distinction is made between external and internal friction. Whereas the relative motions of the welding components cause heating via external friction, the electrical and mechanical damping characteristics of the material and the molecular vibrations lead to heating by internal friction.

Spin welding , a technique employing external friction, is suitable only for bonding components that are rotationally symmetrical. One of the welding substrates is rotated while the other is mounted on a bearing capable of rotating about the same axis, but initially prevented from doing so by a brake, and is lightly pressed against the rotating partner (1 – 2 N/mm^2). The relative motion (0.8 – 2.5 m/s) causes heating of the welding surfaces and finally melting. Once a large enough melt reservoir has been generated, the brake is released, and both components rotate at the same speed. If one component is particularly large or does not have rotational symmetry, rotation of the substrate can be stopped for welding. The weld must be cooled while still under compression. The technique can be carried out straightforwardly on a lathe. A disadvantage is the long setup time.

In vibration welding, direct heating of the weld plane is brought about by relative motion of the two partners while under pressure. An oscillating rotational (with rotationally symmetrical welding surfaces) or translational motion (frequencies of 100 – 300 Hz) is used. Important process parameters that must be adjusted to suit both the geometry of the articles to be welded and the material itself are

1. Friction speed or frequency and amplitude (up to 2.5 mm)
2. Friction time
3. Friction pressure (up to 4 N/mm^2)
4. Weld seam pressure
5. Holding time

Both processes are simple to automate and have short cycle times (ca. 5 s), so they are ideally suited for mass production operations. Additionally, vibration welding techniques can be used in the manufacture of hollow articles (e.g., brake fluid reservoirs and pressurized containers for automobile coolants) and also for bonding larger items (e.g., automobile bumpers) even when relatively soft thermoplastics are used.

A technique that utilizes the internal friction in a material is *ultrasonic welding* at a frequency of 20 – 60 kHz. The mechanical oscillation of a piezoelectric vibrator is introduced into one of the two components to be welded via a booster and a sonotrode. The components are mounted between the sonotrode and a stationary anvil. The sonotrode is shaped so that a standing mechanical wave is generated with its maximum amplitude at the contact surfaces of the two components. With appropriate shaping of the contact surfaces (energy directing), heating of the material by internal friction is rapid and concentrated in the contact area. Hence, short cycle times can be attained (0.2 – 1.5 s).

Many variations of this welding technique exist. The characteristic of near-field welding is the close proximity of the sonotrode contact surface and the welding surface (<6 mm). The method is employed to bond films and sheets of almost all thermoplastics. Only rigid polymers [such as styrene – acrylonitrile (SAN), ABS, PMMA, polyoxymethylene (POM), PC, and polystyrene (PS)] are suitable for distant

field welding, where the energy losses are not too great across the longer ultrasonic pathway between the sonotrode contact and the welding surface. The main area of application of distant field welding involves the bonding of moldings (sometimes made from different polymers). The major process parameters that must be adjusted to suit the specific material and geometry of the welding components include

1. Sonotrode shape
2. Contact pressure
3. Amplitude of oscillation and ultrasonic power
4. Irradiation and holding time

A related process involves embedding metal inserts in thermoplastics (e.g., screw thread sockets) by mounting the metallic component on the sonotrode and pressing it into the polymer under the influence of ultrasonic irradiation. Ultrasonic equipment is also employed for riveting; a shaped sonotrode is used to form the head on a thermoplastic rivet.

Ultrasonic welding is suitable for use in mass production bonding operations and gives highly reproducible weld seam quality. By appropriate design of the welding surface, weld seam bead can be concealed behind undercuts and hence need not be removed in a finishing stage.

In high-frequency welding a polar material is heated by the molecular dipole oscillations generated by the alternating electric field of a capacitor (frequency ca. 27 MHz). By suitable shaping of the capacitor electrodes, heating can be limited to the immediate vicinity of the welding surface. Cycle times are then short. Electrodes are also employed to apply the bonding force to the welding partners. Specially shaped electrodes can be used to emboss the weld seam or to generate a weld seam with a cutting edge.

Suitable materials are polymers with dielectric loss factors greater than 0.01 [e.g., cellulose acetate (CA), PA, PMMA, polyurethane (PUR), and PVC]. This technique is used mainly for large-area welding of sheet materials. Product examples include PVC rainwear and inflatable life rafts.

High-frequency welding can be automated and used in mass production.

2.1.5. Induction Welding

In induction welding, weld fillers that contain electrically conducting particles are heated by eddy currents induced in the particles by an alternating electromagnetic field (frequency range 3 – 10 MHz) (Fig. 11). The weld filler is a (profiled) preform placed in a groove situated in the bonding surface. Welding takes place in an induction field with the components held under slight pressure. The composition and conducting particle content of the filler must be selected to suit the substrate to be welded. The filler can also be applied to the substrate during the manufacturing process by using two-component injection molding (see → Plastics Processing, 1. Processing of Thermoplastics, Section 4.5). Because heating of the substrate takes place by conduction, cycle times are longer than with high-frequency or ultrasonic welding.

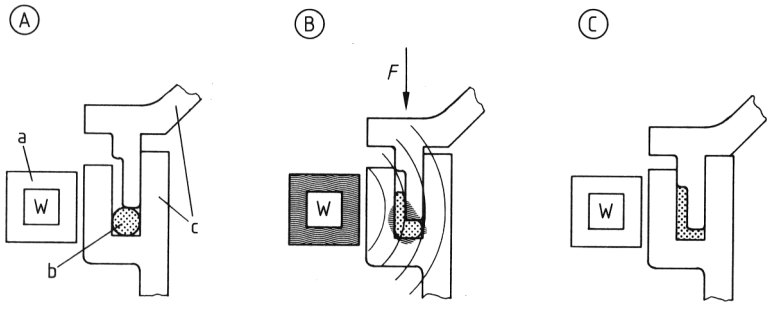


Figure 11. Induction welding
A) Before welding; B) During welding; C) After welding
a) Induction coil; b) Weld filler; c) Parts to be joined

The induction process is also used to open welded seams by placing the welded article in an induction field (e.g., opening containers for transporting corrosive materials).

2.2. Adhesion

In contrast to welding, all polymers can be bonded to themselves, each other, and other materials, such as wood, textiles, glass, and metals, by using adhesives [18–20], with the exception of solvent adhesion, which strictly speaking should be regarded as a welding process. During adhesion the substrates are not brought directly in contact with each other. In this case, a layer of similar or dissimilar polymer that can partially diffuse into the substrate surface is responsible for the bond. No or very little heat is necessary for adhesion, so that the structure and properties of the bonding substrates remain unchanged. In contrast to welding, adhesion can also be used for large-area bonding, a fact that is of considerable importance in the packaging industry. Adhesive bonds can be optically superior to welded bonds, which is important with transparent polymers. However, the manufacture of strong adhesive bonds often requires multistage processes and can take several days. The strength of polymer adhesive bonds can be nondestructively tested only to a very limited extent.

A wide range of adhesives with various adhesion and curing mechanisms are used for bonding plastics (see → Adhesives).

Some polymers can be softened by applying solvents and then fused together. Strictly speaking, this technique should be regarded as diffusion welding. Solvent-based adhesives that harden by evaporation of the solvents are also frequently employed. The solvents can also cause the surface of the bonding substrates to swell and hence can facilitate mutual diffusion of adhesive molecules and the molecules of the substrate. This is possible only with thermoplastics. Although adhesion with solvents or solvent-based adhesives is simple and economical, problems often arise with this process due to aging of the bond because the solvent cannot be removed completely from the joint after bonding.

Heat sealing and melt adhesives have also gained importance in bonding plastics. The highest adhesive bond strengths with polymers are generally obtained with chemically hardening one- or two-component adhesives. In most cases, single-component adhesives require heating for the curing reaction, whereas two-component systems also cure at room temperature.

Adhesion processes can now be extensively automated. Continuous adhesion process and short cycle times can be realized, particularly when heat sealing and melt adhesives are used.

Polymers can be classified by their adhesive bonding behavior as

1. Easily bondable polymers
2. Limitedly bondable polymers
3. Difficulty bondable polymers

The differences in bondability are due to variations in the solubility of the polymers and the polarity of the macromolecules (Table 5).

Further influences are the surface tension and hence wettability. Table 6 lists surface tensions for some polymers and adhesives. A prerequisite for adhesion is that the surface tension of the adhesive be lower than or equal to that of the polymer. Only when this applies does the binder adapt itself to the contours of the solid surface during the wetting stage so that the physical and chemical interfacial reactions required for good adhesion can occur. Only in solvent-based adhesives containing strongly

Table 5. Polarity and solubility of plastics

Plastic	Polarity	Solubility	Adhesive capacity
Polyethylene	nonpolar	very slightly soluble	poor
Polypropylene	nonpolar	slightly soluble	medium
Polytetrafluoroethylene	nonpolar	insoluble	very poor
Polyisobutylene	nonpolar	readily soluble	good
Polystyrene	nonpolar	soluble	good
Poly(vinyl chloride)	polar	soluble	good
Polyterephthalates	very polar		insoluble
medium			
Poly(methyl methacrylate)	polar	soluble	good
Polyamide 66 – 610	polar	slightly soluble	medium
Polyamide 6 – 11	polar	slightly soluble to insoluble	medium to poor

Table 6. Surface tension of plastics and adhesives

	Surface tension, 10^{-3} N/m
Plastics	
Polytetrafluoroethylene	18
Polyethylene	31
Polystyrene	33
Poly(vinyl chloride)	40
Polyester	43
Cellulose film	45
Polyamide 66	46
Adhesives	
Acid-curing phenolic resins	78
Urea – formaldehyde	71
Phenol – resorcinol resins	48
Casein resins	47
Epoxy resins	30 – 47
Poly(vinyl acetate) rubber	38
Nitrocellulose	26

dissolving components can the wetting criterion be neglected to a certain extent. If the surface tension of the plastic is lower than that of the adhesive, the surface must be mechanically prepared or, in the case of difficultly bondable polymers, chemically pretreated.

Easily bondable polymers are: poly(vinyl chloride) with low plasticizer content, polystyrene, polyacrylates, polycarbonates, and polyurethanes, as well as polyester, epoxy, and phenolic resins in unreinforced and reinforced state. Whereas polystyrene can be bonded most easily with solvent-based adhesives, the remaining members of the group can be bonded reliably by a variety of adhesives without pretreatment or after mechanical roughening. The surfaces of the bonding substrates should be cleaned with solvents or mechanically even when easily bondable polymers are involved, to remove contaminants and residual release agents.

The limited bonding polymers include PVC with high plasticizer content, which must be thoroughly cleaned with organic solvents prior to application of the adhesive. The pronounced shrinkage and swelling behavior of PVC can lead to difficulties in using solvent-based adhesives. Plasticized PVC can be bonded quickly and reliably by using solvents alone (e.g., tetrahydrofuran). Greater problems are encountered with adhesion to synthetic rubbers and polyamide. The latter can be diffusion bonded by using formic acid; otherwise, two-component adhesives are required, which however, give strong bonds only if the surface of the polyamide substrate has been mechanically roughened. Furthermore, the adhesion to polyamide is strongly dependent on the chemical structure of the polymer.

Difficult-to-bond polymers include all polyolefins, fluoropolymers, polyacetals, and silicone resins. These polymers cannot be bonded in the untreated state. Polyolefins can be chemically etched and treated electrostatically by using corona discharge equipment or treated with an oxidizing flame (see Section 3.5.1). Care must be taken that the basic structure of the plastic is not altered by surface pretreatment. The greatest difficulties are encountered in adhesive bonding fluoroethylene – propylene copolymers and polytetrafluoroethylene, which can be bonded with adhesives only after etching with sodium in liquid ammonia or sodium naphthalenide. Although both processes are complicated, they give bonds of high mechanical strength and good aging resistance.

Current developments in adhesives are concerned with improving bond strength, resistance and stability, and simplifying processibility. An example involves single-component reactive adhesives based on cyanoacrylates, which are ideally suited for bonding rubber and whose hardening takes only seconds or minutes. High manufacturing speeds can also be attained with heat sealing and melt adhesives, whose major advantage is their freedom from solvents. Melt adhesives based on polyamides, linear polyesters, or aromatic polysulfones exhibit good thermal stability and have processing times of a fraction of a second. Of the two-component reaction adhesives, flexible polyurethanes have a broad range of uses for bonding polymers, including construction bonding and the manufacture of laminates such as packaging materials, light core sheets, film-laminated sheet metals, and metal-coated polymers.

2.3. Mechanical Bonding

Mechanical bonding processes include the conventional methods of bolting and riveting. The bolts and rivets can be made of the same or different materials with respect to the bonding substrates [21, 22]. The use of self-tapping

screws avoids cutting threads in a previous process stage. Screw bonds that are loosened frequently and have a diameter of >4 mm should be equipped with a sunken or embedded metallic thread socket. Rivet bonds can be prepared by using the techniques employed in the metalworking industry. The rivet heads can be formed either by hot forming or cold pressing. Cycle times for riveting processes are short, and the mechanical strength of riveted bonds is satisfactory. Snap-in rivets are inserted in rivet holes and fixed to form a solid bond by spreading of the rivet shaft.

A particularly elegant bonding variation for polymers involves the so-called clamp or snap-in connectors in which protrusions or hooks become interlocked in correspondingly shaped undercuts when the two components are brought in contact. Bonds of this type can be rendered air- or watertight by use of gaskets or sealants. Mechanical bonds of this form can also be formed between polymers and other materials.

3. Surface Treatment

The surfaces of plastic components are treated to meet functional or decorative requirements that cannot be met by the base material alone [23, 24]. Surface treatment processes can be classified as follows:

1. Mechanical processes such as hot embossing and flocking
2. Painting and printing with solvent-based or chemically binding coatings
3. Wet chemical deposition processes such as electroplating or electroless metal deposition
4. Physical deposition of inorganic materials
5. Dry chemical processes such as fluorination, sulfonation, and plasma polymerization

3.1. Mechanical Processes

3.1.1. Hot Embossing

In hot embossing, a multilayer hot embossing sheet is applied to a substrate under pressure by a heated stamp. The term "embossing" is misleading in that it suggests the remolding of the substrate surface, which is not the case. Descriptions such as (color) film printing, (color) hot film printing, or dry printing are more apt, since, because of the way in which the (multilayer) decoration is applied, the initial surface topology remains unchanged, with the only exception being the gloss. Hot embossing can be used to coat the entire surface of an article (equivalent to painting), along with applying letters or a fine pattern of a different color to the substrate (e.g., scales and labeling on dials).

The hot stamp itself has the pattern to be embossed in relief on its surface (Fig. 12). The raised areas activate the hotmelt adhesive layer, which is located nearest the substrate during the stamping process; hence adhesion of the stamping laminate results in these areas. The deeper-cut areas of the stamp do not come in contact with the film, so no heat transfer and hence no activation of the adhesive occur, and the decorative and adhesive layers of the film are removed when the stamp is removed from the substrate.

A relief structure already present in the substrate surface can be highlighted by color by stamping with a flat stamp (relief stamping). With counterstamping, transparent materials are embossed on the reserve surface.

In the displacement stamping process, the stamp is generally planar or can be adapted to the slightly convex or concave shape of the article. In roll stamping, which is especially suited for large-area hot embossing and relief stamping, the stamp has the form of a roll that proceeds across the surface of the substrate with

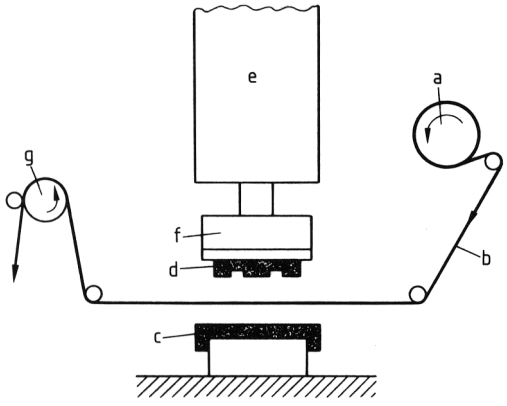


Figure 12. Hot embossing
a) Film roll; b) Film; c) Workpiece; d) Embossing stamp; e) Press; f) Heater; g) Feed roll

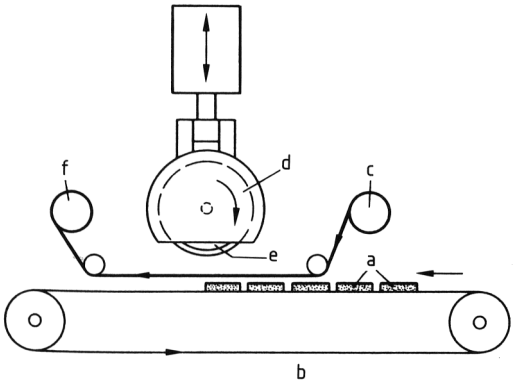


Figure 13. Roll stamping process
a) Workpieces; b) Conveyor belt; c) Roll of film; d) Heater; e) Embossing roll; f) Film windup

the stamping film positioned between them (Fig. 13).

As a rule, a thermoplastic substrate surface is necessary to obtain a satisfactory bond with the embossing film. The required thermoplastic surface can be produced on thermosets, metals, ceramics, or wood by applying paint coating. Embossing films are available in a multitude of decors, as mat or gloss films, in wood colors, single or multicolored, metallized (Fig. 14), etc.

3.1.2. Flocking

Flocking is used to produce a velvetlike surface. Colored fibers 0.3 – 0.5 mm in length are used, made from polyamide or viscose, for example. In mechanical flocking processes, which use vibration or compressed air, the flocks form an unoriented and nonuniform layer on the surface. For this reason, electrostatic processes, sometimes supplemented by mechanical techniques, are almost exclusively employed (Fig. 15). To ensure alignment in the electrostatic field, the

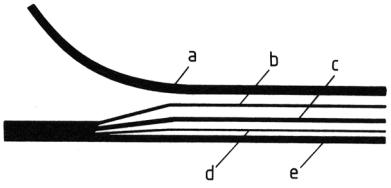


Figure 14. Construction of a metallized film
Layers c – e make up the embossing film.
a) Substrate sheet; b) Release film; c) Protective coating; d) Metallic layer; e) Adhesive layer

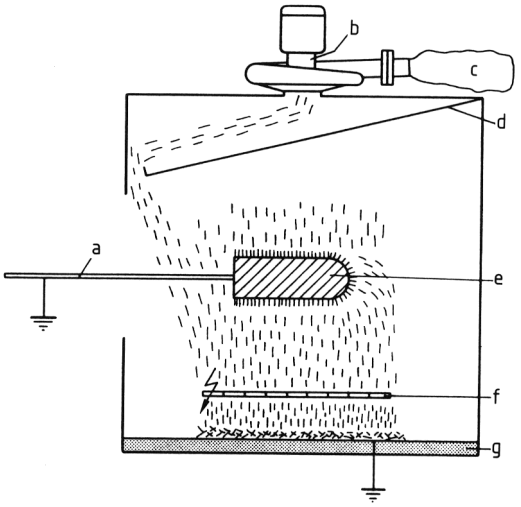


Figure 15. Electrostatic flocking
a) Rod; b) Extractor fan; c) Filter bag; d) Air-guiding plate; e) Molding; f) Electrode; g) Bottom tray

flocks are produced in a free-flowing, conducting form. Prior to flocking, the substrate surface is coated with an adhesive in which the flocks become permanently anchored. Sometimes, surface pretreatment is necessary (see Section 3.5.1). Equipment is available for flocking films, sheets, moldings, and hollow articles employed in the automobile industry, the packaging sector, toys, fashion jewelry, etc.

3.2. Painting and Printing

Whereas printing of plastic articles is carried out almost exclusively for decorative purposes, the reasons for painting polymers can be divided into three categories:

1. To meet functional requirements
2. For decorative purposes
3. As an intermediate step prior to further surface modification techniques, such as printing, film embossing, flocking, and metallizing

3.2.1. Painting

Previously, it was believed that, in contrast to metals, polymers did not have to be painted because they were not prone to corrosion.

However, this situation has changed considerably. Many plastic components can meet their respective specifications regarding optics, light, and weather resistance only when painted.

The thickness of the paint coatings varies between 5 and several hundred micrometers, depending on intended application.

When painting properties are considered, distinctions are drawn between thermosets and thermoplastics, between solvent-sensitive and solvent-resistant plastics, between solid and foamed polymers, and between foams with smooth and those with open-pored surfaces. The polymer and the coating must be matched with regard to their chemical compatibility, adhesion, and elasticity.

Surface State, Pretreatment. Critical demands are placed on the surface of the substrate to be painted and also on the design of the molding itself. The molding must be designed to suit the painting process (i.e., without sharp corners, edges, angles, or deep recesses and undercuts). Due to surface tension effects, paints recede from sharp edges (edge recession) and form a thin coating at these critical wear positions [26]. Undercuts and deep recesses are insufficiently coated in most spray painting processes. With larger planar areas, problems are caused by dust particles, especially with high-gloss coatings and metallization.

The surface to be coated must be clean (i.e., free from grease, dirt, sweat, and residual release agents, particularly those containing silicon). Contamination decreases adhesion and causes surface defects such as spots, dull or glossy areas, and flow disturbances. When necessary, cleaning procedures must be applied: cleaning with trichloroethylene vapor with compact thermosets, mixtures of organic solvents with degreasing and antistatic action, possibly supplemented by ultrasonic techniques or aqueous baths containing surfactants. Electrostatic charging, which causes wetting and flow problems and dust contamination, can be neutralized by blowing with ionized air.

With injection-molded articles, release agents and lubricants may concentrate in and around the weld lines and thus lead to surface defects in the coating. Stresses are often frozen into the molding due to poor selection of injection conditions and inappropriate choice of gate type or gate position [27]. In particular, in solvent-sensitive materials regions of increased internal tensile stress can lead to stress corrosion, deformation, and even loss of mechanical strength. Similarly, the type and amount of pigment in a polymer as well as choice of filler can influence results. Successful surface coating therefore requires knowledge of the type of polymer material, the process parameters for producing the molding, the quality of the coating material, and its processing conditions.

Besides these generally applicable aspects, several polymers require further specific measures prior to coating [26, 27]. Polyethylene, polypropylene, and epoxy resins are nonpolar and have very low surface tensions. To render them wettable and achieve satisfactory adhesion of a coating, they must be oxidized (see also Section 3.5.1) immediately before the coating is applied by

1. Low-pressure methods
2. Plasma treatment
3. Electrical methods at ambient pressure, such as corona treatment
4. Thermal processes with a strongly oxidizing flame (Kreidl – Traver process)
5. Immersion in chromic acid – sulfuric acid

However, antioxidants and stabilizers can reduce the effectiveness of such measures. With polypropylene and ethylene – propylene elastomers, the required paint adhesion can be attained by using special primers. Plasticized PVC and cellulose esters often contain plasticizers that can migrate into coatings and soften them. They must therefore be coated with paints that are resistant to migration of plasticizer.

Application Methods and Paint Systems. All nonelectrostatic coating methods (see → Plastics Processing, 1. Processing of Thermoplastics, Chapter 3) are in principle applicable for use with polymers: high-pressure spraying at 200 – 600 kPa with air atomization, high-pressure airless spraying at 10 – 20 MPa, dipping, flow coating, roller application, pouring, centrifugation, drum application, and brushing (see also → Paints and Coatings, 7. Paint Application, Chapter 3). Electrostatic spraying can be used with nonconducting polymers by coating them with a conducting solution [26, 28].

Apart from economic aspects, the form of the molding and the requirements placed on the surface, as well as the temperature and solvent sensitivity of various polymers, must be considered in selection of the coating method. Curing of the coating is generally accelerated by heating. Manufacturers' information on the heat resistance of the plastics is of limited value here. Heat resistance is determined on standard test specimens, whereas commercially manufactured moldings are seldomly produced under optimal conditions and have internal stresses and variations in wall thickness, and the coating and curing process often takes place under conditions of mechanical loading. This can cause deformation, losses in dimensional stability, and surface defects due to excessive penetration of solvents. Table 7 lists empirical heat resistances for fabricated plastic components. Bubble formation in the coating is possible at elevated temperature as a result of the evolution of formaldehyde from solid thermosets and from residual blowing agents in foamed thermosets.

Paint systems are selected according to the demands placed on the surface of the finished article and the coating characteristics of the substrate itself. These include physically drying paints (i.e., those that dry simply by evaporation of the solvent, e.g., nitrocellulose – resin lacquers and acrylic and vinyl paints); oxidative drying fatty-acid-containing resin paints; chemically drying multicomponent paints based on epoxy resins, polyurethanes, or unsaturated polyester resins; and resin stoving paints (see Section 3.2). For further information on various paint systems, see → Paints and Coatings, 1. Introduction.

Table 7. Empirical short-term heat resistance of fabricated plastic components

Plastic	Heat resistance, °C
Polystyrene – butadiene	50
Polystyrene	60
Poly(vinyl chloride)	60
Cellulose acetate and others	60
Styrene – acrylonitrile	70
Polyethylene	70
Acrylonitrile – butadiene – styrene	80
Poly(methyl methacrylate)	80
Poly(phenylene oxide)	110
Polyamide	110 – 120
Polypropylene	110
Polycarbonate	120
Polysulfone	150
Polyoxymethylene	150
Poly(ethylene terephthalate)	150
Polyurethane (foamed)	60
Urea – formaldehyde resin, melamine – formaldehyde resin	110
Phenol – formaldehyde resin	120 – 150
Unsaturated polyester	150

The solvent sensitivity of many thermoplastics must be taken into account in formulating the paint (Table 8). Generally, solvent sensitivity increases with increasing temperature in the painting and drying process, as well as with increasing contact with the paint (e.g., in dipping). In particular, involatile solvents can diffuse deeper into the substrate surface and thus cause changes in molecular structure that lead to surface roughness and loss of mechanical strength. Highly solvent-sensitive polymers (polystyrene, polystyrene – butadiene, polycarbonate) allow only a limited choice of paints [29].

Polyurethane integral foams, thermosets, and elastomers have a closed, smooth surface. Differences in flexibility and foam weight influence the surface integrity and hence the coating characteristics. Single-layer coatings with smooth surfaces can be achieved if the surface quality is high. The best results are obtained with two-pack polyurethane paints based on aliphatic isocyanates. Apart from self-releasing polyurethane foams, the choice of release agent and its subsequent removal are particularly important. Thermoplastic cast foams exhibit an open-pore surface, which gives good adhesion to coatings and is less sensitive to solvent effects than unfoamed plastics. Smooth surfaces can be obtained only by multilayer coating with intermediate polishing. For this reason, paints with structured surfaces are generally employed.

Areas of Application. A precise distinction between functional and decorative coatings cannot generally be made [26]. Varnishes and paints that absorb UV radiation prevent photochemical degradation of ABS, PC, POM, and poly(propylene oxide) (PPO), which would otherwise result in discoloration, spots, loss of gloss, and embrittlement. Coatings increase the resistance to many aggressive media such as solvents, water, chemical cleaning baths, atmospheric influences, adhesives, and plasticizers. Furthermore, by using

Table 8. Short-term resistance of plastics to solvents during painting*

Plastic	Alcohol and glycol ether	Esters	Ketones	Gasoline	Benzene	Chlorinated hydrocarbons
Polystyrene	+	–	–	+	–	–
Polystyrene – butadiene	+	–	–	+	–	–
Styrene – acrylonitrile	+	–	–	+	–	–
Acrylonitrile – butadiene – styrene	+	○	–	+	○	○
Poly(phenylene oxide)	+	○	–	+	○	–
Poly(methyl methacrylate)	–	○	○	+	+	+
Polycarbonate	+	–	–	+	○	–
Poly(vinyl chloride)	+	+	○	+	+	○
Cellulose acetate and others	+	○	○	+	+	+
Polyamide	+	+	+	+	+	+
Polysulfone	+	○	○	+	○	–
Polyoxymethylene	+	+	+	+	+	+
Polyethylene, polypropylene, epoxy resins	+	+	+	+	+	+
Poly(ethylene terephthalate)	+	+	+	+	+	+
Thermosets	+	+	+	+	+	+

* + resistant; ○ partially resistant; – nonresistant.

colored paints, direct coloration of the polymer, which requires expensive high-quality pigments, can be avoided. Matt metallic coatings are obtained by using aluminum or bronze paints, of either the leafing or the nonleafing type. In leafing products the metal flakes float on the surface, are lighter in color, and are contact sensitive, whereas in nonleafing products they remain embedded in the coating and exhibit greater scratch and corrosion resistance.

The fire resistance of plastics containing flame retardants can be improved further by application of flame-retarding paints.

Antistatic coatings prevent electrostatic charging and consequent collection of dust on nonconducting polymer surfaces. Conductive coatings filled with graphite or metal powders (copper, silver, or their alloys) are used as internal coatings (e.g., in television sets and computers). Nonconducting metallic paints, which are used primarily for decorative purposes, prevent creep currents in electronic equipment.

During the electroplating of polymers (see Section 3.3.2), cover coatings are used for partial chromium plating. The coatings protect the substrate from damage caused by chemical baths; no metal is deposited on the coatings themselves. A sharp interface with the metal-plated areas is, however, practically impossible to achieve. If this is required, the entire molding should be chromium plated, and selected areas should be lacquered (e.g., automobile radiator grills).

Abrasion-resistant coatings consisting of polysiloxane resin are used to protect plastic lenses and mechanically loaded polycarbonate components from scratching.

Molds for polyurethane components can be sprayed with mold-release paints instead of release agents so that a coated molding is formed in the mold (in-mold coating).

Paints also serve as a base layer and adhesion promoter for printing and film embossing with simultaneous coloration.

In the manufacture of consistently colored or mat surfaces, and also to cover faults such as joints, colorless, mat, or pigmented scratch-resistant paints are utilized. Thermoplastic foam castings and glass fiber reinforced plastic components are coated with strongly filling paints to achieve optically satisfactory surfaces.

Solvents and other volatile components released during drying pass into the exhaust air in gaseous form; the exhaust must therefore be treated to comply with emission limits. Because vast amounts of air are involved in paint drying, treatment equipment is large and expensive. A trend toward the use of fewer solvent-based paints in favor of waterborne systems is apparent, particularly in the automobile industry.

3.2.2. Printing

In principle, all printing techniques are applicable to polymers [23, 30, 31]. The most suitable process for a given task depends on the material thickness and the substrate form (film, sheet, molding). Prior to printing, the material may have to be pretreated (see Section 3.5.1). For several applications (e.g., wood grain printing), a primer layer is applied before the actual print layer, and a topcoat protects the print from damage. Because the substrate is generally hard and nonabsorbent, indirect or transfer printing techniques are used, which employ an elastic intermediate substrate, generally made of rubber (e.g., gravure printing with horizontal or vertical rolls). The printed pattern is transferred, via a rubber roll, from a deeply etched, ink-filled steel applicator roll to the planar printing substrate.

Films are generally printed by using rotary techniques (flexo or gravure printing). Sheets that are to be vacuum remolded are printed in an offset process. The distorted printed pattern is straightened during remolding.

The most common technique — silk screen printing — is used for both sheets and moldings. The tightly woven fabric (usually made of polyester or polyamide) is mounted tautly in a frame and partly coated with a UV-cured solvent-resistant layer [30]. The sieve is positioned close to the article to be printed, and the ink is pressed through the screen onto the substrate by using an elastic doctor blade. The tension in the sieve ensures its withdrawal from the surface once the process is complete.

Moldings with complex shapes can be printed by indirect silk screen printing with an intermediate rubber substrate. With the tampo-print technique, also an indirect printing method, a negatively etched printing block is automatically filled with ink and doctored by a steel blade. The ink remaining in the etched areas is then transferred to the substrate by a tampon. The highly flexible printing tampon made of silicone rubber can be manufactured in a variety of forms so that irregularities and curvatures in the surface of the article to be printed do not play a significant role. Even multicolor wet-in-wet printing is possible.

3.3. Wet Chemical Deposition Processes

Wet chemical processes are used to deposit metallic layers on polymers. Because polymers are generally electrical insulators, components that are to be electroplated must first be coated with a metallic, conducting layer in an electroless process.

3.3.1. Chemical Deposition

Chemical deposition processes are based on the techniques used to manufacture mirrors: The metal (in the case of mirrors, usually silver) is deposited from an aqueous salt solution by a chemical reducing agent such as formaldehyde, glyoxal, or hydrazine.

Similar methods have been developed for depositing copper and nickel on polymer surfaces [23, 32]; these are generally immersion processes. The clean, wettable polymer surface is first "activated" or "seeded" with silver or palladium. For example, to obtain silver nucleation sites, the surface is immersed in a solution of tin (II) chloride, rinsed, and dipped in a basic silver nitrate solution. For palladium seeding a palladium salt solution is employed, followed by a reducing agent. A comparable effect can be achieved by immersion in a solution of colloidal palladium. Nucleation with 0.1 – 1.0 mg/dm^2 of noble metal is a prerequisite for specific metal deposition by chemical metallizing techniques. The most common chemical metallizing baths currently employed contain the metal (Cu or Ni) as an aqueous solution of a complex salt along with the reducing agent (e.g., sodium hypophosphite or diethylaminoborane for nickel baths and formaldehyde for copper baths). The composition of the bath is adjusted so that metal deposition begins when the nucleated article is immersed and ceases when it has been removed. A coherent metal layer ca. 0.3 μm thick is deposited on the polymer typically within 10 min. This thin metallic layer can subsequently be thickened by electroplating.

With small production runs (e.g., jewelry), a spray process can also be employed for chemical metallization. A solution of a silver salt and a solution of a reducing agent are sprayed simultaneously onto an activated polymer surface by

using a two-component spray gun. The components react to form a continuous layer of silver.

3.3.2. Electroplating of Plastics

The thin metal layers deposited by electroless methods are extremely sensitive to abrasion and corrosion. When demands other than decoration arise, such as hardness, abrasion resistance, corrosion resistance, and electrical conductivity, the thin layers must be reinforced electrolytically [23, 32]. Total metallic behavior of the layer is reached only with layer thicknesses of ca. 20 μm. However, because the Young's modulus of metals is approximately two orders of magnitude greater than that of the polymer, and the coefficient of thermal expansion is approximately an order of magnitude lower, with thick metal deposits, forces occur at the interface that cannot be withstood by the adsorptive forces arising between polymer and metal as a result of even the smallest mechanical or thermal loading.

Although electrolytic reinforcement normally leads merely to sheathing of the molding with metal, it is suitable for making small spherical articles such as typewriter heads. The poor adhesion of the metal is in fact desirable for electroforming [33] (e.g., for the manufacture of press matrices or injection molds from plastic models). The range of applications of metallizing techniques with polymeric moldings is limited by the poor adhesion of the metal, which cannot be improved by mechanical treatment of the plastic surface.

The term polymer electroplating is currently used to describe a technique that differs from the methods discussed above in that metal adhesion approximately two orders of magnitude greater can be obtained. Development of this process began in 1965 when it first became possible to produce a strong bond between a metal and a specially treated ABS graft polymer [34, 35]. Within a few years, a fully developed technology resulted that was adapted to suit ABS polymers [32] and that is still used to electroplate polymer moldings on a mass production scale with automated equipment.

The special significance of ABS graft polymers is a result of their structure. They have a

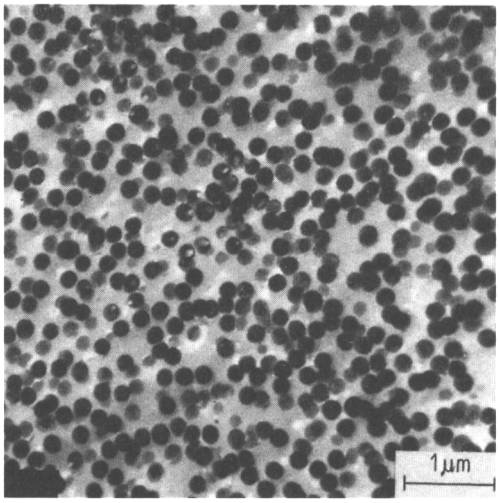


Figure 16. ABS graft polymer

styrene – acrylonitrile copolymer matrix in which fine spheres of an elastomer phase are dispersed (Fig. 16). This elastomer phase can be removed to a depth of ca. 1 μm by oxidation in a chromic acid – sulfuric acid etching bath [32, 36], without damaging the matrix material, in 5 – 10 min at 60 °C. A submicroscopic pore system with dimensions corresponding to the diameter of the elastomer particles is generated in the surface (Fig. 17).

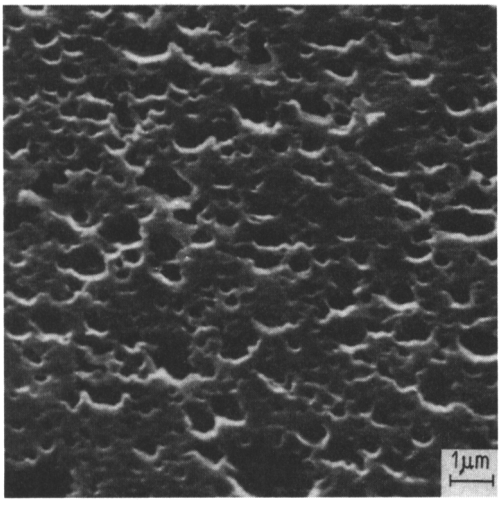


Figure 17. Surface of an ABS graft polymer after treatment in an etching bath

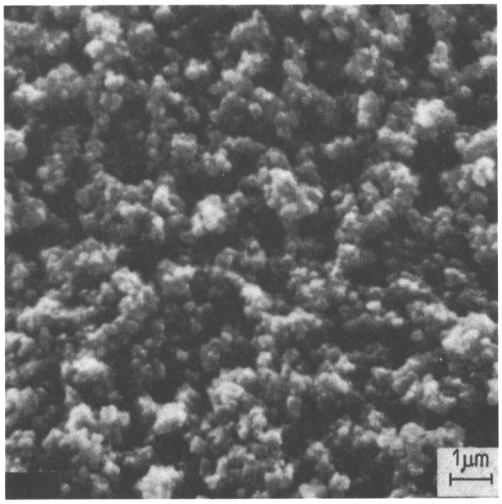


Figure 18. Underside of conducting metal layer (plastic removed by solvent)

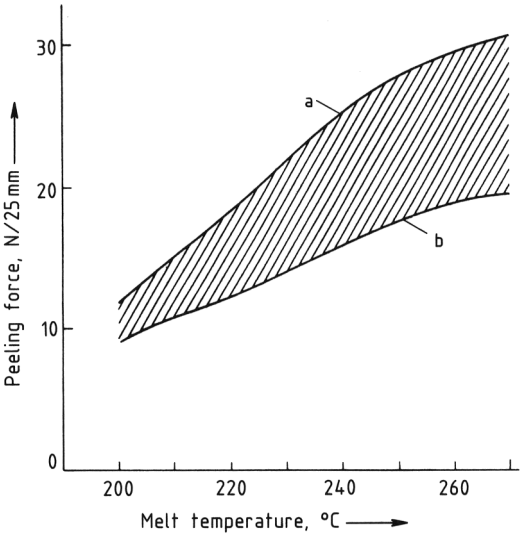


Figure 19. Peeling force as a function of melt temperature in injection molding for a plastic disk of 50 mm diameter and 2 mm thickness
a) Slow injection; b) Fast injection

After etching, the surface is activated, and nickel or copper can be deposited chemically (see Section 3.3.1). Initially the pores are filled, and subsequently a continuous, strongly anchored conductive metal layer is then formed that can be electrolytically reinforced, for example, with 20 µm of copper, 10 µm of nickel, or 0.2 – 0.8 µm of chromium by standard processes (see → Electrochemical and Chemical Deposition). The lower surface of the metal layer (Fig. 18) forms a positive replica of the pore system generated by etching. A polymer – metal composite is thus formed that is bonded so strongly that removal by force of the metal leads to cohesive fracture of the polymer in the vicinity of the metal layer. The adhesion of the metal layer is hence determined by the tensile strength of the outermost polymer layers [32, 37].

During the forming of thermoplastics by injection molding, orientation is frozen into the outermost layers, in particular, which can lead to a significant anisotropy in the mechanical properties. The processing conditions for injection molding (melt temperature, injection speed, mold temperature, wall thickness, position and design of the gate, etc.) often exert a decisive influence on the adhesion and the quality of electroplated moldings [32, 37]. Figure 19 shows the influence of melt temperature on peeling force (see below). Whereas with thick-walled, orientation-free (pressed) moldings, a peeeling force of >100 N per 25 mm can be reached, under less favorable processing conditions (high orientation) this value can fall below 10 N per 25 mm. Peeling forces >15 N per 25 mm are adequate to meet the majority of technical requirements.

Electroplated ABS is a composite material with a specific property profile [32, 37, 38]. The surface properties (gloss, hardness, abrasion resistance, corrosion resistance) are determined by the thickness and the structure of the metal layer.

Due to the reinforcing influence of the metal, the molding stiffness and strength increase proportionally to the ratio of the thickness of the metal to that of the polymer, up to approximately three to five times that of the unplated material. The creep behavior typical of polymers under loading is suppressed. The heat resistance of the plated molding is considerably superior to that of unplated materials.

The ABS electroplating process can also be applied to other polymers with only minor modifications. These include ABS blends with other polymers (e.g., PC) as well as polystyrene and poly(phenylene oxide) modified with butadiene rubber particles.

Polypropylene can be rendered electroplatable by using specific additives. In these PP products, the amorphous and crystalline regions

are attacked by the etching bath to various extents. This leads to extensive fissured roughening of the polymer surface, which gives good anchorage and adhesion of the metal layer [23].

Most polymers can now be electroplated by employing other etching or pretreatment techniques [23, 39].

Quality Test. For planar surfaces, the peel strength (DIN 53 494) is used as a measure of adhesion. The quality of moldings is evaluated by means of alternating temperature tests (DIN 53 496).

Applications. Electroplated ABS moldings are employed where their low manufacturing costs offer advantages over metal components, or where their advantages relative to unplated material due to increased hardness, stiffness, dimensional stability, and reduced weight are apparent [23]. Particularly in the automobile, radio broadcasting, audio, electronic, lining, writing instrument, and watchmaking industries, electroplated polymers find application as fittings, covers, handles, buttons, levers, keys, frames, and housings. Uses range from radiator grills to dials for wristwatches. The emphasis has shifted from decorative effects (e.g., for fashion articles such as buckles, buttons, fasteners, and chains) to functional components such as chassis, shields, waveguides, and switches in the electrical industry.

3.4. Physical Deposition Processes

Various techniques are employed to produce transparent (layer thickness <0.2 μm) or high-gloss (layer thickness >0.2 μm) metallic coatings and abrasion- or scratch-resistant ceramic protective coatings.

Atmospheric Pressure Techniques. Metal spraying permits the rapid buildup of a relatively thick layer.

Metal powder (powder process) or wire (wire process) is melted (e.g., in a plasma burner) and sprayed onto the polymer surface by a gas jet. Rough metal layers with pores are formed rapidly, which exhibit low adhesion to the base material. For more details on thermal spraying of metals, see → Metals, Surface Treatment, Chapter 5.

Vacuum Techniques. The deposition of metals in a high vacuum is of greater importance than atmospheric pressure methods. The metal is evaporated and condenses on the cold surface of the substrate in a vacuum chamber (10^{-2} – 10^{-3} Pa). It forms a dense film with high reflectivity. The following methods are used:

1. Thermal evaporation, whereby heat is generated by electrical heating, induction, or current flowing directly through the molten metal to be evaporated.
2. Electron beam evaporation, in which a high-energy electron beam is focused on the metal to be evaporated.
3. Cathodic sputtering in which a gas discharge (generally in an argon atmosphere) is ignited in the chamber: the chamber walls form the anode, while the metal is located on the bar or plate cathode. The energetic gas ions that bombard the metal surface dislodge particles, some of atomic dimensions, that deposit on the substrate surface. Magnetic fields are frequently employed to increase the efficiency of evaporation and reduce the thermal stress to which the substrate is exposed.

Thermal evaporation techniques do not permit deposition of alloys of defined composition because fractionation occurs as a result of differences in the boiling points of the alloy components. Deposition of alloys is possible by using electron beam evaporation and cathodic sputtering.

All evaporators operate with a directed jet of metal vapor so the vacuum chamber is not completely filled with an atmosphere of metal vapor, which explains why only the substrate surface that is in direct line with the evaporator is coated. For this reason, the molding surface should not be too rough and should have no undercuts.

Because of the time required to generate a high vacuum, substrates are introduced into the chamber in batches and attached to a turntable so that they can be coated successively.

The substrate surfaces are often activated prior to evaporation. A corona discharge is ignited in the chamber at ca. 10 Pa. The ions impinging on the substrate surface cause cleavage of chemical bonds near the surface and thus

a roughening of the surface and the formation of polar structures. In this way, nucleation sites are generated for the condensing metal, and good adhesion of the coating is attained.

Apart from aluminum, which is used in most cases because of the high reflectivity that can be attained, silver, gold, copper, chromium, zinc, nickel, cobalt, tin, titanium, and indium are employed, as well as several nonmetallic materials such as borosilicate glass and silicon monoxide.

The thin metal films are generally extremely sensitive to mechanical damage and are prone to rapid attack by moisture and environmental chemicals (exceptions include aluminum, which on exposure to air immediately forms a hard protective oxide layer, and the noble metals). Therefore, in most cases the metal layers are covered with a protective coating.

All polymers are suitable as substrates providing they do not evolve any materials that could lead to disturbances in the high vacuum (e.g., plasticizer from PVC or moisture from PA 6, PA 66, and cellulose hydrate). Such substrates must be precoated with a primer that hinders degassing.

The metallic deposit reproduces the finest structures and defects of the substrate, and adhesion is seldom adequate. Hence, for these reasons as well, use of a primer can be beneficial.

This primer layer must form a smooth, defect-free, high-gloss surface and exhibit excellent adhesion to the substrate. After drying — almost always at elevated temperature to drive out any residual solvents — no disturbing substances may be released into the vacuum. Furthermore, the primer coating should exhibit good adhesion to the metal film and should not be colored. It should be unaffected by the metal film and resistant to any solvents in the protective coating.

Similarly, the protective coating must exhibit excellent adhesion to the metal and must not have any detrimental effects on the substrate, the primer coat, or the metallic layer.

The primer and protective coatings are colorless or colored with translucent, soluble, lightfast dyes. They can be used to imitate other metals such as chromium, copper, gold, and brass. Highly homogeneous but less lightfast colors are obtained by immersing the colorless protective coatings in dye solutions.

Transparent polymers such as poly(methyl methacrylate) and polycarbonate (Fig. 20) can be first-surface or second-surface metallized. With second-surface metallizing, the primer coating is often unnecessary, and the protective coating is generally highly pigmented and opaque.

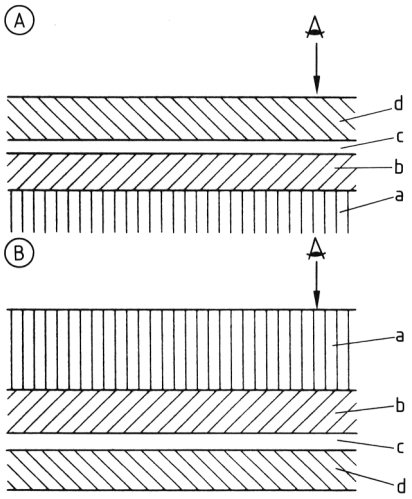


Figure 20. First-surface (A) and second-surface (B) metallization
a) Transparent substrate; b) Primer; c) Metal coating; d) Protective coating

Typical areas of application for polymer metallization include components for automobile interiors, taillight and headlight reflectors, sanitary fittings, signs, flashlight reflectors, lamp components, Christmas tree decorations, toys, fashion jewelry, caps for cosmetic bottles, frames for pictures and mirrors, and wristwatch dials.

3.5. Dry Reactive Processes

Dry reactive processes are employed to functionally modify the surface of a polymer or as a pretreatment for further coating processes.

Differences are drawn between:

1. Processes during which the substrate is itself chemically altered
2. Application of additional layers to the surface

3.5.1. Surface-Modifying Processes

Corona treatment is an electrical pretreatment process. The substrate is located at ambient pressure in a discharge field between two electrodes to which an a.c. voltage of 10 – 20 kV

with a frequency of 20 – 40 kHz is applied. This technique is used mostly to activate the surface of sheets and films by passing them between two roll electrodes with a gap of ca. 1 mm. The attainable surface energies are high despite the relatively short treatment times. The treatment times depend on the electrical performance of the equipment although this is limited by possible electrical breakdown of the substrate. Whereas regularly shaped hollow moldings are relatively amenable to corona treatment by placing them on appropriately formed counterelectrodes, the technique is difficult to apply to irregularly shaped articles. In such cases, counterelectrode-free techniques are used in which, by applying very high voltages, the charge carriers can be sprayed from wire bundles onto the plastic component.

With substrates containing low molecular mass additives (e.g., lubricants, plasticizers), a decrease in surface energy with storage time following treatment can be observed. This is caused by migration of the low molecular mass components.

The toxic substances, such as nitrogen oxides and ozone, generated in large amounts in the discharge field must be removed.

Fluorination is employed not only to activate polymer surfaces for successive coating processes (adhesive bonding, painting, printing, etc.) but also to permanently modify surface properties such as wettability and permeability [42, 44]. The substrate is exposed to a nitrogen atmosphere containing up to 10 % fluorine at slightly reduced pressures and at temperatures up to 110 °C. In *oxyfluorination* [45], oxygen is added to the gas mixture. Apart from the increased surface energy, fluorinated substrate surfaces are characterized by a pronounced diffusion barrier effect toward organic solvents, for example. For this reason, the technique is employed to treat the inner surface of plastic fuel tanks to reduce permeation of the fuel. With oxyfluorination, good barrier effects are achieved even after short treatment times (ca. 10 min). With fluorination, better barrier effects can be achieved but only after extended treatment times. As a process for activating the substrate surface, fluorination has an advantage over corona treatment because it gives higher surface energies. Furthermore, the activating effect remains longer with substrates containing low molecular mass components because the rate of diffusion of these components in the fluorinated substrate layers near the surface (1 – 2 μm) is also reduced. However, longer treatment times are required, and equipment for the continuous fluorination of sheets is more expensive than corona machines. Fluorination has proved relatively problem free for the surface activation of irregularly shaped components.

Because the gaseous fluorinated products that are formed (e.g., hydrogen fluoride) and fluorine gas are severe pollutants, measures to guarantee compliance with permitted workplace and exhaust gas concentrations are necessary (operation at slightly reduced pressure, exhaust gas cleaning).

Flame treatment of plastics is a surface activation process that is operated at atmospheric pressure. The substrate surface is briefly exposed to the flame from a gas burner (propane, butane, town gas, or natural gas) adjusted to give strongly oxidizing conditions (excess oxygen). The substrate is oxidized at the surface, and the polar groups that are formed lead to improved wettability. Significant process parameters include the gas – air ratio, flame temperature, and duration of treatment, all of which must be adjusted so that the substrate is not heated too strongly and the surface is not visibly altered. The process is applicable to films, sheets, and moldings with large smooth surfaces. Flame treatment is employed primarily with polyolefins (e.g., PP automobile bumper linings). Because the activating effect is lost rapidly, flame-treated articles should be coated immediately after treatment.

Plasma treatment of plastics is also a surface activation process. It is carried out in vacuum chambers at 10 – 100 Pa with a nonthermal plasma (gas discharge) in a gas atmosphere consisting of an inert gas or reactive gases (e. g., oxygen). In the plasma, gas atoms and molecules are ionized and accelerated toward the substrate surface, which they impact with high energy, causing cleavage of chemical bonds and formation of polar groups. In *glow discharge* processes the plasma is fed with a d.c. or an a.c. voltage field (frequency range 50 Hz

up to several tens of megahertz). The plasma burns between two electrodes located in the chamber (resistive coupling), whereby one of the electrodes can be an electrically conducting substrate. For treating sheets and films, the separation between electrodes at 200 – 400 V is considerably larger than with corona treatment and amounts to several tens of centimeters. When a glow discharge is used as a pretreatment (e.g., for metallizing) for moldings, the separation between the electrodes can be considerably larger and voltages up to 5 kV are applied.

When energy is introduced into the plasma by using *microwaves* (gigahertz range), significantly shorter treatment times (<1 s) are possible due to the increased charge density in the plasma.

These pretreatment techniques are used, for example, in the physical metallization or coating of films and moldings (automobile bumper covers [46]), and also in the treatment of carbon, aramid, and high-strength PE fibers to improve fiber-to-matrix adhesion when they are employed in fiber – polymer composites [47, 48].

Because plasma techniques require considerable expenditures for equipment due to the low pressures required, they are usually applied only when a subsequent vacuum coating process is intended.

3.5.2. Coating Processes

Gasplating is normally carried out at atmospheric or slightly elevated pressure. It is used in metallizing, where volatile metal compounds (e.g., nickel tetracarbonyl) are employed, which decompose on the preheated substrate surface and form a pore-free, homogeneous metal film.

Plasma polymerization is a vacuum coating process that is suitable for metallic substrates and also for thermally sensitive polymers due to the low thermal loading of the substrate [47, 49–56]. Monomer gases (e.g., ethylene, vinyl chloride, hexamethyldisiloxane) are vented into the vacuum chamber containing the substrate at 1 – 1000 Pa. A nonthermal plasma is ignited in which the monomer gas is activated. The plasma can be fed by an electrical d.c. or a.c. voltage field with frequencies of 50 Hz to several megahertz between two electrodes located within the chamber (resistive coupling) or outside it (capacitive coupling — not applicable to d.c. plasmas). Energy input using microwaves (generally 2.45 GHz) gives the highest attainable coating rate due to the high charge carrier density in the plasma. A distinction is made between processes in which the plasma burns directly on the surface to be coated and those in which it is remote from the surface (so-called downstream processes). In the latter, the monomers and (optional) propellant gas particles that are activated in the plasma (plasma reactor) must flow through a plasma-free zone to the substrate surface, whereby the first recombination reactions occur in the gas phase. Indirect ionization is employed with particularly sensitive monomers. Here, a propellant gas (e. g., a noble gas) is activated in the plasma, and the monomer gas is activated by ionized propellant ejected from the plasma. This prevents fragmentation of the monomer by direct contact with the plasma.

The activated particles and recombined intermediate products meet at the substrate surface and, in the course of further chemical reactions, form layers of highly cross-linked polymer. Low molecular mass, gaseous products that are not incorporated in the layers are removed by the vacuum pump. Apart from the composition of the feed gas, which can contain other inert or reactive gases in addition to the monomers, process parameters that influence the rate of deposition and the properties of the layer include reactor geometry, separation between plasma and substrate in downstream processes, substrate material and temperature, flow of feed gas, process pressure, excitation energy, excitation frequency, and coating time.

Because of the high degree of cross-linking, plasma-polymerized layers exhibit high density, mechanical stability, and chemical resistance. They also have electrical breakdown voltages and good heat resistance. Furthermore, even at very low thicknesses (10 nm) they are free of micropores, so that they are ideally suited as diffusion barrier layers. Due to the high energy of the particles formed during the process, the layers generally adhere well to the substrate.

As in metallizing in high vacuum, the properties of the layer can be varied across its thickness by varying the operating parameters or the composition of the process gas during coating.

The process is used in the coating of reflectors for headlights [46, 57]. These are mounted in charges on a rotating carousel in a high vacuum, where they are pretreated (glow discharge), coated with aluminum, and subsequently coated with a protective layer 20 – 30 nm thick by plasma polymerization with a process gas containing hexamethyldisiloxane and oxygen. Because of their extremely low thickness, the protective layers have no optical influence but are effective diffusion barriers (condensed water resistance is 1000 times greater than without the coating) and also have a high surface energy so that condensing materials (moisture or degassed products from other headlight components) spread across the surface to form thin films and hence have no optical effects. Other applications include the hydrophilic coating of contact lenses and the coating of medical materials to improve biocompatibility [58].

On a laboratory scale, a variety of layer properties are currently being investigated. For instance, with ethylene as a monomer, it has been possible to apply a layer to the inside of PE screw top bottles (1.2 L) that reduces the permeation of gasoline to < 2 % of that of uncoated bottles [59, 60]. The highly crosslinked polyethylene layer was coated onto the substrate within 40 s by using a microwave plasma; it had a high density (>1.5 kg/dm^3) and a thickness of 100 –200 nm. Because the coating also exhibits excellent adhesion and does not suffer appreciable loss of barrier properties even after severe deformation (drop test), it represents a viable alternative to fluorination in the manufacture of plastic fuel tanks.

An advantage of plasma polymerization is that a very high proportion of the monomers employed is incorporated into the film, and only small amounts are present in the evacuated residual gases. The material costs of the process are thus very low. Additionally, environmentally harmless materials are used in many cases so that the exhaust gases need not be cleaned. Because vacuum processes are involved, however, considerable equipment expenditure is necessary. Especially with microwave plasma polymerization, the process cycle time is influenced primarily by the capacity of the vacuum pumps (evacuation time), whereas the actual coating time is low (generally <1 min). For this reason, chambers for rough evacuation of the components to be coated through which the substrate passes to and from the actual process chamber, are useful.

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Plastics, Properties and Testing

ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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1. States of Order of Polymers

The state of order in plastics is, despite some peculiarities, very similar to that of low molecular mass compounds. Amorphous, crystalline, and liquid crystalline phases are observed, which exhibit short- and long-range order in one, two, or three dimensions. Therefore, the *characterization techniques* used to determine the state of order are also very similar. The most common techniques are summarized in Table 1, which also lists the typical dimensions and the principal information that can be obtained. One generally distinguishes among the following typical scales for the state of order:

1. The submolecular scale (typically 0.1 – 10 nm) where the state of order of chain segments and monomer units is considered

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Table 1. Most common techniques for the determination of order in polymers

Technique	Information	Typical dimensions
Wide-angle X-ray scattering (WAXS)	crystallinity, orientation, crystal structure, near range order	0.1 – 1 nm
Small-angle X-ray scattering (SAXS)	morphology, long spacing, density fluctuations	1 – 100 nm
Small-angle neutron scattering (SANS)	chain conformation	1 – 100 nm
Electron microscopy (EM)	morphology,	
Electron diffraction (ED)	long spacing,	10 – 1000 nm
Electron energy loss spectroscopy (EELS)	crystal structure, element distribution	
Light scattering (LS)	larger structures,	
Microscopy	different phases,	1000 nm – 1 mm
Birefringence	orientation	

2. The molecular scale (typically 5 – 20 nm) where the spatial arrangement of one chain is investigated
3. The morphological scale (10 nm to several micrometers) where the superstructure formed by many polymer molecules is envisaged

The crystal structure, crystallinity, and orientation of polymers are determined by X-ray methods [1], whereas the crystal morphology or phase structure is obtained from electron microscopy [2] and light scattering [3]. The use of neutron scattering [4] offers the unique possibility of "seeing" the spatial arrangement or conformation of single molecules in the bulk by selective deuteration (Fig. 1).

The two *principal states of order* in polymers are the amorphous and the semicrystalline states. A peculiarity of polymers is that, in general, amorphous regions are also present in the crystalline state and the crystallinity can be varied over a wide range by means of the crystallization and annealing conditions. It is evident from Figure 1 that mechanical properties, such as the elasticity and the toughness of plastics, are determined largely by the connectivity and entanglement of the molecules. In particular, in the crystalline state the crystallites are interconnected by tie molecules, giving the material its mechanical strength. Hence the physical properties of polymers are determined not only by their chemical nature and composition but also by the state of order—the chain conformation, morphology, phase structure, and orientation of molecules. Therefore, the control and determination of the state of order are important areas of polymer science. They can determine the final use of products and also offer possibilities for modification and new areas of application. Examples include the stress-induced crystallization of rubber, which is undesirable because it makes the material brittle and unelastic, and the production of ultra-high-modulus polyethylene fibers by extreme orientation from a gel state to obtain a material that can be much tougher than steel in terms of the specific modulus.

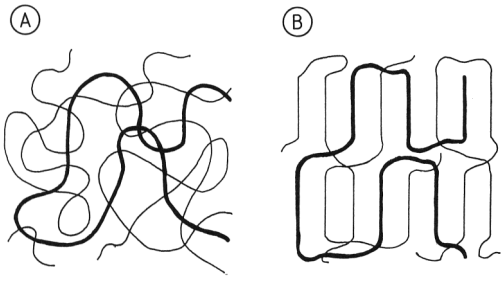


Figure 1. Schematic of chain conformations in the (A) amorphous and (B) semicrystalline state
A single chain is marked by the solid line and may represent a labeled (deuterated) chain among otherwise unlabeled molecules. In the amorphous state (melt or glass), molecules adopt a Gaussian coil conformation, whereas in the semicrystalline state, both amorphous and crystalline regions are present. During rapid crystallization from the melt, the overall chain conformation does not change significantly and chain segments are incorporated into crystalline lamellae.

Special morphologies and superstructures are observed in polymer blends and block copolymers, while the state of order of liquid crystalline polymers is between that of the crystalline and the amorphous materials.

1.1. Glassy State and Melt

Polymers in the glassy state and in the isotropic melt generally have a low degree of order: they are *amorphous.* Only short-range order is present, similar to that observed in simple liquids. Because polymers are large molecules, a distinction can be made between the intra- and

intermolecular order of monomer units. Very stiff macromolecules have a high orientation correlation along the chain, while the center-of-mass positions of molecules with respect to one another are distributed statistically in space (i.e., a large intramolecular and no intermolecular order). However, in many cases, stiff molecules tend to form liquid crystalline phases (see Section 1.3).

Polymer Melt. Flexible chains form a Gaussian coil-like conformation [5], [6] with little intramolecular order. The *random-coil conformation* of the melt (Fig. 1 A) is also observed in dilute solution under theta conditions. In the ideal situation, no effective interaction occurs between a chain and its surroundings. The center-of-mass positions of the molecules are random, and the long-range order observed in the crystalline state is completely absent. This picture can be tested by small-angle neutron scattering in the melt [7], in which the radius of gyration R_g – a measure of the mean dimension of the chain and the chain conformation — can be obtained. Contrast for neutrons is generated by the deuteration of one chain in a matrix of otherwise undeuterated chains (Fig. 1). The deuterated chains are then "visible" against the others for neutrons. The assumption is that deuteration does not change the thermodynamics, and particularly the chain conformation, which to a good approximation is true in most cases [8], [9]. Investigations indicate that the chain conformation in the melt and under theta conditions is identical and, in many cases, can be described by an unperturbed coil. In the random-coil model with a random distribution of chain segments, the radius of gyration R_g should be proportional to the square root of the molecular mass M_w ($R_g = \alpha M_w^{0.5}$) [22], which to a good approximation is true for many polymers (Table 2).

The pair correlation function $h(r)$ of monomer units, irrespective of their connectivity to different chains, is a measure of the *near range order* of the monomer units (Fig. 2 A) [23]. In starting from one monomer unit in the melt, at a certain distance r_0 a peak in $h(r)$ is observed, corresponding to other monomer units at the nearest neighbor position, which form a first shell around the reference monomer. At larger distances, no spatial correlations exist and $h(r)$ becomes constant. It goes to zero at $r = 0$ since a double occupancy is excluded.

Table 2. Molecular dimensions of some polymers in different states of order as determined by small-angle neutron scattering

Polymer	$\alpha = R_g/M_w^{0.5}$, nm $g^{-0.5}$	Reference
Melt		
Polyethylene	0.045	[7]
Polystyrene, atactic	0.028	[10]
Polybutadiene	0.035	[11]
Poly(ethylene oxide)	0.042	[12]
Polypropylene, isotactic	0.035	[13]
Glass		
Poly(methyl methacrylate), atactic	0.027	[14–16]
Polystyrene, atactic	0.028	[17]
Poly(vinyl chloride)	0.040	[18]
Poly(ethylene terephthalate)	0.039	[19]
Semicrystalline state		
Polyethylene	0.045	[20]
Polypropylene, isotactic	0.034 – 0.038	[13]
Polystyrene, isotactic	0.024 – 0.029	[21]
Poly(ethylene oxide)	0.052	[12]

Because of interactions of various kinds this simple picture must be modified. Even in the case of largely noninteracting particles such as in a melt of *n*-alkanes or polyethylene indications can be found of additional near range order effects because of steric reasons [24], [25]. There is a slight tendency for neighboring *trans* sequences to align themselves parallel to one another giving rise to a small intermolecular interaction which can be observed by magnetic birefringence or depolarized light scattering [24]. These interactions do not, however, influence the conformations of the chains significantly as can be seen from small-angle neutron scattering, which is consistent with the unperturbed-coil picture of the single chains. Scattering data of isotactic, syndiotactic, and atactic poly(methyl methacrylate) [16], [26–28] and polycarbonate [29] over a wide angular range have been compared with model calculations [30], [31] based on the rotational isomeric state model [22] in which the rotational configurations (isomers) are taken into account with their proper statistical weight. The agreement is very good in those regimes where first at small angles the overall chain conformation and second at intermediate angles the segmental configuration dominate the scattering. The unperturbed-coil model thus seems to be a good approximation for the spatial arrangement of flexible polymer molecules in the amorphous state.

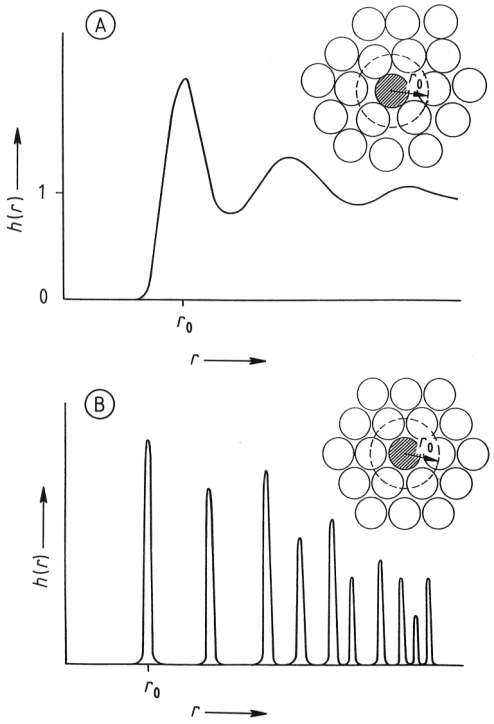


Figure 2. Distribution of monomer units $h(r)$ as a function of distance r in the (A) amorphous and (B) crystalline state for a simplified model in which monomer units are replaced by spheres
Connecting bonds to neighboring monomer units are not shown. The distance distribution $h(r)$ between centers of the spheres is continuous in the amorphous state and discrete in the crystalline state. Figure 2 A exhibits only a short-range, and Figure 2 B a long-range, positional order. The first coordination shell of radius r_0 is also indicated in the insert (dashed line).

Glassy State. The glassy state is of great importance for practical applications of plastics. Many atactic polymers do not crystallize when they are cooled down from the melt but form an amorphous glassy state. This can be described as a frozen melt in which the mobility of the chains is frozen in and the state of order of the melt at the glass transition temperature T_g is retained. The detailed nature of this transition is still not clear, but various aspects have been investigated and analyzed [32]. Many properties, such as mechanical modulus, dielectric constant, and specific heat, change at T_g (Fig. 3). A change in slope occurs at T_g for both volume V and enthalpy H, whereas a jump is observed for the specific heat c_p and the coefficient of thermal expansion α. The smooth transition in V and H and the jump in the second derivatives c_p and α suggests a second-order phase transition, which, however, cannot be demonstrated rigorously.

The glass transition temperature depends on the rate of cooling or heating, the frequency of the measuring technique (e.g., in dielectric or dynamic mechanical investigations), and the annealing conditions [32], [33]. The glassy state is thus not an equilibrium state. Since an equilibrium thermodynamic description of the glassy state [34] is questionable [35], a non-equilibrium free-volume theory [36] is mostly used, which assumes that the volume of the melt consists of the van der Waals volume of the molecules V_0 and an additional free volume V_f. For the movement of chains in the melt a certain number of voids or empty sites are required and

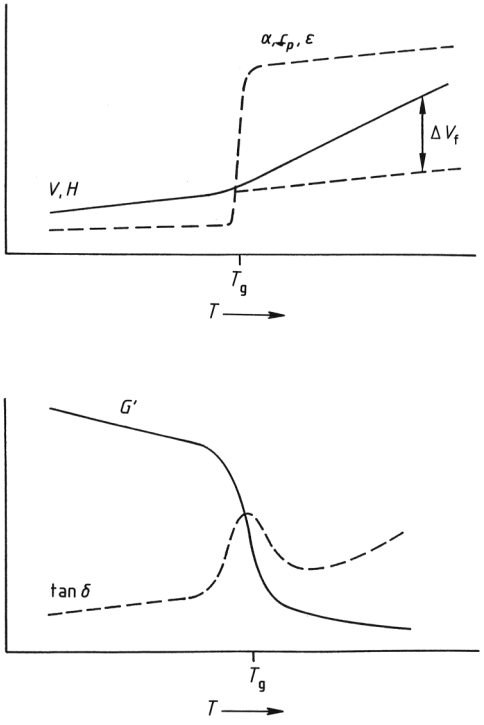


Figure 3. Schematic of the change of various properties of plastics at the glass transition temperature T_g: volume V, enthalpy H, linear coefficient of thermal expansion α, specific heat c_p, dielectric constant ε, shear modulus G', and mechanical loss factor tan δ
Also indicated in the upper figure is the increase of free volume ΔV_f with temperature according to the free-volume theory of the glass transition.

are taken into account by the free volume. The free volume of the melt decreases with decreasing temperature (Fig. 3) and is frozen in at T_g. At T_g the free volume is estimated to be 2.5 % of the total volume.

The empirical Williams – Landel – Ferry (WLF) approach [37] can be used to calculate the time – frequency – temperature behavior of the viscosity, diffusion constant, dielectric or mechanical relaxation, etc., and is an expression of the dynamic nature of the glassy state. Glass transition temperatures can be estimated from the chemical structure [38]. A list of the glass transition temperatures of many polymers is found in [39].

Blends; Polymer Orientation. In *blends* of glassy materials a single glass transition is observed when miscibility on a molecular level is achieved [40]. For blends of immiscible plastics the glass transition temperatures of the pure components are measured, which indicate phase segregation on the microscopic level. The addition of a low molecular mass component to plastics may lower T_g (plasticizer effect) [32], but can also cause crystallization or phase separation.

The order in amorphous polymers can be increased by *orientation* of the molecules, which is achieved, for instance, by mechanical deformation [41]. With some materials, stress-induced crystallization is observed (e.g., rubber) [42], which strongly affects mechanical properties. Similarly, on annealing above T_g some plastics [e.g., poly(vinyl chloride), polycarbonate, poly-(ethylene terephthalate] undergo partial crystallization [32]. In most crystalline plastics a large portion of the material is amorphous, and crystalline lamellae are formed between the amorphous regions.

1.2. Crystalline State

Some plastics can crystallize and form a crystalline state that depends largely on sample history and preparation. Only polymers with well-defined tacticity can crystallize, whereas atactic materials are generally amorphous. In contrast to low molecular mass materials, plastics form only a *semicrystalline state*, and generally both crystalline and amorphous regions are present in the polymeric crystalline state (Fig. 1 B). In the crystalline regions a long-range spatial order is present (Fig. 2), and monomer units occupy well-defined locations within the crystal. Crystal structures of polymers have been determined by X-ray and electron diffraction and are known for most crystalline polymers [39], [43]. The structural parameters depend, however, on sample treatment, and a different crystalline order may result from heating, quenching, annealing, orientation, or the application of pressure. The degree of crystallinity and the morphology (i.e., the superstructure of the crystallites) also depend on sample treatment.

Melt-Crystallized Material. During *crystallization from the melt* a lamellar morphology (Fig. 4) develops in which amorphous regions and crystalline lamellae form alternating layers with a well-defined periodicity L, typically in the range 5 – 30 nm. L is thus significantly smaller than the contour length (total length of the chain along its contour) of a polymer chain, and the molecules fold several times within the lamellar morphology (Fig. 1 B). The detailed chain conformation has long been under discussion [44], and various regular and statistical folding models have been introduced. This question has been investigated [4] in small-angle neutron scattering (SANS) experiments. One of the striking results from melt-quenched polyethylene is that the radius of gyration R_g does not change during crystallization (see Table 2), and the chain conformations in melt

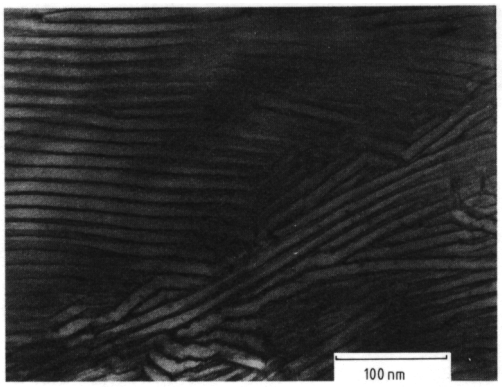


Figure 4. Transmission electron micrograph of polyethylene crystallized from the melt [2]
A thin cut of material has been stained to achieve a contrast between amorphous and crystalline regions. A side view through the crystalline lamellae is shown.

and quenched crystal are quite similar [7], [20]. Due to entanglements of the chains in the melt, long-range diffusion of segments is not possible, and only segments of the chain straighten during crystallization [45]. The overall chain conformation remains, however, essentially constant. The statistical folding model of FLORY [22], [46] for melt-crystallized polymers has been modified to include the true density of chains in the amorphous regions [47] and tie molecules between lamellae [48].

Solution-Crystallized Material. In polyethylene samples crystallized from solution a much more regular folding structure and regular morphology is observed (Fig. 5) [44]. Conformational models include "stacked-sheet" [45] or "superfolding" [49] structures in which crystalline stems of one molecule fold into stacks of an ordered arrangement along the (110) crystallographic direction, which is the main crystallization plane during crystallization from solution. Allowing the molecules during crystallization more time for rearrangement with respect to typical segmental relaxation times results generally in more regular chain folding structures; however, few experiments are performed on slowly crystallized or annealed samples [50]. Good agreement is obtained between SANS and IR experiments [51], which are both sensitive to chain conformation.

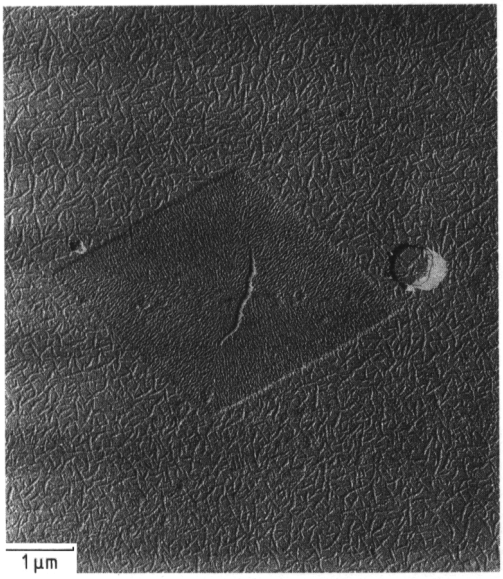


Figure 5. Surface replica [54] of a polyethylene single crystal crystallized from dilute solution
A top view of a crystal lamella is shown. As a result of decoration with low molecular mass polyethylene (evaporation of PE and epitaxial growth on the surface), four quadrants and pleating due to pyramidal shape can be seen.

Degree of Crystallinity and Morphology. The *degree of crystallinity* depends on the material and on sample preparation. For rapidly melt-quenched materials it is near zero, and for some highly tactic or symmetric materials it can reach values of ca. 90 %. Crystallinities of polyethylene and polytetrafluoroethylene for instance may be 80 – 90 %, of highly isotactic polystyrene and isotactic polypropylene 60 – 70 %, and for most other semicrystalline polymers < 50 %.

The crystallinity is determined by X-ray diffraction, whereby the intensity of the amorphous halo is compared to the Bragg peak intensity [52]. The unstructured broad amorphous halo reflects the near range order in the amorphous regions (Fig. 2 A), while the crystalline long-range order gives rise to sharp Bragg peaks. To transform this ratio into absolute values a fully amorphous and fully crystalline sample must be investigated or other techniques (e.g., density measurements) have to be used for comparison. Depending on preparation conditions, different crystalline structures may be observed [43], [52]. Isotactic polypropylene for instance exhibits monoclinic, pseudohexagonal, and triclinic modifications [53].

The *morphology* of crystalline materials is determined by optical or electron microscopy [2], [52]. Whereas single crystals are observed in solution-crystallized material (Fig. 5), various morphologies occur in melt-crystallized materials. Crystalline lamellae (Fig. 4) may be arranged in spherulitic, dendritic, or other supramolecular structures [55]. Specific morphologies (e.g., fibrillar and "shish-kebab" structures) are observed in stretched plastic materials [56–58].

1.3. Liquid Crystals

Plastics can also form liquid crystalline ordered phases in which, like in low molecular mass compounds, smectic, nematic, and cholesteric

phases are formed, depending on the composition and temperature [59], [60]. The state of order is between crystals and amorphous materials. In a nematic phase, for example, the center-of-mass position of the rigid mesogenic groups is random (like in an amorphous liquid), whereas mesogenic groups are preferentially oriented in one direction (as in a crystal). Long-range orientational order is present, but only short-range positional order.

Depending on the location of the mesogenic groups, liquid crystalline polymers are classified as side- chain and main- chain polymers (Fig. 6). A potential advantage of polymeric liquid crystals over the corresponding low molecular mass compounds is the possibility of freezing the ordered state by quenching the polymer below its crystallization or glass transition temperature. A major area of application is thus the production of ordered, high-modulus fibers from liquid crystalline phases [61].

Many main-chain liquid crystalline polymers are believed to be rigid, but they become more difficult to process with increasing rigidity. Various methods have been discussed [60], [62] for making them soluble and processible, including the grafting of flexible side chains (Fig. 6 C) or the introduction of flexible spacers between the mesogenic groups (Fig. 6 B). A potential application is the blending of rigid chains with flexible ones to form reinforced plastics on a molecular level (molecular composites) [63]. The field of liquid crystalline polymers is still growing, and quite different developments and applications may be envisaged.

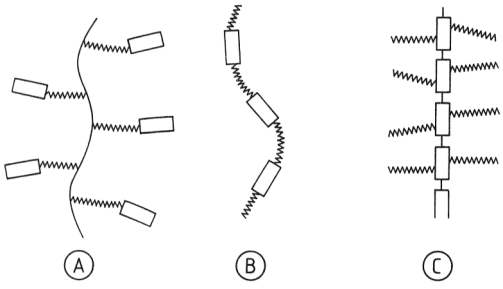


Figure 6. Different types of liquid crystalline polymers
Rigid mesogenic groups (▭), separated by flexible spacers (wiggly line), are incorporated into the side chain (A) and the main chain (B). For better processibility, flexible groups may be attached to a rigid backbone (C).

1.4. Blends and Block Copolymers

Phase-separated structures are observed in blends and block copolymers in which the components are incompatible [64], [65]. The components are mostly amorphous but can also be crystalline. Observed morphologies can be very regular if, for instance, butadiene – styrene diblock copolymers with narrow molecular mass distributions are used. Depending on the molecular composition, cylindrical or lamellar ordered structures are formed [66]. In some cases [67], ordered crystalline (hexagonal) arrangements of phase-separated domains with macroscopic dimensions are observed. Within the domains, polymers may be amorphous or crystalline, while the superstructure of the domains forms a lattice.

The state of order of blends and block copolymers is very important for their applications since many plastics are blended to improve their properties. The structures can be quite complex, and the compatibility effect of additives acting at the interface between phases is not always easy to understand [68].

2. Properties and Testing

The term high polymers or plastics refers to compounds whose molecules contain more than 1000 – 1500 atoms. These substances display a number of special properties that are unknown in low molecular mass compounds. Such features occur in nearly all realms of physical and engineering properties, as described below.

Typically, the properties of plastics depend strongly on the structure and morphology, which result from the manufacturing process, as well as on loading parameters.

Over the course of plastics development, this specific behavior has dictated the methods used to investigate their properties. Plastics testing today is therefore an independent branch of engineering. Its procedures are discussed in parallel with the description of properties.

The standardization of testing methods (ISO, DIN, and other national standards) is also important for plastic materials. Standardization of plastics types based on their profile of properties is no longer customary except for a few groups of thermosets.

For thermoplastics a classification and nomenclature system has been developed that is consistent for ISO, DIN, and several other standards. For compatibility with modern data bank systems, as well as rationalization, a selection has been made from the large number of test methods available, and the profile of properties has been published as a "table of reference values" [69]. The table contains information on specimen preparation and data on properties related to processing, as well as mechanical, thermal, and optical properties. It is highly suitable for data collections because the properties listed can be compared readily.

2.1. Mechanical Properties and Their Testing

2.1.1. Classification of Plastics Based on Mechanical Properties

The mechanical properties of all groups of plastics cannot be discussed within a single context. Rather, three major classes of polymers exist that differ in their behavior under mechanical loading over a wide temperature range: thermoplastics, elastomers, and thermosets. Their differences in behavior result essentially from differences in physical as well as chemical structure.

Thermoplastics. Figures 7 A and 7 B plot the shear modulus versus temperature and the stress – strain curve for thermoplastics. This class includes un- cross-linked amorphous or partially crystalline plastics. At low temperature they are energy elastic, but above a certain temperature they exhibit viscous flow. Softening takes place in the glass transition range for amorphous thermoplastics (see Vibration. Test) and in the crystallite melting range for partially crystalline thermoplastics. Between the elastic and viscous-flow ranges there may be temperature range in which the material behaves in a rubberlike (entropy-elastic) manner.

In un-cross-linked substances such as thermoplastics, or in only partially cross-linked substances, entropy-elastic and viscous properties are superimposed. These substances are said to exhibit viscoelastic behavior (see Section 2.1.2).

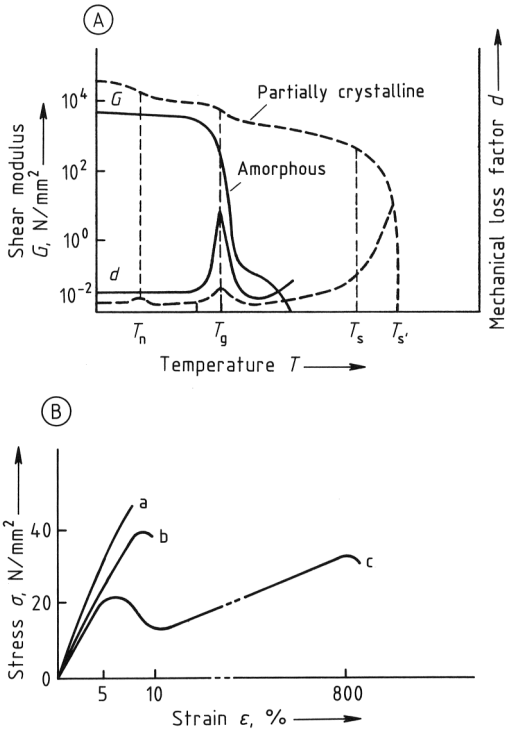


Figure 7. A) Temperature dependence of shear modulus G and mechanical loss factor d for amorphous and partially crystalline thermoplastics (schematic)
T_g = glass-transition temperature; T_n = temperature of a secondary relaxation mechanism; T_s = onset of melting of crystalline regions; $T_{s'}$ = end of melting of crystalline regions B) Stress – strain curve for thermoplastics (schematic) a) Amorphous material at moderate temperature; amorphous and partially crystalline material at low temperature or high strain rate; b) Amorphous and partially crystalline material at moderate temperature and strain rate; c) Partially crystalline material at moderate temperature and strain rate

Thermosets. Figures 8 A and 8 B present typical curves of shear modulus and loss factor versus temperature and of stress versus strain for thermosets (based on the curves for phenolic resins differing in degree of cross-linking). Thermosets are closely cross-linked polymers that exhibit energy-elastic or energy/entropy-elastic behavior at low temperature. At or above 60 °C, they show entropy-elastic behavior with very limited deformability. Figure 8 shows how, as cross-linking increases, the glass transition temperature increases and the main transition step becomes smaller, while the curve becomes flatter and the damping maximum becomes lower and broader. The steps disappear

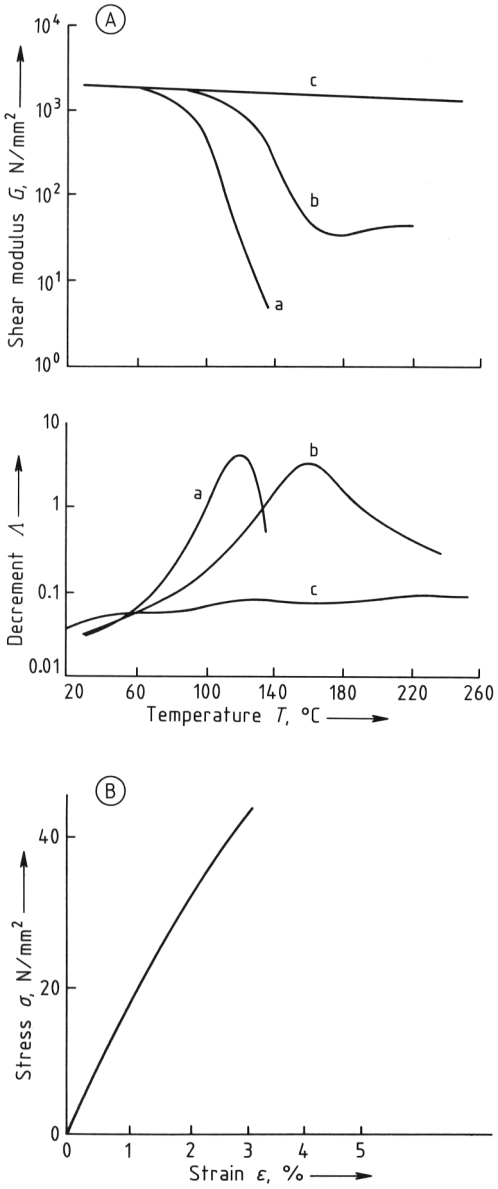


Figure 8. A) Temperature dependences of shear modulus G and logarithmic decrement Λ (as a measure of the loss factor d) for thermosets (phenol – formaldehyde resin) Cross-linking increases in the order a<b<c. B) Stress – strain curve for thermosets (schematic)

altogether upon curing and no main softening occurs in the closely-cross-linked network [70].

Elastomers. Figures 9 A and 9 B show curves of shear modulus and loss factor versus temperature for natural rubber, along with a schematic stress – strain curve. Elastomers are loosely cross-linked polymers that exhibit energy-elastic behavior at low temperature but do not exhibit viscous flow even at high temperature.

Above the glass transition temperature (20 °C or lower), elastomers exhibit rubberlike behavior. In this range, most have shear moduli between ca. 0.1 and 100 N/mm^2 and a high reversible deformability. The stress–strain curve has a characteristic S shape.

The glass transition temperature T_g is the mean temperature of the freezing range of a polymer, in which the microscopic Brownian motion of molecular chain segments becomes frozen and the polymer is converted to the glassy state. The temperature dependences of many physical properties change at the glass transition temperature (see Fig. 3). Some properties, such as the modulus, undergo a step-function change.

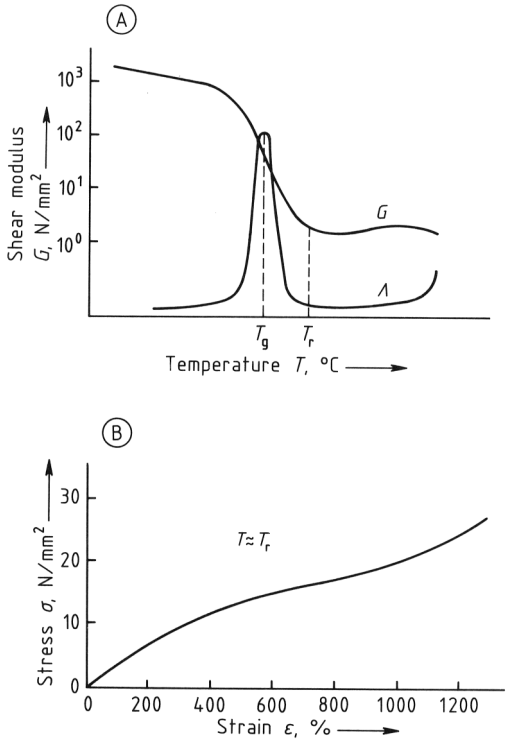


Figure 9. A) Temperature dependences of shear modulus G and logarithmic decrement Λ (as a measure of the loss factor d) for elastomers T_g = glass transition temperature; T_r = room temperature B) Stress – strain curve for elastomers (schematic)

Energy Elasticity, Entropy Elasticity, and Viscous Behavior. Strictly speaking, *energy-elastic* (perfectly elastic), mechanically and thermodynamically reversible behavior, in the sense of classical elasticity theory, does not occur in any material, particularly not in plastics. The main process in deformation is a distortion of the bond angles of the valence bonds, or else work is done against intra- or intermolecular forces (potential forces).

In *entropy-elastic* (rubberlike) substances, elasticity does not result from attractive forces but is a kinetic phenomenon like the volume elasticity of a gas. In the ideal case, the internal energy does not change when an amorphous, loosely cross-linked polymeric material network is deformed. Instead, the entropy decreases as the coiled chains are brought into a more highly ordered state. The hypothesis of constant internal energy implies that the work of deformation must be entirely transformed to heat; that is, a rubberlike substance (elastomer) must become heated when deformed. The assumption of decreasing entropy leads to the conclusion that the stress in a specimen must increase proportionally to the absolute temperature if the strain is held constant, or that if the tensile stress is held constant, the specimen must contract when heated.

Both effects have been the subject of extensive experimental and theoretical studies, initially in thermodynamic terms. However, complete understanding was achieved only with the application of the kinetic theory. This theory cannot be described in detail here [71], but chemical cross-linking of the chains is not absolutely necessary for rubberlike behavior. In partially crystalline polymers, for example, the crystallites act like cross-linking sites. In amorphous polymers under brief loads, entanglements of the chains can act as cross-links. When phase separation occurs in block copolymers, the regions composed of one of the two components play the role of cross-links (physical cross-linking).

Viscous Behavior can manifest itself in mechanically reversible creep (i.e., when stress is removed, the specimen returns to the starting position, not spontaneously but after a delay) or in flow (i.e., slipping of molecular chains past one another). Pure flow occurs (even if only as an approximation) in the melt. It is idealized as Newtonian flow, in which the deformation is mechanically and thermodynamically irreversible. However, this idealized state does not exist in polymers (see Section 2.8.3).

2.1.2. Viscoelastic Behavior of Polymers

In ideally elastic solids, the relationship between stresses and the corresponding strains is described by Hooke's law. The stresses and strains can be represented by diadics (second-order tensors), between whose coefficients linear relationships exist. This statement is the general form of Hooke's law. The mathematical expression is $\sigma_{kl} = c_{klmn} e_{mn}$, where σ_{kl} is the stress and e_{mn} is the strain. The 21 constants c_{klmn} required to describe this relationship in the linear range are known as elastic constants. They can be time dependent. In isotropic materials, the number of constants is reduced to two (Lamé constants), both of which can also be time dependent. In practice, other elastic constants or moduli, which themselves are functions of the Lamé constants, are also used. In particular, they are used as parameters in the attempts to mathematically describe the mechanical properties of elastic materials (see below).

In the nonlinear range, the number of elastic constants increases greatly, especially for anisotropic materials. Those of the 21 constants which vanish in the linear range for symmetry reasons have a finite, time-dependent value in the nonlinear range. The number of constants is so large that the measurement of all required constants and their time dependencies, although theoretically possible, is impractical. Thus, in this respect, there are limits to the exact description of the mechanical behavior. The problem is then to make an appropriate selection of constants so that the values measured adequately describe the mechanical behavior in practice.

For more than a century ago, many materials have been known that do not fit into this scheme because their behavior depends on their history. Such effects, not predicted by classical theory, were called "memory effects" (elastic aftereffects) [72], [73]. For many years, the study of this phenomenon was of only academic interest,

but the situation changed with the development of plastics.

Plastics were found to have properties exhibited by both elastic and viscous substances; hence, the term viscoelasticity.

Mechanical behavior was studied by means of static and dynamic measurements involving static and fluctuating loads and deformations. The resulting coefficients, however, applied to only a limited experiment. The experimental results were systematized by using a heuristic principle, the superposition principle, which has since been recognized as the mathematical formulation of the fundamental assumption in the theory – assumption of the linearity of viscoelastic effects. Within the limits of this hypothesis, a coherent phenomenological theory could be constructed that left nothing unexplained and provided a complete picture of viscoelastic behavior. The theory cannot be derived and explained here; for a comprehensive account, see [74].

The effects and functions of the theory can be classed in two groups:

Group I, which relates to creep experiments or measurements with predetermined stress.

Group II, which relates to relaxation effects or measurements with predetermined strain.

With the superposition principle a linear viscoelastic theory could be constructed but stresses and strains can also be interrelated by linear differential equations of the general form $\mathbf{P}\sigma = \mathbf{Q}\dot{\varepsilon}$, where **P** *and Q* are differential operators with respect to time.

This representation permits an especially advantageous mathematical description of linear viscoelastic behavior in relation to deformation problems with viscoelastic solids. The general explicit form of such differential equations is

$$a_0\sigma + a_1\frac{\mathrm{d}\sigma}{\mathrm{d}t} + a_2\frac{\mathrm{d}^2\sigma}{\mathrm{d}t^2} + \cdots = b_0\varepsilon + b_1\frac{\mathrm{d}\varepsilon}{\mathrm{d}t} + b_2\frac{\mathrm{d}^2\varepsilon}{\mathrm{d}t^2} + \cdots \quad (1)$$

Equations of this type arise when viscoelastic behavior is described in terms of mechanical models consisting of elastic springs subject to Hooke's law, combined with viscous dampers obeying Newton's law of viscosity. Such models are wholly fictitious, except that electrical networks described in a similar way are realistic (see Section 2.4.2).

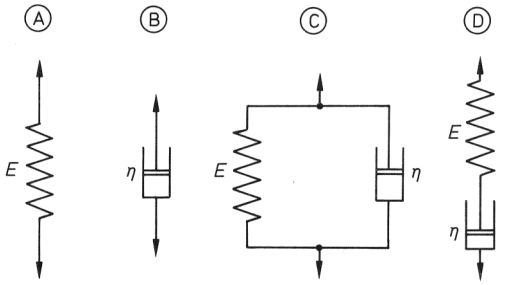


Figure 10. Simple models for describing linear mechanical behavior A) Spring; B) Damper; C) Voigt – Kelvin model [72], [73]; D) Maxwell model E = modulus of elasticity; η = viscosity

Mechanical Models and Relaxation – Time Spectra. The basic models are the Maxwell and Voigt – Kelvin models (see Fig. 10).

Maxwell model. The total strain consists of two parts, $\varepsilon = \varepsilon_{\text{spring}} + \varepsilon_{\text{damper}}$, where the stress is the same in damper and spring: $\sigma = E\ \varepsilon_{\text{spring}}$; $\sigma = E\ \tau \cdot \dot{\varepsilon}_{\text{damper}}$ where $E\ \tau = \eta$. Appropriate manipulations lead to the differential equation $\dot{\sigma} = E\ddot{\varepsilon} - \sigma/\tau$ and hence to the following expressions: for the stress-relaxation test ($\varepsilon = \varepsilon_0$),

$$\sigma = \sigma_0 \mathrm{e}^{-t/\tau} \quad (2)$$

and for the deformation (creep) test ($\sigma = \sigma_0$),

$$\varepsilon = (\sigma_0/E\tau)t + \sigma_0/E \quad (3)$$

Similar arguments for the *Voigt model* lead to the differential equation

$$\varepsilon = (\sigma/E\tau) - \varepsilon/\tau \quad (4)$$

and to $\sigma = E\ \varepsilon_0$ for the relaxation test and

$$\varepsilon = (\sigma_0/E)(1 - \mathrm{e}^{-t/\tau}) \quad (5)$$

for the creep test.

These simple models are not, however, suitable for "correctly" describing creep or relaxation behavior, because the Maxwell model represents relaxation alone (stress-relaxation test) and the Voigt model, retardation behavior alone (creep test). The behavior of real polymers requires a combination of at least three or four basic models. A given viscoelastic behavior can be characterized by two arrangements of basic models: (1) a number of Voigt models in series plus a single spring and a single damper, also in series; and (2) a number of Maxwell elements in parallel.

The constants of the two arrangements are linked to one another, and either model can be calculated from the other. The mathematical proof of equivalence is laborious. The model selected depends on convenience. The Voigt type is preferable when the stress is given and the strain must be calculated, and the converse is true for the Maxwell type. Expanded types are referred to as "generalized" Voigt or Maxwell models.

The final step in the analysis is the transition from a generalized to a continuous mechanical model. Such infinite networks are characterized not by a finite number of constants but by a continuous function of an independent variable. These functions, which define continuous models, are called distribution functions. The extension of the theory is not simply a mathematically elegant solution. The restriction to a finite number of models, each having a well-defined characteristic time (retardation or relaxation time), would imply that processes in real viscoelastic polymers take place with very well-defined characteristic times, but this is true for only a few crystalline materials, not for polymers.

To clarify the situation, consider a generalized Maxwell model with relaxation times $\tau_1<\tau_2<\tau_3<\cdot\cdot\cdot$. The model is determined if the corresponding spring constants M_i are given. The subdivision into different τ_i is made finer and finer, so that in the limit, the variable τ becomes continuous, taking on all values between 0 and ∞.

The "spring constant" associated with relaxation times between τ and $\tau + d\tau$ has a value $h(\tau)\,d\tau$, $0<\tau<\infty$, where $h(\tau)$ is a continuous function of the relaxation time called the "distribution function of relaxation times" or, for brevity, the relaxation spectrum. If the relaxation spectrum $h(\tau)$ is known for all times, the mechanical behavior of the model is completely determined. In particular, the stress-relaxation modulus $M(t)$ is found by integrating over relaxation time (here with the use of a logarithmic time scale):

$$M(t) = \int_0^\infty H(\ln\tau)e^{-t/\tau}d\ln\tau \qquad (6)$$

The relaxation spectrum cannot, however, be measured directly; it must be calculated from measured phenomenological functions by means of special equations. The calculation is not simple in every case and can be done to only a rough approximation; the spectra are therefore of little importance for purposes of phenomenological description. Their value lies, instead, in the thermodynamic and structural interpretation of the relaxation process. Figure 11 shows relaxation spectra $H(\ln\tau)$ of polyethylene and polypropylene at various temperatures [75]. Inclusion of the temperature dependence leads to a threedimensional representation of the relaxation spectrum. Special reduction methods can be used to extend the spectra to shorter or longer times, after which the plots for polypropylene and polyethylene, for example, exhibit distinct maxima, whose interpretation is discussed in [75]. For example, in polypropylene, the principal maximum at short times is a criterion for mechanisms in amorphous domains, whereas the maximum at long times is a criterion for mechanisms in crystalline domains. Figure 12 shows the relaxation spectrum of polypropylene at 23 °C (after extension to short times) and the temperature traces of the two maxima [76].

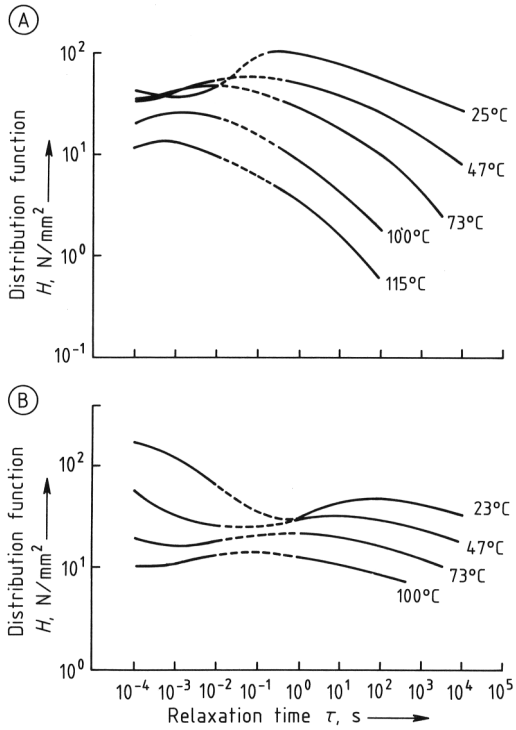


Figure 11. Relaxation spectra at various temperatures A) Polyethylene; B) Polypropylene

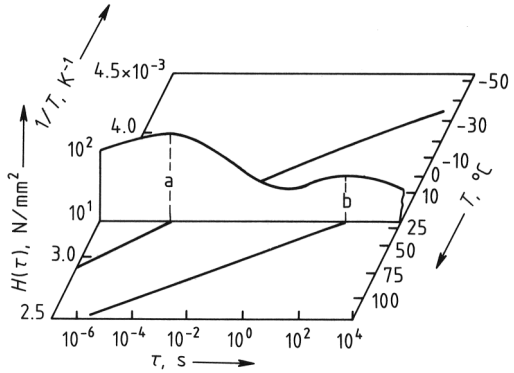


Figure 12. Relaxation spectra of polypropylene as a function of time and temperature [75], [76] a) Principal maximum; b) Crystalline maximum

As has been mentioned, relaxation spectra can be obtained from creep and relaxation tests only by indirect means; for immediate practical purposes, the results of these "phenomenological" experiments are therefore used directly. They cover loading times $t \geq 1$ s, with no upper bound on the time. These experiments are also referred to as static tests. The model theory of viscoelasticity is thus supplemented by a phenomenological treatment of viscoelasticity.

2.1.3. Mechanics of Deformation

Creep Modulus and Relaxation Modulus. The strongly time-dependent behavior of plastics (especially thermoplastics) under mechanical deformation, resulting from viscoelastic properties, is characterized by the time-dependent creep modulus (retardation modulus) and the time-dependent relaxation modulus. General laws for these can be derived from the viscoelasticity theory (see Section 2.1.2). For the relaxation test, this principle leads to an integral representation in the form

$$\sigma(t) = \int_0^t M(t-\xi)\dot{\varepsilon}(\xi)\mathrm{d}\xi \qquad (7)$$

with variable of integration ξ [77].

In Equation (7), $M(t)$ is the relaxation modulus, which replaces the modulus of elasticity E, the shear modulus G, and the bulk modulus K; $\dot{e}$ is the strain rate. The more specific notation $E_r(t)$ should be used for the modulus $E(t)$ derived from the relaxation test, to distinguish it from the reciprocal compliance $1/C(t) = E_c(t)$ discussed below, which is determined from the creep test. The superposition principle applied to the creep test leads to an integral representation

$$\varepsilon(t) = \int_0^t C(t-\xi)\sigma(\xi)\mathrm{d}\xi \qquad (8)$$

which is analogous to Equation (7). As in the representation of $\sigma(t)$, $C(t-\xi)$ is the time-dependent elastic compliance, which is referred to as the creep compliance and takes the place of the elastic compliance $C_E(t)$, the shear compliance $C_G(t)$, and the bulk compliance $C_K(t)$. In practice, $C_E(t)$ is also written as $1/E_c(t)$.

The relaxation modulus $M(t)$ and the compliance $C(t)$ are linked by the general relation

$$\int M(t-\xi)C(\xi)\mathrm{d}\xi = t$$

which implies the condition $M(t)\,C(t) \leq 1$. The equality holds if the time dependence is weak, so that $Er(t) = Ec(t)$; otherwise, $Er(t) < Ec(t)$.

If the time dependence is marked, the elastic modulus measured in the relaxation test is lower than that from the creep test. However, this holds only with no stress dependence in the creep test and no strain dependence in the relaxation test. This is not, however, the case in general, so in practice, $Er(t)$ can also be greater than $Ec(t)$.

The results of creep tests play an important role in construction with plastics. In the creep test, a stress σ is applied to the specimen at time $t = 0$ and held constant thereafter (relative to the initial cross section). The increase in strain with time (creep) $\varepsilon(t)$ is measured. Figure 13 shows how σ and ε vary with time in the creep test. The ε versus t curve is commonly referred to as the creep curve. For sufficiently low stress, Hooke's

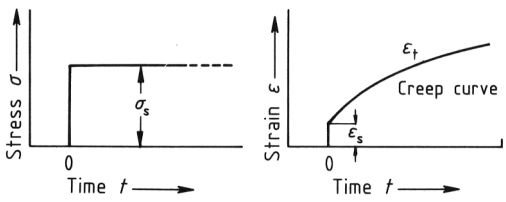


Figure 13. Variation of σ and ε with time in creep test εs = instantaneous strain (immediately after the application of stress)

law in the form $Ec\ (t) = \sigma/\varepsilon\ (t)$ gives the time-dependent modulus $E\ (t)$ from the creep and the constant (initial) stress.

The creep modulus $Ec\ (t)$ is independent of the stress only if the stress lies in the Hooke's law range, where the stress and the strain measured after a given time are proportional to one another. Outside the linear range, the creep modulus decreases with increasing stress. When values are cited for the creep modulus, the stresses at which they were determined must be specified. In practice, uniaxial tensile loads are usually applied in creep testing, chiefly because this loading mode gives an identical state of stress at all points in the specimen. The performance of tensile creep tests is governed by DIN 53 444 [78]. The specimens used are the same as for the tensile test of DIN 53 455 [79]. Tensile specimens are loaded by the impactless application of weights, and strain is measured at fixed time intervals. A plot of the results gives the above-mentioned creep curve. The test involves three variables: stress, determined by load and (initial) specimen cross section; strain; and loading time. Two-dimensional plots, each with two explicit variables and one as parameter, yield the family of curves shown in Figure 14. For clarity's sake, only one stress – time curve (yield limit curve) and one isochron are plotted.

The creep modulus $Ec\ (t)$ is derived from a family of creep curves with stress as parameter; the result can be plotted, for example, versus time, as shown in Figure 15. Plotting points for the respective stress – strain values from the creep curve, with loading time as parameter, gives so-called isochronous stress – strain curves, which show the time and stress

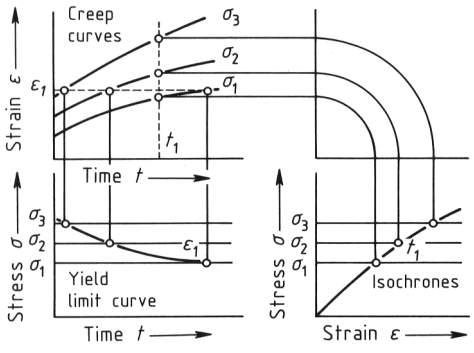


Figure 14. Derivation of yield limit curves and isochrons from creep curves

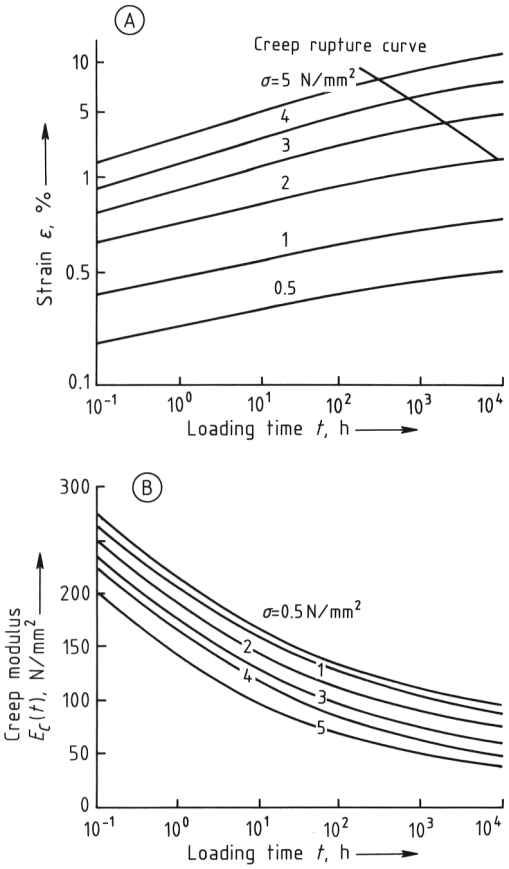


Figure 15. Creep curves and creep-modulus curves
A) Creep curves at 65 °C for high-density polyethylene with creep rupture curve from a long-term pressure test on high-density polyethylene pipes B) Creep-modulus curves derived from creep curves

dependence clearly. Fields of isochrones for a number of temperatures convey much information to the designer (see Fig. 16).

The stress σ that leads to a total strain ε after time t is called the time yield limit $\sigma_{\varepsilon/t}$.

The curve connecting creep stresses for equal strains is now known as a "stress versus time curve" (formerly termed yield limit curve; see Fig. 14). The set of creep curves forms the creep diagram, which may also contain the test stress σ and the time t to fracture (or to a certain sign of damage). These give the creep rupture curve or a certain "damage curve." The term creep strength curve is also commonly used for the creep rupture curve, because ultimately it is the curve joining the creep strengths. The creep strength $\sigma_{B/t}$ is the

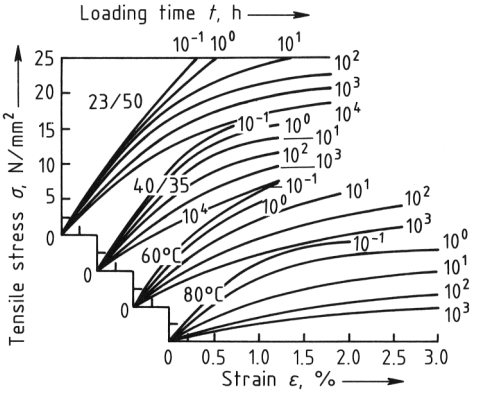


Figure 16. Isochronous stress – strain curves for acrylonitrile – butadiene – styrene; $ak = 12$ kJ/m2 [80] 23/50 = 23 °C/50 % relative humidity; 40/35 = 40 °C/35 % relative humidity

static load B, relative to the initial specimen cross section, that causes fracture of the specimen after a certain loading time t. The creep diagram can be used to estimate the time-dependent deformation occurring under uniaxial tensile loading and is a useful design aid for simple loading modes (Fig. 17). The time-dependent modulus of elasticity, however, is more universal in its application because, in many cases, it can also be used in the equations for materials engineering.

The relaxation test is experimentally far more difficult to perform than the creep test. The deformation must be held constant over time,

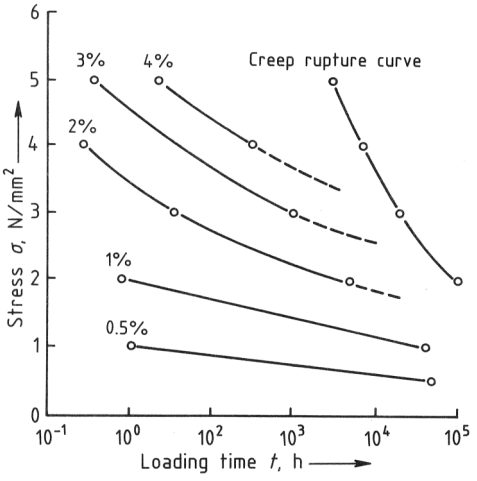


Figure 17. Creep diagram for high-density polyethylene with 0.5, 1, 2, 3, and 4 % yield limit curves and the creep-rupture curve

and the mechanical stress must be measured as a function of time. For details, see [81].

Vibration Tests. Static tests involve loading times longer than ca. 1 s. If information about the millisecond range is needed, vibration tests must be performed. These usually cover two orders of magnitude in frequency; the ranges in conventional vibration tests are roughly between 10^{-1} and 10^{4} Hz, corresponding to time t (if $t = 1/\omega$) in the range of 10^{-5} to 1 s.

As is customary in treatment of vibration, complex quantities are employed to describe the phenomena. The theory leads to the definition of a complex modulus (see Fig. 18):

$$\boldsymbol{M} = |\boldsymbol{M}|e^{i\delta} = M' + iM''$$

where M', the real part of $\boldsymbol{M}$, is called the dynamic modulus (as distinct from the time-dependent modulus $M(t)$; see Creep Modulas and Ralaxation Modulus) or the storage modulus. It is a measure of the recoverable energy transformed in the deformation occurring during one vibration. The parameter M'', the imaginary part of $\boldsymbol{M}$, is called the loss modulus. It is a measure of the vibrational energy unrecoverably transformed to heat (dissipated). The quotient of the real and imaginary parts of $\boldsymbol{M}$, which is the tangent of the phase angle δ of the complex modulus, is known as the mechanical loss factor $d = M''/M' = \tan\delta$. It is a relative measure of vibrational energy losses compared to recoverable energy.

The chief methods used in plastics testing are the torsional vibration test and the bending vibration test. The various techniques for exciting torsional vibrations have in common that a specimen acting as a torsion spring is connected

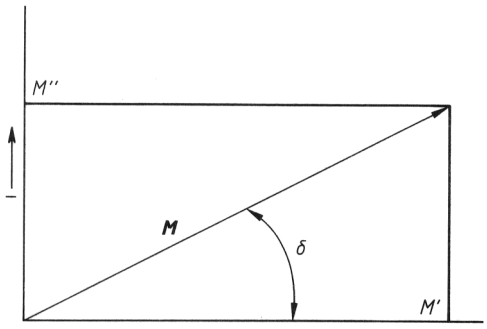


Figure 18. Representation of M in the complex plane

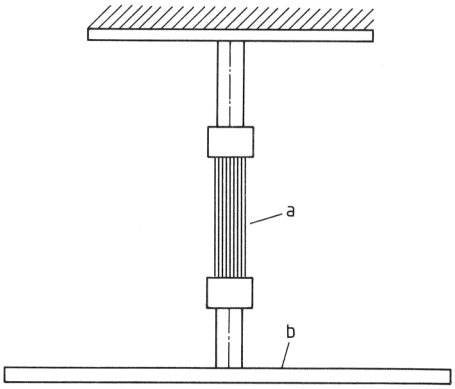


Figure 19. Schmieder – Wolf torsional pendulum a) Specimen; b) Rotating mass

to an oscillating mass. Figure 19 shows one possible arrangement.

If the upper specimen clamp is moved slightly, this torsional pendulum is set into damped natural oscillation. The logarithmic decrement $\Lambda = \ln (A_n/A_{n+1})$ and the mechanical loss factor $d \approx \Lambda/\pi$ (for $\Lambda \leq 2$) are calculated from the amplitudes A of successive oscillations. The shear modulus G is determined from the moment of intertia $\boldsymbol{I}$ of the oscillating mass, the square of the oscillation frequency f, and factors F_g and F_d relating to the dimensions and the damping effect, respectively:

$$G = \boldsymbol{I} f^2 F_g F_d$$

The test method is described in detail in DIN 53 445 [82]. Figure 20 shows how the curve of shear modulus G versus temperature T can be used to separate the various states of high polymers. The glassy range is characterized by high modulus and low damping. The diagram also shows clearly the temperature below which the substance described by this G versus T curve behaves as a solid. Temperature ranges in which the modulus is strongly temperature dependent, while the damping has a maximum, represent softening ranges. The measured results also show whether flow sets in as soon as softening begins or whether cohesive forces are still present. Figure 21 gives examples of shear modulus curves over a wide temperature range.

Because of the amount of information it provides, the torsional vibration test has also been incorporated into the table of reference values mentioned earlier (see Thermoplastics).

In the bending vibration test [83], the top end of a rod-shaped specimen is clamped in a fixed position and the rod is excited to steady-state resonance bending vibrations by an electromagnetic transducer at the bottom. The amplitude of the vibration is measured by a transducer near the clamping point. The modulus of elasticity is calculated from the resonant frequency, and the loss factor from the width of the resonance curve. The wide frequency range employed in this method (1 – 10 000 Hz) is an advantage of the bending vibration test. Because frequencies lie in the audible range, the test is particularly important for studies relating to acoustic applications of plastics for example for noise suppression [84]. The torsional vibration test gives the shear modulus G, whereas the bending vibration test yields the elastic modulus E. To a good approximation, the conversion formulas are

$$E = 2G(1 + \mu) \quad \text{or} \quad E = \frac{3G}{1 + G/(3K)}$$

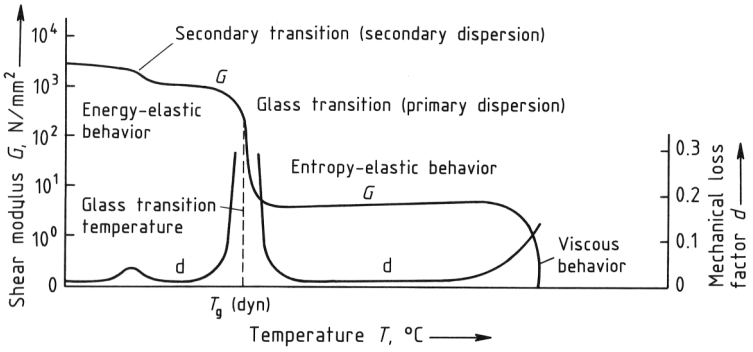


Figure 20. Definition of state regions based on the curve of shear modulus G versus temperature T (DIN 7724)

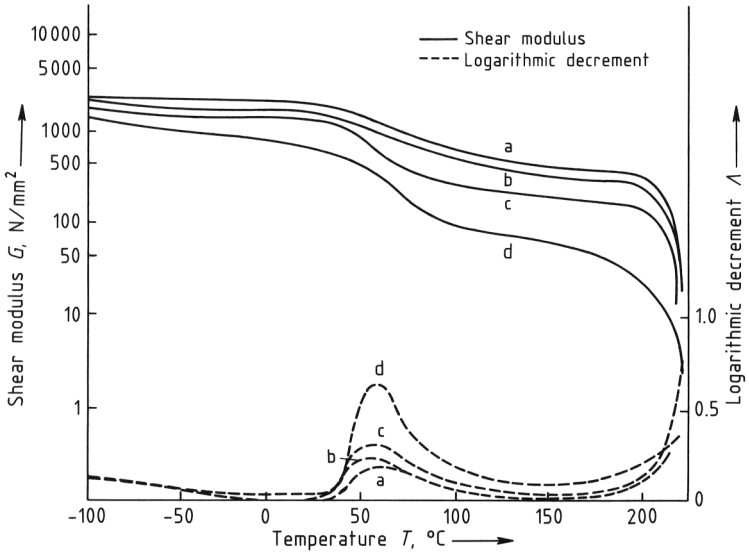


Figure 21. Temperature dependences of shear modulus and logarithmic decrement for poly(butylene terephthalate) a) 30 % Glass fiber; b) 20 % Glass fiber; c) 10 % Glass fiber; d) Unreinforced

where μ is Poisson's ratio and K is the bulk modulus; see also [85].

Behavior under Steady and Fluctuating Loads. To characterize the time-dependent load-deformation behavior, the laborious long-term and vibration tests are supplemented by steady-load and fluctuating-load tests. These techniques are important for product development, inspection, and preliminary materials selection. Tests with steady load include tensile, bending, and compressive tests, as well as hardness measurement; those with fluctuating load include flexural fatigue tests. Studies of friction and wear properties complete the series of mechanical measurements. For the designer, however, by far the most informative results are the temperature and time functions describing the long-term behavior under tensile loading together with the curves of shear modulus versus temperature. The predictive power of all other methods is limited by comparison [86]. The tensile test [87] is, however, largely exempt from the limitations mentioned. The elongation and strength values from this test, given uniform strain and a homogeneous stress distribution, allow a good assessment of the load deformation behavior. Figure 22 A presents three typical curve shapes [86], along with the stress and strain values listed in the table of reference values for plastics.

Outside the linear range of the stress – strain curve, the bending test [88] gives unrealistically high values. This test is therefore no longer included in the table of fundamental values [89].

Compression tests [90] are important in the evaluation of some thermoset molding compounds.

Static Modulus of Elasticity. The elastic modulus derived from stress – strain curves (or force –deformation curves) recorded in steady-load tests, like the values from tensile, bending, and compressive tests, is a single-point value with respect to strain rate. It has adequate predictive power for product development, inspection, and materials preselection in most cases. Derivation of the modulus for a tensile load is illustrated in Figure 16 B.

The applicable standard [91] specifies a uniform rate of extension (crosshead speed) of 1 mm/min and restriction of the evaluation to the stress – strain curve between 0.05 and 0.25 % strain. Because the stress-strain relationship for rigid plastics is quasi linear in this range, what is obtained is an approximate tangent modulus. A secant modulus is found for soft plastics with a nonlinear stress-strain relationship.

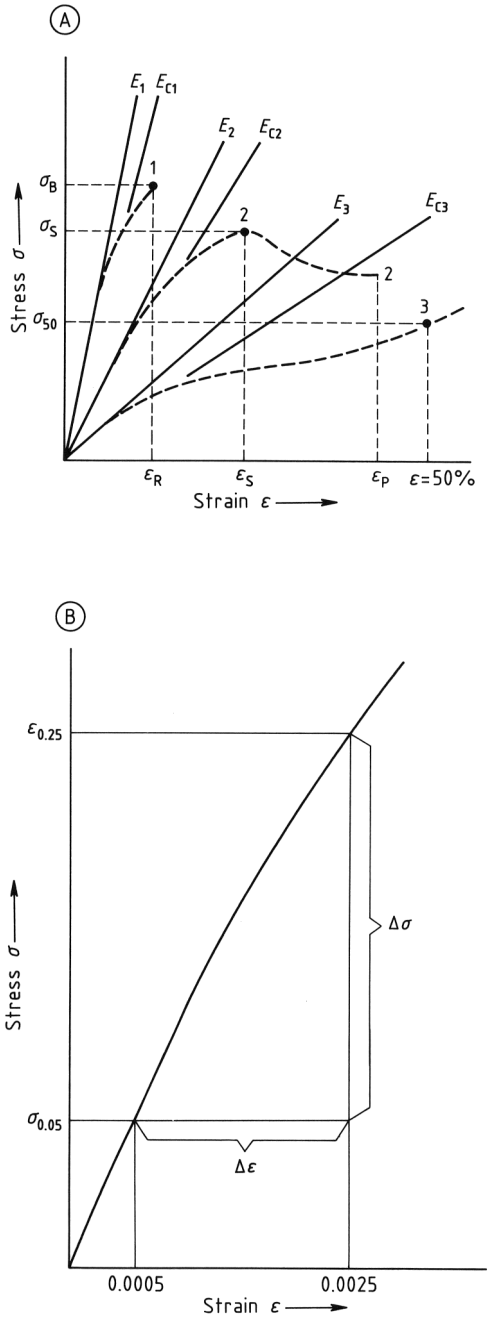


Figure 22. Evaluation of tests with steady load A) Values from tensile test, for three typical shapes of stress – strain curves [86] E = elastic modulus; E_c = creep modulus after 10^3 h; ε_R = elongation at rupture, ε_S = extension; σ_P = tensile strength; σ_S = yield stress; σ_{50} = stress at 50 % strain B) Determination of elastic modulus (DIN 53 457/1987) $\sigma_{0.25}$ = stress at 0.25 % strain; $\sigma_{0.05}$ = stress at 0.05 % strain; $\Delta\sigma = \sigma_{0.25} - \sigma_{0.05}$, $\Delta\varepsilon = 0.002$ (= 0.2 %)

The standard does not, however, distinguish between tangent and secant moduli in the listing of values. Thus, the elastic modulus in this standard is given by

$$E = \frac{\sigma_{0.25} - \sigma_{0.05}}{0.002} \text{(units of } E \text{ and } \sigma: \text{ N/mm}^2\text{)}$$

where $\sigma_{0.25}$ is the stress at 0.25 % strain and $\sigma_{0.05}$ is the stress at 0.05 % strain. Table 3 lists tensile moduli of elasticity for several reinforced and unreinforced plastics.

Table 3. Static modulus of elasticity for unreinforced and reinforced plastics (maximum value in each case)

Product (abbreviations from DIN 7728) *	Elastic modulus E, N/mm^2 **
ABS, moderate impact strength	2 500 (T)
	2 300 (B)
ABS + 30 % GF	6 000 (T)
	4 500 (B)
PS	3 500 (T)
SB	3 000 (T)
SAN	3 800 (T)
ASA	2 900 (T)
PTFE	750 (T)
FEP	700 (T)
PFA	700 (T)
PE-HD (HDPE)	1 400 (T)
PP	1 800 (T)
PP + 40 % T	4 500 (T)
POM (Copolymer)	3 200 (T)
POM + 30 % GF	10 000 (T)
PBT	2 700 (T)
PBT + 30 % GS	4 000 (T)
PBT + 30 % GF	10 000 (T)
PBT + 30 % CF	16 000 (B)
PA 6 (d)	2 500 (T)
PA 6 + 30 % GF (d)	8 300 (B)
PA 6 + 30 % CF (d)	16 000 (B)
PA 66 (d)	3 000 (T)
PA 66 + 30 % GF (d)	10 000 (B)
PC	2 200 (T)
PC + 30 % GF	7 000 (T)
PPO	2 000 (T)
PPO + 30 % GF	9 000 (T)
PEEK	3 800 (B)
PEEK + 30 % CF	13 500 (B)
PPS	4 200 (B)
PPS + 40 % CF	19 600 (B)
PMMA	3 300 (T)
PVC	3 300 (T)
PVC-HI	2 600 (T)
PES	2 600 (B)
PES + 30 % CF	14 300 (B)

* GF = glass fiber; T = talc; GS = glass spheres; CF = carbon fibers; d = dry;

** T = tensile modulus; B = bending modulus.

Multiaxial Loading. The strengths measured under steady load, such as the tensile strength, apply to a one-dimensional load system. Application of these values to multiaxial stresses requires that the multiaxial states be linked with the individual strengths through fracture criteria that reduce the multiaxial state to a single reference stress. Definition of this reference stress depends on the fracture hypothesis selected. Finally, the reference stress is compared with the individual (usually tensile) strength. The fracture criteria used for metals cannot as a rule be applied to plastics, because isotropic fracture behavior – the precondition for most of the classical criteria – is generally not exhibited by plastics [92].

Classical failure criteria must therefore be modified to describe more accurately the failure behavior of polymers. A detailed discussion of these modifications can be found in [93].

Hardness. Hardness is not a fundamental property of plastics; the concept is ultimately subjective. Probably the most widely acknowledged definition is resistance to the penetration of another, harder body.

As in methods for metals, hardness testing on plastics employs a standard penetrator, often a hardened steel ball or steel pin, that is pressed by a defined force into a plane surface of the material being tested, with the depth of penetration being measured [94–97].

The viscoelastic behavior of plastics results in two basic difficulties: (1) the depth of penetration depends on the rate of loading, and (2) measuring the diameter of the impression is difficult. Because the impression springs back after the load is removed, it would have to be measured immediately. Thus, either the depth of penetration is measured after a given time under load, or a transparent penetrator is employed.

Not only does the hardness depend on time, temperature, and the nonlinear stress – strain relationship, it also depends on the magnitude of the forces applied, the modulus, and the shape of the penetrator. Accordingly, hardness measured by a given method cannot be compared with that obtained by another method. The hardness of elastomers and other "soft" materials is characterized by the Shore hardness value [97], while that of rigid thermoplastics and all thermosets is expressed as the ball indentation hardness [95].

Behavior under Fluctuating Load (Fatigue). A large fluctuating load applied many times can lead to material damage that results in failure (fatigue failure) at a load value far below the strengths measured in steady-load tests (tensile strength, tensile creep strength). Test methods devised for metals have been extended to plastics, with allowance for the fact that metals, in contrast to plastics, have low damping and high thermal conductivity. The loading frequencies for plastics are therefore markedly lower than for metals, lying between ca. 600 and 3000 min^{-1}.

Fluctuating loads are classified as loads with constant stress and those with constant strain. The many possible forms of loading cannot be discussed individually here. As Figure 23 shows, three loading ranges are distinguished: fluctuating compressive, alternating, and fluctuating tensile. In the repeated flexural fatigue test (Wöhler method), several (e.g., six to ten) equivalent specimens are subjected to appropriately graduated oscillating loads, and the number of cycles to failure is recorded for each. The same mean stress σ_m is chosen for all specimens, and the initial stress amplitudes are graded. The mean stresses and stress amplitudes, which vary within a test because of relaxation and heating, are then plotted against the common logarithm of the number of cycles. The curves obtained are known as run curves, and the complete set of curves obtained in the test is the family of run curves. In addition, the Wöhler curve proper ($\sigma_a - N$ or stress-life curve) is plotted; its points

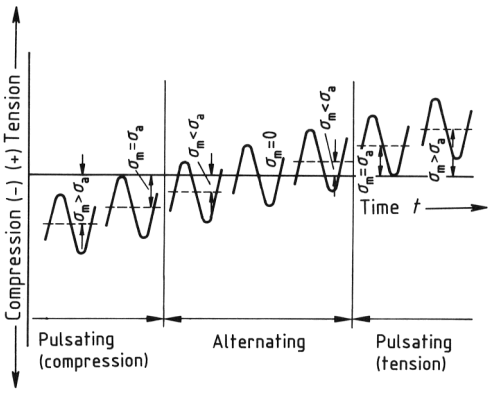


Figure 23. Load ranges in vibrational test σ_0 = maximum stress; σ_u = minimum stress; σ_m = mean stress $[\sigma_m = 0.5(\sigma_0 + \sigma_u)]$; σ_a = stress excursion $[\sigma_a = \pm 0.5(\sigma_0 - \sigma_u)]$

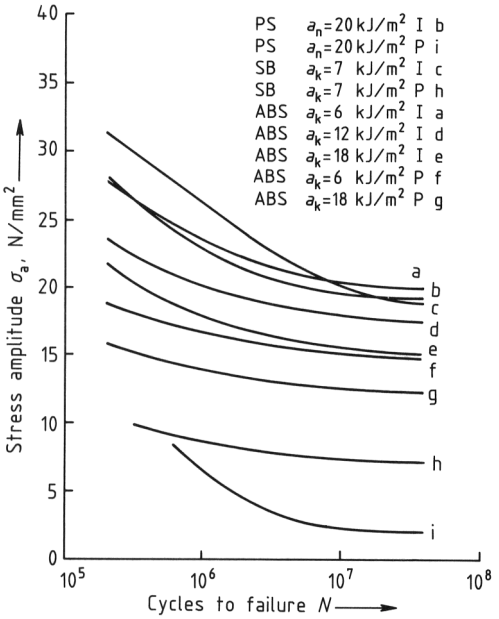


Figure 24. Wöhler curves for polystyrene, styrene – butadiene, and ABS, after Oberbach [71] a_n = impact toughness; a_k = notch impact toughness, S = injection-molded specimen; P = molded specimen

represent pairs of initial stress amplitude σ_a and cycles to failure N, plotted with a logarithmic horizontal (N) axis and a linear vertical (σ_a) axis. Figure 24 presents Wöhler curves for polystyrene, styrene – butadiene, and acrylonitrile – butadiene – styrene (ABS) [80].

Service Temperature Range. The best way of assessing the service temperature range is to use curves showing the properties of interest as a function of temperature. In many cases, functional tests on a finished part can also be employed. Nonetheless, evaluating the service range – in relation to, say, mechanical behavior – by performing standard tests on specimens is often useful. This is successful, with some reservations, for determining the upper limit service temperature (heat stability) but not for determining brittleness temperatures. Attempts to devise a satisfactory technique for measuring these have not been successful.

The DIN heat stability tests are the Martens test [98] and the heat deflection temperature (HDT) test among [99]. The Vicat softening temperature (VST) indicates the softening

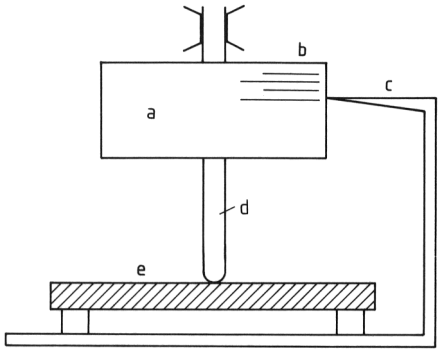


Figure 25. Setup for the HDT method (schematic)
a) Weight; b) Scale; c) Indicator; d) Bending mandrel; e) Specimen

behavior at the upper limit of the service temperature range [100].

Figure 25 shows a schematic of the HDT test. The heat deflection temperature is the temperature at which the bending test specimen, loaded in the middle, deforms by a given amount as its temperature is increased. Various test methods differ in the magnitude of the bending stresses applied. In the Martens test, the bending moment acts in a four-point loading scheme. The VST is the temperature at which a 1-mm^2 circular steel pin under a given force penetrates 1 mm vertically into the specimen as the temperature is increased.

2.1.4. Friction and Wear

Friction is defined in general as the resistance that must be overcome to set or maintain two contacting bodies in relative motion. The coefficient of friction μ is calculated from the normal force N between the contacting surfaces and the frictional force F opposing their motion: $\mu = F/N$. In other words, the frictional force is proportional to the normal force (first law of friction). This formula holds approximately for metals; the coefficient of friction for plastics decreases with increasing normal force. Friction measurements on plastics should therefore employ a graded series of normal forces.

The concept of friction is often broken down into static and dynamic friction, even though perfectly static friction is impossible. The term static friction normally refers to the amount of force required to induce a relative motion

between two surfaces in contact; that is, what is measured is the frictional force with very slow movement.

Dynamic friction means the force that will maintain a constant, perceptible, relative motion between contacting surfaces. Velocity thus plays a role in determining the frictional force, even though for many materials the frictional force changes almost negligibly as relative velocity changes by several powers of ten. This finding corresponds to the third law of friction. For plastics, however, it does not hold perfectly. The frictional force may change by a factor of three or even four as the velocity varies over several powers of ten. Unfortunately, the velocity effect cannot be wholly separated from the temperature effect, but the velocity dependence must still be determined for plastics. The heat produced in a sliding contact is approximately proportional to the coefficient of friction, the sliding velocity, and the normal force.

Figure 26 shows how the coefficient of dynamic friction depends on the sliding velocity for ultrahigh molecular mass polyethylene under various pressures.

In general terms, wear refers to all abrasive processes involving mechanical energy. The mechanisms governing wear are complex and intimately interconnected (see also → Abrasion and Erosion). For plastics, relatively little experience has been gathered with regard to the effects of various parameters. The following methods are considered proven: The wear in dry sliding against a granular material is determined by the friction wheel technique [101]; a similar method is described in [102]. Another method measures

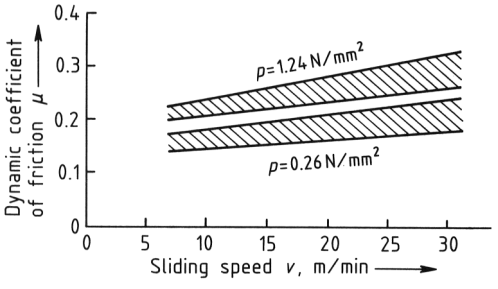


Figure 26. Dynamic coefficient of friction μ as a function of sliding velocity v for ultrahigh molecular mass polyethylene at various surface pressures p = mean surface pressure

Table 4. Wear (reduction in specimen diameter) of some plastics in dry sliding against 16 MnCr 5 steel

Product (abbreviations from DIN 7728)	Wear, μm per km of sliding distance
PA 66	0.09
PA 6	0.23
PA 610	0.32
PA 11	0.8
PET (PETP)	0.5
POM (copolymer)	8.9
PE-HD (HDPE)	1.0
PE-LD (LDPE)	7.4
PP	11
PTFE	21
PS	115
SAN	23
SB	51
ABS	8.4
PMMA	4.8
PVC	5.6
PC	22

the wear of plastics in dry sliding against a rotating steel shaft. This technique is used to test plastics for sliding bearings, especially those designed to run dry [102]. Table 4 lists values measured in a setup of this type.

2.1.5. Fracture Behavior

Plastics exhibit three types of deformation and fracture behavior:

1. Quasi-brittle fracture
2. Fracture after partially or completely irreversible shear deformation
3. Fracture by crazing after irreversible deformation of the specimen

This classification applies mainly to thermoplastics; fracture in thermosets is nearly always brittle. The fracture behavior of elastomers is described by the theory of Bueche and Halpin [103].

Brittle Fracture. The term brittle fracture denotes fracture with virtually no deformation, characterized by a high propagation velocity. If the latter is placed in the foreground, brittle fracture can be said to take place even if some plastic deformation occurs first. Brittleness and toughness as material properties are influenced by test conditions and depend on the temperature, the rate of loading, and the stress

state. In this sense, any plastic experiences low-deformation fracture in some range or ranges.

Despite their brittle behavior, plastics have a relatively high specific fracture energy (energy to produce 1 cm^2 of fracture surface), roughly a hundred times that of inorganic glasses. The reasons for this are that (1) the edges of an advancing fracture undergo substantial irreversible deformation, even in the glassy state; and, (2) the numerous crazes formed in the material act not as energy absorbers but as starting points for new fractures (see Fracture Mechaincs).

Fracture Mechanics. A few words should be said about the applicability of fracture mechanics to plastics. The fundamental idea of fracture mechanics is to analyze the mechanical behavior of an individual crack in a linearly elastic, homogeneous, and isotropic continuum. This basic concept is, however, valid only if the solid shows linearly elastic behavior even in its smallest regions, that is, at the tip of the crack. In other words, the material must be perfectly brittle. The energy transformation is then simply the conversion of supplied elastic energy to pure surface energy. Even for perfectly brittle glasses, however, the energy balance is not this simple; the "supply side" includes elastic energy derived from internal stresses, whereas on the "demand side" the liberation of plastic deformation energy plays a dominant part, especially for crack propagation in plastics. The specific surface energy is orders of magnitude lower than this deformation energy.

To describe this ductile behavior, the concept of crack resistance has been introduced, which describes ductile behavior without the necessity of knowing or postulating details about the shape, size, and time behavior of the plastic zone itself. Fracture mechanics becomes less and less valid as the crack-tip plasticity increases. A number of models of this plastic behavior exist, including that of DUGDALE.

In the area of *quasi-brittle fracture*, however, linearly elastic fracture mechanics (LEFM) offers a fairly good description even of viscoelastic materials. If certain fitting parameters are introduced, the framework of LEFM can also be extended to materials with small plastic deformation components. As the deformation behavior becomes more strongly plastic to completely plastic, the corrections are no longer sufficient and the linearly elastic solution ceases to be meaningful. For such cases, however, viscous fracture mechanics is based on a different set of principles and may provide a fracturemechanical description. The application of fracture mechanics to polymers is reviewed in [104].

Fracture after Partial or Complete Shear Deformation. A ductile fracture, in contrast to a brittle one, is characterized by large amounts of macroscopic deformation. The deformation may arise through uniform elongation or, in true ductile fracture, by yielding or necking. In metals and ceramics, direct inspection reveals lattice defects (dislocations) in this yielding region. Movements of the dislocations are responsible for observed plastic or permanent deformation; such motion does not occur below the tensile yield stress. This behavior provides a basis for clearly distinguishing between elastic and plastic (irreversible) strain in metals and ceramics. The curves plotted for plastics are very similar to those for metals (Fig. 27). The analogous behavior of metals and some plastics is underlined further by the occurrence of necking. In thermoplastics, for example, one or several such necking zones migrate over the specimen until the whole has experienced yielding (unless it has fractured first). The behavior can be described by the Eyring yield equation; detailed discussion and calculations based on a kink model are presented in [105].

In metals, the planes of maximal shear stress (e.g., a plane at 45 ° to the direction of uniaxial loading) exhibit so-called Lüders lines [106]. These are tracks left by slip lines along which the parts of the specimen are displaced. The lines

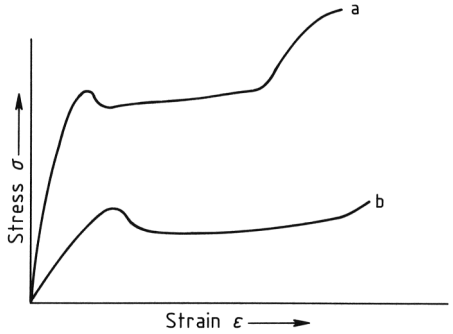


Figure 27. Stress – strain behavior of materials with yielding a) Metals; b) Thermoplastics

are regarded as evidence of a dislocation-dependent deformation process. Similar lines are observed in both crystalline and amorphous plastics. Their occurrence in crystalline plastics is interpreted in terms of a dislocation-dependent slip mechanism, but this interpretation does not apply to amorphous materials. ROSEN advanced a theory based on the observed birefringence [107]. According to this hypothesis, birefringence results from a new, noncrystalline state of aggregation. The lines are a domain of oriented material having a refractive index different from that of the surrounding material.

Fracture after Deformation with the Formation of Crazes (*Flow Zones*). Crazes or flow zones are planar inhomogeneities in a high polymer, produced by plastic deformation in the direction of an applied tensile stress [108–110]. The planar surface of the craze forms perpendicular to the maximum principal tensile stress (Fig. 28). A craze can be as large as 1 cm^2 in area but no more than 4 μm thick.

Surface crazes display arched crack edges or dislocations. In contrast to a crack, a craze contains material in a highly stretched, unthinned state and behaves as an optically homogeneous medium. The craze stands out sharply against the surrounding normal polymer material.

STERNSTEIN et al. have investigated the conditions under which deformation through craze formation (normal yielding) occurs [111], [112]. The results show that crazes can form only in the vicinity of a positive isotropic stress component (stress invariant I_1): $I_1 = \sigma_1 + \sigma_2 + \sigma_3 > 0$. However, even when this condition is fulfilled, crazes only occur when the maximum principal normal stress exceeds a time- and temperature-dependent critical value σ_{crit}.

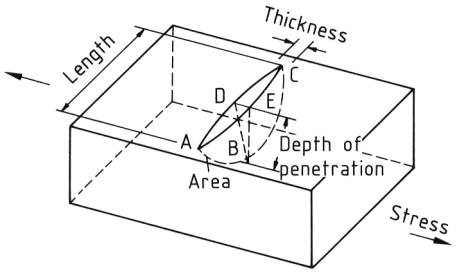


Figure 28. Schematic illustration of a craze AC = length; DE = thickness; EB = depth of penetration

The formation of flow zones in impact-resistant two-phase or multiphase systems is of great engineering importance. When flow zones develop in these systems, they act as energy absorbers. All analyses are based on the assumption that elastomer particles in such a system act as stress concentrators under mechanical load, because their elastic modulus is low compared to that of the matrix. BOHN has further shown that the soft phase must have a sufficiently uniform distribution and must be sufficiently cross-linked and grafted in order to produce and maintain the special dilatation stress state in the hard matrix on cooling [113].

Fracture Morphology of Plastics. So many factors affect fracture morphology in plastics that only a few examples can be discussed here. Brittle plastics exhibit a behavior similar to that studied in detail by SMEKAL for inorganic glasses. According to those findings, the fracture front advances radially in all directions from a primary notch site. The primary notch is surrounded by a smooth surface, the "mirror," which is bounded by a semicircle. SMEKAL states that the transport of heat in the initial phase (i.e., in the "mirror region" of the fracture) is an essential feature of the fracture phenomenon. This region of the fracture, which is traversed at a low velocity, is therefore referred to as the thermal phase of the fracture. The remainder of the process occurs at a very high fracture velocity (i.e., athermally), and this phase is called the athermal phase of the fracture. The fracture mirror and the athermal phase are also observed in brittle plastics, especially in fracturing after high strain rates (Fig. 29) [114]. The fracture mirror often displays periodic fine structures that can yield information about the rate of loading. In ductile materials, fissured morphologies are observed; these depend on, among other factors, orientation, stress distribution, and rate of loading.

A point of special interest is the fracture morphology of fiber-reinforced plastics. Fracture surfaces are observed by optical microscopy or by scanning electron microscopy at a magnification of 60 – 24 000.

Measurement of Fracture Behavior. Instrumental investigation of fracture behavior takes place in the context of steady-load and

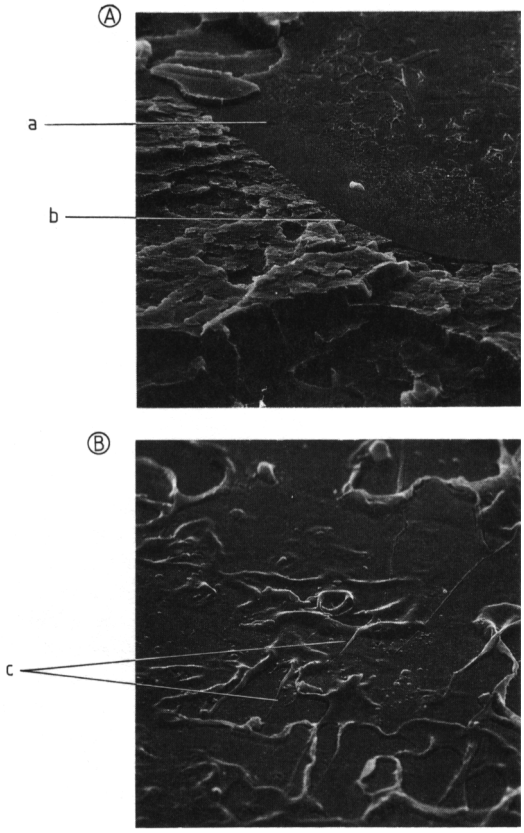


Figure 29. A) Boundary between thermal (mirror) and athermal fracture phases after impact tensile loading of polystyrene, [114] (scanning electron micrograph, ×180); B) Spickle structure in the mirror, with typical "thermal threads" (×1800) a) Mirror; b) Thermal – athermal phase boundary; c) Thermal threads

fluctuating-load mechanical tests, both short- and long-term, with tensile, compressive and bending loads. These tests are performed at moderate to low strain rates.

A special test procedure has been developed to study deformation and fracture behavior at high strain rates (impact behavior). To a large extent, plastics owe their great versatility to high impact strength combined with other qualities. Hence, many studies have dealt with the property of impact strength. The translation from values measured on test specimens to in-service performance (the behavior of moldings and semifinished products in a variety of applications) is more difficult for impact strength than for the mechanical properties already discussed.

For example, the influence of viscoelastic behavior can be estimated only in the quasi-linear range. At the extreme loads, required for evaluating performance under impact loading, which usually far exceed the linear range (especially for unreinforced materials), other tests must be used. These include impact flexural and impact tensile tests, both performed with notched-bar specimens. Studies are also carried out with multiaxial loading modes.

As in low-strain-rate tests, the stress – strain diagram or the deformation energy absorbed up to a certain damage level (usually to fracture) is determined.

Numerous standardized tests have been developed for this purpose. In general, however, they cannot be assessed in terms of how well they correlate with in-service performance under impact and shock loads.

The methods used to obtain impact values for inclusion in the table of reference values were chosen to satisfy a number of criteria, one being that the test should show a distinct difference in energy absorption between ductile fracture (in which the specimen is merely cracked) and brittle fracture.

This condition is met, for example, by the Izod notched-bar toughness test or the Charpy impact bending test; see Figure 30 [115–117]. Notched and unnotched specimens can be tested by either method. Both belong to the class of flexural impact tests in which the impact energy absorbed up to failure is measured. For reasons of measurement technique, no determination of the stress – strain relationship is included in this test. The V-shaped notches used have a 45° angle between sides and various notch root radii. Impact tensile tests are performed on plastics along with the flexural impact test,

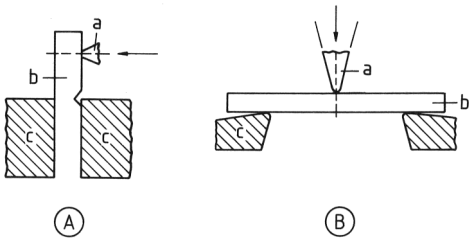


Figure 30. Setups for impact bending test A) Izod test, notched specimen; B) Charpy test, unnotched specimen a) Striker; b) Specimen; c) Clamp or support

especially when the specimens in the flexural impact or notched-bar flexural impact test do not fracture. Notched and unnotched specimens are used in the impact tensile test as well.

The notch action at the root of the notch is described by the theoretical stress concentration factor $a_k = \sigma_{max}/\sigma_n$, where σ_n is the nominal stress with no notch and σ_{max} is the maximum stress in the direction of loading at the root. For a notched flexural impact specimen (0.25-mm radius at notch root), a_k is ca. 2.4, and for a double-notched impact tensile specimen (DIN 53 448, 0.25-mm radius at notch roots), ca. 2.9 (values determined by photoelastic examination [114]). Thus the notch action is roughly comparable in both specimens even though the notch radii are very different. Stress distribution outside the notch region, however, are quite dissimilar.

In specimens with marked partly plastic behavior, the decrease in a_k from blunter to sharper notches is not very great. This is due to the fact that despite the large stress concentration factors, the partly plastic behavior prevents the maximum stress at the notch root reaching the high value predicted by elasticity theory [118].

Flexural impact and impact tensile tests are supplemented by a technique employing biaxial impact loading: the falling-weight impact test. A circular or square flat specimen is laid on a ring-shaped support and loaded in the center by the impact of a falling weight. Experimental setups of this kind are described in [119–121]; they are also used for investigating the impact behavior of films and finished or semifinished parts. Given a well-defined criterion of failure, the damaging energy at which a given percentage of specimens fail can be determined. Results are evaluated either statistically (probit method [122]) or by a staircase technique (up-and-down method [123]).

Methods that allow the plot of applied force versus deformation to be continued up to failure have greater predictive power than the impact and falling-weight tests described here, which yield the damaging energy or the proportion of damaged specimens.

In addition to the damaging force and deformation, these tests also measure the damaging energy for tensile loading or for biaxial loading by impact on the centrally loaded plate [124]. The test apparatus, which features automated performance and evaluation, is complicated.

Table 5. Damaging work W_s per unit thickness d, damaging force F_s, and damaging deformation l_s for several plastics, after DIN 53 443 Sheet 2

Product (abbreviations from DIN 7728)	W_s/d, Nm/mm	F_s, N	l_s, mm
PC	5500	9000	23
ABS	1450	3600	16
PS	30	300	3
PE	1550	2600	20
PVC-HI	3300	5400	18
PF Type 31	30	440	3

The devices for tensile loading are called high-speed tensile testers. Combined machines for high-speed tensile tests and impact penetration tests at high rates of deformation are also available. These devices have a maximum rated tensile force of 100 kN, with an impact velocity up to 20 m/s. The force is measured with piezoelectric pickups, and the strain is measured with inductive strain gauges or high-resolution precision laser systems [125].

Interpretation of results from the biaxial plate-loading test is difficult, chiefly because the state of orientation in the specimen varies from one plane layer to another. Apart from taking extreme orientation distributions into account, apparent anomalies in impact penetration test results can be explained only by analyses based on elasticity theory (e.g., the theory of sheets) [126].

Because of these difficulties, the results of impact tests are not generally regarded as material values.

If specimen fabrication and testing conditions are controlled very carefully, however, the tests are suitable for preliminary materials selection and especially for development in the field of impact-resistant plastics. Table 5 lists impact penetration test results for several plastics.

2.1.6. Control of Mechanical Properties through Orientation, Internal Stresses, and Morphology

The term orientation refers to the alignment of structural elements (i.e., polymer chains or chain segments, crystalline regions, or domains). Orientation takes place in the initial production process or results from subsequent drawing and is frozen in on transformation to the solid state, with simultaneous occurrence of

disorientation processes. A material usually exhibits greater strength and less elongation in the orientation direction. Multiaxial states of orientation in molded parts can often influence mechanical behavior in an unforeseen way. Orientation is used in the production of high-strength monofilaments (fibers and wires) and biaxially drawn (and thus biaxially oriented) films with high impact penetration strength.

Orientation is of particular importance in the fabrication of film ribbons, where drawing ratios up to 1:15 are used. The anisotropy of the strength in the longitudinal and transverse directions, resulting from the orientation, can be so great that the ribbons split when loaded transversely. This splitting tendency is desirable in string and yarn. If splitting is to be avoided, the molecules must be oriented slightly transverse to the drawing direction during processing [127].

Molecular orientation in polymers can be determined by wide-angle X-ray diffraction (limited to polymers that are more than 10 % crystalline); birefringence (the second moment of the distribution is measured); linear dichroism (suitable for determining the amorphous and crystalline orientations separately); acoustic velocity (simple method for fibers); or nuclear resonance. An approximate measure of orientation is the shrinkage at high temperature, which results mainly from the prior molecular alignments and is thus an entropy-elastic effect. In contrast, energy-elastic effects play little part in shrinkage. Figure 31 shows how orientation (characterized by birefringence) influences the notched-bar impact bending strength.

Molded plastic parts can exhibit internal stresses, which may significantly affect mechanical properties. According to WÜBKEN [128], the three main causes of internal stresses in amorphous moldings are cooling stresses, stresses due to the expansion of parts ejected from the mold under pressure, and flow-related Hooke's law stresses. Deformations resulting from internal stresses are energy elastic and therefore very small in comparison to those associated with orientation. The internal stresses in a molding are at equilibrium. If, however, the stresses are not at equilibrium (e.g., on demolding), the injection-molded part deforms until equilibrium is reached. Internal stresses in components subject to compressive loads, such as pressure piping and pressure vessels, require special

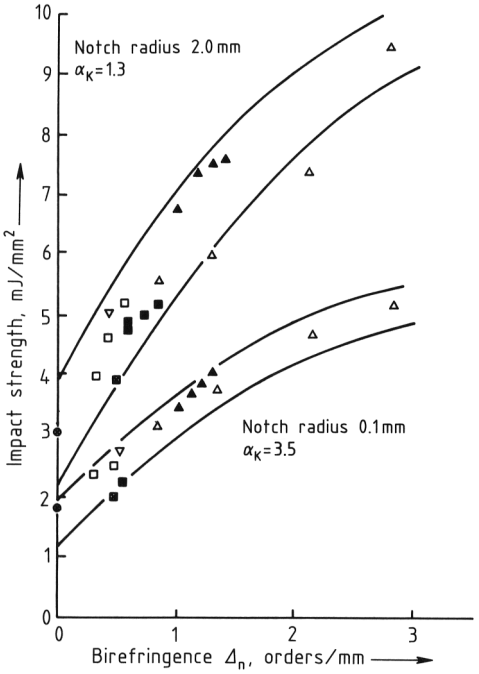


Figure 31. Notched-bar bending strength of polystyrene (specimen with double V notches) as a function of birefringence and notch geometry

attention. The addition of internal stresses to the multiaxial stresses produced by external forces can, under unfavorable conditions, lead to a reduction in the design creep strength. Internal stresses can be determined by deformation measurements on components [128]. A quasi-nondestructive test based on hardness measurements has been described [129] (see Section 2.7.2 for stress cracking).

Of the morphological states that influence mechanical properties, the only ones discussed here are crystallinity and, for amorphous plastics, particle structure. The partially crystalline state and the associated superlattice structures are discussed above (see Section 1.2). Higher crystallinity means higher rigidity and yield stress. Because crystallinity is correlated with density, measuring the density provides a simple criterion for evaluating the crystalline fraction.

Partially crystalline superlattice structures called spherulites (for their spherical shape) are formed when crystallization takes place from solution and especially from the melt. The spherulite diameter depends on the chemical structure of the macromolecules and the

thermal prehistory. Polyethylene, for example, crystallizes mainly in fine spherulites having diameters of 5 – 200 μm (depending on the rate of cooling), whereas polypropylene and poly-1-butylene cooled at similar rates may form spherulites up to several millimeters in diameter.

In polymerization processes, spherulite size is often controlled by addition of nucleating agents in order to achieve desired properties, such as high rigidity or impact strength.

Rigidity (modulus, yield stress) generally increases with increasing spherulite radius, whereas toughness decreases, although exceptions can be found to this rule. Domain structures, which are especially marked in polymer blends and graft and block copolymers, also exhibit surprising engineering properties. The flow behavior, rigidity, and impact strength are improved.

Impact-resistant thermoplastics, which include, among others, grades of polystyrene and poly(vinyl chloride) (PVC), consist essentially of a continuous hard component (polystyrene, PVC) in which a soft component [e.g., polybutadiene, poly(vinyl acetate)] is dispersed in the form of domains. The number, shape, and distribution of the domains, as well as the structure of the matrix – domain phase boundaries, govern the properties of the blend. Other domain structures of engineering interest are found in block copolymers, such as those of butadiene and styrene [130].

If only a reduction in rigidity is required, and no special demands are imposed on the energy absorption in impact loading, internal or external plasticization can be used. Internal plasticization is the copolymerization of two compatible monomers whose glass transition temperatures differ greatly.

External plasticization is a solvation process in which low molecular mass plasticizers are bound to polymer macromolecules.

2.1.7. Reinforced and Filled Plastics

A reinforced plastic is a composite material with a plastic matrix. Such a composite has an elastic modulus and strength, in at least one direction, that far exceed those of the unreinforced matrix. Particle-reinforced composites (e.g., with talc, powdered chalk, powdered minerals, short fibers, or glass spheres) are distinguished from fiber-reinforced composites (e.g., with glass, aramid, or carbon fibers). Particle-reinforced thermoplastics have the advantage that they can be injection molded. The composites exhibit greatly improved rigidity, strength, and heat deflection temperature. Moldings exhibit reduced shrinkage and thermal expansion. Curable molding compounds also include particle-reinforced composites, some of which are free-flowing materials that can be injection molded.

Fiber-reinforced materials most commonly have thermoset matrices of unsaturated polyester (UP) or epoxy (EP) resin. An important class is glass-fiber-reinforced plastics. The various reinforcements (rovings, filaments, mats) have been standardized [131]. For further information and properties, see [132].

Reinforced thermosets tested in the longitudinal direction have moduli of ca. 30 000 N/mm^2 and tensile strengths of 700 N/mm^2; thermoplastics with carbon-fiber reinforcement (50 – 60 wt% carbon fiber) exhibit tensile strengths of 270 – 280 N/mm^2. The high carbon fiber content, however, lowers the volume resistivity to 10 – 100 Ω · cm.

Additives and fillers are also used to modify plastics properties. Only a few examples can be mentioned here. Carbon black lowers resistivity (affording safety against electrostatic charging) and also reduces the coefficient of friction. Graphite, molybdenum disulfide, and carbon fibers lower the dynamic coefficient of friction. Metal powders (bronze, chromium – nickel steel) are used in bearing materials, valves, piston rings, and gaskets. Aluminum flakes provide electromagnetic shielding.

2.2. Acoustic Properties and Their Testing

Because most plastics have relatively high mechanical loss factors (at least two orders of magnitude higher than most metals), they can be used to attenuate solid-borne sound. This application is undoubtedly the most interesting in the field of acoustics, especially for noise suppression. Dimensionally stable plastics with high internal damping (i.e., high mechanical loss factor) include polypropylene and polyamide. Examples of acoustic damping applications are

covers, gears, and rollers made of these materials. Unfortunately, glass-fiber reinforcement greatly lowers the loss factor, so that glass-fiber-reinforced plastics are not well suited to sound attenuation. The hum generated by metal plates can be suppressed by viscoelastic coatings. These are special amorphous thermoplastics, in particular vinyl acetate copolymers, or two-component systems based on polyurethane or epoxy resins. These coatings are improved further by active fillers such as vermiculite, a micalike clay material, or graphite.

To assess the damping properties of such coatings, the dynamic flexural rigidity and the bending wave rate must be known. These quantities are derived from the dynamic modulus of elasticity, which in turn is determined in flexural vibration tests performed at audio frequencies [83], [84].

Figure 32 shows curves of loss factor versus temperature for a 1-mm steel sheet with a 2-mm sound-deadening material and also for a steel – plastic – steel laminate (i.e., a symmetrical composite). Undamped steel sheet has a loss factor $d \approx 0.0001$; the maximum with heavy edge damping is 0.001. The laminates exhibit d values up to 1.0.

Homogeneous solid plastics do not attenuate airborne sound because even the lightest solids do not satisfy the requirement of wave impedance matching between air and absorbing medium. Plastics have a wave impedance several orders of magnitude greater than that of air. To suppress airborne sound, therefore, open-pored foams or fibrous materials are employed. Absorption takes place by friction between air particles and components of the skeleton. Open-pored foamed plastics used in this absorbing role include

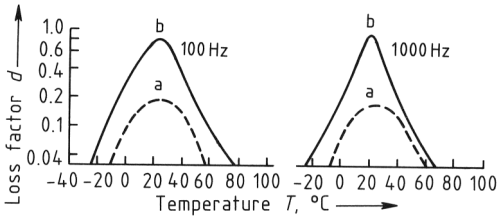


Figure 32. Mechanical loss factor d as a function of temperature T at 100 Hz and 1000 Hz for steel – plastic composite sheets a) 1-mm steel sheet with 2-mm sound-deadening material; b) Steel – plastic – steel composite (0.5 – 0.2 – 0.5 mm)

foamed urea – formaldehyde resin and nonrigid PVC foam. Foamed polystyrene slabs, even though they have closed pores, can be used for acoustic purposes if the surface is perforated.

If solid-borne sound is to be blocked (as opposed to attenuated), soft materials of low dynamic flexural rigidity are required. Low-frequency vibrations from machinery cannot, however, be blocked with plastics; instead, rubberized metal elements, steel springs, or air springs are employed.

Another application represents a far more important use of plastics in blocking solid-borne sound: the suppression of footfall noise by so-called floating floors. Acoustic requirements for buildings [133] are met by insulating slabs based on expanded-bead polystyrene foam, whose resilience is enhanced by postprocessing.

Plastics, even filled materials (e.g., with expanded glass or clay), are not very suitable for blocking airborne sound. They are not considered for this purpose by builders, because this type of soundproofing always requires heavy masses with the lowest possible flexural rigidity. Plastics with heavy fillers (PbO or $BaSO_4$) do meet the mass requirement and also have the high coincidence cutoff frequency needed for soundproofing [84]. Heavy, nonrigid plastic films are used in automobiles and machinery.

2.3. Thermal Properties and Their Testing

A knowledge of the thermodynamic properties of plastics – and, especially, of their temperature dependence – is important for the economics of production and for the quality and functioning of products. Relevant data include specific heat, specific enthalpy, thermal conductivity, thermal diffusivity, specific volume, compressibility, and coefficients of thermal volume and linear expansion. With this information, the processor and the user can calculate the heats needed for processing, mixing temperatures, volume changes on cooling, shrinkages during and after processing, and temperature-related dimensional changes in semifinished products and moldings. Furthermore, several of these quantities must be known if the reactions and internal changes taking place in plastics are to be understood.

2.3.1. Specific Heat

The specific heat of a plastic is not always an unequivocal function of temperature. Crystalline and amorphous polymers do have comparable specific heats at very low temperature, but sizable differences occur in the vicinity of transformations (e.g., glass transition, crystallization, and melting). The specific heat in these ranges depends on the state (e.g., the degree of crystallization) of the polymer and thus on its thermal prehistory [134], [135]. If the specific heat at constant pressure c_p is known, the enthalpy differences ΔH between the initial T_0 and final temperatures T can be calculated by integration:

$$\Delta H\,(T)_{T_0} = H_T - H_{T_0} = \int_{T_0}^{T} c_p(T)\,\mathrm{d}T$$

Enthalpy depends on pressure, and because of the high pressures that frequently occur in plastics processing this dependence must be taken into consideration. Figure 33 A shows schematically the specific heat as a function of temperature for amorphous thermoplastics. The steplike rise in the glass transition range is characteristic. Partially crystalline thermoplastics are distinguished by the fact that an additional enthalpy, the heat of fusion, must be supplied to melt crystalline regions. The heat of fusion results in a maximum in the curve of specific heat versus temperature for partially crystalline plastics, as shown schematically in Figure 33 B. With regard to the temperature dependence of specific heat and enthalpy, see [136], [137].

The enthalpy of the uncured starting product is of interest for the energy balance in the processing of thermosets.

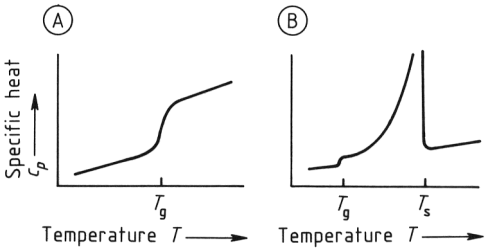


Figure 33. Temperature dependence of specific heat
A) Amorphous thermoplastics; B) Partially crystalline plastics T_s = crystallite melting point

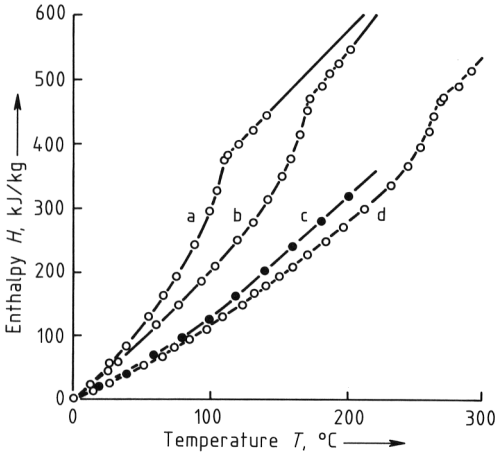


Figure 34. Enthalpy curves for some thermoplastics
a) Low-density polyethylene; b) Polypropylene; c) Polystyrene; d) Poly(ethylene terephthalate)

Measurements of the specific heat of plastics from nearly 0 K to ca. 600 K can be performed only with adiabatic calorimeters. A very simple, quick, and sufficiently accurate measurement can, however, be carried out with dynamic differential calorimeters [138]; the technique is called DSC (differential scanning calorimetry). A review of differential scanning calorimeters can be found in [139].

Not only does DSC yield the same results as adiabatic calorimetry, it also makes new types of measurements possible. Examples are the detection of glass-transition steps, exothermic crystallization, melting, and determination of stabilizer content [140].

Differential scanning calorimetry also permits indirect determination of, for example, crystalline content, degree of cross-linking, degree of curing, thermal stability, and plasticizer content. Studies of reaction kinetics are possible as well [141–143]. Figure 34 shows enthalpy curves for several commercially important thermoplastics.

2.3.2. Thermal Conductivity

Plastics are poor heat conductors, because they have virtually no free electrons available for conduction mechanisms such as those in metals.

For amorphous thermoplastics at 0 – 200 °C, the thermal conductivity lies between 0.125 and 0.2 W m^{-1} K^{-1}. Partially crystalline

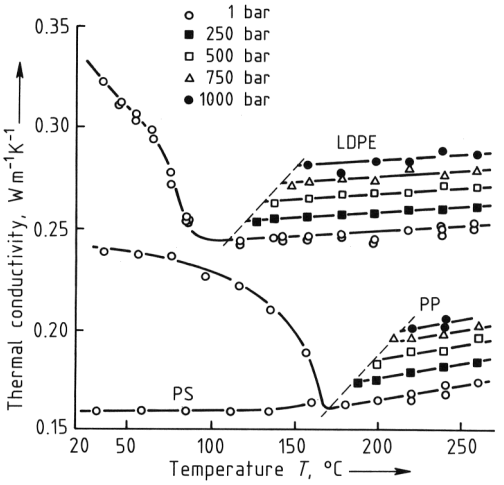


Figure 35. Thermal conductivity of low-density polyethylene, polypropylene, and polystyrene as a function of temperature [144]

thermoplastics, in contrast, have a higher thermal conductivity, because the ordered crystalline regions conduct better than the amorphous regions. As melting of the crystalline regions progresses, the thermal conductivity approaches that of the amorphous regions. Figure 35 plots the thermal conductivities of branched polyethylene, polypropylene, and polystyrene as functions of temperature and pressure [144]. Branching has a marked effect on thermal conductivity; molecular mass and molecular-mass distribution have no influence.

As cross-linking increases (thermosets, elastomers), thermal conductivity rises, because van der Waals bonds are progressively replaced by valence bonds with their greater molecular thermal conductivity. Moreover, the changes and transformations characteristic of polymers are less strongly marked in curves of thermal conductivity (and other thermal values) at higher degrees of cross-linking.

At content below 5 %, additives (air or even metals) do not greatly influence thermal conductivity. For higher filler contents, numerous mixture rules have been developed. They are, however, not universally applicable. The most reliable is still the geometric mean model of PRINGELHOF and THRONE, which was rediscovered by AGARI and UNO [145] and confirmed for many mixtures. According to this model, the logarithmus of the thermal conductivity increases linearly with increasing volumetric filler content:

$$\log\lambda = V \cdot \log\lambda_f + (1 - V) \cdot \log\lambda_m$$

where λ is the thermal conductivity of the mixture, λ_f the thermal conductivity of the filler, λ_m the thermal conductivity of the matrix, and V the filler content in vol %. Oriented plastics and plastics with oriented fillers, whose thermal conductivities differ from that of the matrix, exhibit anisotropic thermal conductivity.

For commercial closed-cell foamed plastics [polystyrene, poly(vinyl chloride), and phenolic resin], the thermal conductivity lies between approximately 0.035 and 0.042 W m^{-1} K^{-1} .

The thermal conductivities of solids are usually measured under steady-state conditions with the Poensgen two-plate apparatus [146]. A setup described by FRITZ and KÜSTER is suitable for the investigation of foamed materials [147]. A very simple device for determining the thermal conductivity of foamed materials with an accuracy sufficient for practical purposes is described in [148].

Two quantities derived from thermal conductivity are important in plastics processing. Cooling takes up a large part of the cycle time in injection molding, and a quantity called the thermal diffusivity a is used in calculating this process: $a = \lambda/c\varrho$, where λ is thermal conductivity, c is specific heat, and ϱ is density. Thermal diffusivity has the units m^2/s or m^2/h.

The second important quantity is the heat penetration coefficient $b = (\lambda\ c\ \varrho)^{1/2}$, expressed in J m^{-2} $s^{1/2}$ K. This coefficient determines the initial contact temperature T_c (in Kelvin) when two bodies A and B come in contact: $T_c = (b_A\ T_A + b_B\ T_B)/(b_A + b_B)$. The formula indicates, for example, the temperature that prevails at the mold wall when a hot plastic mass flows into a cooler mold and before heat removal by the cooling system becomes effective [149].

2.3.3. Thermal Expansion

The linear coefficient of thermal expansion lies between ca. 0.6×10^{-4} and 2.3×10^{-4} K^{-1} for thermoplastics or 0.2×10^{-4} and 0.6×10^{-4} K^{-1} for thermosets (in the service temperature range for each case).

The linear coefficient α can be measured directly with a dilatometer (e.g., a quartz-tube

dilatometer as specified in ASTM D 696) or, more accurately, against a reference material with a differential dilatometer.

This coefficient can also be derived from measurements of the specific volume or of the volume coefficient of thermal expansion β. The approximate formula is $\alpha \approx \beta/3$.

The specific volume V is also measured in dilatometers [150–153].

If the specific volume is plotted against temperature for amorphous thermoplastics, the curve exhibits a kink near the glass-transition temperature. The expansion coefficient, which is the first derivative with respect to temperature, thus has a discontinuity (a step). This phenomenon can be interpreted with Eyring and Hirai's vacancy theory of liquids: As the temperature rises, the equilibrium vacancy concentration begins to increase at the glass transition. This increase manifests itself as an increase either in the free specific volume or in the slope of the specific volume–temperature curve. These effects are more marked for amorphous polymers than for partially crystalline ones, because the thermal behavior of partially crystalline materials is governed chiefly by the melting of crystallites.

At the onset of melting (i.e., as the structure begins to break down), the curve of specific volume versus temperature rises faster than linearly. After melting is complete, the curve becomes linear again but has a steeper slope than before melting; see Figure 36 [151].

On cooling from the melt, however, these discontinuities in the curves of specific volume versus temperature show a dependence on cooling rate. Figure 37 illustrates schematically what happens with amorphous materials. The vacancy concentration is somewhat lower in slow cooling than in fast cooling. The various branches correspond to states differing in vacancy concentration. Among the consequences of this behavior is that V versus T curves are measured only with increasing temperature because the heating curve cannot be reproduced on cooling.

p – V – T *Diagrams.* Because plastics are processed over a wide range of temperatures and pressures, the variation of the specific volume not only with temperature but also with pressure must be known. The literature describes several methods for investigating the relationship of p, V, and T [154–159].

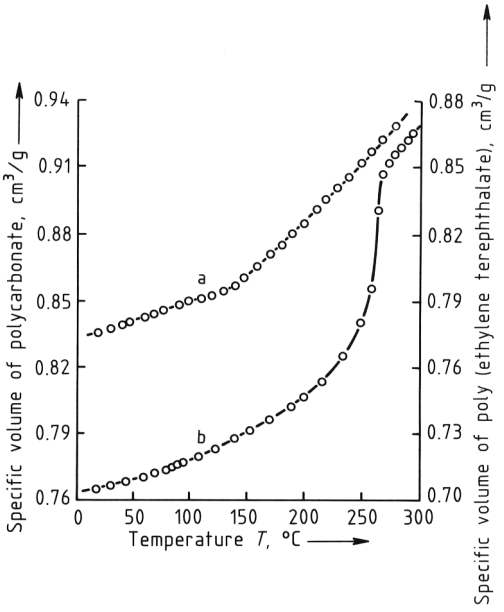


Figure 36. Specific volume as a function of temperature a) Polycarbonate, $\varrho_{20} = 1.2$ g/cm^3 (example of an amorphous product); b) Poly(ethylene terephthalate), $\varrho_{20} = 1.4$ g/cm^3 (example of a partially crystalline product) [154]

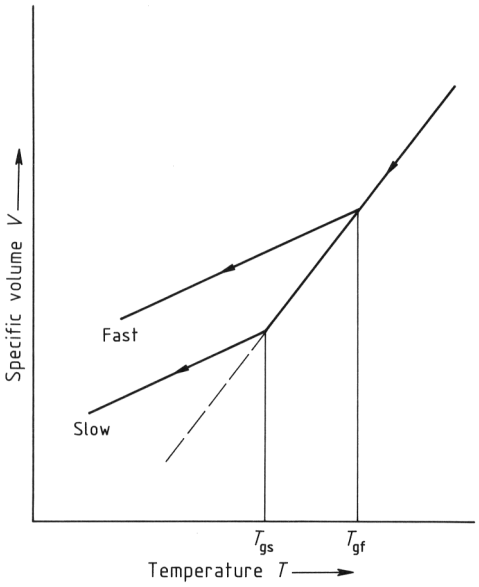


Figure 37. Temperature curves of specific volume for fast and slow cooling of an amorphous plastic T_{gs} = glass transition temperature for slow cooling; T_{gf} = glass transition temperature for fast cooling

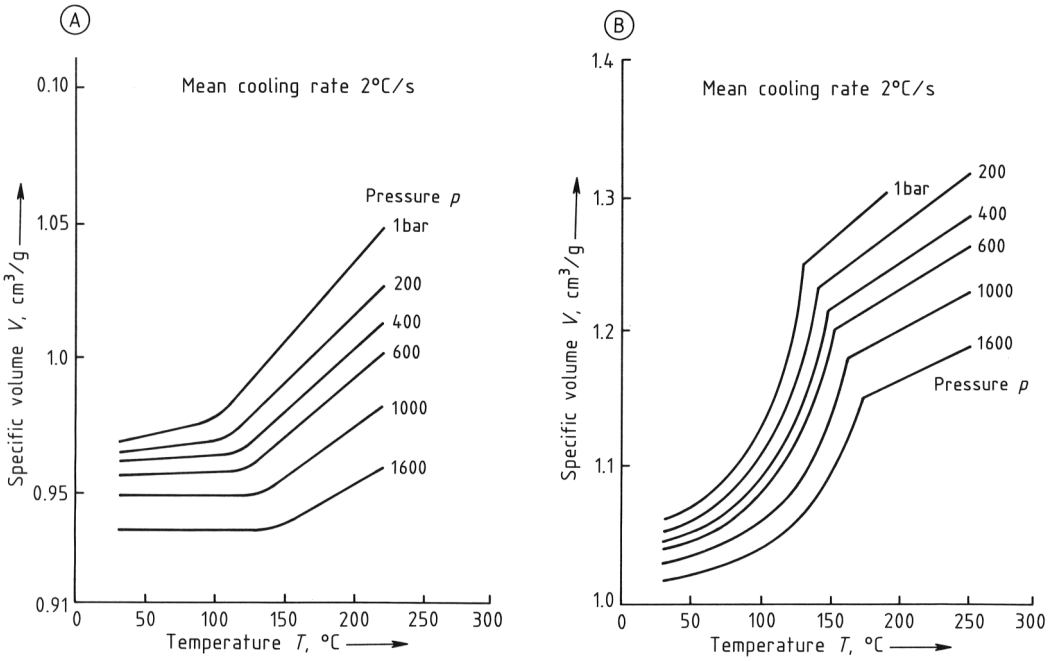


Figure 38. *p–V–T* diagrams A) Polystyrene; B) Polyethylene

In some methods, the specimen is placed in a cylinder and compressed from one or both ends by pistons. In another, the specimen is under hydrostatic pressure in a mercury-filled piezometer located in a pressure vessel filled with silicone oil. Figure 38 shows the $p-V-T$ diagram of an amorphous plastic (polystyrene) and of a partially crystalline plastic (high-density polyethylene). As in the V versus T plots, the shape of the curve depends on the cooling rate.

2.4. Electrical Properties and Their Testing

Plastics owe their great variety of uses in electrical and electronic devices to their combination of electrical properties, rational fabrication methods, and widely variable engineering properties.

2.4.1. Insulating Properties

Volume Resistivity. Plastics used as electrical insulators have volume resistivities of 10^{10}–10^{19} Ω cm. Substantially lower values can be achieved with additives such as carbon black, graphite, carbon fibers, and metal powders or flakes, making possible a reduction in static charging due to high resistance, which can lead to safety problems in some instances (e.g., when flammable liquids are transferred from plastic vessels, when plastic flooring is employed in spaces where an explosion hazard exists, and in mining). In general, no hazardous charging occurs at resistivities of less than 10^{10} Ω cm.

Charge transport in plastics occurs mainly by ions and to only a minor extent by electrons. Whereas Ohm's law holds rigorously for metals, insulators not only have a charge carrier current but also an internal charge current resulting from polarization of the plastic. This internal charge current builds up a space charge, which decays on a scale of hours. The volume resistivity ϱ_D is a function of temperature, having the form $\varrho_D = \varrho_0 \exp(b/T)$, where ϱ_0 and b are constants and T is absolute temperature. Figure 39 shows how the volume resistivity of polypropylene films depends on temperature.

Surface Resistivity and Resistivity between Plugs. Because the insulation surface usually makes a large contribution to leakage, surface resistivity is also defined. This quantity does

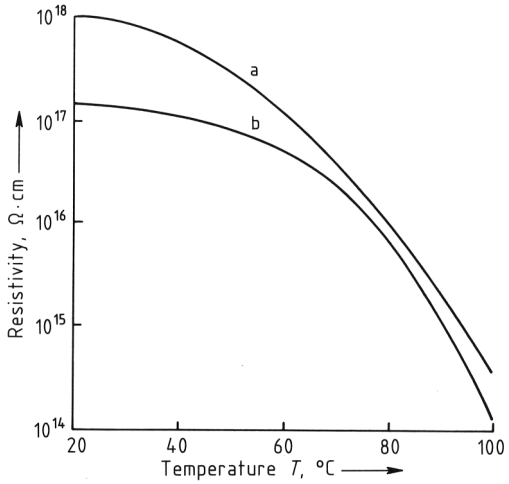


Figure 39. Resistivity of polypropylene films as a function of temperature a) Polypropylene; b) Biaxially drawn polypropylene

not, however, have the predictive power of volume resistivity, which is a material-specific value.

In the case of inhomogeneous insulators such as laminated composites or plastics containing electrically conducting fillers such as carbon black, the insulator resistance is often determined between two metal pins inserted into the material 25 mm apart (resistivity between plugs). This measurement includes an unknown contribution from surface resistivity.

Resistivity measurements are current – voltage measurements, preferably carried out at 100 or 1000 V d.c. with standard electrodes [158].

2.4.2. Dielectric Properties

Certain formal analogies exist between the relaxation behavior of viscoelastic bodies under mechanical loading, which can be described in terms of a complex modulus, and the dielectric behavior of plastics, which is characterized by a complex dielectric constant (permittivity) $\varepsilon^* = \varepsilon'(\omega) - i\,\varepsilon''(\omega)$, where ω is angular frequency, $\varepsilon'(\omega)$ the dielectric constant (permittivity), and $\varepsilon''(\omega)$ the dielectric loss factor. The ratio $\varepsilon''/\varepsilon'$ is equal to the tangent of the phase angle between the voltage and the current: $\tan\delta = \varepsilon''/\varepsilon'$.

Just as viscoelastic behavior in the mechanical case can be simulated by spring – damper

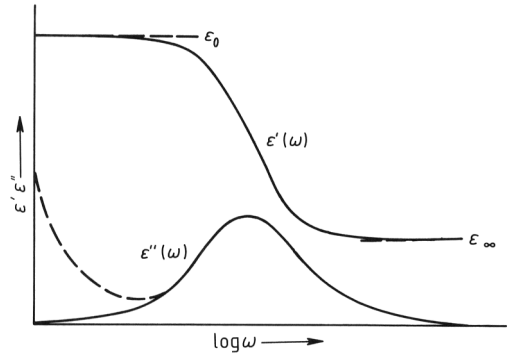


Figure 40. Schematic curves of $'_r$ and $''_r = '_r \tan\delta$ versus frequency for high-polymer electrical insulators

models, dielectric behavior can be described in terms of electrical networks. The analogy is, as already mentioned, merely formal; it has to do with the fact that both phenomena come under a common theory, the theory of the elastic aftereffect (memory effect), advanced as early as 1893 by WIECHERT and extended by WAGNER in 1913 to the theory of the dielectric aftereffect.

The mathematics of viscoelastic and dielectric behavior is the same as that of the magnetic aftereffect, linear network theory, and linear integral equations. Figure 40 illustrates schematically how the dielectric values for high-polymer electrical insulators depend on the frequency of the applied alternating field. Here ε' is the relative permittivity ε'_r, which is a measure of the polarization attainable at any frequency: At low frequencies, the molecules have enough time to orient themselves in the field, so that ε' takes on its largest value. At higher frequencies, the field changes so rapidly that the dipoles can no longer follow and ε' declines to smaller values. The value of ε' falls off substantially when the period of the field is of the order of the dipole relaxation time. The value ε'' is a measure of the energy transformed in one oscillation period; this energy is extracted from the field and converted to heat as the dipoles orient themselves. This quantity passes through a maximum when the period of the field is equal to the relaxation time; it approaches zero at very low and very high frequencies.

Because $\varepsilon''_r/\varepsilon'_r = \tan\delta$, $\varepsilon''_r = \varepsilon'_r \tan\delta$. The product $\varepsilon'_r \tan\delta$ is also called the dielectric loss factor.

The measured ε''_r at low frequencies can be distorted by a metrological effect not related to

polarization: the d.c. conductance, whose contribution to the total loss decreases with frequency (dashed curve in Fig. 40).

If plastics are to be heated in a high-frequency (HF) field, the loss factor must be made as large as possible (HF welding of polar plastics). In insulation, small tan δ values are desirable to minimize the evolution of heat. When polar plastics (e.g., PVC blends) are used in cable manufacturing, the loss factor maximum must be shifted to the highest possible temperature so that thermal breakdown will not be promoted at service voltages.

In nonpolar substances, an external a.c. field brings about polarization only by deforming the electron distribution. This displacement of the charge carriers is, however, independent of frequency, so that ε_r remains virtually constant over a wide frequency range. At very high frequencies (in the infrared), ε_r approaches the square of the optical refractive index.

The Clausius – Mosotti equation holds for nonpolar substances under certain conditions. This equation

$$\frac{\varepsilon - 1}{\varepsilon + 2}\frac{M_r}{\varrho} = \frac{4\pi}{3}N\alpha$$

describes the relationship between the dielectric constant and the density, where ε is the dielectric constant, N is Avogadro's number, M_r is molecular mass, ϱ is density, and α is molecular polarizability.

The temperature curve of tan δ for nonpolar straight-chain polymers generally shows two maxima of the loss factor: the α absorption (e.g., due to motion of the CH_2 dipoles in polyethylene) and the γ absorption (e.g., due to relaxation in crystalline regions in PE). Branching gives rise to a third absorption region, β absorption, which lies between the α and γ absorptions in the tan δ curves; see Figures 41 A and B.

Often, the loss factor and dielectric constant must be measured over a wide range of temperature and frequency (from a few hertz to more than 10 GHz, although most measurements are made between 50 and 100 MHz). The dielectric constant ranges from somewhat over 1 for foamed plastics up to 20 or more. Loss factors range from 3×10^{-5} for polyethylene with no residual catalyst to 0.1 or higher.

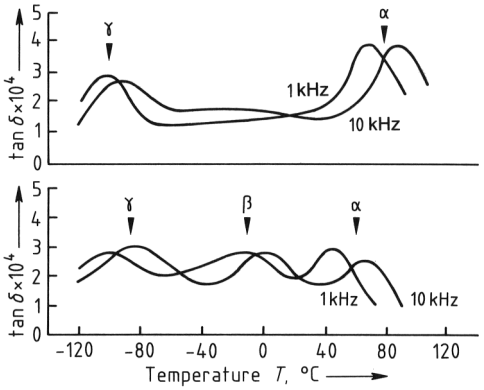


Figure 41. Plot of tan δ versus temperature at 1 and 10 kHz for polyethylene A) High-density polyethylene; B) Low-density (branched) polyethylene

Materials with anisotropic structure may display anisotropic dielectric properties. Measurement is complicated by the variety of methods needed to cover the wide frequency range. Up to about 10^8 Hz, however, only two measuring principles are needed. In general, the circuit used must contain coils, capacitors, and resistors. From the audio frequency range up to 100 kHz, bridge circuits are used without exception. In a.c. measurements, at least one branch of the bridge, not containing the specimen, must have a blind component, either an inductance or a capacitance. Examples of such bridges are the Schering type and the transformer measuring bridge. Automatic, self-balancing transformer bridges, which are unexcelled for quick routine measurements, are now available.

The range from 10 kHz to 100 MHz corresponds roughly to radio frequencies. Measurements in this range are performed by tuned-circuit methods (resonance techniques with tank circuits and a modified capacitance standard).

Above 10^8 Hz, different principles are employed. They include measuring-line methods and techniques with capacitively loaded coaxial resonators.

For further information on measuring methods see [159–162]. Table 6 lists dielectric values at 50 Hz and 20 °C for a number of plastics.

2.4.3. Dielectric Strength

Current theories of breakdown in a solid dielectric start with the assumption that

Table 6. Dielectric properties of some plastics at 20 °C and 50 Hz (mean values)

Product (abbreviations from DIN 7728)	Dielectric constant ε	Loss factor tan δ
PF 31.5	6 – 8	0.4
UP resins	3 – 3.8	0.003 – 0.01
EP resins	3.2 – 4.8	0.002 – 0.006
PE	2.28 – 2.34	0.0005
PP	2.27	0.0005
PVC, rigid (E)	3.8 – 4.3	0.03
PVC, rigid (S)	3.4 – 3.7	0.02
PVC/DOP 60:40	7.5 – 8.0	0.08
PA 6	4.3	0.03
PS	2.5	0.0003
PTFE	2.1	0.0001

breakdown is linked with the free electrons that are always present, which are set in motion by the electric field. Part of the energy obtained from the field is given up to the dielectric, and this process is decisive for the dielectric: If the field is strong enough, the energy absorbed from the field by the electrons exceeds the energy lost to the dielectric, and the electron energy increases without limit. This energy is transformed to heat and ultimately destroys the dielectric.

The theory of collisional ionization assumes that the electrons, after exceeding the maximum loss to the dielectric, are accelerated further until they have sufficient energy to liberate more electrons by collisional ionization. The result is an avalanche-like increase in the number of electrons.

In the theory of collective breakdown, in contrast, the energy excess is assumed to increase the thermal energy of the collective of free electrons. The resulting temperature rise is then transferred to the dielectric [163].

The breakdown voltage is measured with a 100- or 200-kV a.c., 50-Hz power supply, usually on plate or film specimens. The breakdown voltage per unit specimen thickness is the dielectric strength E_d, in kV/mm. This value is not, however, a specific material property; it depends on a number of factors, especially specimen thickness [164], [165].

A quantity of special engineering interest is the long-term dielectric strength – the breakdown strength as a function of the time over which the voltage is applied, often under service conditions [166]. The service life of an insulator is influenced by a variety of aging processes, including the buildup of space charge due to electron enrichment, electrical aging due to microcorona discharges, electrochemical aging due to mobile contaminants (e.g., water), and thermal aging [167].

Tracking Resistance. If contaminants and moisture on the surface of an insulating material form a conducting bridge between two contacts between which a voltage is imposed, surface leakage currents can damage the surface. This process is simulated in testing to assess tracking. Two standard methods are available, one with voltages up to 600 V (low-voltage tracking) [168] and the other up to 6 kV (high-voltage tracking) [169].

In the low-voltage method, contamination is simulated by a test solution dripped onto the surface. At a predetermined voltage selected from a series, five specimens must survive after 50 drops; failure is signaled by the presence of a given current. Variants of the test are described in [168].

The high-voltage method is intended for insulating materials for open-air service at high voltages. The specimen is tilted 45° from the horizontal, and a stream of a test solution is allowed to flow down the bottom of the specimen between two stainless steel electrodes. Two failure criteria can be applied: the current flowing over the specimen surface or the presence of tracks [169].

Other, application-oriented tests on insulating materials should be mentioned briefly.

The ability of insulating materials to withstand surface glow discharges is important for the service life of electrical equipment. The glow discharge is intimately related to breakdown behavior. Such discharges attack the surface both mechanically and chemically. In the test of this behavior, graduated voltages are imposed on a specimen with a point – plate electrode arrangement, and the time to breakdown is measured. The service life curve obtained in this way for the insulating material makes it possible to rank insulators with respect to glow discharge behavior [170], [171].

If insulators are in contact with conductors to which d.c. voltage is applied, corrosion of the conductors can result. This corrosion depends on the insulator – metal combination and is affected by temperature, atmospheric humidity, and exposure time. Electrolytic corrosion can

take place on any base metal. This phenomenon is tested by imposing a d.c. voltage in a humid atmosphere; two brass electrodes are employed. Results are assessed by comparing the colors of the brass foils with a standard color scale [172], [173].

Plastics filled with conductive carbon black, aluminum flakes, stainless steel fibers, or metallized carbon fibers are suitable for shielding electromagnetic fields. These compounds, used for the housings of electronic devices, are supposed to prevent electromagnetic interaction of the devices.

Measurements of dielectric strength and surface resistance are not adequate for the evaluation of shielding qualities, and special methods must be used. Shielding effectiveness is measured in dB. A value of 30 – 40 dB is considered sufficient for plastics. For details, see [174], [175], and literature cited therein.

2.4.4. Electrets; Semiconducting and Conducting Polymers

Electrets are dielectrics bearing a quasi-permanent charge, in which positive and negative charges, either isolated or created by polarization, are kept apart for an extended time. The best-known electrets are fluorinated ethylene–propylene copolymers (EP-F), polycarbonate (PC), polytetrafluoroethylene (PTFE), polypropylene (PP), poly(ethylene terephthalate) (PETP), and polyphenylene ether (PPE).

Electrets are used in electroacoustic transducers (e.g., microphones), radiation dosimeters, and air filters (electrostatic dust collection).

Several polymers now under development exhibit piezoelectric and pyroelectric effects. The most important product in this area is poly(vinylidene fluoride) (PVDF). To achieve the strongest possible piezoelectric effect, the material is drawn and given a permanent dipole orientation in a strong electric field.

The true semiconductive and conductive polymers include polyacetylene, polypyrrole, poly(*p*-phenylene), and poly(*p*-phenylene sulfide). Detailed reviews of this area have been published by Roth [176] and Mair and Roth [177]. Numerous literature references can be found in [178]. See also → Polymers, Electrically Conducting.

2.5. Optical Properties and Their Testing

Optical elements made of plastics include lenses, prisms, rear reflectors, glazings, lighting enclosures, optical-fiber light guides, compact discs, and many others. The most important optical properties for these applications are refractive index and lighting qualities (as defined, for example, in lighting standards), especially transmittance. In many other components for household and industry, aesthetic qualities such as color, gloss, and opacity are more important, but these properties are difficult to correlate with visual impressions.

2.5.1. Refraction and Birefringence

When a ray of light passes from one isotropic medium to another, the sine of the angle of incidence is in a constant ratio to the sine of the angle of refraction (both measured from the normal to the interface). If the light passes from a vacuum (or, less precisely, from air) into a denser medium, this ratio is called the refractive index n. The refractive index is dimensionless and depends on the wavelength of the light and on the temperature.

General methods for measuring refractive indices (i.e., not necessarily restricted to plastics) can be found in optics texts; standards also exist for measurements on plastics [179], [180]. Table 7 lists refractive indices for a number of plastics. Wavelength dependence is characterized by the dispersion. In practical optics, either the "dispersive power" $D_r = (n_F - n_C)/(n_D - 1)$ or its reciprocal, the Abbé number $\nu = 1/D_r$, is employed. Subscripts refer to wavelengths at which the indices are measured.

Birefringence is a measure of optical anisotropy. It is defined as the maximum difference between two refractive indices determined in two perpendicular directions. Some materials show isotropic behavior until they are deformed while in the glassy state. The deformation, which manifests itself in small changes in bond angles and interatomic distances, leads to the phenomenon *stress birefringence*, which is proportional to the applied stress. This behavior is utilized for, among other purposes, photoelastic examination, which enables the

Table 7. Refractive indices n_D^{20} of plastics

Product (abbreviations from DIN 7728)	Refractive index n_D^{20}
CA	1.49 – 1.51
CP	1.47 – 1.48
CAB	1.45 – 1.47
PTFE	1.35
FEP	1.338
PFA	1.35
ETFE	1.4028
POM	1.48
PA 6	1.53
PC	1.586
PE-(LDPE)	1.51
PE-(HDPE)	1.545
PMMA	1.4893 – 1.491
PP	1.5030
PAN	1.5187
PS	1.590 – 1.592
SAN	1.565 – 1.569
PVDC	1.60 – 1.63
PSU	1.633
PVC	1.52 – 1.55
PU	1.5 – 1.6
PVA	1.4665
PVDF	1.42
SB (30 % PS)	1.53
EP	1.55 – 1.60
UP (50 % styrene)	1.523 – 1.540
PVC + DOP 60/40	1.52
PF	1.7
UF	1.54 – 1.56

investigation of plane and even triaxial states of stress in metal structures by using plastic models. The preferred material for this application is phenol – formaldehyde resin because it has a relatively high stress birefringence.

The other cause of birefringence in plastics is orientation of the polymer chains brought about in processing or by drawing. This *orientation birefringence* is greater than the stress birefringence. Birefringence measurement is one of the techniques used to determine the state of orientation in polymers.

Birefringence is measured by the transmission method (Fig. 42) [181]. A ray of monochromatic light is polarized so that the oscillation direction of the electric vector lies in the $x - z$ plane and makes a 45° angle with the z direction. The ray next passes through the specimen, in which the polymer molecules should be aligned preferably with the z axis, and then through an analyzer whose polarization direction $\boldsymbol{P}_z$ is perpendicular to that of the polarizer. The intensity of light transmitted by the analyzer is measured with a photomultiplier. If the polarization in the

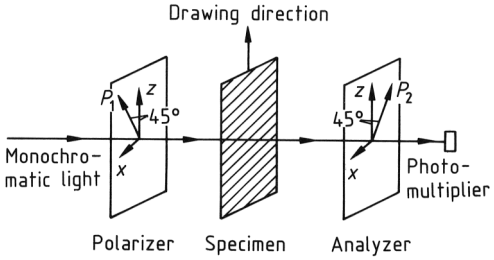


Figure 42. Setup for birefringence measurement [181]

specimen does not change, the transmitted light has zero intensity; if the specimen is birefringent, the intensity will be

$$I_b = I_0 \sin^2 \left[\pi \frac{d}{\lambda} (n_x - n_z) \right]$$

where I_0 is the incident light intensity. From the intensity ratio I_t/I_0, the specimen thickness along the path of the light, and the wavelength of light employed, the birefringence $n_x - n_z$ can be calculated as

$$n_x - n_z = \frac{\lambda}{\pi \cdot d} \arcsin \sqrt{I/I_0}$$

This method is used when the degree of drawing and thus the degree of orientation are high.

A second method for measuring birefringence uses the Babinet compensator, which replaces the analyzer and the photomultiplier. Essentially, it consists of two quartz wedges that are adjusted so as to offset the phase shift δ between the x and z components of the emerging light vector.

2.5.2. Transmittance and Gloss

The light-transmitting qualities of plastics are described in terms of the visual impression that the specimen gives under precisely defined illumination. In the usual order, these terms are clear, almost clear, transparent, translucent, semiopaque, and opaque.

The customary definitions in lighting technology are as follows [182]:

Transmittance is the percentage of light transmitted without deflection. Without deflection means that only the components propagated in the direction of the incident ray are considered. Plastics with particularly high transmittances

include poly(methyl methacrylate) (92 % at 380 – 780 nm), polycarbonate (88 %), and cellulose esters (86 % at 420 nm, 90 % at 660 nm for cellulose acetate). For some applications, the ultraviolet transmittance of these clear products can be reduced by addition of UV absorbers. Modified and filled polymers are clear or transparent only if their components have similar refractive indices or if the particle size of the incoherent phase is smaller than the wavelength of the light.

Haze refers to the portion (intensity) of light transmitted by a specimen that deviates from the direction of the incident light because of forward scattering in the material. Materials with high haze components are said to be semiopaque or translucent.

Both transmittance τ and haze vary with the geometry of the optical measuring system, which must therefore be precisely defined. The same holds for the type of light employed. Examples are Colorimetric Standard Illuminants A (incandescent lamp), C (same as A with Davis – Gibson filter), and D 65 (daylight with a color temperature of ca. 6500 K).

Once the spectral characteristics of the light and the spectral sensitivity of the human eye (characterized by "standard spectral curves") are known, mathematical formulas are applied to relate the wavelength dependence to the measured energy spectrum of the transmitted light. Finally, transmittance is determined.

The most common way of determining absorption spectra is by use of spectrophotometers. If the monochromator is placed in front of the specimen, the light, whose wavelength is continually varied, passes through the specimen, and the transmitted intensity of each wavelength is measured successively by a photocell. Alternatively, the light is dispersed only after it has passed through the specimen, and the intensities of the individual wavelength components are then led to the photocell. With this scanning arrangement, however, the long measuring time can be shortened considerably if all wavelength components are led simultaneously to a series of photocells. The result (spectral curve) is then determined in a few microseconds. Some applications of transmittance measurements in the visible spectrum include determination of the spectral or mean transmittances of colored and colorless plastics; color characterization (tristimulus values or total transmittance) for signal lights in air and marine navigation, railroads, and road transport; color matching; aging tests; damping measurements in light guides; and testing the lightfastness and weather resistance of colored plastics.

The haze of thin specimens with low scattering is measured in a standardized setup [183]. For reasons having to do with experimental technique and to bring the results into accord with subjectively assessed scattering (haze) properties, the scattered light measured is the component lying between two coaxial cones (about the axis of incidence) with opening angles of 12° and 80°.

For specimens with higher scattering (up to 30 %), the measuring system of ASTM 1003–61 is employed. The setup features an integrating sphere and can be reconfigured to measure the incident flux as well as the directly transmitted, scattered, or total transmitted flux. The parameters total transmittance, diffuse transmittance, and haze are then calculated with allowance for the scattering of the integrating sphere. High-quality transparent acrylates have haze values of the order of 0.15 %.

Gloss. HUNTER defines gloss as the ratio of the regularly (specularly) reflected light intensity to that of a high-quality optical mirror. Gloss can be defined in a number of other ways. Most glossmeters measure the specular gloss defined by HUNTER. Most instruments employ fixed incidence and measurement angles (e.g., 45° in the Lange glossmeter).

Highly polished, optically flat black glass plates are often used as reference standards. Their reflectivity can be calculated from the refractive index.

Measurements of the spectral reflectance curve (i.e., the dependence of reflectivity on incidence angle) give a more meaningful description of gloss. The instrument used for these measurements is a goniophotometer [184–187].

The values obtained by gloss measurement techniques, however, do not correlate perfectly with the visual impression of gloss. This becomes obvious when an inspector assessing gloss turns an object one way and another, thus scanning through many incidence and reflection angles. Polarization also plays a role in the impression of gloss.

2.5.3. Color and Colorimetry

Color is not an absolute property but depends on the surface condition of the specimen as well as the conditions under which it is examined. Nor does the term "artificial light" or "daylight" provide enough information; for example, the color of sunlight varies with the position of the sun in the sky. Two colors that the observer subjectively judges to be the same under given illumination may not match under other conditions. These problems are, of course, not specific to the plastics industry. The concepts of colorimetry, measuring methods, and test conditions are specified in DIN 5033 [188]. American and British standards also exist for this field [189], [190]. The CIE international vocabulary for lighting technology defines terms and nomenclature; problems involved in color differentiation are discussed in ISO 2573 [191], [192].

Very simple methods for assessing small color changes or departures from colorlessness in the direction of yellow (yellowing) are described in [191]. The objective determination of color with scales and formulas is a difficult undertaking but is still important in plastics production and applications.

Transparent, translucent, and opaque colored plastics must generally exhibit narrowly defined hues, whether they are to be used in signaling, advertising, or illumination. Consumer products and industrial articles must meet similar requirements, especially when colored plastics have to match other components in perceived color.

Problems of colorimetry can be mentioned only briefly here. The human eye interprets incident radiation with three distinct sensitivity functions at once. These are called the standard spectral curves and relate to the three primary colors red, green, and blue. One of these (green) is taken as the basis for the spectral curve describing the human perception of brightness. The standard spectral curves are now mathematically related to the energy distribution of the radiation giving rise to a color sensation and to the reflectance curve of the specimen in the visible spectrum (see also Section 2.5.2). The relations between the incident energy distribution (e.g., the Colorimetric Standard Illuminants) and the standard spectral curves are tabulated, so all that is necessary is to link

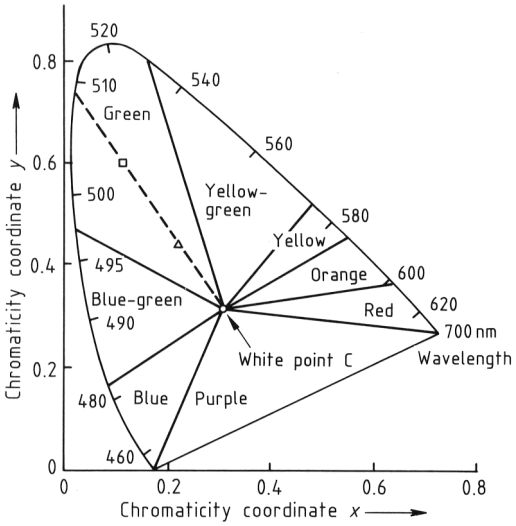


Figure 43. The color triangle

them with the reflectances. The resulting tristimulus values X, Y, and Z are normalized and can be used to generate a two-dimensional representation. The normalized values x, y, and z satisfy the condition $x+y+z=1$; thus the color location in the $x-y$ system, which formally characterizes the color, can be unambiguously determined. The colors of the spectrum, plotted in this way, lie on a horseshoe-shaped curve (Fig. 43). Together with the brightness reference value Y (which cannot, however, be presented in the color triangle), the point (x, y) completely describes a color. All natural colors lie inside the curve. The location of the "white point" depends on the type of illumination. The saturation decreases toward this point. Colors lying on a straight line radiating from the white point have the same hue. In Figure 37, for example, the square and the triangle are color locations with the same hue, and the square is more saturated than the triangle. It is important here that colors with the same color location are the same only for the illumination conditions illustrated, not necessarily under other illumination conditions. Such colors are said to be conditionally the same, or metameric colors. Colors that must appear the same under all illuminations must have identical reflectance curves.

In principle, any spectrophotometer that permits measurements in the visible spectrum and

has a reflector attachment is suitable for colorimetry.

An important class of instruments, especially for routine color measurement, is the three-filter (tristimulus) type, which does not yield complete reflectance curves but facilitates the determination of X, Y, and Z values. These devices use three calibrated filters (tristimulus filters) to evaluate the fraction of incident light reflected from a specimen. The filters, in combination with the light source and the system of photoelectric cells, give the three standard spectral curves. Because the curves are not reproduced perfectly, the measurements do not rank as absolute values. However, these instruments are suitable for relative measurements (e.g., comparing the color of a plastic product with that of a color standard). However, only metameric color matching can be realized. As mentioned above, the geometry of the setup is also important for reflectance measurement. Geometries for colorimetry include "direct" illumination at 45° with observation at 0° and "diffuse" illumination at 0° with the integrating sphere used for reflected-light measurement. The appropriate geometry depends on the surface structure of the specimen. The most commonly used Colorimetric Standard Illuminant is D 65, which resembles the formerly customary type C, because the behavior of nonluminous colors in daylight is of particular interest. For color-matching purposes, fluorescent lamps or, even better, xenon arc lamps are used to provide artificial daylight.

The locations (in the color triangle) of standard and specimen must lie within a certain tolerance if they are to appear "the same." A number of workers have attempted to establish these tolerance ranges. Formulations to match standard colors can be found by computer calculations based on colorimetric measurements (Kubelka – Munk and other methods).

2.6. Density and Physical-Chemical Properties and Their Testing

2.6.1. Density

High-precision density measurements can be performed with relatively simple apparatus. Because some physical properties of plastics are single-valued functions of density, changes in these properties can be characterized indirectly on the basis of density measurements. An example of such a property is crystallinity, which in turn affects certain mechanical properties.

Density often occupies an important place in specifications; in the case of polyethylene, for example, it is essential for classification and identification [192].

The determination of density for solid plastics (except foamed plastics) is described in ISO 1183 [193]. The standard covers four methods, corresponding to the type of plastic in question. These methods are also contained in DIN 53 479 [194]; DIN 53 420 describes density measurements on foamed plastics. Compact, unfilled, unreinforced plastics have densities between ca. 900 kg/m^3 (polypropylene) and 2300 kg/m^3 (polytetrafluoroethylene).

2.6.2. Liquid Absorption and Swelling; Desorption of Plasticizers

Many polymers can absorb liquids (often up to an equilibrium concentration). The processes involved are adsorption, diffusion, and dissolution or swelling. Un-cross-linked amorphous polymers swell without limit in some liquid media and ultimately dissolve entirely (e.g., polystyrene in benzene). A table identifying good and poor solvents for some 60 important polymers appears in [195].

If the polymer is cross-linked or partially crystalline (with the crystallites acting like cross-link sites), swelling may be limited because the entropy-elastic restraint of the network prevents further liquid absorption.

Thermodynamic equilibrium is reached when the free swelling energy $\Delta F = \Delta H - T\,\Delta S$ vanishes or when the heat of swelling ΔH is equal to the product of the temperature T and the entropy of swelling ΔS. The time to equilibrium depends not only on the swelling agent and its concentration, but also on the geometry of the sample and, above all, the diffusion coefficient of the swelling agent in the polymer. Figure 44 shows the equilibrium water uptake of several plastics as a function of relative humidity.

The opposite process, liquid loss, occurs when low molecular mass plasticizers diffuse out of plastics and become desorbed.

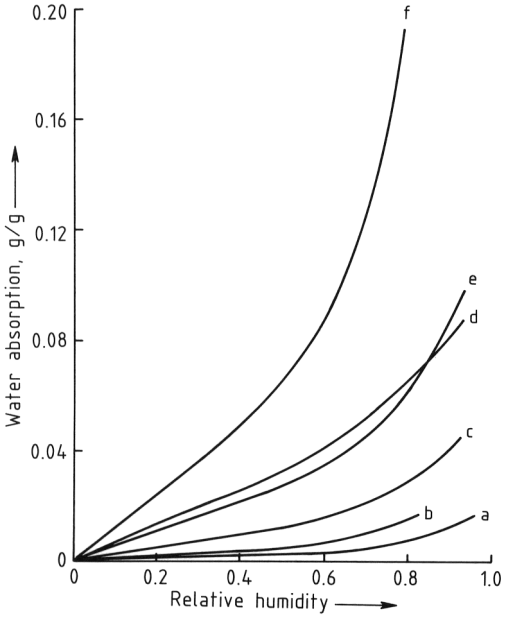


Figure 44. Equilibrium water absorption of some plastics as a function of relative humidity a) Poly(vinylidene chloride); b) Chlorinated rubber; c) Poly(vinyl butyral); d) Polyamide 66; e) Cellulose acetate; f) Poly(vinyl alcohol)

2.6.3. Permeation of Gases and Vapors

The permeation of gases and vapors in plastics can be described as a two-stage process. First, the permeating substance dissolves in the surface of the plastic; second, the molecules diffuse through the material, forming a concentration gradient, and then evaporate again. The concentration c of the permeating gas at the surface depends on the gas pressure p or the volumetric concentration in the gas space. For permanent gases (H_2, O_2, N_2, CO_2, noble gases, etc.), the concentration is directly proportional to the partial pressure p (Henry's law: $c = kp$). This simple relationship does not hold for the diffusion of vapors.

The steady-state diffusion of a gas or vapor is described by Fick's first law:

$$\frac{dQ}{dt}\,\frac{1}{A} = -D\frac{dc}{dx}$$

where dQ/dt is the flow velocity of the medium, A the flow area, D the diffusion constant, and dc/dx the concentration gradient. Transient diffusion is described by Fick's second law.

Consider a layer of finite thickness d and assume that D is independent of concentration. Integrating the above equation over the thickness gives

$$\frac{dQ}{dt}\cdot\frac{1}{A} = \frac{D(c_1 - c_2)}{d}$$

where c_1 and c_2 are the concentrations at the two surfaces. If concentration is expressed in terms of pressure, the result is

$$\frac{dQ}{dt} = D \cdot S \cdot A\frac{p_1 - p_2}{d}$$

where $D \cdot S$ is the permeability P; dQ/dt is constant in the steady state. In experiments, $p_1 - p_2 = \Delta p$ is held constant, so that

$$P = \frac{Qd}{\Delta t A \Delta p}$$

in units of $cm^3\ cm^{-1}\ s^-\ mbar^{-1}$.

The practical quantity gas permeability is easier to work with. It is the volume of gas in cubic centimeters that permeates a 1-m^2 area of the product being tested in 24 h at a given temperature and a given pressure difference (e. g., 1 bar). The corresponding unit is $cm^3\ m^{-2}\ d^{-1}\ bar^{-1}$. The unit employed for vapor permeability, especially water-vapor permeability, is $g\ m^{-2}\ d^{-1}$. The thickness of the test specimen must be stated, along with the gas and water-vapor permeabilities, because the units do not allow for reduction to unit thickness. Furthermore, the pressure difference must be known in the case of water-vapor permeability; in practice, this is accomplished by establishing a given atmospheric humidity difference.

The steady-state transport equation holds only for gases and vapors that are not very soluble in the polymer and do not react chemically with it. Vapors can often act as plasticizers, thus increasing diffusion.

The permeability is temperature dependent in all permeant – polymer systems. The diffusion coefficient for both gases and vapors increases with increasing temperature. With increasing temperature, the solubility factor S increases for gases but decreases for vapors.

Permeation is also influenced by the molecular size and polarity of the permeating substance. The morphology of the polymer

(crystallinity, branching, orientation, etc.) plays an important role in the process.

Multilayer films (laminates) are commonly used in packaging. The P coefficient of such a composite can be calculated from the P values of the individual plies:

$$\frac{1}{P_L} = \frac{1}{L}\sum_{i=1}^{n}\frac{d_i}{P_i}$$

where L is the thickness of the composite, P_L is its permeability, and d_i and P_i are the thickness and the permeability of the ith ply.

This equation, however, applies only when permeability does not depend on pressure. The order of the plies has no effect in this case; otherwise, the overall permeability depends on the order of the plies.

Methods of measuring gas permeability include those employing pressure gauges and those involving carrier gases. In the first group, the quantity of gas permeating the specimen in a given time is found by measuring pressure and volume changes [196], [197]. In carrier-gas methods, gas flows through the specimen while the pressure remains the same on both sides. The test gas flows at a constant rate through a chamber on one side of the specimen, while a second (carrier) gas flows, also at a constant rate, through the chamber on the other side. The carrier gas delivers the permeating test gas to a detector, which can operate on the absorption or thermal conductivity principle [198]. A development in the carrier-gas technique was the insertion of a gas chromatograph column between the measuring cell and the detector [199].

To determine water-vapor permeability, an aluminum test cell filled with calcium chloride, for example, is employed as absorption chamber. The cell is closed by the specimen and sealed with wax at the edges. This apparatus is placed in an atmosphere having a well-defined temperature and humidity, and the weight gain of the absorption cell is measured at regular intervals [200], [201].

2.7. Stability Properties and Their Testing

The usefulness of plastics in many fields depends on their resistance to environmental factors. These complicated effects cannot always be simulated, and testing must often be accelerated. The loads applied are thus greater than would occur in the normal loading cycle. Accordingly, for short-term tests in particular, the correlation with in-service performance must be examined carefully and interpreted critically.

2.7.1. Water Absorption

Like other swelling agents (such as alcohols), water has a plasticizing effect on some plastics (polyamides, polyurethane). This action is based on the cleavage of hydrogen bonds between polar groups of adjacent macromolecules [202]. The result is a decrease in the glass-transition temperature of the amorphous regions in the plastic. The material, which is brittle and fragile at normal service temperatures and completely dry, becomes tough and flexible. Apart from the desired plasticization at room temperature, the dissolution of hydrogen bonds also leads to an increase in density, and thus modulus, at low temperature, although this effect generally has no practical importance.

Polymers whose main chain contains hydrolyzable groups (e.g., polyesters, polyamides) can be irreversibly damaged by water. In addition, water that has diffused into the material acts as a radical donor, thus promoting photochemical aging (see below) and, through the loosening of the polymer structure (hydrogen bond cleavage), facilitates the diffusion of oxygen and free radicals.

A number of standard test methods have been devised to measure water absorption quantitatively: water absorption in cold water [203], [204]; water absorption in boiling water [205], [206]; and behavior in humid air [207]. In the standards, water absorption is measured relative to a well-defined dry condition, to the dry condition with allowance for constituents lost to the water, or to the as-delivered condition of a specimen. Water absorption is stated as a percent weight change or as the absolute weight change in milligrams.

2.7.2. Effect of Chemicals

Water uptake and solubility in water are just one aspect of the more general concept of chemical

resistance. The reason for treating the action of water on plastics separately is the ubiquity of this medium.

Plastics are resistant to the action of many chemicals, with the exception of certain classes of compounds. Organic solvents are among the most corrosive compounds towards plastics, since the plastics are themselves organic materials. Generally, nonpolar plastics are sensitive to nonpolar solvents, and polar plastics to polar solvents.

The standards for determining chemical resistance are ISO 175 and DIN 53 476 [208], [209]. For unstressed specimens, all that is necessary is to investigate how factors such as absorption, extraction, and chemical attack alter physical properties. Detailed tables of chemical resistance can be found in [210], [211].

Plastics in service are often subject to external mechanical stresses or residual stresses from production. A plastic may be stable against a given reagent when unstressed but fail in contact with the same reagent under stress. This phenomenon, called stress cracking, results from purely physical processes, in contrast to the stress corrosion cracking of metals (see also → Corrosion, 1. Electrochemical). The three most important processes are wetting, diffusion, and swelling. Wetting and swelling can increase the notch stress at weak points and microcracks that are always present in the material; diffusion is crucial for the transport of the medium to such weak points.

Methods for studying stress cracking are not completely analogous to practical experience. For example, the Bell test, specially conceived for polyethylene (PE), is very controversial. The Plax test described in ASTM 2561 has been devised for the evaluation of hollow articles made of PE. The setup enables hollow articles to be tested under constant internal pressure. The crack-opening medium is a 10 % aqueous solution of polyoxyethylnonylphenol. Cracking is detected with a simple electrical instrument.

2.7.3. Effects of Heat, Light, and Weathering

In DIN 50 035, Sheet 1, aging is defined as the totality of chemical and physical processes occurring irreversibly in a material over time. In this sense, the consequences of heat, light, and weathering are aging processes. The definition also implies that time is a significant variable in testing and, hence, that aging takes place in not spontaneous processes but relatively slow ones whose effects are seen only over a time span comparable to the service life. Thus the above definition excludes, for example, irreversible processes that are associated with processing operations [212].

Oxidation always accompanies aging due to heat and light. The most important apparatus for tests of thermal aging is the furnace. It can be operated with air recirculation and no fresh air, with fresh air circulation, or with fresh air metered into the recirculating air. Specimens can also be thermally aged by heating in a metal block, heating bath, or thermal analysis apparatus.

Light and Weathering. Weathering includes the action of many components: heat, water vapor, visible light, ultraviolet radiation, and the effects of oxygen and ozone. The synergism among these processes is often difficult to predict. In addition, the varying intensities of the components can have a more severe effect than a steady high level. The variability of the weather at any location and the difference between climatic regions render reliable correlations between an accelerated weathering test and natural weathering doubtful. Only when specimens are subjected to natural processes do weathering tests give reliable results. The possibility of accelerating the test consists in selecting a suitable weathering location. The three most important climatic regions for open-air weathering are temperate (e.g., Germany, with a mean global radiation of 400 MJ m^{-2} a^{-1}), warm-dry (Phoenix, Arizona, ca. 7900 MJ m^{-2} a^{-1}), and warm-humid (Bombay, 6300 MJ m^{-2} a^{-1}). The part of the spectrum responsible for photochemical aging of plastics ($\lambda \leq 380$ nm) accounts for only 4 – 6 % of global radiant energy; the remainder is transformed to heat when it is absorbed by the specimen. Open-air weathering tests are described in [213–215]. Resistance to natural weathering is expressed as the change in properties tested as a function of irradiation. Weatherfastness in the natural weathering test is expressed as the color change.

In many cases, open-air testing is done to determine not the weathering resistance or weatherfastness, but merely the stability to light or lightfastness (change in color only). These tests are governed by ISO 877 [216]. Color changes can be evaluated with the Woll lightfastness scale described in DIN 5003 or ISO 105 [217] or by the (more laborious) spectral method of DIN 5033 Sheet 4 or Sheet 6 (see Section 2.5.3).

Artificial weathering and artificial illumination allow a fairly constant radiation flux to be obtained, so that irradiation is roughly proportional to time. Various types of lamps are employed. High-pressure mercury-vapor lamps are suitable for testing if short wavelengths are filtered out. Carbon arc lamps are still used, even though their spectrum bears no resemblance to sunlight. Xenon arc lamps have recently found wide use in the plastics industry. With suitable filters, sunlight can be modeled well by this light source, although the acceleration over sunlight is not very great. To take one example, the action of xenon light on ABS is about fives times that of sunlight.

Although accelerated tests (i.e., simulated or artificial weathering and illumination) do not yield absolute results as to weather- or lightfastness, a number of standard methods have been in use for years [218–220]. Figure 45 shows how the impact strength of impact-resistant polystyrene decreases with time under xenon arc light. A comprehensive survey of the measurement of aging criteria, the extrapolation to determine service life, and the problem of reference standards is given in [212].

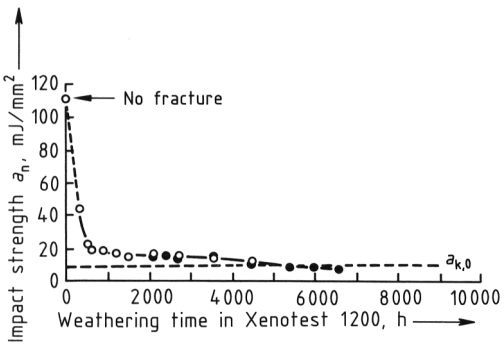


Figure 45. Impact toughness of high-impact-strength polystyrene (SB) as a function of illumination time in the Xenotest 1200 apparatus [212] $a_{k,0}$ is the notched impact strength of the unweathered probe

2.7.4. Effect of High-Energy Radiation

The service properties of all organic polymers are impaired when they are exposed to sufficient doses of high-energy radiation. The type of radiation (e.g., electrons, gamma rays, or reactor radiation) has no influence; only the absorbed dose of energy is important.

The dose rate may, however, be significant in the presence of atmospheric oxygen. In polymers that mainly undergo radiation cross-linking in the absence of oxygen, chain degradation occurs by radiative oxidation, leading to a loss of stability. Oxygen has little effect on polymers that undergo primarily radiative degradation. Degradation by radiative oxidation depends on time, and thus on dose rate, because it is determined on the one hand by oxygen diffusion into the material and on the other by decay of the peroxide radicals formed [221], [222]. The density of the polymer also plays a role in diffusion.

Plastics can be ranked in terms of their stability to high-energy radiation by means of half-value doses. Measurement of the half-value dose for the elongation at rupture has proved useful. Thus, the half-value dose is the dosage, in grays (1 Gy = 1 J/kg = 100 rad), at which the ultimate elongation falls to half the starting value (before irradiation). Figure 46 illustrates the situation with respect to tensile strength and elongation at rupture. At a certain dose rate (e.g., 2 kGy/h), the elongation reaches half of its starting value at a dose of 32 kGy. The tensile strength declines in a similar way, but drops to half the starting value only at 60 kGy.

The stability to high-energy radiation often depends strongly on the stabilizing system of the polymer; see Table 8 [221], which lists half-value doses (elongation) for polypropylene with various stabilizers. WILSKI points out that all the values in this table are "correct" in themselves, but only the value for the product with no stabilizer represents the true value applicable to this product type.

WÜNDRICH [222] and WILSKI [224] have provided a good introduction to this field, presenting detailed summaries of results with extensive references to other publications and values.

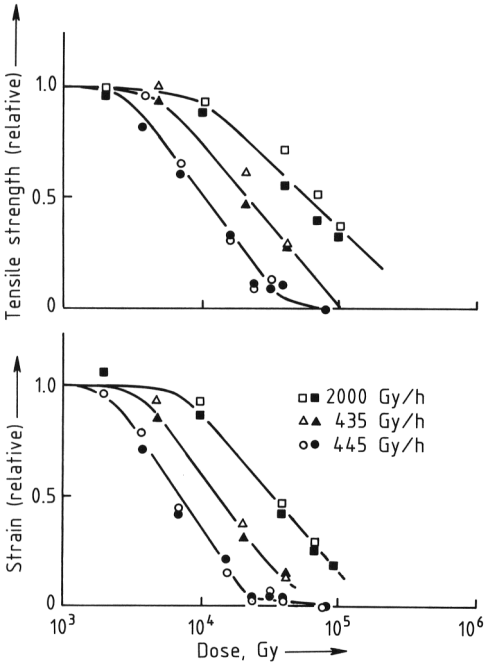


Figure 46. Tensile strength and elongation at rupture of polypropylene monofilaments (0.4-mm diameter) irradiated in air at various dose rates Initial tensile strength: 507 N/mm^2 (solid circles); 397 N/mm^2 (open circles) [223]

2.7.5. Stability against Fire

The combustion of plastics cannot be described quantitatively. It includes a number of steps, some of which have not yet been studied. For combustion to begin, three events are necessary: heating, decomposition, and ignition of the polymer. Table 9 lists the decomposition, flame initiation, and self ignition temperatures, along with the heats of combustion, for several plastics. Thermoplastics tend to soften and melt in the presence of an ignition source. The intensity of burning, smoke evolution, and the formation of residues depend on the chemical structure.

Because of their three-dimensional cross-linked structure, thermosets burn without first softening and flowing. They also generate a smaller amount of decomposition products than thermoplastics. The action of heat on their surfaces results in carbonization. In some cases, ignition does not occur.

The requirements imposed on the fire performance of plastics, especially when they are employed in construction, electrical equipment, transportation, furniture, and appliances, mean that flame retardants must be used in many cases. Flame retardants fall into two classes, reactive and additive. Reactive flame retardants are chemically incorporated in the polymer molecule and are used chiefly in polyester and epoxy resins and in polyurethanes. They have a permanent action. Additive flame retardants are usually added only after polymerization. The use of high molecular mass flame retardants also has a permanent effect.

The most common flame retardants include chlorinated and brominated compounds, as well as phosphorus compounds. The literature contains discussions of synergistic effects between individual additives.

Table 8. Half value dose (extension) of Hostalen PPN polypropylene [223] *

Stabilizer system	Half-value dose, 10^3 Gy
No stabilizer	5
N,N′-Di-*β*-naphthyl-*p*-phenylenediamine (DPPD)	6
Trilauryl phosphite	6
Irganox 1076	14
Irganox 1010	15
Ionox 330	17
Phenothiazine	22
Ionol	26

* Dose rate 24 Gy/h in air, ^{60}Co radiation, molded sheets 0.5 mm thick. All specimens contain 0.2 % calcium stearate, stabilizer concentration 0.5 %.

Table 9. Decomposition temperature ranges T_d, flame initiation temperatures (FIT), self ignition temperatures (SIT), and heats of combustion ΔH for some plastics [225]

Product (abbreviations from DIN 7728)	T_d, °C	FIT, °C	SIT, °C	ΔH, kJ/kg
PE	340 – 440	340	350	46 500
PP	320 – 400	320	350	46 000
PS	300 – 400	350	490	42 000
PVC	200 – 300	390	450	20 000
ABS		390	480	36 000
PMMA	180 – 280	300	430	26 000
PA 6	300 – 350	420	450	32 000
PA 66	320 – 400	490	530	32 000
PTFE	500 – 550	560	580	
PAN	250 – 300	480	560	
Cellulose	280 – 380			17 500
Cotton		210	400	17 000

Fire-protection tests, also called test methods for evaluating fire performance, are so numerous – and the associated problems so complex – that only a few general points can be discussed here.

All authors who have dealt with this topic state that fire performance is not a material property but depends on flammability, flame propagation, heat evolution, and several associated phenomena: fume density, toxicity, and corrosiveness of the combustion gases [225]. A particularly important point is that general statements regarding flammability and combustion – such as flammable, flame resistant, combustible, self-extinguishing, difficultly flammable, and the like – without reference to a specific test method, can lead to serious misinterpretations. A numerical value referred to a specific test method or to an unambiguous code representing flammability test results must always be given.

Tests are performed on bench, laboratory, and full scales. Most of the standards relate to specific applications such as mining, electrotechnology, transportation, furniture and appliances, and construction.

Some important testing standards are listed below.

On a bench scale, the processes in incipient combustion are studied in *reaction to fire* tests. One such is described in ISO 1210.2 [226]: The flame from a Bunsen burner is tilted at 45° and applied to horizontal specimen. The plastic is assigned to one of three categories, depending on the flammability and the duration of burning, if any. The tests DIN 53 438 [227] and ASTM D 635–77 [228] are similar.

A somewhat controversial method is measurement of the *oxygen index*. The oxygen concentration at which the specimen just burns for 3 min is determined [229]. However, the oxygen content in the combustion mixture is unrealistic.

In electrotechnology, flammability measurements are material tests and product tests. The VDE standards include, in the first category, the Schramm–Zebrowski glow-bar test [230] and, in the second, the glowing-wire test [231].

Material-specific tests devised by Underwriters Laboratories (UL) in the United States have achieved worldwide recognition. Especially important test specifications include UL 94, which includes several fire safety tests on materials [232]. The UL 94 test is used in all plastics application areas except building construction.

Tests leading to the ratings 94 HB, 94 V-0, 94 V-1, and 94 V-2 are important. The letter "H" denotes horizontal clamping of the specimen, whereas "V" stands for vertical clamping. In the HB test, the flame from a Bunsen burner inclined at 45° is applied to the free end of the specimen. The evaluation criteria are burning rate or extinction of the specimen before a standard mark is reached.

In the V test, the specimen is suspended vertically and the flame from the upright burner is applied to its bottom end. The response is evaluated from continued burning, afterglow, and ignition of cotton wool by burning droplets. The best rating is 94 V-0. The test result depends on specimen thickness, which must therefore be stated.

The fire performance of plastics used in construction is evaluated in accordance with DIN 4102 [233]. This standard provides for rating as nonflammable (class A) or flammable (class B); flammable materials are further classified as difficultly flammable, normally flammable, and easily flammable. Most plastics, because of their organic nature, achieve only class B. In some cases, such as composites with inorganic materials, they are rated in class A.

2.7.6. Effect of Microorganisms

Synthetic polymers are generally not affected by microorganisms (bacteria, algae, and fungi). The picture is complicated by the presence of additives, reinforcements, plasticizers, and so forth. General instructions for the investigation of this problem in ISO 846 are set forth [234]. The result of any such action is characterized by visual description of the growth of the organisms. Two methods of study are available. In method A, determination is made of the extent to which plastics can serve as a nutrient substrate for microorganisms; in method B, the fungicidal properties of plastics are examined. See also [235].

2.8. Processing Properties and Their Testing

The processing of plastics requires a knowledge of the as-delivered properties of molding compounds, the flow behavior of thermoplastics,

and the simultaneous flow and curing behavior during forming for thermosets. Molding compounds take the form of powders, granules, preformed pellets, liquids, or masses of doughy consistency; chips, sheets, and strips are sometimes encountered.

Important processing qualities of thermoplastics, curable molding compounds, and casting resins are identified and briefly described in the following material.

2.8.1. Molding Compounds

An essential condition for trouble-free automatic processing of thermoplastic and curable molding compounds is that the material flows freely. This quality is determined by measuring the time required for the compound to run through a funnel of a given size [236]. The discharge time of a powder can be influenced, for example, by the addition of aerosols.

The particle size and particle-size distribution govern the packing density and thus the filling of a completely positive mold or, in the case of a polymer in paste form [e.g., poly(vinyl chloride) in plasticizers], the formation of a gel. Screen analyses and visual counting methods are generally employed; microscopic examination is also used. Plastics in powder form are commonly analyzed on screens having openings of 63 – 2000 μm; the series usually has six screens with mesh sizes in a geometric series [237]. Often only two fractions are specified; in the case of vinyl chloride homopolymers and copolymers, for example, the oversize fractions on a 250-μm and a 63-μm screen are stated as the R (250) and R (63) values, respectively.

Particle-counting techniques based on optical measurements are important in the determination of particle-size distribution. In the laser granulometer, the beam from a helium–neon laser is guided through a cuvette that contains the specimen in dispersion form. The particles diffract the coherent beam, forming diffraction rings whose diameters are inversely proportional to the grain size. The size of the diffraction ring determines whether a particle is counted or not, depending on its spherical volume. The number of particles counted in a fraction (a given volume range) is converted to their volume and then to mass. In this way, the mass fraction is obtained as a function of the mean particle size (similar to screen analysis) [238].

The bulk density is informative in relation to metering. This value is the ratio of mass to volume when the molding compound is treated in a particular way (compacted, if apparent density is being measured). For long-strand fibers and chips, an apparent density is measured. The bulk density is easily determined with a filling funnel and a graduated flask.

The essential processing criterion for reaction resins is the viscosity as delivered; the viscosity after warm storage is also used for epoxy resins.

For reaction molding compounds, the time required to reach a given viscosity limit or the gelling time (open time, pot life) is measured under standard conditions [239], and the curing behavior (curing time) is determined.

The curing time is the time after which certain properties (e.g., heat deflection temperature, acetone-soluble matter, or styrene monomer content in the case of unsaturated polyester resins) no longer vary within certain limits.

2.8.2. Conventional Methods for Characterizing Flow Behavior

The only source of adequate information about the flow behavior of polymers is the flow curve (see Section 2.8.3). However, experimentally plotting a family of flow curves at a sufficient number of temperatures is laborious, and only in exceptional cases can this be done in the context of process monitoring. Attempts have therefore been made to characterize the flow behavior by simple, conventional measuring methods. This is especially appropriate for thermosetting molding compounds because curing takes place during processing and makes impossible the analysis of rheological phenomena in a simple way [240].

One of the most frequently used conventional test methods for the flow behavior of thermoplastics is determination of the melt flow index (MFI) or the melt volume index (MVI) [241]. For MFI, the quantity measured is the amount of polymer melt extruded from a nozzle in 10 min when a specified force is applied with a plunger (units of g/10 min). In automatic instruments, the plunger motion is measured as a function of time to give an MVI; the specimen volume expelled through

the nozzle in a specified time under the stated conditions is determined (units of cm^3/10 min).

When the melt index values do not correlate with in-service behavior (chiefly for injection molding), the flow behavior is assessed on the basis of the spiral flow test. A specimen in the form of a spiral is made in an injection-molding machine; the flow qualities are evaluated in terms of the length of the spiral.

In production monitoring and control, the melt viscosity or melt index is measured continuously with bypass rheometers (Fig. 47) [242], [243].

The flow behavior of curable molding compounds is far more difficult to characterize than that of thermoplastics, because in thermosets a chemical curing reaction proceeds while flow continues during the production process. The names of the test methods for these resins reflect the shapes of the specimens molded in the test [244].

If information beyond that offered by these simple methods is required, the measurements must conform to well-defined and easily understood techniques, as in the case of thermoplastics. Such measurements have been described by KANAVEC and others [245], [246]. The variation of viscosity with time is determined in a rotational viscosimeter. Use of this method means that processing conditions can be varied to an extent comparable with plant practice. The Bauer and Eichler kneading-chamber method [247] and the Philips method [248] cannot be described in detail here.

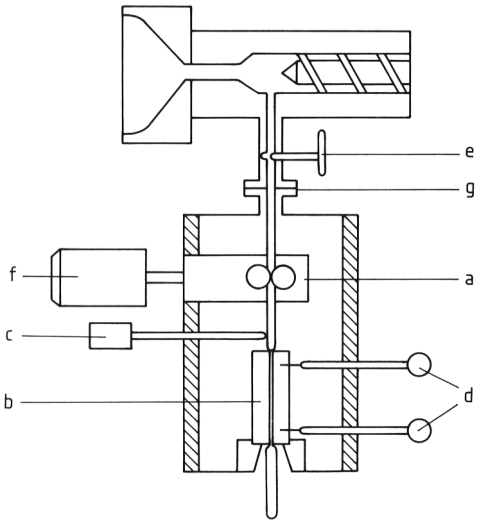


Figure 47. Göttfert bypass rheograph, open one-pump system with independent pressure and temperature controls a) Melt pump; b) Nozzle; c) Pressure pickup; d) Temperature pickup; e) Shutoff valve; f) Pump drive motor; g) Flange

2.8.3. Rheology of Plastics

Earlier (Section 2.8.2), the flow behavior of plastics melts was said to be describable only in terms of flow curves, that is, plots of shear stress versus shearing rate. The measurements are performed with simple shear deformation. Because deformations in processing nearly always involve extension, the extensional properties of the melt must often be investigated as well . For thermoplastics, the term melt refers to the condition above the glass-transition temperature for polymers that solidify in glassy form (e.g., polystyrene or polycarbonate) and to the condition above the maximum melting point of the crystalline regions for polymers that solidify in crystalline form.

The essential features in the rheology of thermoplastic melts are easily observable when a melt is extruded from a nozzle; see Figure 48 [249]. The behaviors illustrated at a, b, and c can be described as follows:

a. *Structural* (*non-Newtonian*) *viscosity.* The flow rate m increases faster than proportionally to the extrusion pressure p; that is, viscosity decreases as the mechanical load applied to the melt increases.
b. *Entropy elasticity* The molecules become oriented by the flow in the nozzle. This corresponds to a rubberlike elastic deformation, which is canceled as soon as the force is released outside the nozzle. The extrudate has a much larger diameter than the nozzle. This phenomenon is called extrudate swelling.
c. *Viscoelasticity* The coupling between viscous and elastic processes is time dependent.

This behavior implies that melts (and also solutions) of polymers are non-Newtonian, rubberlike, viscoelastic liquids.

Shear Viscosity. The flow behavior during shear deformation is described by the shear stress τ and the time derivative of the shear

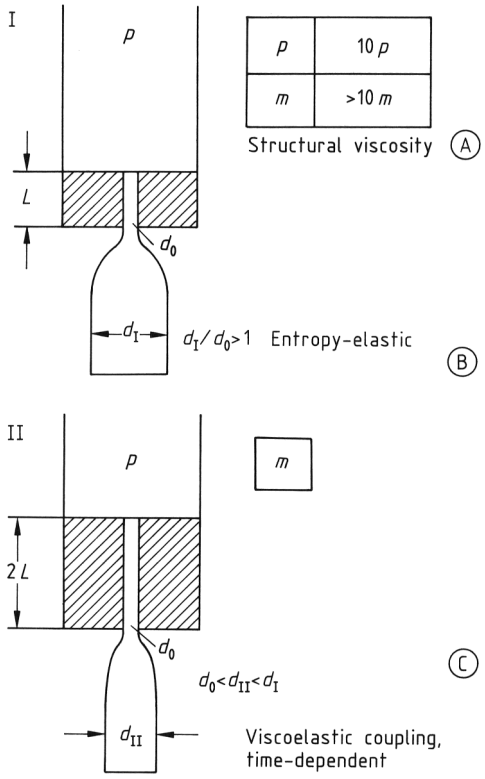


Figure 48. Rheological properties of plastic melts [249]

γ, that is, the shear rate $\dot{\gamma}$. In addition to the nonlinear formulas $\tau = \mathbf{F}(\dot{\gamma})$ and $\ddot{\gamma} = \mathbf{f}(\tau)$, a viscosity η is also defined for polymers: $\eta = \tau / \dot{\gamma}$.

This viscosity is independent of the shear rate only at very low values of the latter; that is, only in this region does a polymer melt behave like a Newtonian liquid (linear flow region). At the high shear rates used in plastics processing, viscosity decreases rapidly. The high rate of deformation obviously changes the tangled-chain structure in the melt. This concept gives rise to the term "structural" viscosity. Thus, quite generally, $\tau = \eta_s(\dot{\gamma})\,\ddot{\gamma}$, where η_s is the structural viscosity.

The shear-rate-dependent viscosity at very low shear rates is called the zero-shear viscosity:

$$\eta_0 = \lim_{\gamma \to 0} \eta_s(\gamma)$$

Figure 49 shows curves of viscosity versus shear rate for a Polyamide 6 melt at various temperatures.

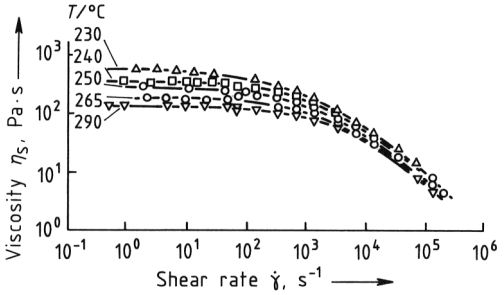


Figure 49. Viscosity of a polyamide 6 melt at various temperatures

In both the linear and the nonlinear regions, viscosity decreases with increasing temperature; see also [250].

The zero-shear viscosity η_0 is strongly dependent on the molecular mass above a critical value $M_r = M_c$. For commercial polymers, which always have $M_r > M_c$, this strong dependence of η_0 on M_r also manifests itself in the viscosity function $\eta(\dot{\gamma})$. The molecular-mass distribution, on the other hand, influences the elastic phenomena associated with viscous flow. Extrudate swelling becomes increasingly marked as the distribution becomes broader. The form of the viscosity function stays the same as molecular mass varies but changes with molecular-mass distribution.

Flow curves are usually determined with capillary viscosimeters. A disadvantage of the generally very convenient capillary viscosimeter is that the shear rate in the melt is not constant from point to point. Shear stress and shear rate increase from the center of the capillary toward the wall. The shear rate is zero at the capillary axis (see Fig. 50). In contrast, all particles of the liquid can be subjected to the same shear rate in rotational viscosimeters. This uniformity of shear rate cannot be achieved in a capillary.

Because it is easy to use, however, the capillary viscosimeter is employed widely in the roudetermination of flow curves. A standard method has been devised so that the results obtained can be compared [252]. The melt is forced through a capillary of specified size; either the test pressure at a specified volume flow rate or the volume flow rate at a specified test pressure is determined. In general, one charge in the cylinder yields several pairs of volume flow rate and test pressure values. The

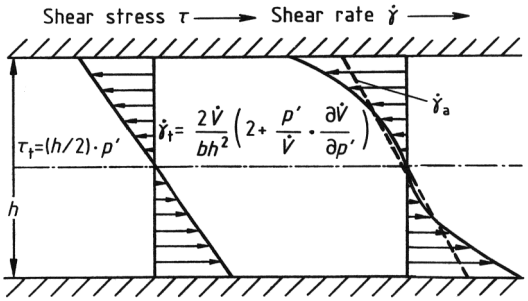


Figure 50. Steady-state shear flow in a flat-slot capillary [251] τ_t = true shear stress at wall; γ_t = true shear rate at wall; γ_a = apparent shear rate at wall; V = volume flow rate; p' = axial pressure gradient; b = capillary width Dashed curve: Newtonian liquid; solid curve: structurally viscous liquid

apparent shear rate $\dot{\gamma}_a$ is calculated from the flow rate and the capillary diameter, and the apparent shear stress τ_a is calculated from the capillary dimensions and the test pressure. The form $\dot{\gamma}_a = f(\tau_a)$ is recommended for flow curves used in comparisons (e.g., in quality control). The capillaries must have identical dimensions. The use of apparent flow curves and viscosity curves for the design of flow channels should be avoided. The Weissenberg and Rabinowitsch correction method [253], which cannot be discussed further here, gives the shear stress at the capillary wall (true shear stress τ_t) and the true shear rate $\dot{\gamma}_t$. The geometry-independent flow curve $\dot{\gamma}_t = f(\tau_t)$ and the viscosity function $\eta(\dot{\gamma}) = \tau_t/\dot{\gamma}_t$ are obtained from these values. The functions cited are indeed measured for the wall layer only, but they are valid in the bulk of the liquid as well, so that the subscript t can be omitted in the notation (units are s^{-1} for shear rate, Pa for shear stress, and Pa · s for viscosity). If the measured flow curves or viscosity functions are to be used for calculating steady-state shear flows in plastics-processing machinery, it is desirable to derive a mathematical approximation to the measured curves. Two approaches have proved useful: the Ostwald/de Waele power law approximation and the Carreau approximation [254], [255]. A large number of flow curves for commercial thermoplastics have been collected in [256].

Extensional Viscosity. During many processes employed in the plastics industry, such as melt spinning, film blowing, blow molding, coating at high takeoff speed, and injection molding, the melt is subjected not only to shearing but also to extension. Often the last deformation process performed on the melt before it hardens is an extension process that establishes the molecular orientation in the finished article. In contrast to low-viscosity Newtonian liquids with low tensile strength, plastic melts can be extended greatly without rupturing. The total extension consists of an entropy-elastic flow component and a viscous flow component; the ratio of the two components depends strongly on the external conditions and the product. The extensional deformation ε is characterized by the length change dl relative to the instantaneous length l: $d\varepsilon = dl/l$ (Hencky's measure).

Thus the Hencky extension ε of a rod l with initial length l_0 is given by $\varepsilon = \int dl/l = \ln(l/l_0) = \ln\lambda$. The Hencky extension is thus equal to the natural logarithm of the degree of stretching λ, and the rate of extension is $\dot{\varepsilon} = \dot{l}/l_0$.

The measurement of stress – strain or tensile creep curves of melts is described in [256], [257]. An arrangement described by Münstedt is shown in Figure 51, whereas Figure 52 shows

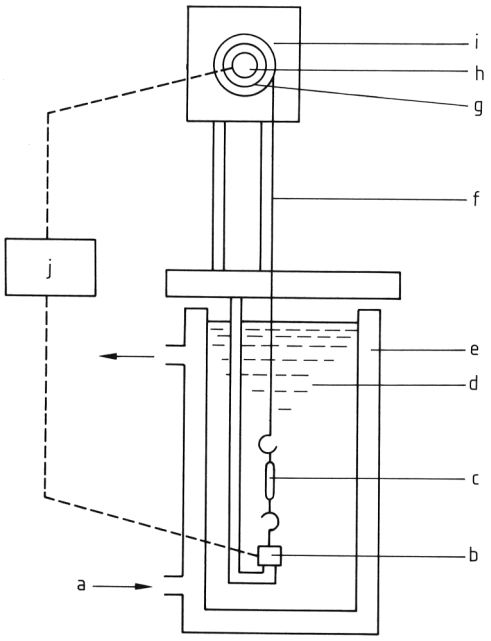


Figure 51. Münstedt extensional viscosimeter [256] a) Heating liquid; b) Load-measuring cell; c) Specimen; d) Oil bath; e) Temperature-controlled vessel; f) Belt; g) D.c. motor; h) Strain gauge; i) Takeup spool; k) Monitoring and control unit

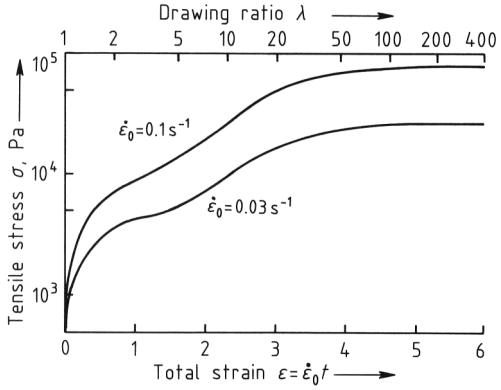


Figure 52. Stress – strain curves for low-density polyethylene melt at 150 °C for various constant rates of extension

stress – strain curves of a low-density polyethylene specimen at various constant extension rates [258].

The extensional viscosities derived from stress-strain curves are plotted as a function of either extension at constant tensile stress σ_0 or extension at constant extension rate $\dot{\varepsilon}$. The extensional viscosity $\eta_F(t)$ is given by $\eta_F(t) = \sigma(t)/\dot{\varepsilon}_0$, where $\sigma(t)$ is the measured tensile stress relative to the true cross-sectional area at time t, and $\dot{\varepsilon}_0$ is the extension rate determined in an extensional rheometer, which is constant over time; see also [259].

Finally, some flow anomalies of importance in plastics processing should be mentioned [259]. When a critical flow rate or wall shear stress value is exceeded, rough areas, termed melt fractures, are seen on the extrudate surface. These phenomena cannot be attributed to the critical turbulence of a flow, determined by the Reynolds number; they are due to the viscoelasticity of the melt (elastic turbulence). The onset of elastic turbulence is associated with a critical state of stress. This critical stress decreases as the molecular-mass distribution of the melt broadens. Modifications in the nozzle inlet reduce the occurrence of melt fracture [260].

If the melt is subjected to extensional loading at the nozzle outlet, periodic rupturing of the extrudate surface can be induced. The scaly surface is referred to as sharkskin. A periodic alternation of wall adhesion and wall slipping is observed at a critical wall stress in the nozzle, particular in high-density polyethylene melts. This phenomenon can also lead to a surface structure resembling melt fracture.

Abbreviations

a	constant
a	thermal diffusivity
a_k	impact strength (notched)
a_k	stress concentration factor
A	amplitude
A	flow area
b	constant
b	heat penetration coefficient
B	static load
c_p	specific heat
C	elastic constants
$C(t)$	compliance
d	mechanical loss factor
d	thickness of layer
D	diffusion constant
D_r	"dispersive power"
e	strain
$\dot{e}$	strain rate
E	modulus of elasticity
$E_c(t)$	creep modulus
E_d	dielectric strength
$E(t)$, $E_r(t)$	time-dependent modulus of elasticity
f	oscillating frequency
F	friction force
F_d	factor for damping effects
F_g	factor for dimensional effects
G', G	shear modulus
$h(\tau)$	distribution function of the relaxation time or relaxation spectrum
$H(\ln \tau)$	relaxation spectra
I	isotropic stress invariant
$\boldsymbol{I}$	moment of inertia
I_0	incident light intensity
K	bulk modulus
l	length
L	thickness of composite
M	complex modulus
M'	dynamic modulus
M''	loss modulus
$M(t)$	relaxation modulus
M_i	spring constant
n_C	refractive index at C-line
n_F	refractive index at F-line
N	cycles of failure
N	normal force
P	permeability
P	differential operator
P_z	polarization direction

Q	differential operator
t	loading time
T_c	contact temperature
v	Abbé number
α	linear coefficient of thermal expansion
α	molecular polarizability
β	volume coefficient of thermal expansion
γ	shear
$\dot{\gamma}$	shear rate
$\dot{\gamma}_a$	apparent shear rate
$\dot{\gamma}_t$	true shear rate
δ	phase shift
$\tan \delta$	loss factor
ε	total strain
$\dot{\varepsilon}$	strain rate
ε_0	constant strain during relaxation test
ε	dielectric constant
ε	extensional deformation
$\dot{\varepsilon}$	extension rate
$\varepsilon'(\omega)$	dielectric constant (permittivity)
$\varepsilon''(\omega)$	dielectric loss factor
ε^*	complex dielectric constant
$\varepsilon', \varepsilon'_r$	relative permittivity
ε''	dielectric loss factor
η	viscosity
η_0	zero shear viscosity
η_F	extensional viscosity
η_S	structure viscosity
λ	thermal conductivity
λ	logarithm of the degree of stretching
Λ	logarithmic decrement
μ	friction coefficient
ξ	integration variable
ϱ	density
ϱ_0	constant
ϱ_D	volume resistivity
σ	stress
$\dot{\sigma}$	stress rate
σ_0	constant stress during creep test
σ_a	initial stress; stress amplitude
$\sigma_{B/t}$	creep strength
σ_{crit}	stress exeding a critical value
$\sigma_{\varepsilon/t}$	"time yield limit"
σ_m	mean stress
σ_{max}	maximal stress
σ_n	nominal stress
τ	relaxation time
τ	shear stress
τ_a	apparent shear stress
τ_t	true shear stress
ω	angular frequency

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Plastics, Additives

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1. Introduction

As plastics find new applications, they face increasingly stringent requirements regarding their service life, durability, and many other properties. A variety of approaches are taken to meet these requirements. One approach is to modify the chemistry of the macromolecules from which plastics are made (e.g., by using new monomers or copolymerization). Current developments in the area of polymer blends also offer a great deal of scope for innovation. Another important way of improving the properties of plastics is to employ additives. These agents have made a decisive contribution to the widespread use of plastics and promise to be useful tools for solving future problems.

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Plastics additives can be classified into three main groups:

1. Additives that stabilize plastics against degradation and aging during processing or in use. Degradation usually involves chain cleavage of the macromolecules and can proceed through the addition of energy (e.g., shear forces, heat, UV light) or chemical attack (e.g., oxidation, hydrolysis). These additives are called antioxidants, light stabilizers, or heat stabilizers.
2. Additives that facilitate or control processing (e.g., lubricants, mold-release agents, or blowing agents).
3. Additives that impart new, desirable qualities to plastics, such as resistance to burning, transparency or color, improved mechanical or electrical properties, dimensional stability, and degradability. Such additives include flame retardants, fillers, dyes, pigments, antistatic agents, nucleating agents, optical brighteners, impact modifiers, and plasticizers. Plasticizers are discussed elsewhere, → Plasticizers.

Surveys of additive groups are given in [1], [2]. New developments are published monthly in [3]. The total amount of additives (excluding fillers and pigments) used worldwide by the plastics industry in 1990 is estimated at ca. 1.7×10^6 t (Fig. 1).

The concentration of additives varies greatly, ranging from a few parts per million for some stabilizers to more than 50 % for certain flame retardants or fillers.

Although additives can be added to the monomer prior to polymerization, they are usually introduced immediately after polymerization, blended, and extruded to form granular (pelletized) products and compounds. Many additives are not introduced until the granules are processed into moldings, films, or fibers.

Additives with monomer functions can be incorporated chemically into the plastic if they are introduced before polymerization. In the case of agents added before processing, the use of "masterbatches" (i.e., granular products containing the concentrated additive in a polymer vehicle) is often advisable.

Plastics generally contain many additives. Preblended additive systems and combination masterbatches are commercially available; they contain optimal proportions of additives that are mutually compatible or have a synergistic action.

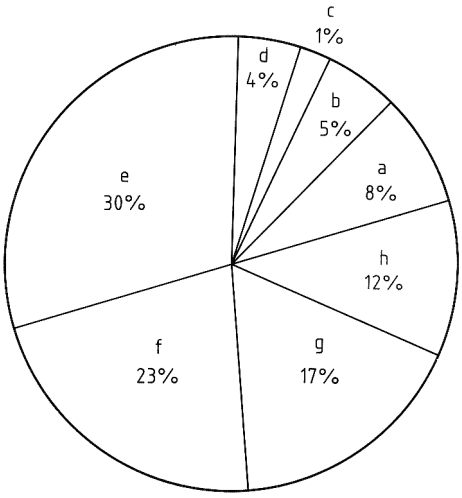


Figure 1. World consumption of plastics additives excluding fillers and pigments in 1990 (100 % = 1.7×10^6 t) a) Lubricants and related compounds; b) Antioxidants; c) Light stabilizers; d) Miscellaneous additives; e) Flame retardants; f) Plasticizers; g) Poly(vinyl chloride) heat stabilizers; h) Impact modifiers

2. Antioxidants

See also → Antioxidants.

2.1. Purpose and Requirements

Antioxidants prevent or retard the autoxidation of polymers and minimize associated damage (e.g., discoloration, reduction in gloss, cracking, embrittlement); i.e., they stabilize the physical properties of plastics. Oxidation reactions generally proceed via different mechanisms that depend on the structure of the polymer. They are often catalyzed by catalyst residues and contaminants. They are also accelerated by the addition of thermal or mechanical energy during plastics production and processing.

Three forms of stabilization are used: prestabilization, stabilization during processing, and long-term stabilization.

Most antioxidants are themselves oxidized and consumed in performing their function, so that the oxidation behavior of the additive in a given polymer is crucial for its effectiveness [4]. A number of other requirements apply to antioxidants:

1. They must be thermally stable and nonvolatile at processing temperatures
2. They must be soluble in polymers and no chalking should occur at service temperatures
3. They must not have an intrinsic color, and their oxidation products must have minimal color
4. Any acidic hydrolysis products must not corrode machinery
5. They must resist extraction
6. They must be odorless and tasteless
7. They must not create toxicity problems (many must be approved as indirect food additives)

2.2. Chemical Classes

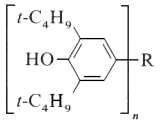
Antioxidants are divided into two classes on the basis of their mode of action (see Section 2.3):

1. *Primary antioxidants*: sterically hindered phenols, secondary aromatic amines, and sterically hindered amines (HALS)
2. *Secondary antioxidants*: phosphites, phosphonites, thioethers (sulfides), and metal salts

Primary antioxidants can be used by themselves for prestabilization and long-term stabilization. Secondary antioxidants are used in combination with primary antioxidants, especially for stabilization during processing and for long-term stabilization under severe thermal conditions. Synergistic effects often occur in such systems (e.g., phenol and phosph(on)ites or phenol and thioethers). Antagonistic effects are also observed, however (e.g., between thioethers and HALS) [5].

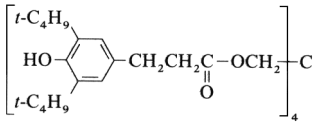
The stabilizer system often includes other components that complex or neutralize degradation-promoting catalysts or acid traces. These may be metal deactivators (oxamides, hydrazones, and hydrazides) or acid scavengers [calcium or magnesium stearate, hydrotalcite (basic Mg/Al carbonate), and epoxy compounds].

Sterically Hindered Phenols. Industrial products are mostly derived from 2,6-di-*tert*-butylphenol (**1**; $n = 1$, R = H); or, less often, from 2-*tert*-butyl-6-methylphenol, 2-*tert*-butyl-5-methylphenol, or other hindered phenols. Tabulations are given in the literature [1], [6].

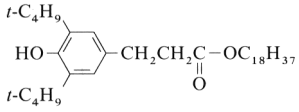


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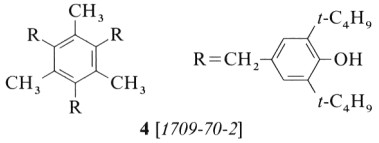
The simplest representative and oldest product of this class is 2,6-di-*tert*-butyl-4-methylphenol [*128-37-0*] (butylated hydroxytoluene, BHT) with $n = 1$ and R = CH_3. Variation of n from 1 to 4 and of R results in a range of hindered phenols with high molecular mass and thus low volatility, good solubility in certain polymers, and only slightly colored oxidation products. Products **2–4** are commonly used.



2 [*6683-19-8*]

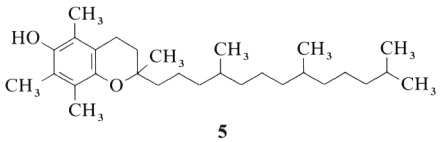


3 [*2082-79-3*]



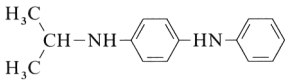
4 [*1709-70-2*]

The natural compound α-tocopherol [*59-02-9*] or vitamin E (**5**) is also used as an antioxidant [8], [8].



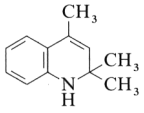
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Secondary Aromatic Amines and Dihydroquinolines. Industrial products are derived chiefly from diphenylamine or *p*-phenylenediamine. A widely used representative of this class is 4-isopropylaminodiphenylamine [*101-72-4*] (**6**):



6

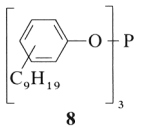
2,2,4-Trimethyl-1,2-dihydroquinoline [*147-47-7*] (**7**) should also be mentioned:



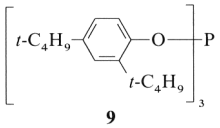
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Sterically Hindered Amines (HALS). The abbreviation HALS stands for "hindered amine light stabilizers." They are described in more detail in Chapter 3 and are based on the 2,2,6,6-tetramethylpiperidine structure.

Phosphites and Phosphonites. The simplest industrial phosphite antioxidants are tris(nonylphenyl) phosphite [*26523-78-4*] (TNPP) (**8**) and tris(2,4-di-*tert*-butyl) phosphite [*31570-04-4*] (**9**).

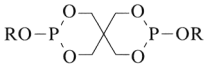


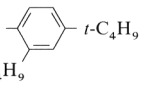
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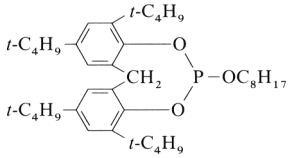
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The cyclic phosphites 10, 11 [9], and 12 [10] are also available:

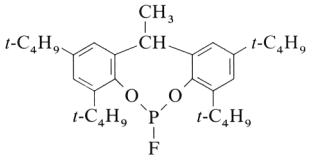


10a [*26741-53-7*], R = 

10b [*3806-34-6*], R = $C_{18}H_{37}$

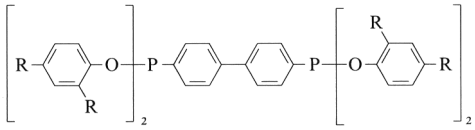


11 [*126050-54-2*]



12 [*118337-09-0*]

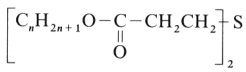
Compound **13** is an industrially used phosphonite antioxidant [11]:



13 [*38613-77-3*], R = *t*-C_4H_9

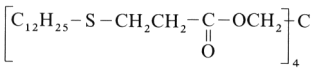
The substituents influence not only the volatility and the solubility in polymers, but also the stability of the product to hydrolysis.

Organosulfur Compounds. Organosulfur antioxidants in practical use are the dilauryl [*123-28-4*] (**14**, $n = 12$), dimyristyl [*16545-54-3*] (**14**, $n = 14$), and distearyl [*693-36-7*] (**14**, $n = 18$) esters of thiodipropionic acid (**14**) which are abbreviated as DLTDP, DMTDP, and DSTDP, respectively.



14

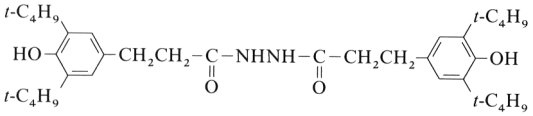
Disulfides such as dioctadecanyl disulfide [*2500-88-1*] or higher molecular mass products such as **15** are used less often.



15 [*29598-76-3*]

Metal Compounds. Zinc and nickel dithiocarbamates or mercaptobenzimidazoles are sometimes used.

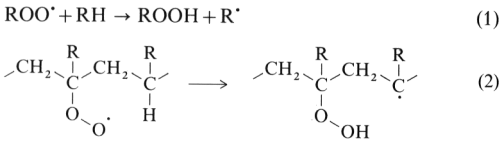
Metal Deactivators. The oxamides or hydrazine derivatives used as metal deactivators often have hindered phenol functions in the molecule as well, so that they also have a primary antioxidant action [1]. A typical structure is:



16 [*32687-78-8*]

2.3. Mechanism of Action

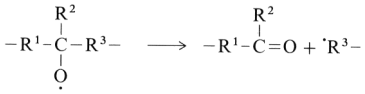
Thermooxidative degradation is an autocatalytic, free-radical chain reaction that involves initiation, propagation, branching, and termination stages. Primary radical sites $R^{\bullet}$ are initially formed by the abstraction of labile hydrogen atoms (e.g., tertiary or allylic hydrogens or those in the α-position to ether oxygen or amide nitrogen atoms). In the presence of oxygen, the primary radicals are oxidized to peroxy radicals $ROO^{\bullet}$. The peroxy radicals then take part in intermolecular (Eq. 1) and intramolecular (Eq. 2) chain propagation reactions to form new radical sites and hydroperoxides:



(1)

(2)

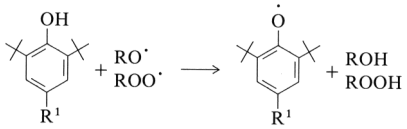
The chain propagation reactions are rate determining for thermooxidative degradation. Tertiary hydrogen atoms are about three times more reactive than secondary hydrogens. The hydroperoxides undergo thermal decomposition or participate in reactions catalyzed by trace metals to form oxy ($RO^{\bullet}$, $HO^{\bullet}$) or peroxy radicals ($ROO^{\bullet}$), which cleave additional bonds in the polymer and generate new radical sites in the chain or break the polymer chain to give carbonyl groups:



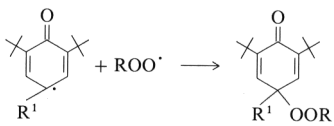
The extent of thermooxidative degradation in many polymers can be estimated via the concentration of peroxy radicals, hydroperoxide groups, and carbonyl groups. Macroradicals can also react with C=C bonds in the polymer, especially with vinyl groups [12], or can recombine and result in undesirable cross-linking (gel formation).

Antioxidants act by trapping free radicals formed in the polymer (primary antioxidants), reduce hydroperoxides to hydroxyl groups (secondary antioxidants), or form complexes with trace metals that would otherwise catalyze hydroperoxide decomposition (metal deactivators). Antioxidant mechanisms are described in [13–18]; see also → Antioxidants, Section 3.2.→ Antioxidants.

Hindered Phenols. Hindered phenols are radical-trapping antioxidants for oxy and especially peroxy radicals:



The phenoxy radicals with their bulky substituents are stabilized by steric hindrance and cannot attack the polymer. These radicals are transformed to quinonoid structures that can recombine with other peroxy radicals:



The formation of yellow quinonoids is a drawback of this class. The intensity of the color

depends on the structure of R^1; it is particularly high in the case of BHT due to the formation of stilbenequinones.

Secondary Aromatic Amines also act by trapping peroxy radicals. Since the products derived from secondary aromatic amines are generally dark in color, their use is restricted to colored elastomers. Their stabilizing action against ozone degradation should be noted.

HALS are used primarily as light stabilizers. They can trap both carbon radicals and peroxy radicals at ambient temperatures. The active species is a hindered nitroxyl radical, which is regenerated (see Chap. 3). HALS are effective long-term stabilizers [19], [20]; nonvolatile, high molecular mass derivatives are especially useful [21].

Phosphites and Phosphonites. The secondary phosphite and phosphonite antioxidants reduce hydroperoxides and are themselves oxidized to phosphates and phosphonates:

$$P^{III} + ROOH \rightarrow P^{V} + ROH$$

Peroxy radicals are analogously reduced to oxy radicals. Phosphites and phosphonites may also complex and thus deactivate trace metals (e.g., polymerization catalyst residues). Their oxidation products are colorless, so they are particularly successful as color stabilizers. Their action is especially useful in the processing of polymer melts, where they also protect phenolic antioxidants against premature oxidation.

Organosulfur Compounds decompose hydroperoxides. Sulfides, for example, are converted to sulfoxides, sulfenic acids, and sulfur dioxide, which in turn can reduce further hydroperoxides. Sulfur-containing stabilizers can also regenerate phenolic antioxidants from their quinonoid structures. Their action is most pronounced at higher temperatures in solid plastics. The odor of the reaction products can be a drawback.

Metal Deactivators act by chelating metal ions [22], particularly metals that have a number of oxidation states and catalyze hydroperoxide decomposition even at low temperatures. These metals include copper (from cablewires), iron, manganese (from fillers), and titanium (from polymerization catalysts).

For the effects of metals and metal deactivators, see [23].

2.4. Test Methods

The two most important test methods for antioxidants are the multiple extrusion test and the oven test (DIN 53 383, ASTM D 1870–68).

The *multiple extrusion test* examines degradation in the polymer melt (i.e., stabilization during processing). The antioxidant is blended with the polymer, and the resulting granules are regranulated up to ten times in succession in an extruder under defined temperature conditions. The yellowness index (ASTM D 1925–70) and the melt viscosity (melt flow index, MFI, ASTM D 1238–70) or solution viscosity are measured. The melt viscosity can also be determined online in an extruder equipped with a bypass [24].

In the *oven test*, polymer degradation is studied in the solid phase (i.e., long-term stabilization is determined). Test plates of the polymer are placed on rotating trays in special furnaces with air recirculation. Their appearance (browning, reduction in gloss and transparency), mechanical properties (brittleness, tensile strength, impact strength), and analytical data (carbonyl bands in the IR) are evaluated after various times. To shorten the test period, the oven test is often run at 100 – 150 °C, but correlation of the results with room temperature is problematic especially in the case of metal deactivators.

Other test methods include

1. Thermogravimetric analysis, especially for plastics such as polyoxymethylene that tend to undergo thermal depolymerization
2. Torque measurements on polymer melts in the Brabender, especially for plastics that tend to cross-link (e.g., polyethylene)
3. Transparency measurements on extruded films
4. Determination of the induction period in an oxygen absorption test at elevated temperature (OIT test)

2.5. Uses

Polyolefins. The optimal antioxidants for polyolefins depend on the type of resin, production

process (catalyst; solution, suspension, or bulk polymerization), comonomer, filler, application (moldings, films, fibers), and other factors. Modern bulk polymerization processes, in which purification steps are omitted or polymers are produced directly as spherical granules, have led to reformulation of stabilization systems.

The primary antioxidant BHT, with its high volatility and yellowing tendency, is losing ground to higher molecular mass hindered phenols (e.g., **2-4**). For prestabilization up to 250 ppm of **3** is usually added at the polymerization stage; ca. 500 – 1000 ppm of a phenolic antioxidant is subsequently added for stabilization during processing and service. Higher concentrations are seldom used because of the risk of yellowing.

The main secondary antioxidants used during processing are the phosphites **8-10** and the phosphonite **13**, whereby especially **13** not only stabilizes the melt viscosity but also offers much better color stabilization than phosphites such as **8** and **9**. The phosph(on)ites are used at concentrations of 500 – 2000 ppm.

Figures 2 and 3 illustrate the stabilization obtained with phosphites and phosphonites during the processing of polypropylene and linear low-density polyethylene (LLDPE), respectively. Whereas polypropylene exhibits an increase in melt flow index (degradation by chain cleavage), LLDPE shows a decline (degradation dominated by cross-linking).

The selection of antioxidants also depends on the solubility in the polymer, which is especially critical for LLDPE. If the polymerization process already yields a granular product in the reactor, antioxidants can be applied to the reactor granules by spraying on the surface. Low-melting products such as **14** are especially suitable for this purpose.

Thioethers are preferentially used as synergists when severe thermal requirements apply to long-term stabilization. They are employed at concentrations of ca. 1000 – 3000 ppm.

Metal deactivators are used at the 500 – 5000 ppm level (higher concentrations in talc-filled polypropylene).

Other formulation guidelines are given in [1].

Styrene Polymers. Phenolic antioxidants (up to 2000 ppm) are added to high-impact polystyrene modified with polybutadiene. They are usually introduced before polymerization. Phosphites and phosphonites are sometimes employed as color stabilizers.

In acrylonitrile – butadiene – styrene copolymers (ABS), the antioxidants are usually introduced into the polybutadiene latex phase by

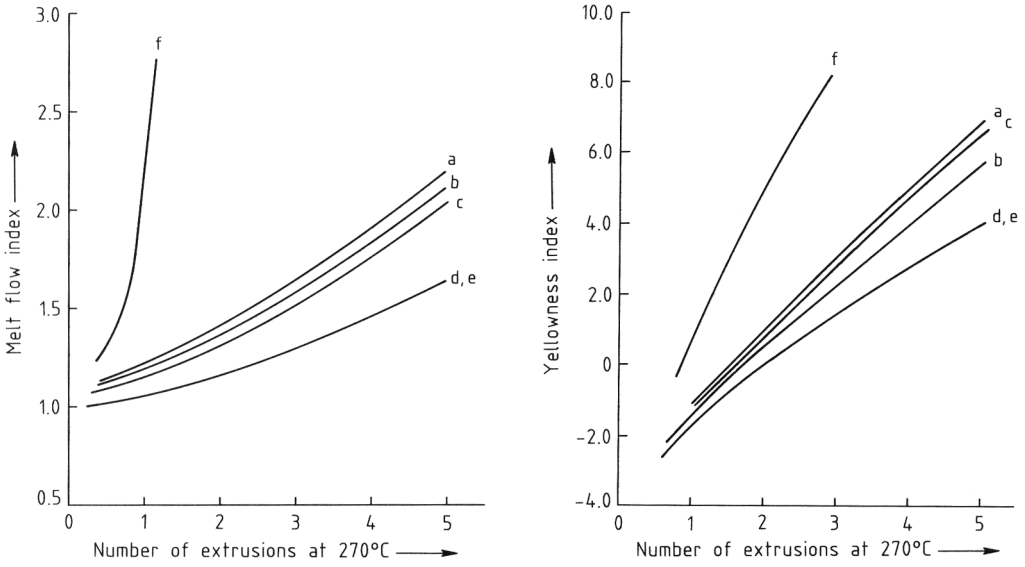


Figure 2. Stabilization of polypropylene in a multiple extrusion test with 0.1 % phenolic antioxidant (**2**) and 0.1 % calcium stearate as basic stabilization and 0.1 % phosph(on)ite process stabilizer a) Phosphite (**9**); b) Phosphite (**10a**); c) Phosphite (**12**); d) Phosphonite (**13**); e) Phosphite (**11**); f) No process stabilizer

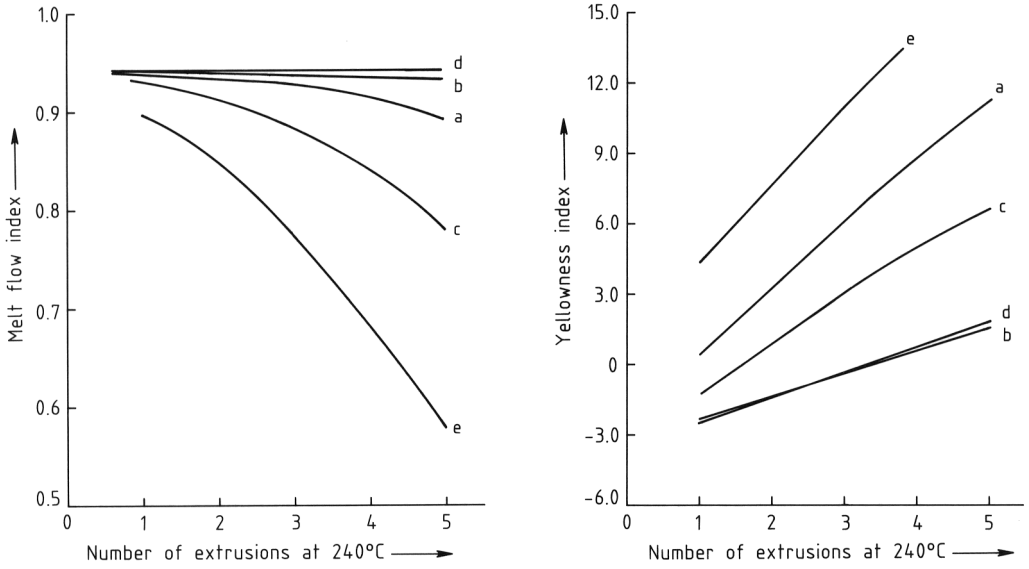


Figure 3. Stabilization of linear low-density polyethylene in a multiple extrusion test with 0.1 % phenolic antioxidant (**3**) and 0.1% calcium stearate as basic stabilization and 0.15% phosph(on)ite process stabilizer a) Phosphite (**9**); b) Phosphite (**10a**); c) Phosphite (**10b**); d) Phosphonite (**13**); e) No process stabilizer

emulsification before it is blended with polystyrene – polyacrylonitrile. Along with 1000 –2000 ppm of phenolic antioxidants, larger amounts of phosphite **8** or DLTDP are used.

Other Plastics [1]. Antioxidants play a less important role in plastics other than polyolefins and the styrene polymers described above. Secondary aromatic amines, BHT, TNPP, as well as high molecular mass phenols are used in elastomers and polyurethanes.

Although engineering thermoplastics (e.g., polycarbonates, polyesters, polyamides) are less sensitive to thermooxidative degradation, hindered phenols and phosph(on)ites are used for color stabilization or long-term stabilization.

2.6. Legal Aspects

Because plastics are widely used in food packaging and agriculture, antioxidants must be approved as indirect food additives by national agencies such as the FDA (USA) and the Bundesgesundheitsamt (Federal Health Office, Germany). Unified approvals are expected to apply throughout the EC as of 1993. Approval is based on toxicity and extraction tests (extraction of antioxidants from plastics by food simulants). Most well-established antioxidants have received broad approval for food use.

2.7. Economic Aspects

Table 1 presents 1990 market volumes of antioxidants. Polyolefins, ABS, and polystyrene account for ca. 80 – 90 % of the antioxidant market. Prices of antioxidants are given in [25].

Antioxidants are often marketed in the form of powder blends. The most important producers and trade names are listed in Table 2.

Table 1. Estimated market volume of antioxidants in 1990 (10^3 t)

Region	Phenols	Thioethers	Phosph (on)ites	Other	Total
United States	14	3	6	2	25
Western Europe	15	3	7	3	28
Japan	8	2	3	2	15
Other	10	2	3	2	17
Total	47	10	19	9	85

Table 2. Manufacturers and trade names of antioxidants

Manufacturer	Trade names	Phenols	Phosph(on)ites	Thioethers	Aromatic amines	Metal deactivators	Blends
Adeka Argus	Mark	X	X	X		X	X
Akzo Chemie	Perkanox	X					
American Cyanamid	Cyanox	X		X			X
BASF	Sicostab	X					X
Bayer	Vulkanox	X			X		
B. F. Goodrich Chem.	Goodrite	X			X		
Chem. Werke Lowi	Lowinox	X	X				
Ciba-Geigy	Irganox, Irgafos	X	X	X		X	X
Daiichi Kogyo Seiyaku	Lasumit			X			
Dover Chemicals	Doverphos		X				
Eastman Chemicals	Tenox	X				X	
Enichem Synthesis	Anox, Alkanox	X	X				X
Ethyl Corporation	Ethanox	X	X				
Ferro Corporation	Oxi-chek	X					
General Electric	Ultranox, Weston	X	X		X		X
W. R. Grace				X			
Hitachi	Cunox					X	
Hoechst	Hostanox	X	X	X		X	
ICI	Nonox, Topanol	X			X		X
Jokoku Chemicals			X				
Mitsubishi Petrochem.	Seenox	X		X			
Monsanto	Santonox, Santowhite Flectol	X			X		
Morton Thiokol	Carstab			X			
Olin Chemicals	Wytox	X	X				
Pennwalt	Anoxyn			X			
PMC Specialities Group	Prodox	X					
Raschig	Ralox	X					
Rhône-Poulenc	Rhodianox, Garbafix	X	X				
R. T. Vanderbilt	AgeRite, Vanox	X	X	X	X		
Sandoz Chemicals	Sandostab		X				
Schenectady Chemicals	Isonox	X					
Shell	Ionol, Ionox	X					
Shipro Kasei	Seenox	X		X			
Sumitomo	Sumilizer	X	X	X			
Ube Industries						X	
Uniroyal	Naugard, Aranox	X	X		X	X	X
Witco	Mark	X	X	X			X
Yoshitomo				X			

3. Light Stabilizers

3.1. Purpose and Requirements

Synthetic and natural polymers vary in their sensitivity to environmental influences. Ultraviolet radiation in sunlight plays a critical role because it has sufficient energy to break chemical bonds. The cleavage sites react with atmospheric oxygen and accelerate degradation (free-radical chain reactions; see Section 2.3). Many plastics therefore suffer yellowing, surface cracking, embrittlement, reduction of gloss, or chalking after a short time in outdoor service, and ultimately disintegrate. Light stabilizers are used to maximize protection against photodegradation.

Ultraviolet radiation is subdivided into UV-A (λ = 320 – 400 nm), UV-B (λ = 280 – 320 nm), and UV-C (λ <280 nm). Only UV-A and UV-B reach the Earth's surface in sunlight, and UV-B is largely responsible for the degradation of plastics.

The difference in damage (yellowing) caused by UV-A and UV-B in poly(vinyl chloride) (PVC) is shown in Figure 4. Plastics are generally fairly stable in the long-wavelength UV-A (350 – 400 nm). Most plastics are sensitive to wavelengths of 290 – 320 nm.

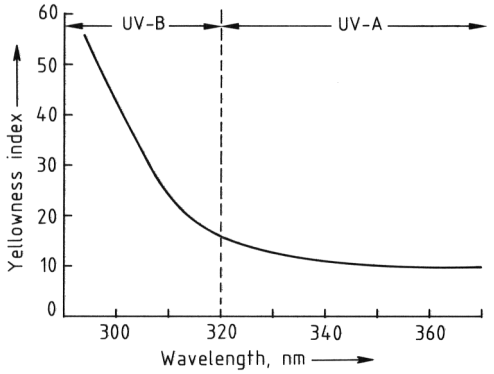


Figure 4. Damage in PVC as a function of the wavelength of UV light (300-h radiation)

Two methods are used to protect plastics against photodegradation: (1) incorporation of light stabilizers in the bulk plastic, and (2) coating with a light-stable or light-stabilized material that is largely opaque to the dangerous UV range.

Light stabilizers must have high light absorption; must resist extraction with water, hydrolysis, and thermal volatilization; and must themselves be stable toward UV radiation. Ideally, a light stabilizer should not be consumed while carrying out its function; it should operate in a closed cycle so that it still exists in active form even after a long period of weathering or use.

Other requirements include solubility in the polymer, stability under processing conditions, compatibility with other additives, and colorlessness. In certain applications, light stabilizers must be approved as indirect food additives.

The service life of a plastic is more than doubled by light stabilizers. Modern systems extend service life by a factor of 10 – 20 in many plastics, thus permitting their outdoor use.

3.2. Chemical Classes

Light stabilizers are classified in three groups according to their mode of action:

1. UV absorbers: 2-hydroxybenzophenones (BP-UVA), 2-hydroxyphenylbenzotriazoles (BT-UVA), oxalanilides (OA-UVA), 2-hydroxyphenyltriazines (TA-UVA), cinnamates (CA-UVA), salicylates (SA-UVA), and formamidines (FA-UVA)
2. Energy quenchers: nickel complexes (NIC)
3. Radical scavengers: hindered amines (HALS) and 4-hydroxybenzoates (HB)

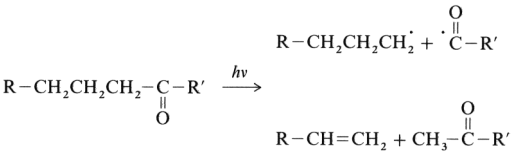
Table 3 lists some of the most important light stabilizers now in use, along with their trade names and producers.

Stabilization can also be achieved by incorporation of carbon black, titanium dioxide, or zinc oxide. The effect of colored pigments varies: phthalocyanine blue pigments have a stabilizing action; organic red and yellow pigments sensitize photodegradation.

3.3. Mechanism of Action

Photodegradation of Polymers. Photodegradation is initiated when radiation is absorbed by chromophores in the polymer structure itself (e.g., C=C, C=O) or by impurities or defects. Energy can be dissipated from excited states by emission of radiation (fluorescence from short-lived singlet states or phosphorescence from long-lived triplet states), release of heat, or energy transfer to nearby chromophores. If none of these mechanisms is available, photodegradation takes place with bond cleavage and formation of radicals. These radical sites react with oxygen and initiate autoxidative chain reactions. Excited molecular segments can also transfer energy to oxygen, converting it to higher-energy singlet oxygen, which accelerates oxidative degradation.

Oxidation to carbonyl groups in the macromolecules results in chain cleavage via the Norrish reactions:



Many plastics with aromatic residues (e.g., polycarbonates, polyesters, polyamides) tend to participate in "photo-Fries reactions", whose products may be colored or may be precursors of colored products:

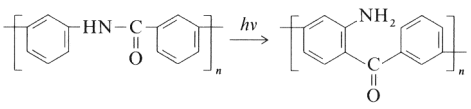
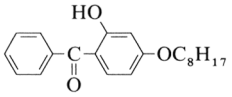
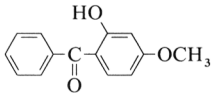
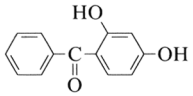
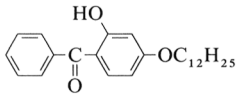
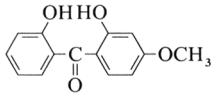
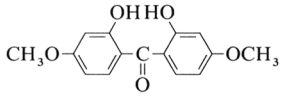


Table 3. Light stabilizers

Structure, CAS registry no., code	Trade name (producer)
2-Hydroxybenzophenones	
 [*1843-05-6*] BP-UVA 1	Cyasorb UV 531 (American Cyanamid) Mark 1413 (Adeka Argus) Chimassorb 81 (Ciba-Geigy) UV-Chek AM 300 (Ferro) Hostavin ARO 8 (Hoechst) Rhodialux P (Rhône-Poulenc) Uvasorb 3 C (Sigma) Seesorb 102 (Shipro Kasei) Aduvex 248 (Shell) Lowilite 22 (Chem. Werke Lowi) Sumisorb 130 (Sumitomo) Viosorb 130 (Kyodo Yakuhin) Uvinul 408 (BASF)
 [*131-57-7*] BP-UVA 2	Cyasorb UV 9 (American Cyanamid) Uvinul M-40 (BASF) UVA Bayer 325 (Bayer) Chimassorb 90 (Ciba-Geigy) Gafsorb 2H 4M (GAF) Rhodialux A (Rhône-Poulenc) Uvasorb MET (Sigma) Seesorb 101 (Shipro Kasei) Viosorb 110 (Kyodo Yakuhin) Sumisorb 110 (Sumitomo)
 [*131-56-6*] BP-UVA 3	Uvinul 400 (BASF) Aduvex 12 (Shell) Gafsorb 24 DH (GAF) DHB (Riedel de Haen) Rhodialux D (Rhône-Poulenc) Seesorb 100 (Shipro Kasei) Viosorb 100 (Kyodo Yakuhin)
 [*2985-59-3*] BP-UVA 4	Chimassorb 125 (Ciba-Geigy) Eastman Inhibitor DOBP (Eastman Chem.) Gafsorb 2H 4DD (GAF) Rhodialux 1200 (Rhône-Poulenc) Seesorb 103 (Shipro Kasei)
 [131-53-3] BP-UVA 5	Cyasorb UV 24 (American Cyanamid) Aduvex 24 (Shell) Sumisorb 140 (Sumitomo)
 [*131-54-4*] BP-UVA 6	Univul D-49 (BASF) Aduvex 424 (Shell)

(*continued*)

Table 3. (*Continued*)

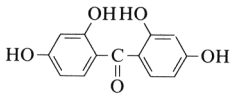
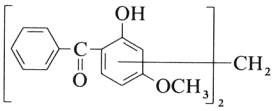
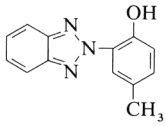
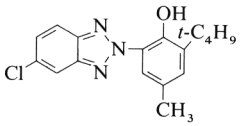
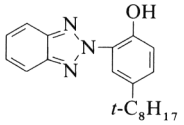
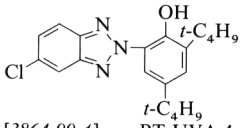
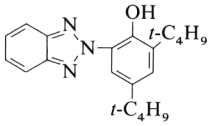
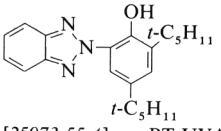
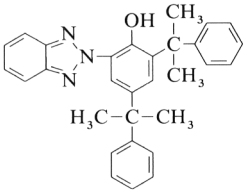
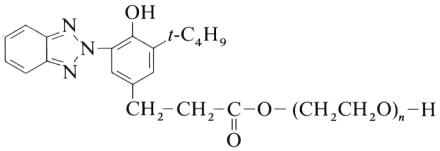
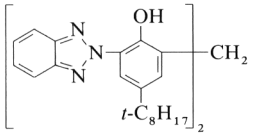
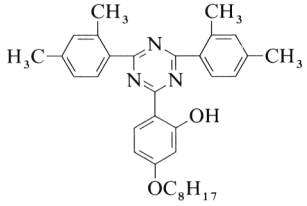
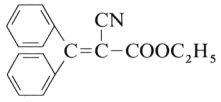
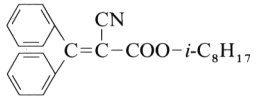
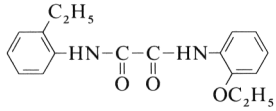
Structure, CAS registry no., code	Trade name (producer)
 [*131-55-5*] BP-UVA 7	Aduvex 412 (Shell) Uvinul D 50 (BASF)
 [69119-80-8] BP-UVA 8	Mark LA 51 (Adeka Argus)
2-Hydroxyphenylbenzotriazoles	
 [2440-22-4] BT-UVA 1	Tinuvin P (Ciba-Geigy) Mark LA 32 (Adeka Argus) Uvasorb SV (Sigma) Seesorb 701 (Shipro Kasei) Lowilite 55 (Chem. Werke Lowi) Viosorb 520 (Kyodo Yakuhin) Sumisorb 200 (Sumitomo)
 [*3896-11-5*] BT-UVA 2	Tinuvin 326 (Ciba-Geigy) Mark LA 36 (Adeka Argus) Seesorb 703 (Shipro Kasei) Viosorb 550 (Kyodo Yakuhin) Sumisorb 300 (Sumitomo)
 [*3147-75-9*] BT-UVA 3	Cyasorb UV 5411 (American Cyanamid) Sumisorb 340 (Sumitomo) Viosorb 583 (Kyodo Yakuhin) Seesorb 709 (Shipro Kasei)
 [*3864-99-1*] BT-UVA 4	Tinuvin 327 (Ciba-Geigy) Mark LA 34 (Adeka Argus) Seesorb 702 (Shipro Kasei) Viosorb 580 (Kyodo Yakuhin)
 [*3846-71-7*] BT-UVA 5	Tinuvin 320 (Ciba-Geigy) Seesorb 705 (Shipro Kasei) Viosorb 582 (Kyodo Yakuhin) Sumisorb 320 (Sumitomo)
 [*25973-55-1*] BT-UVA 6	Cyasorb 2337 (American Cyanamid) Tinuvin 328 (Ciba-Geigy) Seesorb 704 (Shipro Kasei) Viosorb 591 (Kyodo Yakuhin) Sumisorb 350 (Sumitomo)

Table 3. (*Continued*)

Structure, CAS registry no., code	Trade name (producer)
 [*70321-86-7*] BT-UVA 7	Tinuvin 234 (Ciba-Geigy) Tinuvin 900 (Ciba-Geigy)
 [*104810-48-2*] BT-UVA 8	Tinuvin 1130 (Ciba-Geigy)
 [*103597-45-1*] BT-UVA 9	Mark LA 31 (Adeka Argus)
2-Hydroxyphenyltriazines	
 [*2725-22-6*] TA-UVA-1	Cyasorb 1164 (American Cyanamid)
Cinnamates	
 [*5232-99-5*] CA-UVA-1	Uvinul N-35 (BASF) Seesorb 501 (Shipro Kasei) Viosorb 910 (Kyodo Yakuhin)
 [*6197-30-4*] CA-UVA-2	Uvinul 539 (BASF)
Oxalanilides	
 [*23949-66-8*] OA-UVA-1	Sanduvor VSU (Sandoz) Tinuvin 312 (Ciba-Geigy)

(*continued*)

Table 3. (*Continued*)

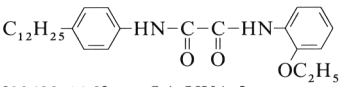
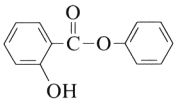
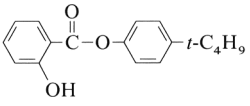
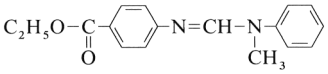
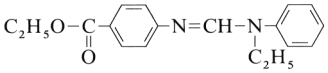
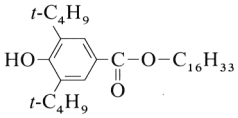
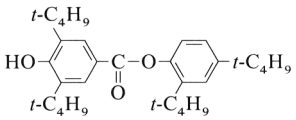
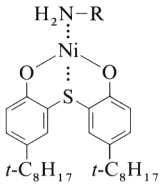
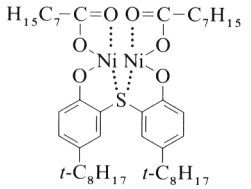
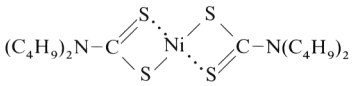
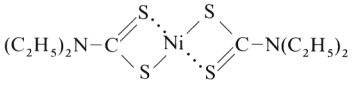
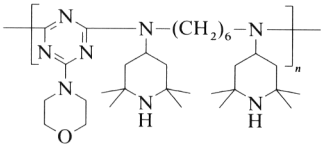
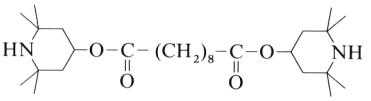
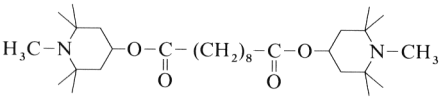
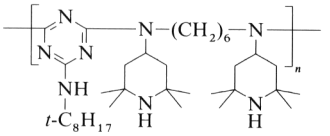
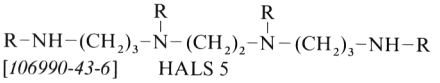
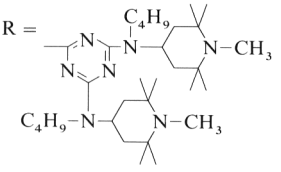
Structure, CAS registry no., code	Trade name (producer)
 [*82493-14-9*] OA-UVA-2	Sanduvor 3206 (Sandoz)
Salicylates	
 [*118-55-8*] SA-UVA-2	Eastman Inhibitor OPS (Eastman Chem.) Seesorb 201 (Shipro Kasei)
 [*87-18-3*] SA-UVA-2	Seesorb 202 (Shipro Kasei) Rhodialux K (Rhône-Poulenc) Viosorb 90 (Kyodo Yakuhin)
Formamidines	
 [*57834-33-0*] FA-UVA-1	Givsorb UV-1 (Givaudan)
 [*65816-20-8*] FA-UVA-2	Givsorb UV-2 (Givaudan)
4-Hydroxybenzoates	
 [*67845-93-6*] HB-1	Cyasorb UV 2908 (American Cyanamid)
 [*4221-80-1*] HB-2	Tinuvin 120 (Ciba-Geigy) Seesorb 712 (Shipro Kasei) UV-Chek AM 340 (Ferro) Viosorb 80 (Kyodo Yakuhin) Sumisorb 400 (Sumitomo)
Nickel complexes	
 R = C_4H_9 [*14516-71-3*] NIC-1	Cyasorb UV 1084 (American Cyanamid) Chimassorb N 705 (Ciba-Geigy) Rhodialux Q 84 (Rhône-Poulenc) Uvasorb Ni (Sigma)
same, R = C_8H_{17} [*67668-65-9*] NIC-2	Seesorb 612 NH (Shipro Kasei)

Table 3. (*Continued*)

Structure, CAS registry no., code	Trade name (producer)
 [*89073-38-1*] NIC-3	UV-Chek AM 205 (Ferro)
 [*13927-77-0*] NIC-4	UV-Chek AM 104 (Ferro) Antigene NBC (Sumitomo) Vanox NBC (R. T. Vanderbilt)
 [*14267-17-5*] NIC-5	Robac Ni PP (Robinson Brothers)
Hindered amines	
 [*90751-07-8*] HALS 1	Cyasorb UV 3346 (American Cyanamid)
 [*52829-07-9*] HALS 2	Tinuvin 770 (Ciba-Geigy) Mark LA 77 (Adeka Argus) Sanol LK 770 (Sankyo) Lowilite 77 (Chem. Werke Lowi)
 [*41556-26-7*] HALS 3	Tinuvin 765 (Ciba-Geigy) Tinuvin 292 (Ciba-Geigy) Sanol 292 (Sankyo)
 [*71878-19-8*] HALS 4	Chimassorb 944 (Ciba-Geigy)
 [*106990-43-6*] HALS 5	Chimassorb 119 (Ciba-Geigy)
	

(*continued*)

Table 3. (*Continued*)

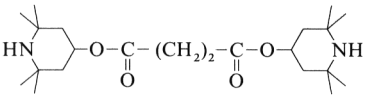
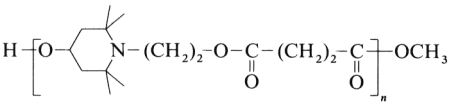
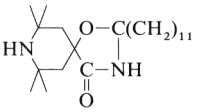
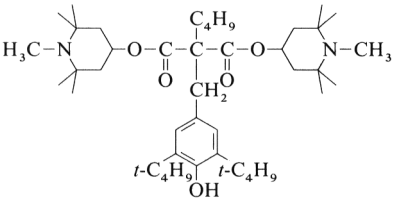
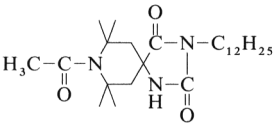
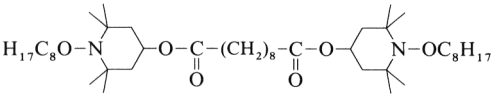
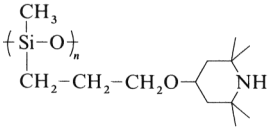
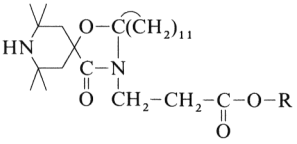
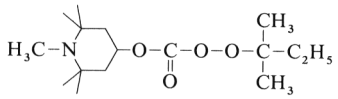
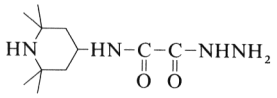
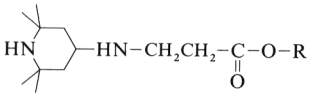
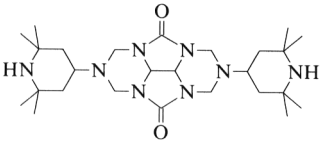
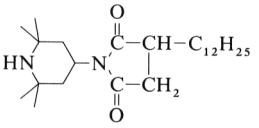
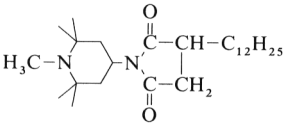
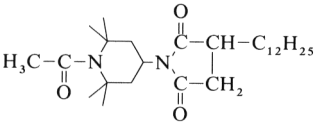
Structure, CAS registry no., code	Trade name (producer)
 [62782-03-0] HALS 6	Tinuvin 780 (Ciba-Geigy)
 [*70198-29-7*] HALS 7	Tinuvin 622 (Ciba-Geigy)
 [*64338-16-5*] HALS 8	Hostavin N-20 (Hoechst)
 [*63843-89-0*] HALS 10	Tinuvin 144 (Ciba-Geigy)
 [82537-67-5] HALS 10	Tinuvin 440 (Ciba-Geigy)
 [*122586-52-1*] HALS 11	Tinuvin 123 (Ciba-Geigy)
 M_r 1100 – 2500 [*102089-33-8*] HALS 12	Uvasil 299 (Enichem)
 R = $C_{12}H_{25}$ [*85099-51-0*] HALS 13 R = $C_{14}H_{29}$ [*85099-50-9*]	Sanduvor 3050 (Sandoz)

Table 3. (*Continued*)

Structure, CAS registry no., code	Trade name (producer)
 [*116214-18-7*] HALS 14	Lupersol HA 505 (Atochem)
 [*122035-71-6*] HALS 15	Luchem HA-R 100 (Atochem)
 $R = C_{12}H_{25}$ [*119530-69-7*] HALS 16 $R = C_{14}H_{29}$ [*119530-70-0*]	Sanduvor 3052 (Sandoz)
 [*109423-00-9*] HALS 17	Uvinul 4049 H (BASF)
 [*79720-19-7*] HALS 18	Cyasorb UV 3581 (American Cyanamid) Sanduvor 3055 (Sandoz)
 [*106917-30-0*] HALS 19	Cyasorb UV 3604 (American Cyanamid) Sanduvor 3056 (Sandoz)
 [*106917-31-1*] HALS 20	Cyasorb UV 3668 (American Cyanamid) Sanduvor 3058 (Sandoz)

In semicrystalline plastics, UV radiation is scattered by the crystallites and increases the quantum efficiency of polymer degradation. Photodegradation occurs mainly in the amorphous, oxygen-permeable regions.

Ultraviolet Absorbers. The UV absorbers listed in Table 3 have intense absorption bands in the UV-B and some of them in the UV-A as well. They therefore filter out harmful radiation before it reaches the chromophores in the plastic.

The UV absorbers must dissipate the absorbed energy quickly as heat and not as radiation. Mechanisms proposed for this action include proton transitions in the excited singlet state [26–28]. Other quenching mechanisms have also been postulated [29].

The position and intensity of absorption can be modified by substituents on the aromatic rings. For example, alkoxy substituents in the 4- and 4′-positions of 2-hydroxybenzophenones bring about bathochromic shifts in the absorption maxima, as do alkyl substituents in the phenyl ring of 2-hydroxyphenylbenzotriazoles. The steepness of the UV absorption curve on the long-wavelength side is important with respect to intrinsic color—even slight residual absorption around 400 nm causes yellow coloration.

The UV absorbers hinder the photolysis of polymers by competing for UV absorption. They are thus particularly effective when degradation is due primarily to photolysis and not to oxidation. Since the intensity of radiation depends on the thickness of the absorbing layer (Lambert – Beer law), these substances are more effective within the plastic than at its surface. They are therefore only marginally effective in thin films and fibers.

Energy Quenchers. Light stabilizers based on nickel complexes, like some UV absorbers, are energy quenchers. They absorb energy from excited polymer regions or from singlet oxygen, and dissipate it as heat. The action of quenchers depends on concentration, not on layer thickness.

Radical Scavengers. Sterically hindered 4-hydroxybenzoates and amines act chiefly as radical scavengers. 4-Hydroxybenzoates can be regarded as photostable phenolic antioxidants [30]. The hindered amines (HALS) are much more important, however; they all have a 2,2,6,6-tetramethylpiperidine ring [31]. The cyclic mode of action of HALS is shown in Figure 5 [32–43]. The stabilizing action is due not to the HALS compound itself (N – R^1) but to the nitroxyl radical (N – $O^{\cdot}$) formed by photooxidation during weathering. The nitroxyl radical reacts with the polymer radicals formed by photolysis to give ethers (N – O – R), which then react with peroxy radicals to regenerate the nitroxyl radical. Other mechanisms are based on the trapping of acyl peroxide radicals [44] or the decomposition of hydroperoxides [45].

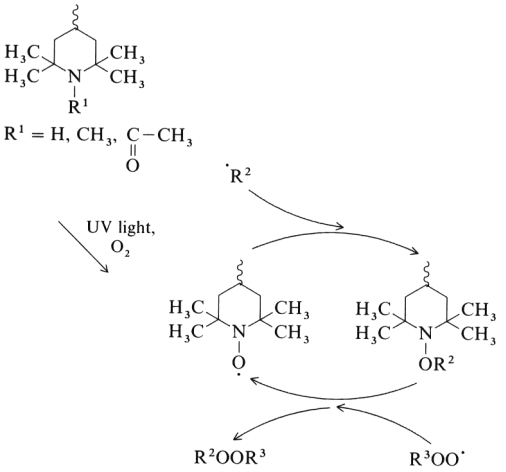


Figure 5. Stabilization mechanism of HALS

The action of HALS depends on their concentration and not on layer thickness. They are therefore equally as effective at the surfaces of plastics in films, fibers, coatings, and thick layers. They are, however, sensitive to certain chemicals, such as organic thioether costabilizers [5], halogen flame retardants [46], kaolin fillers, pesticides [47], and acids. Synergistic effects between HALS and UV absorbers are widely used in industry, and synergies have also been observed with nickel quenchers [48]. A combination of low molecular mass HALS (which migrate to the surface) and high molecular mass compounds (which are more strongly anchored in the bulk polymer) is also recommended [21]. Recent developments include 2,2,6,6-tetramethylpiperazinones [49] and HALS that are chemically bound to polyolefins [50].

3.4. Test Methods

Light stabilizers are incorporated into polymers; processed into specimens in plate, film, fiber, or coating form; and then exposed to radiation in the presence or absence of moisture to determine their weather resistance and lightfastness, respectively.

Weathering may be natural or artificial (i.e., accelerated). Changes in color (DIN 53 236), yellowness index (ASTM D 1925–70), gloss (DIN 67 530), cracking (ISO 4628 Part 4), tensile strength, elongation at break (ASTM D 638, ISO IR 527), or impact resistance (ASTM D 256, ISO R 179) are used to assess lightfastness and weather resistance. The intensity of the IR carbonyl bands is also very often used as a criterion of photodegradation. See also → Paints and Coatings, 1. Introduction; → Plastics, Properties and Testing, Section 2.7.3..

Open-Air Weathering Tests are performed on a commercial basis in all climatic zones. Important sites are located in Central Europe (temperate climate), southern Florida (subtropical), Arizona (desert climate), Okinawa, Thailand, Australia, South Africa, Israel, and Singapore.

In *accelerated sunlight tests*, Fresnel reflectors are used to focus sunlight on the specimens (ASTM E 838–81). Examples of such tests include the Equatorial Mount with Mirrors for Acceleration (EMMA) test and the Equatorial Mount with Mirrors for Acceleration plus Water Spray (EMMAQUA) test, which are performed in Arizona.

In *artificial weathering* the specimens are subjected to precisely defined climatic conditions (temperature, irradiation, rainfall) in specially designed apparatus. Xenon arcs, carbon arcs, and fluorescent lamps are used as illumination sources (see Table 4); filtered xenon light best simulates global irradiation [51], [52].

Standards for artificial weathering tests include DIN 53 384, DIN 53 231, and ANSI/ ASTM G 53–57.

Table 4. Devices for accelerated weathering tests

Producer	Device	Light source
W.C. Heraeus GmbH, Hanau, Germany	Xenontest	xenon lamps
	Suntest	
Atlas Electric Devices Company, Chicago, USA	Weather-Ometer	xenon lamps
	Fade-Ometer	carbon-arc lamps
	Sunchex	UV fluorescent tubes
	UV-CON	
Q-Panel Company, Cleveland, USA	Q-U-V	UV fluorescent tubes
Weiss Technik AG, Reiskirchen, Germany	Global-UV-Testgerät	special UV lamps
	Bauart BAM	
Dainippon Plastics, Tokyo, Japan	Eye Super UV Tester	special UV lamps

3.5. Uses

Light stabilizers are employed mainly in plastics for outdoor service (e.g., garden furniture, stadium seating, window frames, floor coverings) films for protective coverage and agriculture; light fixtures and illuminated signs; automotive parts such as bumpers and body paints; and sports equipment and clothing. Light stabilizers extend the service lives of these articles by years.

The approximate breakdown of light stabilizer uses according to type of plastic is as follows:

Polyolefins (polyethylene, polypropylene)	55 %
Acrylic and polyurethane coatings	20 %
PVC	10 %
ABS and polystyrene	5 %
Unsaturated polyester resins	4 %
Miscellaneous substrates	6 %

The stabilizers are generally used in concentrations of 0.05 – 0.5 %, reaching 3 % in especially critical applications. Recommended formulations can be found in [1].

Polypropylene is particularly sensitive to photodegradation. The photostabilization of polypropylene is reviewed in [53]. Thick moldings are stabilized with 0.2 – 0.6 % of UV absorbers (e.g., BP-UVA 1, BT-UVA 2) and/or radical scavengers (e.g., HB-1 and 2, HALS 1 – 8). HALS (chiefly of high molecular mass, such as HALS 1, 4, or 5) are employed to stabilize films and fibers.

Polyethylene. Although polyethylene is more stable to light than polypropylene, it requires good stabilization for outdoor service. The

selection of light stabilizers is especially critical because of the danger of surface chalking due to migration of incompatible additives. Low-density and linear low-density polyethylene (LDPE and LLDPE) films contain up to 0.4 % of a nickel quencher and UV absorber combination (e.g., NIC-1 and BP-UVA 1) or of a polymeric HALS (e.g., HALS 1, 4, or 7). In filled grades, higher concentrations (ca. 1.5 %) can also produce more than a tenfold increase in service life in open-air weathering. In high-density polyethylene (HDPE) the best results are obtained with HALS (e.g., HALS 2, 4, or 7); 0.1 % is often sufficient.

Styrene Polymers. The UV absorbers and UV absorbers – HALS combinations (e.g., BT-UVA 1 with HALS 2) are recommended for polystyrene, ABS, and styrene – acrylonitrile copolymers (SAN) at a total concentration of ca. 1 % [54].

Poly(Vinyl Chloride). The lightfastness of PVC depends heavily on its heat stabilization or fillers. Barium and cadmium stabilizers, tin carboxylates, and titanium dioxide substantially improve lightfastness. Tin mercaptides are unsuitable for outdoor service or necessitate high levels of titanium dioxide. HALS are not very effective. For transparent PVC in particular, the use of 0.1 – 0.3 % UV absorbers (e.g., BP-UVA 1 or 2, BT-UVA 1 or 5, OA-UVA 1) is recommended.

Miscellaneous Plastics. Polyurethanes, especially those derived from aromatic isocyanates and polyether polyols, tend to yellow and show a deterioration of mechanical properties when exposed to light. Ternary combinations of HALS, UV absorbers, and phenolic antioxidants have a good stabilizing action, especially in foamed plastics [55].

The UV absorbers (e.g., benzotriazoles such as BT-UVA 1 and 2) and HALS are used to stabilize poly(methyl methacrylate) [56]; when colorlessness is important, oxalanilides (OA-UVA 1) are employed. Oxalanilides are also used in unsaturated polyesters and polycarbonates, but a satisfactory solution still has to be found to the problem of light-induced yellowing in polycarbonates.

Table 5. Estimated market volume of light stabilizers in 1990 (10^3 t)

Region	BP-UVA	BT-UVA	HALS	Others	Total
United States	1.1	1.7	2.4	0.6	5.8
Western Europe	1.0	1.4	2.2	0.6	5.2
Japan	0.4	1.3	1.3	0.3	3.3
Other	0.4	0.9	1.1	0.3	2.7
Total	2.9	5.3	7.0	1.8	17.0

3.6. Economic Aspects

Market volumes for light stabilizers are given in Table 5. The most important producers and trade names are listed in Table 3.

Roughly 50 % of the light stabilizers are sold to plastics processors in the form of masterbatches (concentrates containing $\leq$ 20 % light stabilizers in appropriate polymer vehicles). Combination masterbatches supplemented with pigments or flame retardants are being developed.

4. Heat Stabilizers for Poly (Vinyl Chloride)

4.1. Purpose and Requirements

Poly(vinyl chloride) (PVC) is thermally unstable. Heating results in elimination of HCl, the formation of polyene sequences, and rapid discoloration. This autocatalytic reaction begins at ca. 100 °C; at 180 °C a marked brown color occurs after a few minutes. Special heat stabilizers are therefore required for the processing and use of this high-tonnage plastic. These additives are rated according to several criteria besides their efficiency as heat stabilizers:

1. Versatility (use with mass, suspension, and emulsion PVC)
2. Effect on melt rheology of PVC
3. Lubricant action
4. Migration, plate-out
5. Compatibility with other additives and pigments
6. Effect on transparency
7. Effect on lightfastness
8. Effect on electrical insulation
9. Fogging (especially for automotive interior parts)

10. Occupational hygiene and approval as indirect food additives
11. Easy handling and costs

Combinations of stabilizers and costabilizers are normally used to obtain optimal effects. Many systems are employed in industry; PVC stabilization is discussed in detail in [57], [58].

4.2. Chemical Classes

Heat stabilizers for PVC are divided into metal-containing and metal-free stabilizers (costabilizers).

4.2.1. Metal-Containing Stabilizers

The strengths and weaknesses of the main metal-containing heat stabilizer classes are summarized in Table 6.

Lead Stabilizers include basic lead carbonates (e.g., $x\,PbO \cdot PbCO_3$), sulfates, phosphites, stearates, maleates, phthalates, salicylates, and silicates, as well as neutral lead stearate $Pb(OOC{-}C_{17}H_{35})_2$. They have an excellent cost – performance ratio.

Mixed Metal Stabilizers include systems of barium – cadmium, barium – zinc, and calcium – zinc compounds, mainly carboxylates (e.g., stearates, laurates, oleates, or alkylbenzoates) naphthenates, or phenolates. The Ba – Cd types are most effective, followed by Ba – Zn, and Ca – Zn. They must always be reinforced with costabilizers. Recent developments include a zinc glycinate $H_2NCH_2COOZnOOCCH_3$ [59], which is also used in combination with barium or calcium carboxylates.

Organotin Stabilizers are characterized by their tin content (4 – 25 %). They are classified as those containing sulfur (tin mercaptides, i.e., thiolates) and those containing none (tin carboxylates). The first group are the most efficient heat stabilizers. They can be employed without costabilizers and include mainly mono- and dialkyltin mercaptides, mercaptoacetates, mercaptopropionates, and thioglycolates with the following formula:

$$(R^1)_n Sn(SR^2)_{4-n}$$

where $n = 1$ or 2; R^1 = methyl, *n*-butyl, *n*-octyl, or *n*-dodecyl; and R^2 is, for example, $-CH_2COO$-alkyl, $-CH_2CH_2COO$-alkyl, or $-CH_2CH_2OOC$-alkyl. The alkyl group is often isooctyl.

"Methyltin stabilizers" (R^1 = methyl) offer better thermal stability than products containing higher alkyl groups, because the latter suffer thermal β-elimination. Cyclic dialkyltin sulfides are also employed, especially in multicomponent additive systems.

Most of the sulfur-free organotin stabilizers are dibutyltin or dioctyltin carboxylates,

Table 6. Strengths and weaknesses of metal-containing heat stabilizers for PVC *

Property	Lead stabilizers	Mixed metal stabilizers		Tin mercaptides	Tin carboxylates
		Ba – Cd	Ba – Zn, Ca – Zn		
Versatility	−	−	−	+	+
Lubricant action	− (+ for stearates)	+	+	−	−
Migration/plate-out	+	−	+/−	+	+
Transparency of PVC	−	−	−	+	+
Light stability	+	+	−	−	+
Sulfur staining	−	−	+	−	+
Odor	+	−	+	−	+
Electrical insulating properties, water absorption	+	−	−	−	−
Toxicology, food approval in some cases	−	−	+	+	−

* + No problems, often beneficial effect; − Problematic

especially cyclic maleates, semiesters of maleic acid, or laurates.

Antimony Stabilizers include antimony thiolates [e.g., $Sb(SCH_2COOR)_3$].

4.2.2. Metal-Free Stabilizers

These costabilizers always have to be used in conjunction with metal-containing stabilizers. The most important costabilizers follow.

Phosphites. Tris(nonylphenyl) phosphite and mixed aromatic – aliphatic phosphites, such as diphenyldecyl phosphite, are often used.

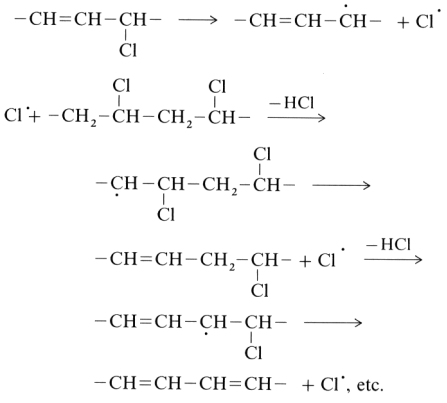
Epoxy Compounds. The principal epoxy stabilizers are epoxidized plant oils, chiefly epoxidized soybean oil.

Polyols include pentaerythritol, trismethylolpropane, and tris(hydroxyethyl) cyanurate.

Other Costabilizers include β-aminocrotonates, dihydropyridines, and 1,3-diketones.

4.3. Mechanism of Action

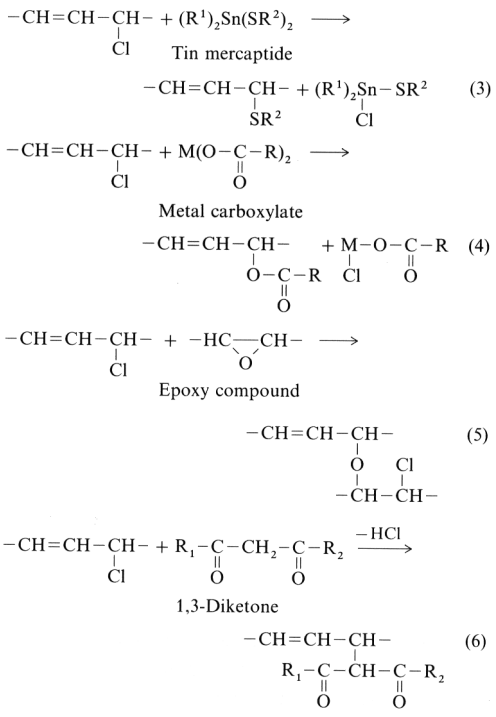
The primary step in the thermal degradation of PVC is free-radical formation by the elimination of activated chlorine atoms, such as those on allyl groups or in tertiary positions. The chlorine atoms attack the polymer, resulting in hydrogen abstraction (formation of HCl) and double-bond formation [60].



Double-bond formation occurs in preference to oxidation of the radical sites to peroxy radicals in the presence of oxygen. Elimination of HCl with the formation of polyene structures continues. Products containing ≥6 – 7 conjugated double bonds are colored.

Ionic mechanisms have also been proposed, but these are less prominent at higher temperature. The formation of carbenium chlorides in the polymer backbone results in deepening of the color ("halochromy"). Thermooxidative processes accelerate degradation.

Stabilizers neutralize labile chlorine atoms by reacting with them to form more stable compounds:



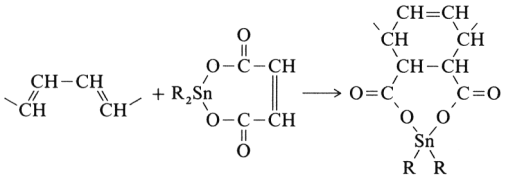
The exchange reactions (Eq. 3 and 4) (Frye – Horst theory [61]) form the basis for many mechanistic analyses. The metal stabilizers are finally converted to chlorides: R_2SnCl_2, $ZnCl_2$, $CdCl_2$, and $PbCl_2$. The metal stabilizers also react with and neutralize hydrogen chloride, which would catalyze further PVC degradation.

The metal chlorides $CdCl_2$ and especially $ZnCl_2$ are, however, Lewis acids and have a destabilizing influence because they catalyze further elimination of HCl. Consequently,

although initial stabilization is excellent, further heating leads to a sudden deep coloration of the PVC ("zinc burning"). The remedy is to exploit the synergism of mixed metal stabilizers. Cadmium and zinc carboxylates are always used in combination with barium or calcium carboxylates, which exchange anions with zinc chloride and cadmium chloride. The zinc and cadmium stabilizers are therefore regenerated, with the formation of barium and calcium chlorides which do not enhance PVC degradation. Barium and calcium carboxylates also react preferentially with HCl.

No catalytic effect on degradation is observed with lead chloride and (di)alkyltin chlorides; the alkyl groups in the latter compounds have a deactivating action. For the effects of metal chlorides, see [62], [63]; for the mechanism of organotin stabilizers, see [64].

Costabilizers, such as polyols [63] and epoxy compounds, also neutralize harmful metal chlorides and improve long-term stabilization with calcium – zinc stabilizers. β-Diketones [65], [66] and dihydropyridines, in contrast, improve the initial color stabilization; the dihydropyridines hydrogenate polyene sequences and thereby shorten their length. Tin mercaptides and the thiols formed by their reaction with HCl can also react with polyene double bonds. The double bond in tin maleates can react with polyenes (Diels – Alder addition):



Finally, alkyltin mercaptides and phosphite costabilizers act as hydroperoxide decomposers, thus protecting against oxidative degradation.

4.4. Test Methods

The most important test methods are based on static and dynamic heating. Analytical methods such as the determination of dehydrochlorination at 180 – 200 °C are also common.

In the *static heating test*, films produced in a two-roll mill or plastisols applied to a substrate are heated in a furnace (e.g., to 180 – 200 °C), and the specimen color is observed as a function of time. In the *dynamic test*, PVC is treated in a two-roll mill, Brabender plastograph, or extruder at specified temperatures. Samples are withdrawn after various times or numbers of extrusion passes and pressed into films, whose color is then determined (usually via the yellowness index).

Because color development in PVC is fairly rapid, these tests (i.e., heat treatment) seldom require more than a few hours. The profile of the yellowness index curves reflects the effects of stabilizers, particularly with regard to short-term and long-term stabilization, and improvements due to costabilizers.

The effect of heat stabilizers on the processing and service qualities of PVC is the concern of extensive testing programs [67].

4.5. Uses

The choice of stabilizer system depends on the processing methods used (extrusion, injection molding, calendering, plastisol application), the intended uses of the PVC, and compatibility with other additives. Technologies and regulations vary greatly. The following survey can therefore give only general indications and trends. For further details, see the producers' literature.

Rigid PVC. Solid stabilizers or stabilizer blends are generally preferred for rigid PVC. Organotin stabilizers have found wide use because processing conditions are more severe than those for flexible PVC.

Window Frames and Sidings. Tin mercaptides are used in the United States; in Europe a shift from Ba–Cd stabilizers has been observed into Ca–Zn costabilizer systems via Ba–Cd–Pd and Pb formulas. Tin carboxylates are also used, especially for transparent or colored frames, because of their good weather resistance.

Pipes, Including Water-Supply Pipes. Tin mercaptides are used in the United States. Lead stabilizers predominate in Europe (except France) and Japan.

Beverage Bottles and Bottle Caps. The PVC is stabilized with food-approved tin mercaptides or Ca–Zn costabilizer systems containing epoxidized soybean oil, 1,3-diketones, or polyols as costabilizers.

Flexible PVC. Most of the stabilizers used for flexible (plasticized) PVC are in liquid form; Ba–Cd and Ba–Zn systems occupy the leading position, with a trend toward cadmium-free systems including Ca–Zn products, e.g., in foils, films, leather imitates (shoes, automotive interiors), hoses, and floor coverings. Lead stabilizers are used in electrical cables.

Stabilizer Content. Heat stabilizer contents of 0.3 – 5 % are common. Levels of organotin stabilizers are at the low end of the range (≤ 2.5 %), mixed metal stabilizers in the middle, and lead stabilizers for cable insulation at the high end. Phosphite or 1,3-diketone costabilizers are generally used below 0.5 %, whereas epoxidized soybean oil is added in concentrations of 5 % or higher.

Legal Aspects. Some countries place strict limits on the use of certain stabilizer classes; for example Sweden and Japan restrict the use of cadmium stabilizers. Similar provisions are under discussion for the EC. Other broad limits apply to lead stabilizers in drinking-water pipes in France and the United States.

Stabilizers for products that come in contact with food (e.g., beverage bottles, packaging films) must be officially approved as indirect food additives. Many octyltin and dodecyltin mercaptides [e.g., di-*n*-octyltin bis(isooctylthioglycolate)], most of the Ca–Zn stabilizers, and many costabilizers (especially stearylbenzoylmethane, dihydropyridine and epoxidized oils) have such approval.

4.6. Economic Aspects

Table 7 lists estimated 1990 market volumes for metal-based heat stabilizers that are used as solids, pastes, or liquids. Dust-free solid forms such as granules, flakes, or "small bags" are preferred. "One-pack" systems, which contain primary and secondary stabilizers preblended with lubricants and other additives, are widely used. Most producers offer broad assortments, with individual products that are continually being modified and tailored to specific applications. Among the nonmetallic costabilizers, epoxidized soybean oil holds a dominant position with more than 100 000 t/a used worldwide in PVC.

Table 8 lists the most important producers and trade names of PVC heat stabilizers.

Table 7. Estimated market volume of PVC heat stabilizers in 1990 (10^3 t)

Region	Tin	Lead	Mixed metal	Total
United States	20	10	25	55
Western Europe	10	50	40	100
Japan	10	30	15	55
Other	10	30	15	55
Total	50	120	95	265

Table 8. Producers of PVC heat stabilizers

Producer	Trade name	Type *
Acima	Metastab	Sn, Me
Adeka Argus	Mark	Me, Pb, C, Sn
Akishima Chemicals		Me, Sn
Akzo	Interstab, Stanclere, Estabex	Me, Sn, Pb, C
BASF	Sicostab	Me
Bleiberger Bergwerks Union	Austrostab	Pb, Sn, Me, C
Cardinal Chemicals	CC	Sn
Chemson	Naftovin, Strandex	Pb, Me, Sn
Ciba-Geigy	Irgastab, Reoplast	Sn, Me, C
Commer	Prosper	Sn, Me, Pb, C
CWM O. Bärlocher	Bärostab, Okstan	Me, Sn, Pb, C
Ferro Corporation	Therm Chek	Me, Sn, C
Hammond Lead Products	Halstab	Pb
Hebron	Vinstab	Sn, Me, Pb, C
Henkel	Edenol, Stabilox, Stabiol	C
Hoechst	Hostastab	Sn, C
Katsuta Kako	Advastab	Me, C, Sn
Kemichrom	Kemistab	Sn, Me, Pb, C
Kyodo Chemicals		Sn, Me
Lagor	Lastab, Synesol	Me, Sn, C
Meister	Meister	Sn, Me, C
Morton Thiokol	Advastab	Sn
M & T Chemicals	Thermolite	Sn, Me, Pb, C
Nissan Ferro Organic Chem.	Therm Chek	Me
Nitto Kasei		Sn
Plastics Specialities & Technologies		Me
Reagens	Reatinor, Reablend	Sn, Me, Pb, C
Rhône-Poulenc	Rhodiastab	C
Sakai Kagaku		Me, C, Sn
Sankyo Organic Gosei	Stann	Sn
Swedstab	Swedstab	Sn, Me, C
Synthetic Products	Synpron	Sn, Me
Tinstab SA	Tinstab	Sn, Me, C
Tokyo Fine Chemicals	Embilizer	Sn
R. T. Vanderbilt	Vanstray, Barostab	Me
Witco Corporation	Mark	Me, Sn

* C=costabilizer; Me=mixed metal; Pb=lead; Sn=organotin.

5. Lubricants, Slip, Antiblocking, and Mold-Release Agents

5.1. Purpose and Requirements [68], [69]

Lubricants (→ Lubricants and Lubrication), slip, antiblocking, and mold-release agents (→ Release Agents) control the frictional and adhesive properties of plastics during processing and in service.

Lubricants also improve the dispersion of pigments and fillers in plastics. Uniform colors can be obtained by breaking up agglomerates in pigment preparations. Better dispersion of fillers (e.g., talc) improves flow limits and material properties.

Internal Lubricants reduce friction between polymer particles and molecules during the melting (plastication) of plastics and transport of the melt. They thus reduce energy consumption on plastication, lower melt viscosity, improve flow properties, increase output of processing machinery, and allow processing under less stringent conditions.

External Lubricants reduce the friction and adhesion of polymer melts on hot metal surfaces of processing machinery (e.g., extruder screws and cylinders, rolls). This reduces abrasion between the polymer melt and the metal, and improves melt flow. It also improves the gloss, smoothness, and regularity of the surface of the plastic.

Mold-Release Agents prevent the adhesion of molded plastics to metal cooling rolls and molds. *Slip agents* improve the frictional qualities of finished plastic surfaces (e.g., bearings and gears) and prevent adhesion between stacked films. *Antiblocking agents* prevent adhesion between film layers on rolls or in stacks when pressure and heat are applied.

Antislip Agents (adhesion promoters) impart limited tack to finished articles to reduce slip (e.g., between filled bags made of plastic films).

It is not always possible to assign a particular product to one of the above classes. For example, the boundary between internal and external lubricants depends on the type of polymer, the additive concentration, the presence of other lubricants, and the processing temperature. Many products also perform multiple functions: external lubricants are often effective as mold-release or slip agents. Carefully matched combinations of additives are often required. This group of additives must also comply with standards of odor and taste, migration behavior, product stabilization [70], and thermal stability.

Lubricants and related compounds may have disadvantageous effects on some product properties. Internal lubricants can act as plasticizers and thus reduce the heat distortion temperature. External lubricants can reduce transparency and impair the printability, cementability, and weldability of plastics. These additives also affect mechanical properties, especially in case of overlubrication, which causes inhomogeneities due to inadequate fusion of the material.

5.2. Chemical Classes

Many lubricants are amphoteric compounds containing both a long hydrocarbon chain and polar groups (e.g., hydroxyl, ester, or acid groups). Lubricants are characterized by their molecular mass, acid or hydroxyl number, saponification number, metal content, melting or dropping point, cold-setting temperature, thermal stability, volatility, density, viscosity, and (for solid agents) particle size. The action of a lubricant depends on its polarity. Polar molecules act as internal lubricants in polar polymers such as PVC and as external lubricants in nonpolar polymers such as polyolefins, and vice versa. The polarity is strongly influenced by the length of the hydrocarbon chain. Lubricants can be classified as fatty acids and their derivatives (C_{12} – C_{22} chains), montanic acids and their derivatives (C_{28} – C_{32}), paraffins (C_{20} – C_{70}), and polyolefin waxes (molecular mass 2000 – 10 000).

The substances of greatest practical importance are listed below; for further details, see → Lubricants and Lubrication.

Fatty Acids, Fatty Alcohols, and Their Derivatives comprise the following groups:

1. Stearic, 12-hydroxystearic, palmitic, and behenic acids
2. Cetyl and stearyl alcohols

3. Metal stearates (Zn, Ca, Pb, Al, Mg, and Na)
4. Butyl stearate, tridecyl stearate, glycerol monostearate (GMS), glycerol monoricinoleate, glycerol monooleate, glycerol tristearate, glycerol tri-12-hydroxystearate (hydrogenated castor oil), trimethylolpropane tristearate, and pentaerythritol tetrastearate
5. Distearyl adipate, distearyl phthalate, cetyl palmitate, cetyl stearate, stearyl stearate, and behenyl behenate
6. Isostearamide, oleamide, erucamide, ethylene bisstearylamide (EDS or "amide wax")
7. Oligomeric fatty acid esters ("complex fatty acid esters") are also used. These are obtained by polycondensation of dicarboxylic acids (e.g., adipic acid), polyols (e.g., pentaerythritol), and monocarboxylic acids (e.g., stearic acid). They may be partially saponified or may contain calcium.

Montanic Acids and Their Derivatives (Montan Waxes). Montanic acids are obtained from lignite and consist of mixtures of $C_{28} - C_{32}$ acids. Derivatives include calcium montanates, sodium montanates, and esters with ethylene glycol, butanediol, glycerol, or pentaerythritol.

Paraffins may be derived from petroleum (straight-chain members are solids, branched-chain members are liquids) or are synthetic (Fischer – Tropsch) paraffins.

Polyolefin Waxes. The most common polyolefin waxes are polyethylene waxes with branched and linear structures; partially crystalline polypropylene waxes are less common. Polar polyethylene waxes are obtained by oxidation; they have acid numbers of ca. 20 – 70.

Other Chemical Classes. Fluorinated polymers, chlorinated paraffins, silicones, graphites, and other substances are used as lubricants and related compounds. Silica gel, chalk, and other minerals are employed as antiblocking agents and slip aids.

This article does not cover externally applied mold-release agents (e.g., waxes, fluorinated polymers, silicones, and metallic soaps), which are sprayed or brushed onto mold surfaces. These methods are used chiefly with thermosetting resins (e.g., polyurethane, unsaturated polyester, epoxy).

5.3. Mechanism of Action

The friction-lowering property of *lubricants* is due to their long hydrocarbon chains ($> C_{12}$). The lubricating effects depend on interactions between the lubricant and the polymer matrix (solubility of the lubricant in the polymer) and on the association between the lubricant and the metal surfaces. Unlike plasticizers, which are completely soluble in the polymer, lubricants should have only limited solubility; this is ensured by their amphoteric character.

Internal Lubricants [71] have a relatively high affinity for polymers. Polar lubricants in, for example, PVC are either dissolved in or strongly bound to the surface of the associations of polymer molecules that occur in the plastic state. Typical effects are a lowering of the softening temperature due to swelling, a reduction in melt viscosity, and frictional damping between polymer particles. Good internal lubricants have high saturation limits and haze points.

External Lubricants are strongly associated to the metal surfaces of processing equipment or form discrete phases within the polymer melt. They only have a low affinity for the polymers. Typical effects are a reduction in adherence to the metal and in friction between polymer particles, which leads to slower plastication. External lubricants often cause haze. Overlubrication must be avoided because some adhesion to the metal is necessary for conveyance of the melt in the extruder and also in calendering.

Mold-Release Agents form a film between the metal surface and the cooled plastic. *Slip agents* migrate to the plastic surface, where their hydrocarbon chains act as a lubricant. *Antiblocking agents* slightly roughen the film surface so that air is trapped between stacked layers. *Antislip agents* artificially create surface roughness where nonlubricating particles incorporated in the melt protrude from the film.

5.4. Test Methods

Methods based on practical applications are applied to lubricant testing. One of the most

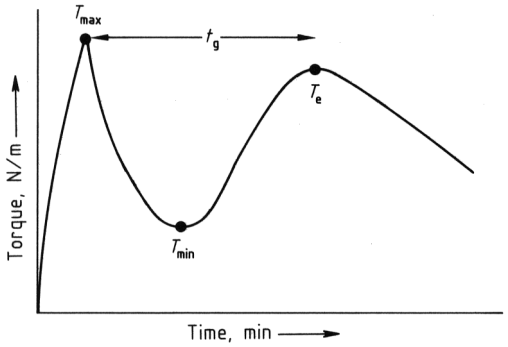


Figure 6. Schematic plastogram of PVC with lubricant (Brabender Plasticorder)

important is the plastograph (e.g., the Brabender Plasticorder). The formulated plastic powder is placed in a kneading chamber at a preset temperature (e.g., 140 – 160 °C) and plasticated by a twin-shaft device running at constant speed. The torque is plotted as a function of time (Fig. 6). The curve passes through a maximum torque value T_{max}, marking the onset of plastication in the powder mixture. It then declines to a minimum T_{min}, followed by an increase to a second maximum T_e as a result of growing friction. Plastication is complete at T_e. The time between T_{max} and T_e is called the plastication time t_g. The test is used to establish suitable ratios of internal and external lubricants. For example, a shorter t_g or an increase in the ratio $(T_{max} - T_{min})/t_g$ indicates internal lubrication. As the hydrocarbon chain in the lubricant becomes longer, the maximum kneading resistance declines.

Other tests employ extrusiometers (measurement of polymer melt temperature and pressure in the extruder cylinder and at the die), capillary viscometers (quantity of material discharged per unit time at constant pressure and temperature) [72], or roller mills (time that elapses between charging and adhesion of the polymer sheet on the rolls). In the spiral test, material is injected into a spiral mold and the distance the material travels in the runner is measured.

Slip and blocking effects are studied in skid and adhesion tests with films (e.g., ASTM D 1893 or D 3354). Haze and surface gloss measurements are an important component of all lubricant tests.

5.5. Uses

The main application of lubricants is in PVC (ca. 50 %), followed by styrene polymers, polyolefins, engineering thermoplastics, and thermoplastic elastomers.

Rigid PVC always requires lubricants for processing (usual content 1 – 4 %), and lubricant combinations (preformulated systems) are often employed. Selection of lubricants is dictated by the type of heat stabilizer used: stearic acid with lead stabilizers; 12-hydroxystearic acid with barium – cadmium stabilizers (to reduce plate-out); glycerol monostearate, montan waxes, or oxidized polyethylene waxes with tin stabilizers; and complex fatty acid esters with calcium – zinc stabilizers.

Fatty acid esters, calcium stearate, and fatty alcohols are typical internal lubricants. Montan waxes, amide waxes, paraffins, oxidized polyethylene waxes, and fatty acids act as external lubricants. Heavy-metal soaps and complex fatty acid esters fall between the two types. Lubricants allow processing under gentler conditions and thereby contribute to stabilization. A combination of calcium stearate as internal lubricant, paraffin wax as external lubricant, and oxidized polyethylene wax as mold-release agent has been used with success for PVC pipes.

Flexible PVC requires less lubricant (ca. 0.5 %). Liquid types,such as glycerol monooleate or paraffin oils, are used. Amide waxes serve as antiblocking agents.

The flow behavior of *ABS, SAN, and polystyrene* can be improved with butyl stearate, glycerol monostearate, fatty acid esters, paraffin oils, oxidized polyethylene waxes, and montan waxes. Zinc stearate and amide wax (0.1 – 2 %) are used as mold-release agents.

The calcium stearate used as an acid radical scavenger is often sufficient for *polyolefins*. Neutral polyethylene and polypropylene waxes are added to pigment preparations for polyethylene and polypropylene. Talc-filled polypropylene can contain ca. 0.5 % of partially saponified montan wax. A suitable mold-release and slip agent for films is 0.1 – 0.3 % of a fatty acid amide in polyethylene or of erucamide in polypropylene. Finally, 0.05 % of fluorinated polymers can be added to LLDPE films to

combat melt fracture (a surface defect occurring at high viscosity and resulting from the alternating wall adhesion and slip of the extrudate). Highly effective slip aids for polyolefin films include micronized synthetic silica gels.

For *engineering thermoplastics* [polycarbonates, polyamides, poly(ethylene terephthalate) (PETP), poly(butylene terephthalate) (PBT)], thermally stable pentaerythritol esters of fatty acids are preferred; they have a better transparency than montanate esters. Amide wax can also serve as a mold-release agent. Filled thermoplastics represent a broad field for lubricants.

Because most lubricants are derived from natural sources, they are often approved for food packaging products.

5.6. Economic Aspects

Current worldwide consumption of lubricants and related compounds is ca. 130 000 – 140 000 t, with Western Europe, the United States, and the rest of the world accounting for a third each. Consumption is equally divided between the five following groups: fatty acids and esters, metallic soaps, amide waxes, paraffin and polyethylene waxes, and miscellaneous types.

Table 9 lists some important producers and trade names of lubricants and related compounds. The number of products on the market is relatively large because new formulations and easy-to-handle forms are continually appearing. Most products for PVC are sold to converters; those for other polymers are often sold to the polymer producers.

6. Flame Retardants [73–78] See also → Flame Retardants

6.1. Purpose and Requirements

The replacement of classical materials by combustible plastics in buildings, equipment, and vehicles creates a fire risk. Flame retardants are used to combat this danger. A useful measure of flammability for plastics is the limiting oxygen index (LOI), which denotes the volume fraction of oxygen in an oxygen – nitrogen mixture that just supports combustion of a well-defined

Table 9. Producers and trade names of lubricants and related compounds

Manufacturer	Trade name
Abril Industrial Waxes	Abril Wax
Akzo Chemicals	Dopral, Interstab, Armoslip, Aramid
Allied Signal	AC Polyethylene
Ashland Chem.	
Astor Wax	Comboloob
Axel Plastics Res. Labs.	Mold Wiz
CWM O. Bärlocher	Bärolub
BASF	Sicolub, Wachs BASF
Dr. T. Böhme	Tebestat
Chemson	Naftolube, Naftozin, Listab
Ciba-Geigy	Irgawax
Corriel	Lubriol, Synthewax, Glycmonos
Commer	Vinlub
Croda Universal	Crodamid, Crodacid
Deer Polymer	
Du Pont	Zonyl, Viton
Durham Chemicals	Durolube
Eastman	Epolene, Myverol, Myvaplex
Th. Goldschmidt	Tego, Tegin
Grace	Sylobloc
C. P. Hall	
Harcros Chemicals	Harochem, Harowax, Harogel, Lankroplast
Harwick Chemicals	Lubrox, Lubrex
Henkel	Loxiol, Loxamid
Hoechst	Hostalub, Hostamont, Hoechst Wachse
Hüls	Vestowax
Humko Chemicals (division of Witco)	Kemamide, Kemester, Mold Pro, Micro-ken
ICI	Atmer
Kao Corporation	
Kemichrom	Kemfluid
Lion Akzo	
Lonza	Glycolube
3 M	Dynamar
Marabushi Oil Chemicals	
Mathe Co.	Coad
Mazer Chemicals (division of PPG)	
Morton Thiokol	Advawax
M & T Chemicals	Stavinor
New Japan Chemical Co.	
Nippon Oil & Fats	
Nitto Kasei	
Reagens	Realube
Rohm & Haas	
Rousselot	
Sakai	
Speciality Products	Zn-Stearate
Struktol Co.	Polydis TR
Swedstab	Swedlub, Swedstab
Tonnan Kagaku Kogyo	
Unichema Chemie	Unislip, Uniwax, Estol, Priolube, Prifrac, Pristerene

specimen under standard conditions. A high LOI indicates a low flammability. The LOI values for the most important plastics follow:

Polyoxymethylene	15.5
Polyethylene	17.3
Poly(methyl methacrylate)	17.5
Polypropylene	17.6
Polyurethane	17–19
Polystyrene	18.0
Unsaturated polyester	18.5
ABS	18–19
Epoxy resin	19.0
PBT	21.5
Polyamide 12	21.6
PETP	22.0
Polycarbonate	23–25
Polyamide 6	23–26
PVC, flexible	24–25
Poly(phenylene oxide) – polystyrene	24–25
Polyamide 66	24–26
PVC, rigid	40–45
Polytetrafluoroethylene	95.0

Flame retardants in plastics affect ignitability, combustion rate, heat release, fuel contribution, smoke evolution, and the formation of toxic or corrosive gases. The significance of these parameters depends on the situation. Although flame retardants can be especially effective in the early stages of a fire and can reduce flammability, plastics modified with these additives are still combustible.

In many cases and especially at high concentrations, flame retardants lower the quality and increase the price of a plastic. They are therefore used only when mandated. Selection is determined by the effectiveness and price of the flame retardant, as well as the processibility of the plastic, and influences on its mechanical, optical,and electrical properties.Interactions with other additives (e.g., light stabilizers) must also be considered.

6.2. Chemical Classes

Flame retardants may be inorganic substances, halogenated organic compounds, organophosphorus compounds, or other organic substances. They are further classified as additive or reactive. Reactive flame retardants are incorporated into the polymer molecule by copolymerization, cross-linking, or grafting.

Inorganic Flame Retardants. Producers and trade names are summarized in Table 10.

Aluminum Trihydroxide, $Al(OH)_3$, and *magnesium dihydroxide,* $Mg(OH)_2$, [79] are the largest group of flame retardants in terms of

Table 10. Producers and trade names of inorganic flame retardants

Compound	CAS registry no.	Producer (trade name)
Aluminum trihydroxide, $Al(OH)_3$	[21645-51-2]	Aluchem; BA Chemicals, Alcan Aluminium (Baco Superfine, Ultrafine); Alcoa (Hydral, Flameguard); Atochem; Kaiser Aluminium; Martinswerke, Lonza (Martinal); Reynolds Metals; Solem Industries, J. M. Huber (Micral, Zerogen); Vereinigte Aluminium Werke (Apyral); Showa Aluminium Industries; Sumitomo Aluminium Smelting
Magnesium dihydroxide, $Mg(OH)_2$	[1309-48-4]	Dead Sea Bromine (FR-20); Kyowa Chemicals; Lonza (Magnifin); Morton Thiokol (Versamag); Solem Industries, J. M. Huber (Zerogen); Veitscher Magnesitwerke
Antimony trioxide, Sb_2O_3 (some as concentrate or in wetted form)	[1309-64-4]	Anzon (Firebloc, Envirostrand, Oncor); Asarco; Laurel Industries (Fire Shield); M & T Chemicals (Thermoguard); Amspec Chemical; BA Chemicals (Timonox)
Antimony pentoxide, Sb_2O_5	[1314-60-9]	Nyacol Products (Nyacol)
Sodium antimonates, e.g., $Na_2Sb_2O_6 \cdot x\,H_2O$		M & T Chemicals (Thermoguard)
Zinc borates, e.g., $4\,ZnO \cdot 6\,B_2O_3 \cdot 7\,H_2O$	[12536-65-1]	Borax Holdings; Climax Performance Materials (ZB-223); US Borax & Chemicals (Firebrake ZB)
Barium metaborate, e.g., $BaB_2O_4 \cdot x\,H_2O$		Buckman Laboratories (Busan)
Ammonium polyphosphate, $(NH_4PO_3)_n$ (some coated or encapsulated, some in systems with flame retardants containing N)	[68333-79-9]	Albright & Wilson (Amgard MC); Hoechst (Exolit); Monsanto (Phos-Chek); Great Lakes (Char Guard 329, CN 1197)
Red phosphorus	[7723-14-0]	Albright & Wilson (Amgard CRP); Hoechst (Exolit 405)

consumption. Particle size varies from 1 to 30 μm. High concentrations (40 – 60 wt %) of these additives are required and are associated with a severe impairment of mechanical properties. To overcome this, products coated with coupling agents (e.g., silanes, fatty acid esters) are recommended. The coating may, for example, improve the impact strength of the modified plastic or reduce the viscosity of prepolymers. Aluminum and magnesium hydroxides often suppress smoke evolution. Use is limited by their thermal stability (dehydration); $Al(OH)_3$ decomposes above ca. 200 °C, and $Mg(OH)_2$ above 300 – 340 °C.

Antimony Compounds. Antimony trioxide, Sb_2O_3; antimony pentoxide, Sb_2O_5; and sodium antimonates (e.g., $Na_2O \cdot Sb_2O_5 \cdot x\ H_2O$) are largely used as synergists with halogenated organic flame retardants or in PVC. In the absence of halogen compounds they have little effect. Antimony trioxide is sold in various purities, whitenesses, and grain sizes (mainly 1 – 3 μm, down to <1 μm for special grades). Antimony pentoxide is available in colloidal form (0.03 μm). Because of occupational health issues relating to antimony trioxide dust, nondusting preparations are preferred (i.e., concentrated masterbatches containing ca. 80 % of active agent, granules, or wetted grades).

Zinc Borates [80] often serve as a partial replacement for antimony trioxide, giving some advantages in suppression of smoke evolution, afterglow, weaker pigmentation, and lower cost. Combinations with aluminum trihydroxide are also employed. Negative effects on the stability of halogen-containing plastics must be considered.

Ammonium Polyphosphate, $(NH_4PO_3)_n$, is included in intumescent systems [81], [82] that contain polyols and melamine derivatives (→ Flame Retardants). The products are also marketed in coated or microencapsulated form to reduce water absorption, for example.

Microencapsulated or inertized *red phosphorus* is a very effective flame retardant that can be processed at up to 280 °C [82],[83]. Its drawbacks are a dark color and potential handling hazards.

Other Inorganic Flame Retardants include iron oxides (Fe_2O_3 and Fe_3O_4); hydrated calcium and magnesium carbonates; bismuth oxides and carbonates [84]; boric acid and borates; zinc hydroxystannate [$ZnSn(OH)_6$], zinc stannate ($ZnSnO_3$), and other zinc compounds [85]; and mineral substances that decompose endothermically at certain temperatures to release water or noncombustible gases. Smoke-inhibiting additives for PVC, unsaturated polyesters, or polyurethanes include calcium carbonate, tin oxides, copper oxide, molybdenum trioxide, and ammonium molybdate.

Halogenated Organic Flame Retardants. Halogenated compounds are effective flame retardants, especially in conjunction with antimony trioxide. They can therefore be used in low concentration so that they do not greatly affect product properties. A drawback is the fact that corrosive gases (HBr, HCl) are always produced in the event of fire and can cause secondary damage. Light stability of the plastic is also reduced, especially by brominated compounds.

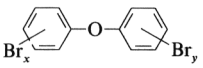
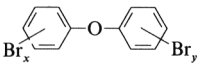
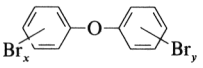
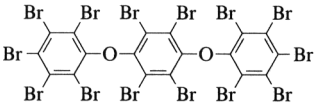
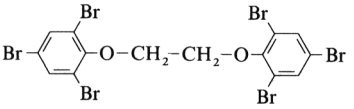
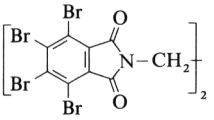
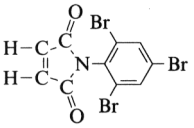
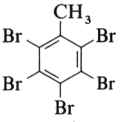
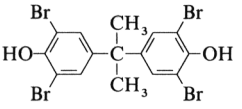
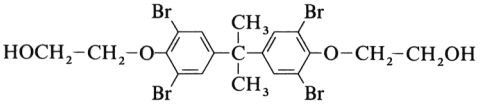
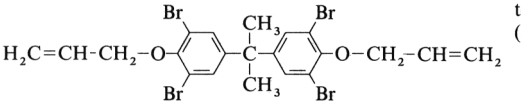
The most important members of this group are brominated aromatics, above all decabromodiphenyl oxide and polymeric compounds. Some important producers and trade names are listed in Table 11. Aliphatic bromine compounds are often more effective but less thermally stable. This disadvantage is partially offset in brominated neopentyl structures that do not have hydrogen atoms in the α-position to the bromine. Hexabromocyclododecane is an example of a brominated cycloaliphatic compound; tetrabromobisphenol A is the most important reactive type.

Chlorinated flame retardants (Table 12) are only about half as effective as brominated ones because of the higher bond energy of chlorine. Chlorinated paraffins and chlorinated cycloaliphatics are mainly used [86]. Fluorine and iodine compounds are not employed as flame retardants.

Organophosphorus Flame Retardants. Important products and trade names are listed in Table 13.

The most important organophosphorus flame retardants are halogen-free triaryl phosphates. Phosphonates (e.g., dimethyl methylphosphonate), phosphine oxides, and halogenated

Table 11. Producers and trade names of brominated organic flame retardants

Structure	Name, CAS registry no.	Producer (trade name)
	decabromodiphenyl oxide [*1163-19-5*]	Dead Sea Bromine (FR 1210) Ethyl Corporation (Saytex 102) Great Lakes Chem. (DE-83)
	octabromodiphenyl oxide [*32536-52-0*]	Dead Sea Bromine (FR 1208) Ethyl Corporation (Saytex 111) Great Lakes Chem. (DE-79)
	pentabromodiphenyl oxide	Dead Sea Bromine (FR 1205) Ethyl Corporation (Saytex 115) Great Lakes Chem. (DE-71)
	tetradecabromodiphenoxybenzene [*58965-66-5*]	Ethyl Corporation (Saytex 120)
	bis(tribromophenoxy)ethane [*37853-59-1*]	Great Lakes Chem. (FF 680)
	ethylene-bis(tetrabromophthalimide) [*32588-76-4*]	Ethyl Corporation (Saytex BT 93)
	*N*-(2,4,6-tribromophenyl)maleinimide [*59789-51-4*]	Dead Sea Bromine (FR 1033)
	pentabromotoluene [*87-83-2*]	Dead Sea Bromine (FR 705)
	tetrabromobisphenol A [*79-94-7*]	Dead Sea Bromine (FR 1524) Ethyl Corporation (Saytex RB 100) Great Lakes Chem. (BA 59)
	tetrabromobisphenol A-bis(2-hydroxyethyl ether) [*4162-45-2*]	Dead Sea Bromine (FR 1525) Great Lakes Chem. (BA 50)
	tetrabromobisphenol A-bis(allyl ether) [*25327-89-3*]	Dead Sea Bromine (FR 2124) Great Lakes Chem. (BE 51)

(*continued*)

Table 11. (*Continued*)

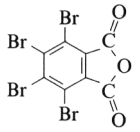
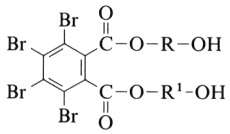
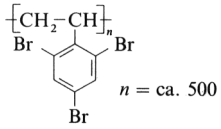
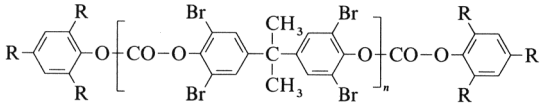
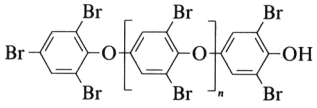
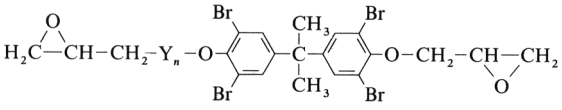
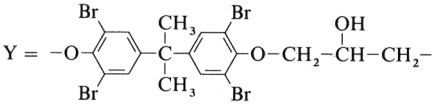
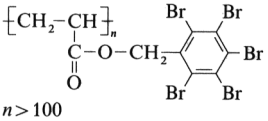
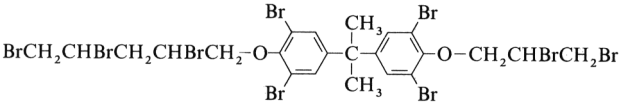
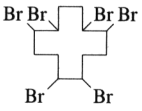
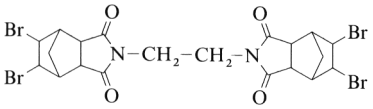
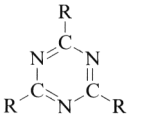
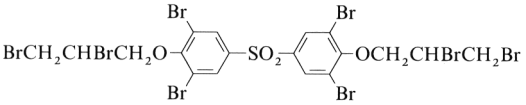
Structure	Name, CAS registry no.	Producer (trade name)
	tetrabromophthalic anhydride [*632-79-1*]	Ethyl Corporation (Saytex RB 49) Great Lakes Chem. (PHT 4)
	mixed esters of tetrabromophthalic acid [*77098-07-8*] with diethylene glycol and propylene glycol [*75790-69-1*]	Ethyl Corporation (Saytex RB 79) Great Lakes Chem. (PHT 4-diol)
	poly(2,4,6-tribromostyrene) [*57137-10-7*]	Ferro Corporation (Pyro-chek 68, Pyro-chek LM)
	poly(tetrabromobisphenol-A)-polycarbonate [*28906-13-0*], [*71342-77-3*]	Great Lakes Chem. (BC 52, 58)
	poly(dibromophenylene oxide) [*26023-27-8*]	Great Lakes Chem. (PO 64)
	brominated epoxy resins	Makhteshim Chemical Works (F 2000 Series) M & T Chemicals (Thermoguard)
		
	poly(pentabromobenzyl acrylate) [*59447-57-3*]	Dead Sea Bromine (FR 1025)
	tetrabromobisphenol A-bis-(2,3-dibromopropyl ether) [*21850-44-2*]	Great Lakes Chem. (PE 68) Riedel de Haen (OBPE)
	hexabromocyclododecane [*3194-55-6*]	Dead Sea Bromine (FR 1206) Ethyl Corporation (Saytex HBCD) Great Lakes Chem. (CD 75-P) Riedel de Haen (HBCD)

Table 11. (*Continued*)

Structure	Name, CAS registry no.	Producer (trade name)
	ethylene-bis(dibromonorbornane dicarboximide) [*41291-34-3*]	Ethyl Corporation (Saytex BN 451)
 $R = OCH_2CHBrCH_2Br$	1,3,5-tris(2,3-dibromopropoxy)-2,4,6-triazine [*52434-59-0*]	Akzo Chem. (Interstab FR 930)
$(HOCH_2)_2C(CH_2Br)_2$	2,2-bis(bromomethyl)-1,3-propanediol [*3296-90-0*]	Dead Sea Bromine (FR 522) Ethyl Corporation (Saytex FR 1138)
$HOCH_2-C(CH_2Br)_3$	2,2-bis(bromomethyl)-3-bromo-1-propanol [*1522-92-5*]	Dead Sea Bromine (FR 513)
	3,5,3′,5′-tetrabromo-4,4′-dihydroxydiphenylsulfone-bis-(2,3-dibromopropyl ether) [*42757-55-1*]	Marubeni (Non Nen 52)
Brominated polyols, some also containing chlorine		Dead Sea Bromine Solvay (IXOL B 251)

phosphate esters and phosphonates are also used. Advantages include low corrosivity of the combustion gases, lack of effect on polymer transparency, and suppression of afterglow. Drawbacks include volatility, sensitivity to hydrolysis, and negative effects on the heat distortion temperatures of plastics. Cyclic organophosphorus compounds (phosphorinanes, phosphazenes) overcome some of these problems.

Miscellaneous Organic Compounds. Organic additives occasionally used in flame retardant systems or for special types of plastics include the following:

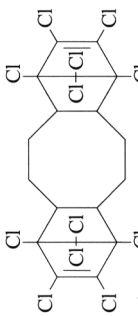
1. Polyols (e.g., pentaerythritol) for intumescent systems [81]
2. Nitrogen-containing compounds (e.g., melamine or melamine cyanurate), often combined with $(NH_4PO_3)_n$
3. Silicones [87] as smoke inhibitors and impact modifiers when high concentrations of $Al(OH)_3$, $Mg(OH)_2$, or $(NH_4PO_3)_n$ are used as flame retardants
4. Free-radical formers (e.g., dicumyl peroxide or 2,3-dimethyl-2,3-diphenylbutane) together with brominated compounds, especially in expandable polystyrene [88]
5. Alkali-metal salts of organic sulfonates for polycarbonates [89]
6. Ferrocene as a smoke inhibitor in PVC

6.3. Mechanism of Action

Three elements are essential for a fire: heat, fuel, and air (oxygen) (Fig. 7). When heated, plastics undergo pyrolysis, forming characteristic degradation products, some of which appear as smoke whereas others serve as fuels that can be ignited once they are mixed with air. Oxidative combustion reactions in the gas phase (the "fire") are strongly exothermic. Thus, large amounts of thermal energy are returned to the plastic and to the surroundings. Pyrolysis and the associated fuel generation are thereby accelerated, and the fire propagates. Flame retardants interfere with these processes by one or more chemical or physical mechanisms [90].

Fuel Dilution. Noncombustible products (CO_2, H_2O) are generated by thermal decomposition of the flame retardant and released into the gas phase. Examples of such flame retardants are $Al(OH)_3$, $Mg(OH)_2$, hydrated carbonates, boric acid, and borates. The decomposition

Table 12. Producers and trade names of chlorinated organic flame retardants

Structure	Name	CAS registry no.	Producer (trade name)
Chlorinated paraffins, 30 – 70 % Cl, some also containing bromine			Atochem (Electrofine), Dover Chemical (Chlorez), Ferro, Hoechst, Hüls, ICI (Cerechlor), Occidental Chemical (Chlorowax)
	1,2,3,4,7,8,9,10,13,13,14,14-dodecachloro-1,4,4a,5,6,6a,7,10,10a,11,12,12a-dodecahydro-1,4 : 7,10-dimethanodibenzo(a,e)cyclooctene	[*13560-89-9*]	Occidental Chemical (Dechlorane Plus)
	1,4,5,6,7,7-hexachlorobicyclo[2.2.1]-5-heptene-2,3-dicarboxylic acid corresponding anhydride	[*115-28-6*] [*115-27-5*]	Occidental Chemical, Velsicol

temperature of the flame retardant must be compatible with the processing temperature and pyrolysis temperature of the plastic.

Endothermic Action. If the pyrolytic decomposition of the flame retardant is endothermic, it can absorb part of the energy released during combustion. This mechanism often accompanies fuel dilution.

Protective Coating. The flame retardant forms a protective coating on the surface of the pyrolyzing plastic. It acts as thermal insulation and a barrier to oxygen, and also prevents combustible pyrolysis products and smoke particles from escaping into the gas phase. Most of the inorganic and organophosphorus flame retardants function by this mechanism. The protective layer can be glassy or have a porous carbon structure (intumescent char). In the latter case, the flame retardant system includes components that are responsible for char formation (e.g., polyols and phosphates) and expansion (e.g., melamine derivatives) [81], [91].

Pyrolysis Modification. Pyrolysis of the plastic can be chemically modified, for example, by dehydration in cellulosic polymers and polyurethanes or by inhibition of thermal depolymerization [e.g., in poly(methyl methacrylate)] to reduce the amount of combustible products generated. The proportion of solid carbon residue (char) is increased, and a noncombustible product (e.g., water) is formed. Organophosphorus compounds employ this mechanism; it is particularly effective in plastics containing oxygen. This mechanism may, however, increase smoke density.

Gas-Phase Quenching. Combustion processes in the gas phase are highly exothermic, free-radical chain reactions in which the fuel is oxidized by oxygen or hydroxyl radicals, for example:

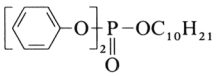
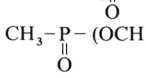
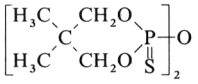
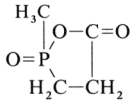
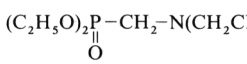
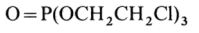
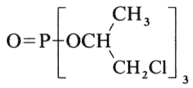
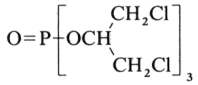
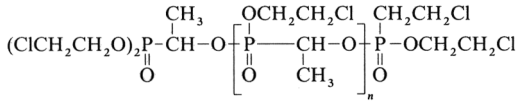
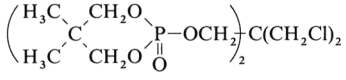
$$CO + HO^{\bullet} \rightarrow CO_2 + H^{\bullet} + \text{heat}$$

$$H^{\bullet} + O_2 \rightarrow HO^{\bullet} + O^{\bullet} + \text{heat}$$

$$RH + O^{\bullet} \rightarrow HO^{\bullet} + R^{\bullet} + \text{heat}$$

Flame retardants that are active in the gas phase must neutralize the highest-energy radicals,

Table 13. Organophosphorus flame retardants

Type or structure	Name, CAS registry no.	Producer (trade name)
Triaryl phosphates		
Triphenyl phosphate	[*115-86-6*]	Akzo (Phosflex)
Tricresyl phosphate	[*1330-78-5*]	Ciba-Geigy (Reofos)
Isopropylated triphenyl phosphate		FMC (Kronitex)
		Monsanto (Santicizer)
Other phosphates, phosphonates, or phosphinates		
	diphenyl decyl phosphate [*14167-87-4*]	Monsanto (Santicizer)
	dimethyl methylphosphonate [*756-79-6*]	Akzo (Fyrol DMMP) Albright & Wilson (Amgard DMMP) Ciba-Geigy (Reoflam DMMP)
	1,3,2-dioxaphosphorinane-2,2′-oxybis-(5,5-dimethyl-2,2′-disulfide) [*4090-51-1*]	Sandoz (Sandoflam 5060)
	2-methyl-2,5-dioxo-1,2-oxaphospholane [*15171-48-9*]	Hoechst
	diethyl *N,N*-bis(2-hydroxyethyl)amino-methylphosphonate [*2781-11-5*]	Akzo (Fyrol 6)
Polyols containing phosphorus		Akzo (Fyrol 35) Hoechst (Exolit 413)
	tris(2-chloroethyl) phosphate [*115-96-8*]	Akzo (Fyrol CEF) Albright & Wilson (Amgard TCEP) Bayer (Disflamoll) Hoechst (Genomoll P)
	tris(2-chloroisopropyl) phosphate [*13674-84-5*]	Akzo (Fyrol PCF) Albright & Wilson (Amgard TMPC)
	tris(2,2′-dichloroisopropyl) phosphate [*13674-87-8*]	Akzo (Fyrol FR-2) Albright & Wilson (Amgard TDCP)
	polyphosphonate [*59036-37-2*]	Sandoz (Sandoflam 5087)
Halogenated phosphate esters and other proprietary phosphorus compounds		Akzo (Fyrol) Albright & Wilson (Amgard) Ciba-Geigy (Reoflam) FMC (PB-460, PB-528) Great Lakes Chem. Sandoz (Sandoflam)
	1,3,2-dioxaphosphorinane-2,2′{[2,2-bis (chloromethyl)-1,3-propanediyl]bis(oxy)}-bis(5,5-dimethyl-2,2′-dioxide) [*83044-97-7*]	Sandoz (Sandoflam 5085)

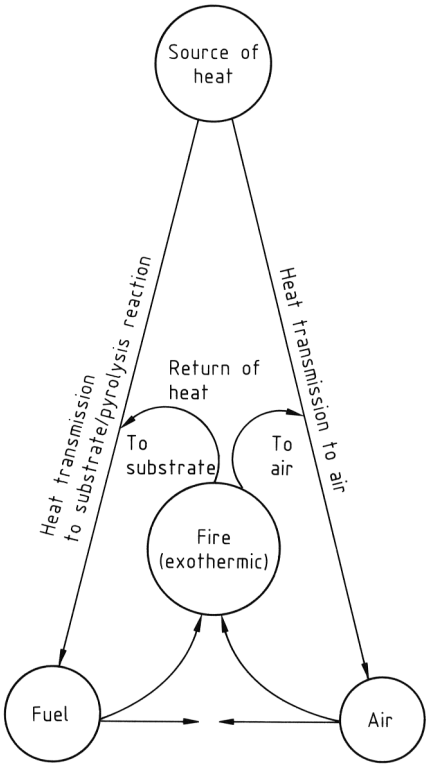


Figure 7. The Emmons fire triangle

such as $HO^{\bullet}$ or $H^{\bullet}$. Halogenated compounds are especially effective in this respect. Pyrolysis produces hydrogen halides or, if antimony trioxide is present [92], antimony halides, which react as follows:

$$HBr + HO^{\bullet} \rightarrow H_2O + Br^{\bullet}$$

$$HBr + H^{\bullet} \rightarrow H_2 + Br^{\bullet}$$

$$SbBr_3 + H^{\bullet} \rightarrow HBr + Br_2Sb^{\bullet}$$

Reactions of this type are less exothermic and block free-radical chain reactions. A drawback of this mechanism is that the gas phase becomes more corrosive. The smoke density may also increase due to inhibition of the combustion reactions.

6.4. Test Methods and Standards

The use of flame-retardant materials (especially in building materials, furnishings, electrical or electronics equipment, mining, and transportation) is covered by application-specific regulations. Many test methods and standards have been created to classify the burning behavior of materials but there is little correlation between them. The small-scale tests performed in materials development can only simulate actual burning behavior within limits; full-scale tests must therefore be performed.

Test methods and standards are specified by (inter)national standards organizations, industry groups or organizations, and government agencies. Numerous test methods are described in [78]. See also, → Flame Retardants, Chap. 3.. The methods encountered most frequently in development and testing laboratories are listed in Table 14. The relatively simple UL 94 test is most widely used and recognized. A standard test rod is clamped in a vertical position, and an igniting flame is applied to the lower end twice for 10 s. The second ignition takes place as soon as the flame from the first ignition is extinguished. The rating criteria are the afterburning time and the ignition of cotton wadding placed under the specimen caused by molten drops of material. The test gives a rating of V-0, V-1, or V-2:

V-0: = afterburning time of single specimen <10 s, of five specimens with two ignitions each <50 s; no ignition of wadding
V-1: = afterburning time of single specimen <30 s, of five specimens with two ignitions each <250 s; no ignition of wadding
V-2: = same as V-1, but with ignition of wadding

The specimens must not be completely burned, otherwise no such classification is given.

6.5. Uses

About 10 % of all plastics (chiefly PVC, ABS, polystyrene, unsaturated polyesters, polypropylene, polyethylene, and polyurethanes) contain flame retardants. The main applications are in building materials and furnishings (structural elements, roofing films, pipes, foamed plastics for insulation and furniture, wall and floor coverings); transportation (equipment and fittings for aircraft, ships, automobiles, and railroad cars); and in the electrical industry (cables; housings and components for television sets, office

Table 14. Test methods and standards (selected)

Test	Standard	Criteria	Applications
LOI test	ASTM D 2863	flammability	development laboratory
Vertical test	UL 94, UL 94–5 V	ignitability dripping	development laboratory electrical industry
Vertical test	DIN 54 332	ignitability	development laboratory floor coverings
Horizontal test	ASTM D 635	burning rate	development laboratory
Miscellaneous tests	FAR 25	ignitability burning rate smoke density	aircraft interiors
Horizontal test	FMVSS 302	burning rate	automotive interiors
Cone colorimeter	ISO DP 5660	ignitability heat release smoke toxic gases	development laboratory materials in buildings
Epiradiator	NF P 92–501	ignitability burning rate	materials in buildings
Surface spread of flame test	BS 476, Parts 5–7	ignitability burning rate	materials in buildings
NBS smoke chamber	ASTM E 662	smoke density	development laboratory aircraft interiors
Toxicity test	DIN 53 436	toxicity of pyrolysis gases	development laboratory materials in buildings
Brandschachttest	DIN 4102	flammability heat release	materials in buildings
Room corner test	NT Fire 025	flame spread smoke toxic gases	materials in buildings
Steiner tunnel test	ASTM E 84	flame spread smoke	materials in buildings

machines, and household appliances; lamination of printed circuits).

More than 90 % of the flame retardants used in thermoplastics are of the additive type. They are added before, during, or after polymerization, but usually when the polymers are processed into compounds or finished products. In the latter case, the retardant is often used as a highly concentrated masterbatch containing 50 – 80 % of the agent.

Reactive flame retardants are added to thermosetting resins before the cross-linking reaction.

Poly(Vinyl Chloride). Up to half of the dioctyl phthalate plasticizers in *flexible PVC* can be replaced by chlorinated paraffins or phosphate esters (e.g., triphenyl or tricresyl phosphate) [93]. Other common additives are Sb_2O_3 (2 – 4 %) and $Al(OH)_3$ (40 %).

In *rigid PVC*, Sb_2O_3 (1 – 4 %) and $Al(OH)_3$ (10 – 20 %) are employed and in some cases zinc borate and zinc stannate. MoO_3, ferrocene, or $CaCO_3$ can be used as smoke inhibitor.

Acrylonitrile – Butadiene – Styrene. A variety of halogenated flame retardants are used for ABS in conjunction with Sb_2O_3; most common for V-0 formulations is a combination of octabromodiphenyl oxide (ca. 20 %) and Sb_2O_3 (ca. 6 %). Halogen-free formulations, for example with $Mg(OH)_2$, are still under development.

Expandable Polystyrene. Hexabromocyclododecane is used at the 3 – 5 % level to comply with building codes; 0.5 % dicumyl peroxide or another free-radical former is added as synergist [88].

High-Impact Polystyrene. The V-0 grades contain ca. 12 % decabromodiphenyl oxide or tetrabromobisphenol A together with 3 – 4 % Sb_2O_3. Ethylene-bis(tetrabromophthalimide) and low molecular mass brominated polystyrenes are also suitable. For V-2 grades, brominated aliphatics are used. Red phosphorus (15 %) has been proposed for halogen-free V-0 grades.

Polyester Resins. The use of 50 – 60 % Al $(OH)_3$, preferably coated, is widespread. Halogenated reactive retardants, such as tetrabromophthalic anhydride and (for more light-stable grades) 2,2-bis(bromomethyl)-1,3-propanediol are also employed.

Low molecular mass brominated epoxy polymers of the F – 2000 series, together with Sb_2O_3, offer another alternative. Zinc borate or dimethyl methylphosphonate is also used.

Polyolefins. In polypropylene, 5 – 20 % tetrabromobisphenol A-bis(2,3-dibromopropyl ether) is used, along with 3 – 8 % Sb_2O_3 [94]. Other halogenated compounds are also used in combination with Sb_2O_3: ethylene-bis (tetrabromophthalimide), ethylene-bis(dibromonorbornane dicarboximide) or Dechlorane Plus. Halogen-free V-0 grades are obtained by using 25 – 35 % of an intumescent system based on ammonium polyphosphate – pentaerythritol – melamine derivatives or 50 – 60 % Al $(OH)_3$ or $Mg(OH)_2$ [95].

Chlorinated paraffins combined with Sb_2O_3 are used in LDPE films. Brominated aromatics or Dechlorane Plus with Sb_2O_3 are used for HDPE and cross-linked polyethylene. Levels of 30 % halogenated organics and 10 % Sb_2O_3 are required for V-0 grades. Halogen-free V-0 grades (e.g., cable sheathing compounds) must contain at least 60 % $Al(OH)_3$ or $Mg(OH)_2$; addition of zinc borate, zinc stannate, or silicones is recommended. Intumescent systems have also been proposed.

Polyurethanes. Flexible polyurethane foams (e.g., for upholstery) contain 20 – 30 % melamine together with a few percent of halogenated phosphate [tris(chloroethyl) phosphate, tris(2-chloroisopropyl) phosphate] or chlorinated paraffins. A combination of graphite and tris(2-chloroisopropyl) phosphate has also been successful. Other formulations include $Al(OH)_3$ or phosphorus-containing products such as dimethyl methylphosphonate, tris(2-chloroethyl) phosphate, tris(2-chloroisopropyl) phosphate, and ammonium polyphosphate.

Rigid foams employ phosphorus-containing or (preferably) halogenated diols and polyols [e.g., diethyl-*N,N*-bis(2-hydroxyethyl)aminomethyl phosphonate, 2,2-bis(bromomethyl)-1,3-propanediol or IXOL B 251] in combination with dimethyl methylphosphonate or halogenated phosphates.

Thermoplastic polyurethane can be rendered flame resistant with brominated compounds and Sb_2O_3 [96] or intumescent systems.

Polyamides. A variety of formulations are used for V-0 grades of polyamide 6 and polyamide 66 [97]. In systems based on brominated aromatics (15 – 20 %) and Sb_2O_3 (4 – 5 %), ethylene-bis (tetrabromophthalimide) and polymeric flame retardants such as poly(tribromostyrene), poly (dibromophenylene ether), and F – 2000 products dominate. Dechlorane Plus is also employed with synergists (e.g., Sb_2O_3, zinc borate, or Fe_2O_3 and Fe_3O_4).

In halogen-free systems, polyamides contain 7 – 10 % red phosphorus or, in the absence of glass-fiber fillers, melamine cyanurate. Tests with $Mg(OH)_2$ are under way.

Polyesters (PBT and PETP). The products used for polyesters are similar to those for polyamides, but combinations of brominated compounds (10 – 20 %) with Sb_2O_3 (3 – 5 %) clearly dominate. A cyclic methylphosphinic acid derivative 2-methyl-2,5-dioxo-1,2-oxaphospholane is chemically incorporated into polyester fibers at the condensation step.

Polycarbonates. Tetrabromobisphenol A is incorporated into polycarbonates as a comonomer; very small amounts of the alkali salts of aromatic sulfonic acids improve flame retardance [89]. Opaque V-0 polycarbonate grades are obtained by using 2 – 4 % brominated aromatics and 1 – 2 % Sb_2O_3 as additive retardants.

Poly(Methyl Methacrylate). The cast plastic can be treated with 13 – 20 % of a halogenated polyphosphonate (Sandoflam 5087) [98].

Poly(Phenylene Oxide) – Polystyrene. V-0 grades of blends of polystyrene and poly(phenylene oxide) can be obtained with ca. 15 % halogen-free triaryl phosphates.

Epoxy Resins. Reactive flame retardants (tetrabromobisphenol A and derivatives, glycidyl ethers of brominated aromatics) are employed for epoxy resins (minimum bromine content

20 %). For printed-circuit laminates, the use of Sb_2O_3 must be avoided. Tests on epoxy resins are being carried out with red phosphorus, $Al(OH)_3$, and zinc borate.

6.6. Toxicology

The question arises whether flame retardants, especially those with chemical action, increase the toxicity of combustion gases. Animal studies have shown that pyrolysis gases emitted by flame-retarded plastics are often less toxic than those from untreated plastics [99]. Standards governing toxicity tests on combustion gases include DIN 53 436 [100] and ISO/IEC/TR 9122–1. Carbon monoxide is the most significant factor in combustion-gas toxicity.

The inherent toxicity of some flame retardants and potential hazards during their processing and use in plastics have been discussed. Of special concern are the polybrominated diphenyl ethers because polybrominated dibenzodioxins and dibenzofurans have been detected in their decomposition products. The Verband der Chemischen Industrie (Chemical Industry Association) in Germany has decided to gradually phase out these retardants. In the United States, an initiative of the Brominated Fire Retardant Industry Panels (BFRIP) has led to in-depth studies on the relevance of the findings [101].

Chlorinated paraffins must be labeled in the United States if their residual carbon tetrachloride content exceeds 0.1 %.

6.7. Economic Aspects

The estimated current world market (1990) of flame retardants is 500 000 t, which is subdivided as follows:

Inorganic	290 000 t
Brominated organic	80 000 t
Chlorinated organic	50 000 t
Organophosphorus	60 000 t

The dominant inorganic product is $Al(OH)_3$, which is also the cheapest flame retardant available.

Producers and trade names of flame retardants are listed in Tables 10–13.

7. Fillers and Coupling Agents

7.1. Purpose and Requirements

Filled (or reinforced) plastics contain large amounts of fillers (20 – 50 wt % referred to the polymer or even occasionally higher). Fillers are divided into *extenders*, which merely provide bulk and lower product cost, and *reinforcements*, which improve several of the polymer properties. *Coupling agents* improve the adhesion between filler and polymer, preferably via chemical bonds; their use confers reinforcing properties on inexpensive extenders, improves the performance of reinforcements, and allows the filler content to be increased. The reinforcing effect of fillers depends on their chemistry, shape (fibers, flakes, spheres), and size (fiber length, particle size). The most important reinforcement effects are

1. Increased strength, ultimate elongation, rigidity (modulus of elasticity), and in some cases impact strength
2. Improved heat distortion temperature and dimensional stability, reduced shrinkage, and improved stability of mechanical values at high temperatures and over extended times (fatigue)
3. Modification of density (usually increased)
4. Improved chemical resistance and lower water absorption
5. Better surface quality and surface hardness

Special fillers are used to obtain compounds with the following properties:

1. Low flammability
2. Electrical conductivity and electromagnetic shielding
3. Radiation and UV shielding
4. Biodegradability
5. Noise suppression

Fillers are characterized by a number of parameters that include geographic origin (minerals); particle size and size distribution or fiber length; purity, especially heavy-metal content; water content; whiteness; oil adsorption value or plasticizer adsorption value (ASTM D 281–31, for PVC fillers); density; specific heat; and

thermal conductivity. Consistency, especially with respect to purity and particle size, is an important criterion of quality.

Occupational health aspects (e.g., dust) and processing qualities (e.g., abrasive behavior toward machinery, effects on viscosity, and wettability – dispersability in the melt) are also important factors influencing the selection of fillers.

7.2. Forms and Chemical Structures

Spherical Fillers and Powders. Calcium carbonate is quantitatively the most important filler. Natural forms (e.g., chalk, marble, or limestone) are ground to powder in dry or wet form. Finer synthetic or precipitated forms [often abbreviated as CCPs (calcium carbonicum praecipitatum)] are obtained by passing carbon dioxide through milk of lime or by reacting calcium chloride and sodium carbonate.

Other mineral fillers include ground dolomite [$CaMg(CO_3)_2$], calcium sulfate (gypsum), and barium sulfate (ground barite or precipitated forms, which have a very high density of 4.5 g/cm^3).

Silica is used as a natural crystalline product (sand, quartz powder) or amorphous synthetic product. The latter is obtained by precipitation from a waterglass solution with acid or by flame hydrolysis from silicon tetrachloride (pyrogenic silica gel).

Solid and hollow glass microspheres of various sizes are employed. Hollow microspheres have the lowest density of all fillers (0.2 – 0.4 g/cm^3).

Other powders include wood flour, cork flour, starch, metal oxides (e.g., Al_2O_3, MgO, ZnO, TiO_2, iron oxides), and metal powders (e.g., Al, Cu, Ni, bronze, Zn, Ag-coated silicate spheres).

Carbon black is obtained by incomplete combustion of gaseous and liquid hydrocarbons. The quality and potential applications (black pigment, conductivity additive, or reinforcement) depend on the production process, purity, and particle size.

Flake fillers include talc, kaolin (China clay), mica, silicon carbide, aluminum trihydroxide, graphite, and metals (e.g., aluminum).

Fibrous Fillers and Reinforcements. A wide variety of inorganic and organic fibrous fillers and reinforcements are used. New ceramic and mineral fibers are being developed.

Carbon fibers are made primarily by oxidative thermal cyclization of polyacrylonitrile fibers. They are classified by their strength. Short fibers (e.g., 3 or 6 mm) are cut from filament yarns.

The starting material for the production of *glass fibers* is glass filament, which is cut into textile glass a few millimeters long. This product is milled to short fibers (e.g., 0.2 – 0.6 mm) when the reinforcement is blended with the polymer in the extruder.

Aramid fibers are obtained, for example, by the polycondensation of terephthaloyl chloride and *p*-phenylenediamine. They are cut to various lengths and used as reinforcement.

Single-crystal fibers (i.e., *whiskers*) can be based on metals, metal oxides, or metal carbides.

Coupling Agents. Typical silane finishes have the general structure $(X)_3Si(CH_2)_3$-Y, in which X is a short-chain alkoxy group (OCH_3, OC_2H_5), an acyloxy group, OH, or Cl; Y is a functional group such as mercapto,amino,azido, methacrylate, epoxy, an anhydride function, or a longer hydrocarbon chain.

Functional groups (e.g., vinyl) can also be attached directly to the silicon. Polymeric silanes [102] containing alkoxy groups and functional groups, as well as bis(trimethoxy) silyl, are also used. New developments include blends of silanes having different functions [103].

The *titanate and zirconate systems* have the general formula $X_mM(O\text{-}X\text{-}R\text{-}Y)_n$, where M denotes Ti or Zr; X denotes an alkoxy group; Z may be a carboxyl, sulfonyl, phosphate, or pyrophosphate group; R can be a long hydrocarbon chain; and Y is a functional group such as amino or methacryloxy. Not all the groups Z, R, and Y need be present. A survey of recommended types is given in [104].

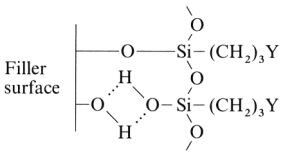
Miscellaneous Coupling Agents. These include aluminates [104], zirconium aluminates [105], stearic acid and stearates, chlorinated paraffins, polyolefin waxes, and carboxylated polybutadienes, or polypropylenes modified with acrylic or maleic acid.

7.3. Mechanism of Action

Reinforcement depends on the transmission of mechanical energy (impact energy, tensile

stress, etc.) from the polymer matrix to the filler. It increases with the strength of (chemical) bonding between the fillers and the matrix. Bonding also limits the mobility of the polymer chain and stiffens the material. Fibrous and flake fillers and reinforcements give rise to anisotropic properties.

Chemical bonding seldom occurs directly between the matrix and the filler; it is usually mediated by coupling agents. In silanes, zirconates, and titanates, for example, the X groups react directly, or after hydrolysis, with hydroxyl or carboxyl groups on the filler surface. The finish materials, particularly silanes, also undergo condensation to form higher molecular mass units:



The Y functional groups react with the polymer (especially in thermosets) or are anchored to the polymer by physical mechanisms, for example, by penetration into the coiled structure in thermoplastics.

7.4. Test Methods

Fillers are tested on receipt, particularly for particle size (screen or sedimentation analysis), acidity, whiteness, density, oil adsorption, and plasticizer adsorption value [dioctyl phthalate (DOP) number]. Tests can be performed by standard methods [106]. Testing the adhesion between the filler and the polymer matrix and correlating it with important physical properties is especially difficult. Publications in this area deal chiefly with fiber-reinforced polymers [107].

7.5. Uses

Nearly all thermosetting and thermoplastic resins are filled or reinforced for special applications. The main applications are in PVC, followed by polyesters, polypropylene, and polyamides. The following examples give a brief summary of the types of fillers and reinforcements used and their effects. Further information can be found in the literature (e.g., [108]).

Calcium Carbonate is important in PVC. Natural forms of calcium carbonate are preferred for flexible PVC because they have lower plasticizer values than precipitated forms. Filler contents of 30 – 60 % or higher are common for cables, film, and floor covering, leading to substantial reductions in cost and additional savings of lubricants, plasticizers, white pigments, or stabilizers.

Precipitated calcium carbonates with surface treatments (coated CCPs) are preferred for rigid PVC. Contents of 10 – 20 %, occasionally up to 50 %, are used for window frames and other profiles, foam, and pipes. Important considerations, in addition to lower cost, are improved impact strength and stiffness, higher production rate, and improved surface appearance. $CaCO_3$ is valued for its low abrasivity in processing.

Other areas for $CaCO_3$ use include polyolefins. Coated types are used for polypropylene in industrial applications (increased heat distortion temperature, dimensional stability, rigidity, and impact strength). Films of LDPE and LLDPE can also be filled with 30 – 40 % $CaCO_3$, which provides slip and antiblocking effects (e.g., trash bags). Calcium carbonate is also used in polyamides, PETP, PBT, and semiopaque grades of other thermoplastics, such as poly(methyl methacrylate).

Barium Sulfate is employed in thermoplastics and provides acoustic damping, X-ray absorption, and increased density.

Kaolin is used in elastomers and flexible PVC for electric cables because of its high water resistance and excellent insulating properties. Kaolin has a high whiteness but also a higher plasticizer adsorption value than, for example, $CaCO_3$.

Mica is employed, for example, in automotive parts made of polypropylene.

Talc is a widely used filler for PVC and polyolefins. Polypropylene components gain in heat distortion temperature and rigidity but lose impact strength and thermooxidative stability.

Aluminum Trihydroxide and Magnesium Dihydroxide are used as flame retardants in polymers such as polypropylene, polyethylene (cable), PVC (carpet backing), and unsaturated polyesters. Filler contents are high (>50 %).

Zinc Oxide serves as an UV absorber in polyolefins.

Wood Flour and Starch. Wood flour is employed in acoustical components made of, for example, HDPE or PVC. The addition of starch, preferably in conjunction with oxidation promoters, is reported to render polyethylene films biodegradable.

Metal powders and carbon black are added to many polymers to improve thermal or electric conductivity.

Silica gel has many applications in thermoplastics (PVC, polyamides) and thermosets (polyester resins, epoxy resins). It is also used as antiblocking and slip agent in LDPE.

Glass spheres are used in polyolefins (including foams) and engineering thermoplastics (polyamides, PETP, PBT). Hollow glass spheres lower the density and result in high transparency.

Glass fibers are by far the most important reinforcement for plastics. For further details, see → Fibers, 5. Synthetic Inorganic, Section 2.1.. They are generally used at levels of 30 – 40 %, and improve tensile and flexural strength, elastic modulus, and heat distortion temperature. The reinforcing effect increases with fiber length and coupling agent. Fiber length must be matched to the elastic modulus of the matrix. Engineering thermoplastics [e.g., polyamides, poly(phenylene oxide), PETP, PBT] and ABS are usually supplied with glass-fiber reinforcement (typical length 0.2 mm) and used for housings or injection moldings in electrical and electronics equipment.

Polypropylene with glass-fiber reinforcement (typical length 0.66 mm) is also important, especially for automotive parts in the United States. Reinforcement results in polypropylene with properties similar to those of engineering thermoplastics. In the thermoset area, long fibers are used for reinforcement. Glass-fiber reinforcement is less common in polyethylene, PVC, and polystyrene.

Carbon Fibers are used mainly as short fibers processed into granular compounds. They provide dimensional stability, electrical conductivity, and (especially metal-coated grades) electromagnetic shielding. They are used in engineering thermoplastics, and epoxy resins. For further details, see → Fibers, 5. Synthetic Inorganic, Chap. 5..

Aramid Fibers (see also, → Fibers, 2. Structure, Section 4.2.) are used chiefly as long fibers (in thermoplastics, their length corresponds to that of the compound granules). They lend rigidity with a low density. Preferred substrates are polyamides, PETP, and epoxy resins.

Coupling Agents are employed at levels of 0.1 – 4 % referred to the filler. They are usually applied to the filler (coated fillers). Aqueous solutions, emulsions, and liquid products are applied by spraying. Coupling agents can, however, be also incorporated directly into the polymer or supplied as powdered concentrates in inert fillers and blended in at the compounding stage.

Silane Coupling Agents are applied to glass fibers, glass beads, and silicates such as mica, talc, wollastonite, and kaolin. They are also used in polymers treated with the flame retardants $Al(OH)_3$ and $Mg(OH)_2$. Silanes (except for special grades) are not, however, suitable for $CaCO_3$, carbon fibers, or metal oxides. They are useful for service in a humid atmosphere because they afford hydrolysis-resistant adhesion.

Titanates are especially good for $CaCO_3$, $BaSO_4$, carbon fibers, aramid fibers, metals, and metal oxides. They tend to become discolored in the presence of phenolic antioxidants. *Zirconates* are used for both $CaCO_3$ and silicates; they do not discolor with phenolic antioxidants.

Stearic Acid and Stearates are mainly used in $CaCO_3$, especially CCP grades. *Chemically modified polypropylene and polybutadiene* are used on glass fibers, mica, $CaCO_3$, and other fillers, chiefly in polypropylene.

Functional groups in the finish should be selected in accordance with the type of polymer.

Table 15. Producers and trade names of coupling agents

Producer	Trade name	Type
Akzo		titanates
BP Performance Polymers	Polybond	functionalized polymers
Cavedon	Cavco	zirconates, zirconium aluminates
Degussa		silanes
Dow Corning		silanes
Du Pont		titanates
Eastman	Epolene	functionalized polymers
Hercules	Az-cup	silanes
Hüls	Dynasilan, Polyvest	silanes, titanates, functionalized polymers
Kenrich		Petrochemicals
Ken-React	titanates,	zirconates, zirconium aluminates
Nippon Soda		titanates
PRC	Prosil	silanes
Titanium Intermediates		titanates
Union Carbide	Ucarsil PC	silanes
Wacker Chemie		silanes

Amino groups are suitable for polyamides, polycarbonates, PETP, PBT, PVC, and many thermosets. Methacrylate groups are used with polystyrene, ABS, SAN, and thermosets, as are epoxy and mercapto groups. Vinyl groups are employed for polystyrene, polyolefins, and PVC. Azido groups are recommended for polyolefins; inert, long-chain hydrocarbon groups can also be used instead of functional groups.

7.6. Economic Aspects

The market volume for fillers and fiber reinforcements is difficult to estimate but is probably on the order of at least 5×10^6 t/a. Mineral fillers are most important, followed by synthetic fillers and glass fibers. Coupling agents have reached a market volume of ca. 10 000 t/a. Because of the large number of suppliers, reference must be made to the literature [108], [109]. Table 15 lists some important producers and trade names of coupling agents.

8. Dyes and Pigments [110–112]

Although the main function of a colorant (i.e., a dye or a pigment) is to impart decorative character and sales appeal, it may also influence the functional properties of the substrate. The selection of colorants from a complex group of minerals and chemical substances has been cited as one of the higher forms of the "black art" of plastics compounding. The problem of colorant selection has become more acute because of the growing complexity of legislation dealing with product safety, occupational safety, and environmental protection. Thus the coloration of plastics is becoming an increasingly precise science.

8.1. Requirements [113], [114]

Modern color-delivery systems (particularly masterbatches) provide overall economy and ease of application. The main requirements for a colorant used in plastics include

1. Inertness under processing conditions (visible and invisible thermal fatigue)
2. Physical and chemical inertness toward the polymer
3. Compatibility with other additives (antagonism/synergism)
4. Required performance during the intended service life of the plastic product
5. Nontoxicity
6. Ability to be disposed of in discarded plastic items without causing extensive environmental nuisance (ecological safety)

Colorants are chosen from a wide range of organic and inorganic compounds. Pigments are particulate organic and inorganic solids that are virtually insoluble in the medium into which they are incorporated. The pigment particles must be dispersed in this medium. Dyes are organic compounds that are usually dissolved in the substrate. Incompatibility is manifested by "crocking", the migration of colorant to the free surface of the plastic from which it can be rubbed off.

Colorants are introduced into plastics by several methods [115]. The dry colorant may be blended with the polymer before processing (dry blending); dispersion or dissolution is less efficient than with color concentrates (masterbatches). Masterbatches are predispersed colorants in a physical form that is easy to handle and use (usually pellets, but also liquid or paste). They offer numerous advantages over powdered colorants, particularly more hygienic working conditions.

8.2. Pigments

8.2.1. Inorganic Pigments [116], [117] See also → Pigments, Inorganic, 1. General

Inorganic pigments are insoluble in plastics and hence do not bleed or migrate; they are therefore the colorants of choice for plastics. They generally exhibit good opacity and hiding power. Colors range from dull earth tones (iron oxides) to bright yellows and reds (pigments based on lead and cadmium).

Titanium Dioxide is the most widely used pigment; it imparts opacity and whiteness to all plastics. Rutile grades are preferred. They are produced by the chloride process, which gives a brighter product, or the sulfate process, which gives a product with a slight "bone" undertone but a lower abrasiveness. To enhance dispersibility and lower the photo- and antioxidant reactivity toward polymer resins, the pigments are usually coated with inorganic materials (e.g., silica or alumina). They are also aftertreated with organic compounds to render them hydrophobic and make them easier to disperse. Plastic-grade titanium dioxide pigments of high hiding power usually have a much finer particle size, in the 0.17 – 0.24 μm range.

Zinc Pigments. Although not as important as titanium dioxide, white zinc-based pigments do have technical advantages, particularly where wear of processing equipment and damage to the polymer during processing or in service are crucial.

Iron Oxide Pigments constitute a very important class of plastics colorants, especially because of their relatively low cost and because of toxicology and environmental considerations. The major shortcomings of iron oxide pigments are their rather dirty shades, ranging from buff yellow to brick red, brown, and black; their abrasiveness with respect to processing equipment; and the fact that they promote the degradation of sensitive polymers (e.g., PVC, polyolefins, and polyamides) by light and weathering. Moreover, the yellow, brown, and black iron oxides are stable only up to 180 °C.

Chromium Oxide Green. The dull green chromium oxide pigments have a poor tinting strength but outstanding heat, light, and chemical stability, making them suitable for all polymers. They are, however, difficult to disperse.

Lead Chromate Molybdate Pigments. The versatile group of lead chromate molybdate pigments ranges in color from primrose to lemon yellow, orange, scarlet, and even green. Silica-coated chromate and molybdate pigments have been developed to provide heat and weather resistance in plastics. Although they offer a combination of bright shades, high hiding power, excellent lightfastness, and low cost, the trend now is toward pigments that do not contain heavy metals.

Cadmium Pigments are ideal for coloring plastics and are the only bright colors available for many industrial polymers. They have excellent heat stability, even in highly aggressive industrial polymers such as nylons; a distinct hue ranging from yellow to orange, deep red, and maroon; and very good lightfastness. Stability under wet conditions is rather limited, however. Cadmium pigments do not cause dimensional instability in colored plastics. As with lead chromate pigments, however, stringent regulations and greater environmental consciousness are forcing plastics colorant users to phase out pigments based on cadmium.

Mixed Metal Oxide Pigments. In the search for lead- and cadmium-free formulations, metal oxide pigments (especially nickel antimony titanate and chromium antimony titanate) have recently attained prominence in both coating and plastics applications. Although their color intensity is low, they are usually combined with color-intense organic colorants to produce the required shades. Titanate pigments have exceptional heat, weather, and chemical stability. Cobalt aluminate pigments are used mainly as shading components.

Ultramarine Blue. Apart from their poor acid resistance, ultramarine blues exhibit excellent all-round fastness. Unlike the blue phthalocyanine pigments, ultramarine blues do not induce distortion in polyolefins. With their excellent heat stability, ultramarines are ideally suited for color correction of white and clear polymers.

Special-Effect Pigments [118]. Pearlescent (nacreous), iridescent, and metallic colorants are increasingly used in plastics. Synthetic nacreous pigments consist of TiO_2-coated mica. Colored pearlescent pigments (e.g., Iriodin, Merck) have an additional coat of iron oxide or chromium oxide. These pigments provide a pearly luster and are used, for example, in cosmetic packaging and fashion articles.

A metallic appearance can be imparted by metal flakes (e.g., aluminum).

8.2.2. Organic Pigments [116], [117], [119], [120] See also → Phthalocyanines, → Pigments, Organic

Organic pigments have cleaner and brighter shades and a much higher tinting strength than inorganic pigments. They tend to dissolve in polymers, however, particularly at very low concentration. The dissolved pigment can undergo thermal degradation [121]. Organic pigments generally produce translucent or semitransparent coloring. Many color formulations are derived from a combination of inorganic and organic pigments whose properties complement one another.

In contrast to inorganic pigments, it is difficult to indicate a particular class of organic pigments for a particular application.

The newer types of monoazo yellows and oranges (e.g., C.I. Pigment Yellow 180, 181, and 182; Orange 64) and monoazo yellow toners (C.I. Pigment Yellow 183, 190, and 191) possess improved heat stability up to 280 °C in polyolefins and even ABS, similar to those of disazo condensation pigments. Among monoazo red toners, C.I. Pigment Red 151 and 247 show good heat stability but rather poor lightfastness.

Diarylide yellows, oranges, and reds tend to undergo thermal decomposition in polyolefins above 200 °C, particularly at low concentration, generating potentially toxic 3,3′-dichlorobenzidine. Their use has recently been limited to PVC.

Azo condensation pigments have adequate heat stability for use in polyolefins and other resins processed at moderate temperature. They generally tend to be dirty in mass tones, however, especially reds. An exception is C.I. Pigment Red 242, a brilliant scarlet, which is of great interest as a heavy-metal replacement.

Except for their tendency to induce distortion in polyolefins, the phthalocyanine pigments, especially the blues, represent the nearest approaches to ideal pigments on the market. Not only are they thermally and photochemically stable, but they also exhibit excellent chemical stability (unlike many inorganic pigments).

Metal-complex pigments are generally rather dirty in shade, particularly in white reductions. C.I. Pigment Orange 68, a heterocyclic metal-complex pigment, is one of the substitutes for heavy-metal formulations in nylons and polycarbonates.

Polycyclic and some heterocyclic pigments (including diketopyrrolopyrrole pigments [122]) generally have very good heat stability in nonpolar polymers. In polar resins, especially nylons, they tend to poor heat and light stability. Of particular importance is the novel heterocyclic perinone pigment C.I. Pigment Yellow 192, which is an ideal cadmium substitute in nylons and polyesters.

Other organic pigments used to color plastics include isoindolines, isoindolinones, dioxazines, anthraquinonoids including indanthones, perylenes, perinones, thioindigoids, quinacridones, and quinophthalones.

8.2.3. Dyes [123]

Because of economy and ease of application, polymer-soluble dyes have been used to color polymers in brilliant and transparent shades. They show reasonably good lightfastness in transparent colorations. In combination with opacifying inorganic pigments, especially titanium dioxide, their lightfastness is rather poor. Polymer-soluble dyes are usually suitable for transparent plastics but not for polyolefins.

Dyes for plastics have a variety of chemical structures. Azo dyes are generally heat- and light-sensitive. Metal-complex azo dyes, especially the chromium complexes, exhibit good stability in nylons. Anthraquinone, quinophthalone, methine, naphthazine, perinone, cumarin, thioindigo, and thioxanthene dyes are usually employed.

Fluorescent pigments are used to produce eye-catching colorations, but tend to plate out in plastics [118]. They consist of finely divided resin particles that contain fluorescent dyes; see → Fluorescent Dyes, Chap. 12.

9. Miscellaneous Additives

9.1. Nucleating Agents

The properties of thermoplastics depend on their degree of crystallization and the morphology of their crystalline phases. Plastics may be amorphous (e.g., PVC, polystyrene, LDPE), of moderate crystallinity (e.g., LLDPE, polypropylene, polyamide 6, PETP), or highly crystalline (e.g., HDPE or polyamide 66). Chain mobility, tacticity, and side-chain volume determine the degree of crystallinity, as do the temperature profile, pressure, and orientation during polymer processing.

During cooling of polymer melts the disordered coiled structure is transformed into an ordered state with the formation of lamellar crystallites. The crystal nuclei can be residual, unmelted polymer crystallites already present in the melt (self-nucleation) or added agents (nucleating agents). The latter make crystallization energetically more favorable and increase the number of nuclei [124–127]. The resulting crystallites form a morphological superlattice structure (e.g., spherulites), which have a central primary nucleus and a radially symmetric structure with amorphous domains occurring between the spherulites. Scattering of light by coarse spherulites (> 0.5 μm) reduces the transparency of plastics.

Nucleating agents control the crystallization behavior of moderately crystalline plastics in the following ways:

1. Increasing the crystallization temperature by ca. 10 – 20 °C
2. Accelerating crystallization rate
3. Decreasing the spherulite diameter and narrowing the size distribution

Classification. Nucleating agents can be divided into

1. Inorganic fillers and pigments: talc, kaolin, silica gel, TiO_2
2. Salts of carboxylic acids [128]: sodium benzoate, aluminum 4-*tert*-butyl benzoate, sodium montanate, sodium β-naphthenate
3. Sodium organophosphates [129]
4. Dibenzylidene sorbitols [130], [131]
5. Waxes [132] and ionomers [133]
6. Systems of carboxylic acids and amines [134]

Some producers and trade names are listed in Table 16.

Properties. Nucleating agents offer some or all of the following advantages. Cycle times in injection molding are reduced by as much as 30 %. They improve optical properties (particularly transparency and gloss), mechanical properties, dimensional stability, and oxidation resistance(less oxygen diffusion in crystalline phases). They also decrease water absorption (polyamides).

Preferred nucleating agents have a high melting point, insolubility in polymer melts, good wettability and dispersability in melts, small particle size (e.g., 1 μm), adequate thermal stability and no odor. They are also approved as indirect food additives (desirable).

Test Methods. Several methods are employed to measure crystallinity.

FT – IR spectroscopy is the simplest way of determining the degree of crystallinity, (i.e., the mass fraction of the crystalline phase) [135].

Differential scanning calorimetry is used to measure the crystallization rate and the temperature at which the maximum crystallization rate occurs [136].

Table 16. Producers and trade names of nucleating agents

Manufacturer	Trade name	Type
Adeka Argus	Mark NA	organic sodium phosphates
Allied Signal	Aclyn	ionomer
Du Pont	Surlyn	ionomer
EC Chemical Co.	EC-1	dibenzylidene sorbitol
Hoechst	Hostalub, Hostamont	sodium montanate
ICI Speciality Chemicals	SCS, Clarifex	proprietary
Milliken Chemical Co.	Millad	dibenzylidene sorbitol
Mitsui Toatsu	NC	dibenzylidene sorbitol
New Japan Chem.	Gellal	dibenzylidene sorbitol
Sandoz Chemicals	Sandostab	aluminum *tert*-butyl benzoate
Schering	Geniset MD	dibenzylidene sorbitol
Shell	AL-PTBBA	aluminum *tert*-butyl benzoate
Witco Corp.	Mark	organic sodium phosphates

Polarization microscopy is useful for measuring spherulite size. Wide-angle X-ray diffraction is used for more detailed studies, for example, of allomorphic forms.

Uses. Nucleating agents are used mainly in polyamide 6, PETP, polyethylene, and polypropylene. Product applications include packaging films, beverage containers, video cassettes, and automotive parts. They are added at a level of 1000 – 5000 ppm and incorporated by dry blending, at the polycondensation stage, or in masterbatch form.

Shortening the injection-molding cycle time is a primary consideration for PETP; inorganic additives, waxes, or sodium salts are used. The situation is similar for polyamide 6, in which many mechanical properties can be improved. Sodium benzoate, aluminum benzoate, phenyl phosphates, and dibenzylidene sorbitols (clarifiers) are employed with polyolefins.

9.2. Antistatic Agents [137]

Plastic surfaces can become electrostatically charged through friction. Charge can build up during processing or service, for example, by the friction of air against the plastic surface. This has several disadvantages:

1. Dirty surface due to attracted dust (a problem with furniture, records, packaging, bottles, and cassettes)
2. Electric shock from walking on plastic floor coverings
3. Adhesion problems in processing films, fibers, foams, and powders
4. Functional disorders in electronic devices and computers
5. Spark generation and dust explosions

Surface-Active Antistatic Agents form a conductive surface layer, in the simplest case a thin film of water, that allows the charge to dissipate quickly or prevents it from building up. In some cases, other additives must be used to impart volume conductivity throughout the bulk of the plastic; these are referred to as *conductivity additives*.

Most plastics have surface resistances of $10^{14} - 10^{16}\ \Omega$, which can be lowered to $10^{8} - 10^{10}\ \Omega$ by antistatic agents utilizing the water-film mechanism. Certain applications, such as explosion hazard areas or electromagnetic shielding, call for even lower surface resistance or lower volume resistivity; conductivity additives can be used to obtain volume resistivities of $10^{1} - 10^{-2}\ \Omega \cdot \text{cm}$.

Quality criteria for antistatic agents include the permanence of their effect, thermal stability, nonvolatility, color, product form, interaction with stabilizers (especially in PVC), and surface effects (tack, weldability, printability). Approval for use as an indirect food additive is often required.

Surface-Active Antistatic Agents are applied by solution spraying (external antistatic agents, nonpermanent) or incorporated into the plastic mass (internal antistatic agents). They are used at levels of 0.1 – 2.5 %, reaching 5 – 7 % in flexible PVC. Internal antistatic agents are amphoteric compounds with limited polymer compatibility (i.e., they tend to migrate to the surface, where their polar moieties "attract" and build up a water-film). Their rate of action depends on their diffusion rate, which is determined by their solubility, molecular mass, and structure, as well as on polymer type and morphology and the presence of other additives and fillers. Internal antistatic agents have a degree of permanence because when they are removed from the surface they are replaced by migration from the reservoir in the bulk plastic.

Surface-active antistatic agents may be cationic, anionic, and nonionic, or organometallic.

Cationic Antistatic Agents include quaternary ammonium salts and sulfonium or phosphonium salts, mainly chlorides, nitrates, hydrogen phosphates, or 4-toluenesulfonates with long hydrocarbon chains. Products derived from imidazoline and pyrazoline are also used.

These agents are employed in rigid PVC (although they may impair heat stabilization) and in polystyrene. Cationic antistatic agents are generally not approved for food contact and are relatively expensive.

Anionic Antistatic Agents include sodium alkyl sulfonates, alkyl phosphonates, and alkyl dithiocarbamates. They are used in rigid PVC (with less detrimental effect on heat stabilization).

Nonionic Antistatic Agents include ethoxylated (or propoxylated) fatty alcohols, fatty amines, or fatty acid amides: polyethylene glycol esters of fatty acids and alkylphenols; glyceryl esters of fatty acids; and sorbitol esters. They are used for many polymers, in particular polyolefins, flexible PVC, polystyrene, and ABS. Most of these agents have a liquid or waxy consistency.

Organometalic Compounds include neoalkyl titanates and zirconates [138] that have a high thermal stability and low migration; their effectiveness is less influenced by humidity. They are especially recommended for polyolefins, but also for PVC and polystyrene.

Conductivity Additives reduce the resistivity in a threshold fashion: when their concentration reaches a certain level (the percolation point), conductivity increases abruptly [139]. They are used at levels of 5 – 10 % and occasionally up to 20 %. Examples are carbon black, metal powders or fibers (e.g., Al or Cu), silver-coated silicates, nickel-coated chopped carbon or glass fibers, or highly conjugated organic polymers (e.g., polyacetylenes, polypyrroles, polythiophenes, and polyanilines), which are oxidized or reduced (doped) to form semiconducting polymers. A survey of conductive additives is given in [140].

Test Methods. The most important test methods measure the surface or volume resistivity (e. g., ASTM D 257 or DIN 53 482, respectively). The frictional charging tendency and the half-life of the accumulated charge (in seconds) can also be measured (DIN 53 486 E).

Empirical soiling tests (e.g., with cigarette ash) should also be mentioned. All testing should be performed under a controlled atmosphere (e.g., 22 °C and 50 % R.H.).

Economic Aspects. The annual worldwide consumption of surface-active antistatic agents is ca. 10 000 t; ethoxylated fatty amines are the leading group in terms of volume. Polyolefins, PVC, and polystyrene use more than 90 % of these products.

Important producers (and trade names) include Aceto Chem. (Catafor), Akzo (Armostat, Interstat), American Cyanamid (Cyastat), CWM Bärlocher (Bärostat), Bayer (Statexan), Dr. Th. Böhme (Tebestat), Chemax Inc. (Chemstat), Dai-ichi Kogyo Seiyaku (Resistat), Dow Chemical (Stature), Eastman (Myvaplex) B. F. Goodrich (StatRite), Henkel (Dehydat), Hoechst (Hostastat), ICI (Atmer), Kao Chem., Kenrich Petrochem. (Ken-Stat), Lonza (Glycolube), Marubishi Oil, Mazer Chemical Division of PPG (Larostat), Nippon Oil & Fats, Sandoz (Sandin), Sherex (Varstat), Swedstab (Swedstat), and Witco (Markstat, Kenamine).

Many producers are in the market with antistatic masterbatches that contain 10 – 50 % of the active ingredient in polymer vehicles, making the usually hygroscopic compounds easier to process.

9.3. Impact Modifiers

High-tonnage plastics such as PVC, polyolefins, or polystyrene have high rigidity but are brittle. Additives (impact modifiers) must therefore often be used to improve impact strength, especially at low temperature [141], [142]. In contrast to plasticizers, impact modifiers must not reduce but increase the heat distortion temperature. Other important selection criteria are their effect on weather resistance and transparency.

Impact modifiers are elastomeric copolymers with low glass transition temperatures. They are dispersed as discrete soft phases in the thermoplastic. Transfer of impact energy to the elastomer phases requires not only a good distribution but also adhesion at the interface between the two phases by chemical bonding or physical cross-linking. Elastomeric properties and adhesion dictate the structural principle of impact modifiers, which are naturally very substrate specific. Most such agents become active above a certain concentration (transition point), between 5 and 15 %.

Classification. Impact modifiers are frequently incorporated into the polymer during compounding; in PVC, they are blended in by the converter. The most important impact modifier classes follow.

Methyl Methacrylate – Butadiene – Styrene Copolymers (MBS). The MBS agents are prepared by graft polymerization of styrene and methyl methacrylate on polybutadiene. They are

used chiefly in PVC, where they offer advantages in clear products (bottles) and, to a lesser extent, in polycarbonates (automotive parts). Because of their sensitivity to light, they are less suitable for outdoor service.

Acrylates include weatherfast polyacrylate esters based on poly(butyl acrylate) and poly (2-ethylhexyl acrylate), as well as skin – core graft copolymers of butyl acrylate and methyl methacrylate. In addition to pure polyacrylates ("all acrylics"), butyl acrylate – styrene – methyl methacrylate terpolymers are used which have good transparency and weather resistance. Acrylate impact modifiers are employed mainly in PVC (e.g., pipes, window frames, sidings). Polyacrylates functionalized with carboxyl groups are recommended for polyamides.

Graft Copolymers of Acrylonitrile and Styrene on Polybutadiene (ABS). ABS is a classical impact modifier for PVC (profiles, sheets, pipes, housings, bottles). The transparency of articles produced depends on the composition. ABS is less suitable for outdoor applications.

Chlorinated Polyethylene. Polyethylene containing 30 – 40 % chlorine is employed in PVC, lending high impact strength especially at low temperature.

Ethylene – Propylene – Ciene Copolymers (EPDM) are used in polypropylene, for example, in automotive parts (bumpers, instrument panels). Functionalized derivatives have been developed for engineering thermoplastics (polyamides, PBT, PETP), for example, by grafting on acrylic acid, maleic acid, or maleic anhydride. The carboxyl groups react with the end groups of the polymers.

Styrene – Butadiene Rubber. Finely divided styrene – butadiene rubber in polystyrene gives high-impact products with a better transparency than high-impact polystyrene (HIPS) produced by graft polymerization of styrene on polybutadiene.

Other Impact Modifiers include ethylene – vinyl acetate, acrylonitrile – styrene – acrylate, and styrene – maleic anhydride copolymers. New functionalized products are being developed for special applications, including those in the thermoset area.

Test Methods. Impact strength tests are specified in the following standards: ASTM D 256, ISO R 179, DIN 53 453. In PVC, for example, modifiers increase the impact value by a factor between 10 and 30.

Economic Aspects. Annual demand for impact modifiers is ca. 150 000 t; ca. 60 % of this is used in PVC. The most important class is MBS, followed by ethylene – propylene – diene copolymers, acrylates, and ABS.

Important producers (and trade names) include Arco Chem. (Arvyl), BASF (Vinuran), Bayer (Baymod, Novadur, Levapren), B. F. Goodrich, Dow Chemical, DSM (Keltan), Du Pont (Elvaloy), Exxon Chemical (Vistalon), General Electric Specialty Chemicals (Blendex), Hoechst (Hostapren), Hüls (Vestolit), Kanegafuchi Chem./Kaneka Texas/Kaneka Belgium (Kane Ace), Kureha Chem., M.A. Industries (MA),Metco America/Metablen b. V.(Metablen, Durastrength), Mitsubishi Rayon, Mobay (Baymod), Monsanto (Elix, Cadon), Nippon Gohsei (Soarblen), Nova Polymers (Novalar, Novalene), Polysar (Taktene), Rohm & Haas (Acryloid, Paraloid), Shell (Kraton), and Wacker Chemie (Vinnol).

9.4. Chemical Blowing Agents

Plastics are often converted into foamed products with physical or chemical blowing agents to obtain substantial savings in weight and improve insulating properties (thermal and acoustic). See also → Foamed Plastics. Physical agents include permanent gases (N_2, CO_2, air) and substances that are gases at the processing temperature (e.g., chlorofluorocarbons, dichloromethane, C_5 – C_7 hydrocarbons). Chemical blowing agents are usually insoluble in the polymer and undergo thermal decomposition or chemical reactions during processing to give gaseous products [143]. While there are technological limits to the use of permanent gases, chlorofluorocarbons have come under severe criticism because of their potential for depleting the ozone layer (Montreal Protocol, October 1987).

The most important criteria for chemical blowing agents are

1. Their decomposition temperature must be matched to the processing temperature of the plastic (150 – 250 °C). Decomposition should not take place spontaneously, should be only slightly exo- or endothermic, and should occur within a relatively narrow temperature window (5 – 15 °C).
2. The gas should be produced with a high yield (usually 100 – 225 mL/g) and should not be toxic, flammable, or corrosive.
3. The solid decomposition products should not interfere with processing (plate-out, migration, or discoloration).
4. They should have a small particle size, a narrow particle-size distribution, and be easily dispersed in the polymer.
5. Approval as an indirect food additive is often required.

Classification. The following are the most important classes of chemical blowing agents.

Azodicarbonamide [123-77-3], thermal decomposition 205 – 215 °C, gas yield 220 mL/g, gases produced N_2, CO (ca. 2 : 1), some NH_3, CO_2. The decomposition temperature can be lowered to 155 °C with "kickers", which are either metal compounds (e.g., ZnO, zinc stearate, Ba – Zn and K – Zn systems, and lead salts) or organic substances (e.g., acids, bases, urea). Azodicarbonamide is used in PVC, polyolefins, polystyrene, ABS, polyamides, poly(phenylene oxide), acrylates, and other resins.

4,4'-Oxybis(benzenesulfohydrazide) [80-51-3], thermal decomposition 150 – 160 °C, gas yield 125 mL/g, gases produced N_2, H_2O. This compound is suitable for plastics that are foamed at relatively low temperature: PVC, LDPE, ethylene – vinyl acetate copolymer, and polystyrene. In comparison with azodicarbonamide it has the advantage of colorlessness.

Cyanuric Trihydrazide [10105-42-7], trihydrazinotriazine, thermal decomposition 275 °C, gas yield 225 mL/g, gases produced N_2, NH_3. This compound is used in ABS, polypropylene, and polyamides.

p-Toluenesulfonyl Semicarbazide [10396-10-8], thermal decomposition 220 – 245 °C, gas yield 140 mL/g, gases produced N_2, CO_2. This compound is used in ABS, polypropylene, HDPE, polyamides, polystyrene, rigid PVC, and PBT.

Isatoic Anhydride [118-48-9], thermal decomposition 210 – 225 °C, gas yield 115 mL/g, gas produced CO_2. This compound is used in polystyrene, ABS, poly(phenylene oxide), PBT, polycarbonates, and polyamides.

5-Phenyltetrazole [18039-42-4], thermal decomposition 240 – 280 °C, gas yield 200 mL/g, gas produced N_2. This compound is used in high-temperature processing, especially in polycarbonates, PBT, poly(phenylene oxide), and polyamides.

Citric Acid and Sodium Bicarbonate, thermal decomposition 150 – 200 °C, gas produced CO_2. In contrast to the compounds listed above, this system generates blowing gases by an endothermic reaction. It can be used in polystyrene, polypropylene, ABS, PVC, and other plastics.

Inorganic Carbonates decompose to form CO_2 and are used in PVC, polystyrene, and polyolefins.

Most chemical blowing agents (ca. 60 %) are used in PVC, followed by polyolefins, including cross-linked polyethylene (ca. 30 %), polystyrene, and engineering thermoplastics. Polyurethanes and polystyrene are foamed mainly with physical blowing agents.

Chemical blowing agents are used at a concentration of 1 – 3 %, higher in cross-linked polyethylene. They are employed as powders or in other forms [144], including nondusting granules, masterbatches, or pastes in combination with plasticizers, kickers, and other additives. The blowing agent can be injected into polymer melts or preblended with the polymer granules and the compound fed to extrusion or injection molding.

Economic Aspects. The annual consumption of chemical blowing agents is ca. 15 000 t; azodicarbonamide is by far the most important product.

Important producers (and trade names) include Bayer/Mobay (Porofor), Boehringer Ingelheim (Hydrocerol), Dong Jim Chem. (Unicell), Eiwa Chem. (Neocellborn, Vinyfor), Fairmount Chem. (Azocel), Hebron (Vinstab, Hebron), Hoechst (Hostatron), J. M. Huber (Activex), Kum Yang (Cellcom), Lucidol/Pennwalt (Luperfoam), M & T (Azubol), Otsuka Chem. (Unifoam), Sankyo Kasei (Cellmic), Schering/Sherex (Ficel, Genitron), Toyo Hydrazine Ind. (Azobis), and Uniroyal/Olin (Celogen, Expandex, Kempore).

9.5. Optical Brighteners

Optical brighteners [145] enhance the whiteness and brilliance of plastics that have a slightly yellow intrinsic color (→ Optical Brighteners). They absorb UV light and emit part of it as fluoresence in the blue – violet region of the spectrum after 10^{-7} – 10^{-9} s.

Important criteria for optical brighteners are the hue of the emitted light (bluish, greenish, or reddish) and their lightfastness. They must also be soluble in the polymer substrate, thermally stable during processing, and resistant to migration.

Optical brighteners have conjugated systems based on stilbene, benzoxazole, coumarin, thiophene, oxadiazole, naphthalene, or triazine building blocks.

They are used in many plastics, at levels between 0.005 and 0.1 %; formulations with TiO_2, especially rutile, require the higher levels. Overdosing produces a greenish tinge. Optical brighteners are also used as concentrates in fillers or plasticizers, or as masterbatches.

Producers (and trade names) of optical brighteners suitable for use as plastics additives include BASF (Ultraphor), Bayer (Blankophor), Ciba-Geigy (Uvitex, Tinopal), Eastman Chemicals (Eastobrite, Kodel), Hoechst (Hostalux), ICI (Fluolite), Sandoz (Leucopur), Sigma (Optiblanc), and Sumitomo (Whitex, Whitefluor).

ABS	acrylonitrile – butadiene – styrene polymer
HIPS	high-impact polystyrene
PBT	poly(butylene terephthalate)
HDPE	high-density polyethylene
LDPE	low-density polyethylene
LLDPE	linear low-density polyethylene
PETP	poly(ethylene terephthalate)
PVC	poly(vinyl chloride)
SAN	styrene – acrylonitrile copolymer

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Plasticizers

ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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1. Introduction

1.1. Definition

A plasticizer is a substance incorporated into a material to increase its flexibility, workability, or distensibility. A plasticizer may reduce the melt viscosity, lower the temperature of the second-order transition, or lower the elastic modulus of the product. Plasticizers are inert, organic substances with low vapor pressures, predominantly esters, which react physically with high polymers to form a homogeneous physical unit, whether it be by means of swelling or dissolving or any other [1].

At present some 300 plasticizers are manufactured, of which at least 100 are of commercial importance. A list of some of the most widely used plasticizers is given in Table 1.

1.2. Types of Plasticization

Two principle ways of obtaining the plasticization effects described above are commonly utilized. Firstly, a rigid polymer may be *internally plasticized* by chemically modifying the polymer or the monomer so that the flexibility of the polymer is increased. A rigid polymer, however, can also be *externally plasticized* by addition of a

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Table 1. Plasticizers in Common Use

Plasticizer	Abbreviation	Alcohol carbon number	CAS registry no.	M_r	Density at 20 °C, g/cm^3
Phthalates					
Diisobutyl phthalate	DIBP	4	[*84-69-5*]	278.3	1.039
Dibutyl phthalate	DBP	4	[*84-74-2*]	278.3	1.046
Diisoheptyl phthalate	DIHP	7	[*41451-28-9*]	362	0.991
L79 phthalate	L79P, 79P	7 – 9	[*71888-89-6*]	380	0.985
L711 phthalate	L711P, 711P	7 – 11	[*68648-91-9*]		0.971
Dioctyl phthalate	DOP	8	[*117-81-7*]	390	0.984
Diisooctyl phthalate	DIOP	8	[*27554-26-3*]	390	0.983
Dinonyl phthalate	DNP	9	[*84-76-4*]	419	0.97
Diisononyl phthalate	DINP	9	[*28553-12-0*] [*68515-48-0*]	419	0.975
Diisodecyl phthalate	DIDP	10	[*68515-49-1*]	447	0.967
L911 phthalate	L911P, 911P	9 – 11	[*68515-43-5*]	454	0.96
Diundecyl phthalate	DUP	11	[*3648-20-2*]	474	0.953
Diisoundecyl phthalate	DIUP	11	[*85507-79-5*]	474	0.962
Undecyl dodecyl phthalate	UDP	11 – 12	[*68515-43-5*]	488	0.957
Diisotridecyl phthalate	DTDP	13	[*27253-26-5*]	531	0.952
Butyl benzyl phthalate	BBP	4 – 7	[*68515-47-9*]	312.3	1.119
Adipates					
Dioctyl adipate	DOA	8	[*103-23-1*]	370.6	0.929
Diisononyl adipate	DINA	9	[*33703-08-1*]	398	0.929
Diisodecyl adipate	DIDA	10	[*27178-16-1*]	427.1	0.915
Trimellitates					
Trioctyl trimellitate	TOTM	8	[*3319-31-1*]	530	0.991
L79 trimellitate	L79TM	7 – 9	[*68515-60-6*]	530	0.996
L810 trimellitate	L810TM	8 – 10	[*67989-23-5*]	592	0.973
Phosphate esters					
Tri-2-ethylhexyl phosphate	TOF	8	[*78-42-2*]	434	0.926
2-Ethylhexyl diphenyl phosphate	Santicizer 141	6 and 8	[*1241-94-7*]	362.4	1.091
Tricresyl phosphate	TCP	6	[*1330-78-5*]	368.2	1.165

plasticizer, which imparts the desired flexibility but is not chemically changed by reaction with the polymer. The latter process has the advantage of lower cost and permits the fabricator freedom in devising formulations to manufacture items of differing flexibility simply by adding different amounts of plasticizer, within the constraints of polymer – plasticizer compatibility.

1.3. Types of Plasticizer

Plasticizers can be divided into two principal groups: primary and secondary. *Primary plasticizers* lower the glass transition temperature T_g and increase the elongation and softness of the polymer. *Secondary plasticizers*, when added to the polymer alone, do not bring about such changes and may also have limited compatibility with the polymer. However, when added to the polymer in the presence of a primary plasticizer, secondary plasticizers enhance the plasticizing performance of the primary plasticizer.

2. Plasticizers in Common Use

2.1. Market Overview

The list of commercially available plasticizers, covering applications throughout polymer science, is extensive. This reflects the development of plasticizers to meet the increasing demand for polymers, especially PVC, for new and higher quality applications. This article discusses the main groups of plasticizers; for further details, see [1–4] and references therein.

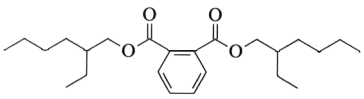
The Western European plasticizer market had a capacity of 969×10^3 t/a in 1989 and at that time was growing at a rate of 3 % per annum [5]. In 1996 production of plasticizer in Western Europe amounted to 1253×10^3 t/a and in the United States to 636×10^3 t/a [6]. In terms of plasticizer types, the majority of this tonnage (>85 %) is standard phthalate (esters of phthalic anhydride with C_8 – C_{10} alcohols). Reasons for this are the relatively low price and ready availability of feedstocks. The remainder of the

market is taken up by phthalate esters of other alcohols, speciality phthalates, adipates, trimellitates, and other esters.

2.2. Phthalate Esters (see also → Phthalic Acid and Derivatives)

Diesters of phthalic anhydride are produced commercially from $C_1 - C_{13}$ alcohols, although the $C_1 - C_3$ esters are generally too volatile to find widespread use. Di-*n*-butyl phthalate (DBP) and diisobutyl phthalate (DIBP) (linear and branched C_4 esters) are used in many PVC formulations, principally for ease of gelation. Owing to their relatively high volatility, in comparison with other phthalates, they are often used in conjunction with higher molecular mass esters. Diisopentyl phthalate (DIPP) is generally used in a similar manner. Diisoheptyl phthalate (DIHP), an ester based on a C_7 iso-alcohol from the oxo alcohol process, shows good plasticizing action with PVC as well as with a number of other polymers [4]. Its principle use in PVC, when compared with higher molecular mass plasticizers, lies in its gelation characteristics and balance of volatility and viscosity, the volatility of DIHP being only slightly higher than the corresponding C_8 phthalate (DIOP).

Di-2-ethylhexyl phthalate (DEHP) (also known as dioctyl phthalate, DOP) has long been accepted as the industry standard general purpose primary plasticizer.

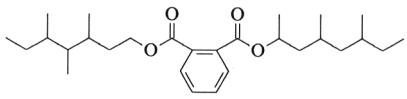


Di-2-ethylhexyl phtalate, DEHP
(dioctyl phthalate, DOP)

This is because its properties are adequate for many applications in the flexible vinyl industry. DEHP shows good gelation characteristics, good softening action, and adequate viscosity properties in emulsion PVC pastes. Diisooctyl phthalate, produced from C_8 oxo alcohols, shows performance in PVC which is generally similar to DEHP. Di-*n*-octyl phthalate (DnOP), a C_8 phthalate ester derived from a linear alcohol, is also produced, but in far smaller quantities than the branched phthalates. The linear structure imparts improved low-temperature performance and lower viscosity.

Diisononyl phthalate (DINP) is produced from C_9 oxo alcohols and has similar plasticizing properties to DEHP. Its slightly higher molecular mass results in a somewhat lower plasticizer efficiency which requires a greater addition of plasticizer to impart an equivalent softness (these effects are discussed in detail in Section 4.2.1). The higher molecular mass alcohol also imparts improved high-temperature performance and resistance to extraction. Other C_9 phthalates are also produced [e.g., DNP, DINP(S)] and vary in the linearity of the alcohol component in the ester, the more linear varieties giving improved properties.

Diisodecyl phthalate (DIDP), the phthalate ester of C_{10} oxo alcohols, exhibits superior high-temperature performance to DINP and DEHP due to its higher molecular mass (lower volatility).



Diisodecyl phthalate, DIDP
(one of the possible isomers)

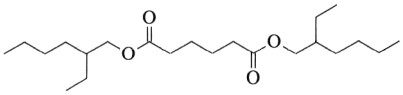
Its lower plasticizing efficiency compared to the lower phthalates requires greater plasticizer addition to impart the same softness, although this can, in some cases, be advantageous. Diundecyl phthalate (DUP), diisoundecyl phthalate (DIUP) and undecyl dodecyl phthalate (UDP) continue this trend. Ditridecyl phthalate (DTDP) is the highest molecular mass phthalate ester generally available in commercial quantities. Its high molecular mass results in low plasticizing efficiency, and some compatibility problems may occur at high plasticizer loadings. Its low volatility, however, also results in superior high-temperature performance and allows some strict electrical cable insulation and sheathing specifications to be met.

2.3. Adipate Esters

Alkyl esters of adipic acid have two principle advantages in the plasticization of PVC resins in comparison with the corresponding phthalate ester: (1) their lower intrinsic viscosity confers

lower plastisol viscosity and good plastisol storage stability, enabling use in demanding applications and (2) they give superior low-temperature flexibility properties.

Of adipate esters in use in the flexible vinyl industry, di-2-ethylhexyl adipate, DEHA (also known as dioctyl adipate, DOA) is the most common.

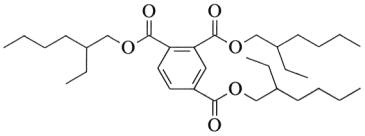


Di-2-ethyl hexyl adipate, DEHA
(dioctyl adipate, DOA)

It is widely used in flexible PVC food film (cling film). DEHA has good plasticizing efficiency and compatibility with PVC, and its very low viscosity enables it to be used in PVC plastisol applications where low viscosity is required, often in conjunction with a phthalate. Diisononyl adipate (DINA) is the ester of adipic acid with isononanol produced from oxo alcohols. It shows similar properties to DEHA. Its higher molecular mass does, however, increase its viscosity compared with DEHA, but this is accompanied by a reduction in volatility. The lower efficiency in comparison with DEHA, which requires a greater plasticizer addition, can result in lower plastisol viscosities. These effects are extended in moving to diisodecyl adipate (DIDA). Higher adipates (e.g., ditridecyl adipate, DTDA) are of limited use due to their lower compatibility with PVC.

2.4. Trimellitate Esters

Esters of trimellitic anhydride (TMA) have grown in popularity due to their excellent thermal properties and resistance to extraction. Tris-2-ethylhexyl trimellitate (TOTM), produced from trimellitic anhydride and 2-ethylhexanol, is the ester most widely used.

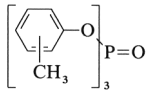


Tris-2-ethylhexyl trimellitate
(trioctyl trimellitate, TOTM)

Although of a lower plasticizing efficiency than the corresponding phthalate, the thermal stability and extraction resistance of TOTM are superior. These properties can be improved still further by using trimellitate esters produced from mixed linear alcohols, e.g., L79 trimellitate and L810 trimellitate. The improved properties brought about by these esters are discussed further in Chapter 4.

2.5. Phosphate Esters

The principle advantages of phosphate esters such as tricresyl phosphate as plasticizers for PVC is their low volatility and their ability to impart fire-retardant properties to a PVC formulation.



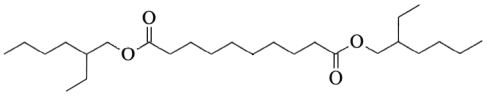
Tricresyl phospate

Tris(2-ethylhexyl) phosphate shows good compatibility with PVC and also imparts good low-temperature performance in addition to good fire retardancy.

2-Ethylhexyl diphenyl phosphate has widespread use due to its combination of plasticizing efficiency, low-temperature properties, migration resistance, and fire retardancy.

2.6. Sebacate and Azelate Esters

Esters from the linear sebacic and azelatic acids are used in PVC applications for the same reasons as the corresponding adipates, i.e., low viscosity and good low-temperature performance. Di-2-ethylhexyl sebacate (DOS) and di-2-ethylhexyl azelate (DOZ) are the most widely used.

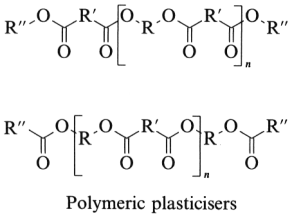


Di-2-ethylhexyl sebacate, DOS

In comparison to adipates, however, these esters tend to have a significantly higher cost and consequently only find use in extreme low-temperature applications.

2.7. Polyester Plasticizers

Polyester plasticizers, or polymeric plasticizers as they are more generally known, have found use due to their low volatility and high extraction resistance.



Polymeric plasticisers

They are typically based on condensation products of propane- or butanediols with adipic acid or phthalic anhydride. The growing polymer chain may then be end-capped with an alcohol or a monobasic acid, although non-end-capped polyesters can be produced by strict control of the reaction stoichiometry. Due to their higher molecular mass compared to other plasticizers they have much higher viscosities (3 – 10 Pa · s), which in some cases can make processing with PVC difficult.

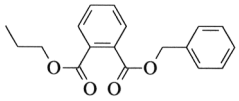
2.8. Sulfonate Esters

Sufonate ester plasticizers for PVC are typically aryl esters of a C_{13} – C_{15} alkane sulfonic acid. They are relatively efficient and easily processable plasticizers with good extraction properties.

2.9. Specialty Phthalate Esters

In addition to the phthalate plasticizers described in Section 2.2, other phthalate plasticizers are also commercially available. These are speciality products which find use as high-quality plasticizers in specific applications. Their quality tends to be reflected in their price since they require either a further manufacturing stage (e.g., transesterification) or the use of alcohol feedstocks of greater linearity than the standard phthalates.

Benzyl butyl phthalate (BBP) shows excellent compatibility and fusion characteristics with PVC and is widely used in vinyl flooring for these reasons and also due to its superior stain resistance.



Benzyl butyl phthalate, BBP

Linear and semilinear phthalates (e.g., DnOP, 911P, DUP) have lower viscosities than the corresponding branched ester. This results in lower plastisol viscosity and also lower plasticizer volatility. 911P, a phthalate ester based on linear and semilinear C_9 – C_{11} alcohols, is the premium plasticizer for flexible PVC in automotive applications due to its low fogging (the condensation of volatile material on a car windscreen, causing impaired visibility); see Section 4.2.7.

2.10. Secondary Plasticizers

Secondary plasticizers (also referred to as extenders) continue to play a major role in flexible PVC technology. They do not have the same mode of softening action as a primary plasticizer but do impart softening behavior when used in combination with a primary plasticizer. In some very hard PVC formulations, however, a secondary plasticizer alone may be of use. The major secondary plasticizers are chlorinated hydrocarbons. These are hydrocarbons chlorinated to varying amounts, typically 30 – 70 %. For a given hydrocarbon, plasticizer viscosity increases with increasing chlorine content. Chlorinated hydrocarbons of the same chlorine content may, however, have different volatilities and viscosities if they are based on different hydrocarbons. The principal advantages of such materials are: (1) they improve fire retardancy due to their chlorine content and (2) formulations containing a secondary plasticizer are often cheaper. Precise knowledge of compatibility between standard plasticizers and chlorinated paraffins is required since some mixtures become incompatible with each other and the PVC resins at certain concentrations. Phthalate – chlorinated hydrocarbon compatibility decreases as the molecular mass of the phthalate and the plasticizer loading in the PVC increases; for specific examples, see [1].

3. Mechanism of Plasticizer Action

Several theories of plasticizer action have been proposed, ranging in detail and complexity. Whilst each theory is not exhaustive, an understanding of the plasticization process can be gained by combining ideas from each theory. The theories are discussed in detail in [1].

3.1. The Lubricity Theory

The lubricity theory is based on the assumption that the rigidity of the resin arises from intermolecular friction binding the chains together in a rigid network. On heating, these frictional forces are weakened so as to allow the plasticizer molecules between the chains. In the resulting mixture at room temperature the plasticizer molecules act as lubricants for the polymer chains.

3.2. The Gel Theory

The gel theory extends the lubricity theory in that it deals with the idea of the plasticizer acting by breaking the resin – resin attachments and interactions and by masking these centers of attachment from each other, preventing their reformation. Such a process may be regarded as being necessary but by itself insufficient to explain a completely plasticized system since while a certain concentration of plasticizer molecules will provide plasticization by this process the remainder will act more in accordance with the lubricity theory, with unattached plasticizer molecules swelling the gel and facilitating the movement of plasticizer molecules, thus imparting flexibility. Molecules acting by this latter action may in fact constitute the bulk of plasticizer molecules.

3.3. The Free-Volume Theory

The free-volume theory extends the above ideas and also allows a quantitative assessment of the plasticization process. The free volume of a polymer is described by Equation 1 and Figure 1

$$V_f = V_t - V^0 \quad (1)$$

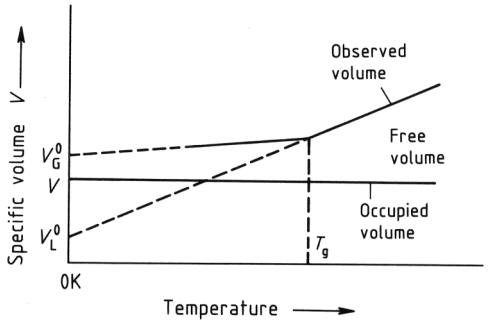


Figure 1. The free-volume concept [4]

where

V_f = the free volume of the polymer
V_t = specific volume at temperature t
V^0 = specific volume at arbitrary reference point, usually 0K

and V_G^0 and V_L^0 are the specific volumes of the glass and liquid extrapolated to 0K.

Free volume is a measure of the internal space available in a polymer for the movement of the polymer chain, which imparts flexibility to the resin. Figure 1 shows how the amount of free volume in the polymer increases sharply at the glass transition temperature T_g. Consequently, the study of plasticization is a study of how to lower T_g, thus creating a polymer that is flexible at ambient temperature. Plasticizers therefore increase the free volume of the resin and also ensure that free volume is maintained as the resin – plasticizer mixture is cooled from the melt. Combining these ideas with the gel and lubricity theories implies that plasticizer molecules that do not interact with the polymer chain must simply fill free volume created by those molecules that do. These molecules may also be envisaged as providing a screening effect that prevents interactions between neighboring polymer chains, thus preventing reformation of the rigid polymer network on cooling.

For the plasticized resin, free volume can arise from:

1. Motion of the chain ends
2. Motion of the side chains
3. Motion of the main chain

These motions can be increased in a variety of ways, including:

1. Increasing the number of end groups
2. Increasing the length of the side chains
3. Increasing the possibility of main chain movement by the inclusion of segments of low steric hindrance and low intermolecular attraction
4. Introduction of a lower molecular mass compound which imparts the above properties
5. Raising the temperature

The introduction of a plasticizer, which has a lower molecular mass than the resin, can impart a greater free volume per volume of material since (1) there is an increase in the proportion of end groups and (2) it has a lower glass transition temperature T_g than the resin. A detailed mathematical treatment of this [7] can be carried out to explain the success of some plasticizers and the failure of others. Clearly, the use of a given plasticizer in a certain application will be a compromise between the above ideas and physical properties such as volatility, compatibility, high- and low-temperature performance, and viscosity. This choice will be application dependent, i.e., there is no ideal plasticizer for every application.

3.4. Solvation – Desolvation Equilibrium

Since plasticizer migrates from plasticized polymers, it is clear that plasticizer molecules are not bound permanently to the polymer as in an internally plasticized resin, but that an exchange or equilibrium mechanism is present. This implies that there is no stoichiometric relationship between polymer and plasticizer, although some quasistoichiometric relationships appear to exist [8], [9]. This idea is extended in Section 3.6.

3.5. Generalized Structure Theories

In their simplest form generalized structure theories attempt to produce a visual representation of the mechanism of plasticizer action [1]. The theories are based on the concept that if a small amount of plasticizer is incorporated into the polymer mass it imparts slightly more free volume and gives more opportunity for the movement of macromolecules. Many resins tend to become more ordered and compact as existing crystallites grow or new crystallites form at the expense of the more fluid amorphous material. For small additions of plasticizer, the plasticizer molecules may be totally immobilised by attachment to the resin by various forces. These tend to restrict the freedom of motion of small portions of the polymer molecule necessary for the absorption of mechanical energy. Therefore it results in a more rigid resin with a higher tensile strength and modulus than the base polymer itself. This phenomenon is therefore termed antiplasticization. A study by Horsley [10] used X-ray diffraction to show that small amounts of dioctyl phthalate (DOP) progressively increase the order in the PVC. Above these concentrations the order decreases and the polymer becomes plasticized (see also Section 3.6).

3.6. Specific Interactions and Interaction Parameters

Early attempts to describe PVC – plasticizer compatibility were based on the same principles as used to describe solvation, i.e., "like dissolves like" [11]. To obtain a quantitative measure of PVC – plasticizer compatibility a number of different parameters have been used. These are briefly described below.

The Hildebrand Solubility Parameter δ gives a measure of compatibility between plasticizer and a resin based on the solvating power of the plasticizer for the resin under investigation. For complex molecules this can be estimated [12] by using a set of additive constants for the more common groups in plasticizer molecules. These constants are designated F and the overall value for the plasticizer is given by the equation

$$\delta = \sum F/V \tag{2}$$

i.e., a summation of each solubility constant for each molecular portion of the plasicizer molecule divided by the molecular volume. Data so calculated for different plasticizers can be compared, with the higher values suggesting greater compatibility.

The Polarity Parameters Φ were evaluated by Van Veersen and Meulenberg [13] and despite their apparent simplicity they show a good

correlation with plasticizer activity for nonpolymeric plasticizers. The parameter is defined as:

$$\Phi = \frac{M(A_p/P_o)}{1000} \quad (3)$$

where
M = molecular mass of plasticizer
A_p = number of carbon atoms in the plasticizer, excluding aromatic and carboxylic acid carbon atoms
P_o = number of polar (e.g., carbonyl) groups present

The factor of 1000 is used to produce values of a convenient size.

The Solid-Gel Transition Temperature $\mathbf{T}_m$ is a measure of plasticizer activity. It is the temperature at which a single grain of PVC dissolves in excess plasticizer. More efficient plasticizers have lower values of T_m due to their higher solvating power.

The Flory – Huggins Interaction Parameter χ**.** These ideas, based on a study of polymer miscibility, were applied to plasticizers by ANAGNOSTOPOULOS [14] according to the equation:

$$1/T_m = 0.002226 + 0.1351(1 - \chi)/V_1 \quad (4)$$

where V_1 is the molar volume of the plasticizer, calculated from the molecular mass and the density at T_m.

The Activity Parameter α is based on work by BIGG [15]. It is another measure of plasticizer activity and is defined as

$$\alpha = 1000\frac{(1 - \chi)}{M} \quad (5)$$

Summaries. Over the past few years these methods have been assessed and extended by many workers, in particular the Loughborough group [16], [17]. It was shown that solubility parameters are capable of classifying plasticizers of a given family in terms of their compatibility with PVC but that they are of limited use for comparing plasticizers of different families (e.g., phthalates with adipates). Polarity parameters provided useful predictions of the activity of monomeric plasticizers but again were not able to compare activity of plasticizers from different families. In all cases it was not possible to predict the behavior of polymeric plasticizers.

Specific Interactions. Ideas on the subject of specific interactions between PVC and a plasticizer molecule, as a basis of plasticization, can be considered a more detailed form of some of the ideas discussed above. Clearly some mechanism of attraction and interaction between PVC and plasticizer must exist for plasticizer to be retained in the polymer after processing.

The role of specific interactions in the plasticization of PVC has been proposed from work on specific interactions of esters in solvents (e.g., hydrogenated chlorocarbons) [18], work on blends of polyesters with PVC [19–25], and work on plasticized PVC itself [26–28]. Modes of interaction between the carbonyl functionality of the plasticizer ester or polyester were proposed, mostly on the basis of results from Fourier transform IR spectroscopy (FTIR). Shifts in the absorption frequency of the carbonyl group of the plasticizer ester to lower wavenumber, indicative of a reduction in polarity (i.e., some interaction between this functionality and the polymer) were reported [25–27]. Work performed with dibutyl phthalate [27] suggested an optimum concentration at which such interactions were maximized. Spectral shifts were in the range 3–8 cm^{-1}. Similar shifts were also reported in blends of PVC with polyesters [19–25], again showing a concentration dependence of the shift to lower wavenumber of the ester carbonyl absorption frequency.

Recent Studies. Some recent work has extended these ideas by using new analytical techniques, in particular molecular modeling and solid-state NMR spectroscopy.

Molecular Modeling. The computer modeling of molecules is a rapidly growing branch of chemistry (→ Molecular Modeling) [29–31]. High-resolution graphics and fast computers allow the operator to build molecules in minimum energy configurations and view them in real time. This model can be constructed from crystallographic coordinates available from data bases or by simple intervention from the operator. Molecular mechanics or quantum mechanics programs are then used to arrive at a likely structure.

A range of plasticizer molecule models and a model for PVC were generated and energy minimized to observe their most stable conformations. Such models highlighted the free volume increase caused by the mobility of the plasticizer alkyl chains. More detailed models were also produced to concentrate on the polar region of the plasticizer and its possible mode of interaction with the polymer. These showed the expected repulsion between areas on the polymer and plasticizer of like charge as well as attraction between the negatively charged portions of the plasticizer and positively charged portions of the PVC.

Solid-State NMR Spectroscopy. Recent advances in technology have made the study of solids by NMR techniques of considerably greater ease than in previous years. For the accumulation of solid state ^{13}C NMR spectra, cross polarisation magic angle spinning (CP-MAS) can be utilized to significantly reduce signal broadening effects present in the solid state but not in the liquid state. The technique was used to study the molecular effects of plasticization by comparing spectral shifts of PVC and plasticizer under various degrees of processing. For PVC plasticized with DIDP two processing temperatures, 130 °C and 170 °C, were used, representing a low degree and high degree of plasticization, respectively. The comparison of the spectra showed no shift in the resonance frequency of the carbonyl group with processing temperature. The most significant difference in the two spectra was in the aliphatic carbon resonances. The spectra of the more plasticized sample showed resonance shifts and increased resolution for these carbon atoms. This again shows a strong dependence of successful plasticization on the conformation of the alkyl chains of the plasticizer ester (linked to the increased free volume).

4. Plasticized PVC

4.1. Applications Technology

Over 90 % of plasticizer sales by volume are into the PVC industry. The reason is that the benefits imparted by the plasticization of PVC are far greater than those imparted to other polymers. PVC stands alone among polymers in its ability both to accept and retain large concentrations of plasticizer. This is due to a morphological form consisting of highly amorphous, semicrystalline, and highly crystalline regions. Without the wide range of additives available (e.g., plasticizers, stabilizers, fillers, lubricants, pigments) PVC would be of little use. The development of PVC as a commodity polymer is fundamentally linked to the development of its additives.

The two principle types of PVC are suspension and emulsion PVC. The plasticizer applications technology associated with these two forms are different and are discussed separately here. Details of the polymerization techniques giving rise to these two distinct polymer types are discussed in [32], [32]; see also → Poly(Vinyl Chloride)).

4.1.1. Suspension PVC

PVCs produced by suspension polymerization have a relatively large particle size (typically 100–150 μm). Additionally, these particles are highly porous and are therefore able to absorb large amounts of liquid plasticizer during a formulation mixing cycle. Flexible PVC formulations based on a suspension polymer are typically processed by a dry-blend process, during which all formulation ingredients are heated (typically 70–110 °C) and intimately mixed to form a dry powder (PVC dry-blend) which contains all formulation ingredients. This dry-blend can be either stored or processed immediately. Processing of suspension resin formulations is performed by a variety of techniques such as extrusion, injection molding, and calendering to totally fuse the formulation ingredients and form the desired product.

4.1.2. Emulsion PVC

Emulsion PVC resins differ from those manufactured by the suspension process principally in terms of particle size but also in the presence of emulsifiers and surfactants not used in suspension polymerization. The particle size of an emulsion polymer (typically 1–2 μm) is much lower than that of a suspension resin. This low particle size imparts a lack of porosity to the resin and thus the mixing of formulation ingredients in a dry-blending process is not possible.

A typical flexible PVC formulation prepared with an emulsion polymer will be a liquid or paste (plastisol). This consequently leads to a different applications technology area. PVC plastisols can be fused by techniques such as spreading, rotational molding, and slush molding. Plastisols may also be semi-gelled (i.e., enough heat is imparted to convert the plastisol into a solid but without the full development of tensile properties brought about by complete fusion) for storage.

As the formulation ingredients in a plastisol are in the liquid form, the viscosity of the plastisol is of major importance, and the intrinsic viscosity of the plasticizer has a major contribution to the plastisol viscosity, as do the polymerization conditions of the resin. The desired plastisol viscosity can be obtained by careful selection of polymer, plasticizer, and other formulation ingredients but also by shear rate. PVC plastisols are either (1) pseudoplastic or shear-thinning (viscosity decreases with shear), (2) near-Newtonian (viscosity remains nearly constant with shear), or (3) dilatant (viscosity increases with shear). Choice of plastisol ingredients to give desired viscosity effects will depend on the application requirements of the plastisol.

4.2. Effect of Plasticizer Choice on the Properties of Flexible PVC

This section discusses the effect of plasticizer choice on a range of properties of flexible PVC articles. Certain properties are more important for some applications than others, and hence some plasticizers find more extensive use in some application areas than others. The PVC technologist must ascertain the most important properties for the application in question and then make the correct choice of plasticizer.

4.2.1. Plasticizer Efficiency

Plasticizer efficiency is a measure of the concentration of plasticizer required to impart a specified softness to PVC. The softness may be measured as a British Standard Softness (BSS) or a Shore hardness (BSS 35 is equivalent to a Shore A hardness of 80 — test method BS 2782). For a given acid constituent of plasticizer ester, plasticizer efficiency decreases as the carbon number of the alcohol chain increases; e.g., for phthalate esters efficiency decreases in the order DBP > DIHP > DOP > DINP > DIDP > DTDP. For example, an additional six parts per hundred of PVC (phr) of DIDP than DOP is required to give a hardness of Shore 80 when all other formulation ingredients remain constant. In addition to the size of the alcohol chain, the amount of branching is also significant, with the more linear isomers being of greater efficiency. Choice of the acid constituent can also be significant. For the same alcohol constituent, phthalate and adipate esters are approximately equivalent but both are considerably more efficient than the corresponding trimellitate.

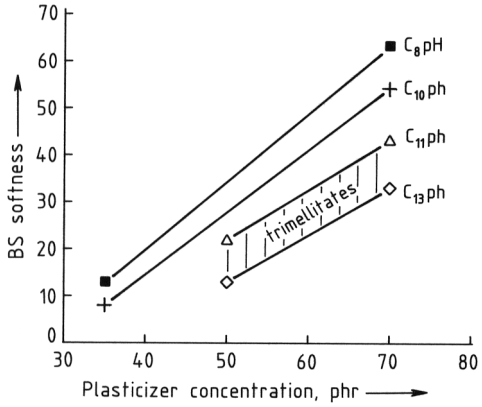


Figure 2. Relative efficiency of plasticizers
ph = phthalate

Figure 2 compares various plasticizers with respect to their ability to impart flexibility to a PVC resin. This shows the lower plasticizing efficiency of a C_{10} phthalate relative to a C_8 phthalate and also the lower plasticizing efficiency of the trimellitate esters compared to the phthalates.

4.2.2. High-Temperature Performance

High-temperature performance in flexible PVC is related to (1) plasticizer volatilization and (2) plasticizer degradation. Plasticizer volatilization, both from the finished article during use at elevated temperatures (e.g., electrical cable insulation) and also during processing (i.e., release of plasticizer fume) is directly related to the volatility of the plasticizer in use. Hence the higher molecular mass plasticizers give superior performance in this area. Figure 3

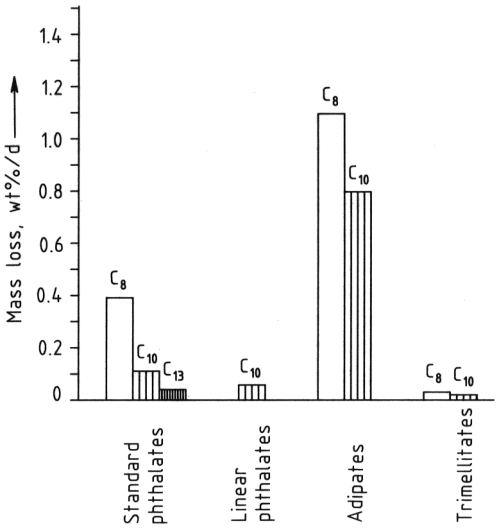


Figure 3. Volatile loss in use from plasticized PVC (50 phr plasticizer) for various plasticizers

shows the percentage mass loss from plasticized PVC (50 phr of plasticizer) for various plasticizers at 100 °C. The superior performance of the trimellitate esters and inferior performance of adipate esters, relative to the phthalate, is illustrated.

For phthalate plasticizers thermal stability decreases in the order DTDP > DIDP > DINP > DOP > DIHP > DBP. Higher molecular mass esters such as trimellitates improve this still further and are used in demanding cable specifications which have strict mass loss requirements. Polyester plasticizers give the best performance in this area, with performance improving with increasing molecular mass. Additionally, branched esters have somewhat higher volatilities than their linear equivalents.

High-temperature performance also includes the generation of fume in the workplace, for which the same structure relationships apply. Not only does excessive plasticizer volatilization have environmental consequences but inaccuracies in formulation can be incurred since not all the plasticizer enters the PVC resin, resulting in a harder material than calculated.

Plasticizer molecules can undergo thermal degradation at high temperature. Esters based on the more branched alcohol isomers are more susceptible to such degradation. This can, however, be offset by the incorporation of an antioxidant, and plasticizer esters for cable applications frequently contain a small amount of antioxidant.

4.2.3. Low-Temperature Performance

The ability of plasticized PVC to remain flexible at low temperature is of great importance in certain applications (e.g., external tarpaulins, underground cables). For this property the choice of the acid constituent of the plasticizer ester is of major importance, with the linear aliphatic adipic, sebacic, and azeleic acids giving excellent low-temperature flexibility compared to the corresponding phthalates and trimellitates.

There is also a major contribution to low-temperature performance from the alcohol portion of the ester; the greater the linearity of the plasticizer the greater the low-temperature flexibility. Figure 4 shows the cold flex temperature (the lowest temperature at which a sample of flexible PVC of standard dimensions can be twisted by 200° in the Clash and Berg test) for various PVC – plasticizer combinations. The increasing low-temperature performance with increasing alkyl chain length is illustrated, as is the superior low-temperature performance of the adipate esters.

4.2.4. Gelation Properties

The gelation characteristics of a plasticizer are related to its efficiency, and both properties are

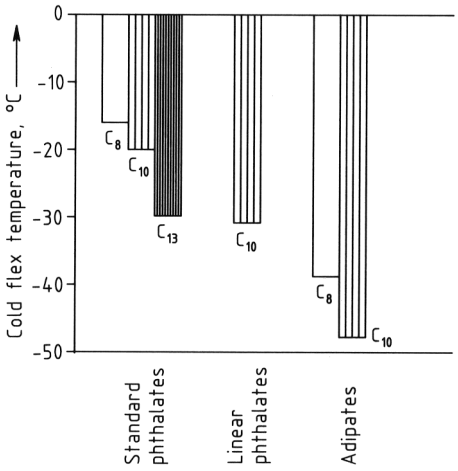


Figure 4. Cold flex temperature for various PVC – plasticizer combinations (50 phr plasticizer)

often discussed together. The gelation characteristics are a measure of the ability of a plasticizer to fuse with the polymer to give a product of maximum elongation and softness (i.e., maximum plasticization). Gelation properties are often measured either (1) as a processing temperature — the temperature to which the plasticizer and polymer must be heated in order to obtain these properties or (2) as a solution temperature, the temperature at which a grain of polymer dissolves in excess plasticizer, giving a measure of the solvating power of the plasticizer. Ease of gelation is related to plasticizer polarity and molecular size. The greater the polarity of a plasticizer molecule the greater the attraction it has for the PVC polymer chain and the less additional energy, in the form of heat, is required to cause maximum plasticizer – PVC interaction. The most active plasticizers are able to bring about these effects soon after the T_g of the polymer (70–80 °C) is reached, whereas the less active plasticizers require temperatures of ca. 180 °C for maximum elongation properties to be obtained. The polarity of the plasticizer is determined by both acid type and alcohol chain length. Aromatic acids, being of greater polarity, tend to show greater ease of gelation than aliphatic acid esters.

Molecular size also has a key contribution and explains why molecules of similar polarity can show different gelation properties. The smaller the plasticizer molecule the easier it is for it to enter the PVC matrix; larger molecules require more thermal energy to establish the desired interaction with the polymer. Since branching influences molecular size, this too has a contribution to gelation properties, with the more branched isomers showing greater activity. Thus for the phthalate esters ease of gelation decreases in the order BBP > DBP > DIHP > DOP > DINP > DIDP > DTDP. Figure 5 shows the greater ability of the more molecularly compact plasticizers to impart full gelation properties (i.e., maximum tensile strength).

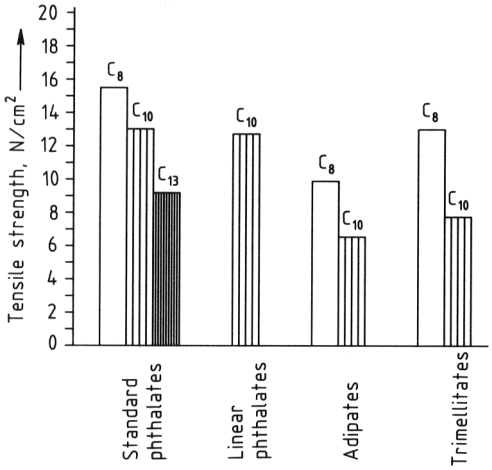


Figure 5. Tensile strength of various PVC – plasticizer combinations at 160 °C (50 phr plasticizer)

4.2.5. Migration and Extraction

When plasticized PVC comes into contact with other materials, plasticizer may migrate from the plasticized PVC into the other material. The rate of migration depends not only on the plasticizer employed but also on the nature of the contact material.

Plasticizer can also be extracted from PVC by a range of solvents, including water. How aggressive a particular solvent is depends on its molecular size and its compatibility with both the plasticizer and PVC. Water extracts plasticizer very slowly, oils are slightly more aggressive, and low molecular mass solvents are the most aggressive.

The key characteristics for migration and extraction resistance is molecular size. The larger the plasticizer the less it tends to migrate or be extracted. The extreme case is seen by the use of polymeric plasticizers in applications where excellent migration and extraction resistance is required. There is also a contribution from the linearity of the alcohol component of the plasticizer ester. The greater the linearity of the ester the greater its migration and extraction rate in comparison to the more branched isomers. Figure 6 shows the results of a standard test for the migration of plasticizer into rigid (unplasticized PVC). Equivalent masses of plaques containing different plasticizers were sandwiched between two rigid PVC discs and the plasticizer migration into the rigid PVC after the test was measured. The improved performance of the longer-chain esters and the trimellitate esters is illustrated.

4.2.6. Plastisol Viscosity and Viscosity Ageing

Plastisol viscosity and viscosity ageing are of great importance in emulsion PVC applications.

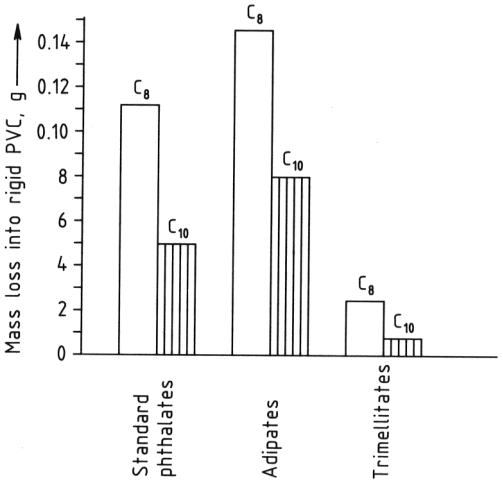


Figure 6. Mass loss into rigid (unplasticized) PVC (11d at 70 °C)

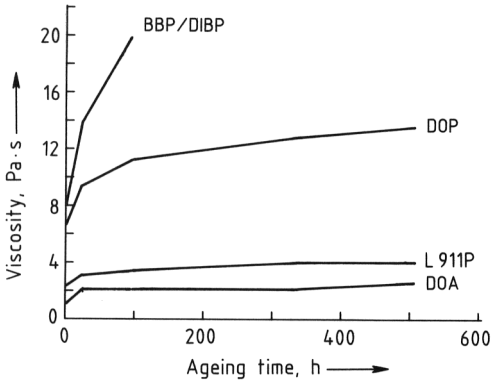


Figure 7. Viscosity ageing of PVC plastisols at 23 °C

Plastisol viscosity, for a given emulsion PVC resin, has a strong dependence on plasticizer viscosity, with the lower molecular mass and more linear esters showing the lowest viscosity and hence the lowest plastisol viscosity (i.e., plastisol viscosity, for a common set of other formulation ingredients, increases in the sequence DBP < DIHP < DOP < DINP < DIDP). In spite of these viscosity differences, however, if plastisols are formulated to equal softness, i.e., taking into account the efficiency of the plasticizers involved, more of the less efficient plasticizer must be employed to impart the same softness to the product being manufactured. The addition of this extra liquid to the plastisol may produce an equivalent viscosity to that of the plastisol with the less viscous plasticizer. Esters based on aliphatic acids, being of lower viscosity than the corresponding aromatic acids, show lower plastisol viscosities, and adipate esters have found widespread use in plastisol applications although to meet other requirements (e.g., volatility, gelation characteristics) they are often employed in a blend with other esters.

Plastisols are often mixed and then stored rather than processed immediately. It is of great importance in this case for the plasticizer to show little or no paste thickening action at the storage temperature, and clearly in this instance it is not advisable to use a plasticizer of too great an activity, since grain swelling, leading to plastisol viscosity increase, can occur at low temperatures for some active plasticizer systems. Figure 7 compares the ageing of plastisols based on various plasticizers. The molecularly compact plasticizers such as BBP and DIBP can enter the PVC matrix easily and cause a rapid increase in viscosity with time. The ageing characteristics improve as the polarity of the plasticizer is reduced. Greater linearity of the plasticizer (e.g., 911 phthalates) also improve this further, with adipates also showing very good viscosity stability.

4.2.7. Windscreen Fogging

The phenomenon of car windscreen fogging has been known for some time. Fogging is the condensation of volatile material on the car windscreen causing a decrease in visibility to the driver. Although this volatile material may arise from a variety of sources (e.g., exhaust fume sucked in through the ventilation system), material from inside the car (e.g., crash pads, rear shelves) may also contribute to windscreen fogging on account of the high temperatures which can arise in a car standing in sunlight. In the case of flexible PVC such a contribution may arise from emulsifiers in the polymer, stabilizers, and plasticizers. In each case manufacturers have studied their products in detail and now recommend low-fogging polymers, stabilizers, and plasticizers. Tests have been designed (e.g., DIN 75 201) to assess the fogging performance of both the PVC sheet and the raw materials used in its production. These tests involve heating a sheet of raw material for a specified period at a set temperature in an enclosed apparatus with a cooled glass plate

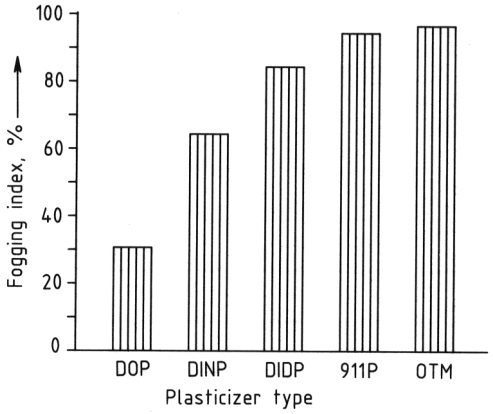


Figure 8. Fogging index of various plasticizers (6 h at 90 °C)

above the sheet or raw material. The reflectance of the glass plate before and after the test is then compared to ascertain the degree of fogging. Figure 8 shows the relationship between plasticizer molecular mass and linearity with fogging performance. The test was carried out at 90 °C for a 6 h duration (a variety of tests, each with their own specified temperature and time, are in use). In such a test, the fogging performance of a plasticizer is related to its (1) volatility, (2) refractive index, and (3) surface tension. The precise nature of (2) and (3) is somewhat complex [33] and attempts to improve the test are currently in progress. In the case of plasticizer volatility it is clear that a higher concentration of plasticizer leads to increased fogging in the test. The higher molecular mass and more linear plasticizers give superior performance, and trimellitate esters (in suspension PVC applications) and L911 phthalates, with their high degree of linearity, and consequently low viscosity for plastisol applications, have achieved widespread use as low-fogging plasticizers for these applications.

4.2.8. Summary

Table 2 gives a summary of the properties described above. For each criterion the effect of (1) increasing plasticizer concentration, (2) increasing the size of the plasticizer molecule, (3) increasing the linearity of the plasticizer molecule, and (4) changing the acid constituent of the ester is discussed. A tick indicates improved performance, a cross indicates poorer performance, and a dash indicate no effect; ticks and crosses in parentheses indicate that any changes tend to be marginal.

Table 2. Summary of the effect of plasticizer choice on the properties of flexible PVC

Property (at equal softness)	Increased concentration	Increased size	Increased linearity	Acid used*
Efficiency (higher)	—	×	✓	ph=ad>tr
High-temperature properties	×	✓	✓	tr>ph>ad
Low-temperature properties	✓	✓	✓	ad>ph=tr
Gelation temperature	(✓)	×	(×)	ph>ad≥tr
Migration/ extraction	×	✓	×	tr>ph>ad
Plastisol viscosity	✓	(✓)	✓	ad>ph
Plastisol ageing	—	✓	(✓)	ad>ph
Fogging	×	✓	✓	tr>ph>ad
Price	✓	✓	×	ph>ad>tr

*ph=phthalate; ad=adipate; tr=trimellitate.

It can be seen from this section that there is clearly no perfect plasticizer for every application: choice will depend on the performance requirements of the article being manufactured and additionally price.

5. Plasticization of Polymers Other Than PVC

5.1. Requirements for Plasticization

The plasticization of PVC accounts for the vast majority of plasticizer sales. However, significant amounts of plasticizers are used in non-PVC polymers and this may become increasingly important in the future. Although PVC is unique in its ability to accept and retain large quantities of plasticizer, effective plasticization of other resins with slightly modified plasticizers may be possible if certain conditions, specific to the polymer, are met.

The factors which must be considered for the plasticization of a polymer are

1. The need — even though some polymers may be compatible with large concentrations of plasticizer the resultant softening may be of little use
2. Short- and long-term compatibility — the ability of a polymer to accept and retain the plasticizer

For a plasticizer to enter a polymer structure the polymer should be highly amorphous (e.g., crystalline nylon will retain only a small quantity of plasticizer if it retains its crystallinity). Once it has penetrated the polymer the plasticizer fills free volume and provides polymer chain lubrication, increasing rotation and movement.

The plasticizer content of a polymer may be increased by suppressing crystallization in the polymer, but if crystallization subsequently occurs the plasticizer is exuded. For highly crystalline resins, the small amounts of plasticizer allowable can change the nature of the small amorphous regions with a consequent change in properties.

Plasticizer compatibility has been studied in many resins and a summary of these studies is given in [4].

5.2. Plasticization of Other Polymers

Acrylic Resins. Although considerable information of the plasticization of acrylic resins is available, the subject is complicated by the fact that acrylic resins constitute a large family of polymers rather than a single polymeric species. An infinite variation in physical properties may be obtained through copolymerization of two or more acrylic monomers selected from the available esters of acrylic and methacrylic acid [34].

Plasticizers are used in the acrylics industry to produce tough, flexible coatings. Compatabilities with common plasticizers are up to 10 wt %, although in some cases (for low molecular mass plasticizers) it can be higher (e.g., a formulation of 100 phr PMMA, 150 phr DBP, 225 phr chalk, 25 phr resorcinol has been used [4]). PMMA is used in small amounts with PVC. Cast acrylics, however, require a high glass transition temperature and high rigidity, hence no plasticizer is required.

Listed plasticizers include all common phthalates and adipates.

There has been interest in the development of acrylic plastisols similar to those encountered with PVC. Clearly the same aspects of both plastisol viscosity and viscosity stability are important. Patents appear in the literature [35] indicating that the number of available plasticizers which show both good compatibility with arcrylic resins and satisfactory long term plastisol stability may be fewer than those showing equivalent properties with emulsion PVC resins.

Polyamides. The high degree of crystallinity of polyamides means that plasticization can occur only at very low levels. Plasticizers are used in nylon but are usually sulfonamide based since these are generally more compatible than phthalates (DEHP is 25 phr compatible, other phthalates less so; sulfonamides are compatible up to 50 phr).

Poly(ethylene terephthalate) (PETP) is crystalline and hence difficult to plasticize. Additionally, since PETP is used as high-strength film and textile fiber, plasticization is not usually required, although esters showing plasticizing properties with PVC may be used in small amounts as processing aids and external lubricants. Plasticizers have also been used to aid the

injection molding of PETP, but only at low concentrations.

The main interest in plasticizers for PETP is in dyeing. Due to its lack of hydrogen bonds PETP is relatively difficult to dye. Plasticizers can increase the speed and intensity of dyeing. The compounds used, however, tend to be of low molecular mass since high volatility is required to enable rapid removal of plasticizer from the product.

Polyolefins. Interest has been shown in the plasticization of polyolefins [4], but their use generally results in a reduction of physical properties [16], and compatibility may be only 2 wt%. Most polyolefins give adequate physical properties without plasticization.

Plasticizers have been used with polypropylene to improve its elongation at break [15], although the addition of plasticizer can lower the glass transition temperature, room-temperature strength, and flow temperature. This can be overcome by simultaneous plasticization (ca. 15 wt%) and cross-linking. Plasticizers used include DOA.

Polystyrene is compatible with common plasticizers, but the modification of properties produced is of little value. Small amounts of plasticizer (e.g., DBP) are used as a processing aid.

Fluoroplastics. Conventional plasticizers are used as processing aids for fluoroplastics up to a concentration of 25%. However, certain grades of Kel-F (polychlorotrifluoroethylene) contain up to 25 wt% plasticizer to improve elongation and increase softness. The plasticizers used are usually low molecular mass oily chloroethylene polymers [4].

Rubbers. Plasticizers have been used in rubber processing and formulations for many years [36], although phthalic and adipic esters have found little use since cheaper alternatives, e.g., heavy petroleum oils, coal tars, and other predominantly hydrocarbon products, are available for many types of rubber. Esters (e.g., DOA, DOP, DOS) can be used with latex rubber to produce large reductions in glass transition temperature. More polar elastomers such as nitrile rubber and chloroprene rubber are insufficiently compatible with hydrocarbons and require a more specialized type of plasticizer, e.g., a phthalate or adipate ester. Approximately 50% of nitrile rubber used in Western Europe is plasticized at 10–15 phr (a total of $5-6\times10^3$ t/a), and 25% of chloroprene at ca. 10 phr (ca. 2×10^3 t/a). Usage in other elastomers is very low but may increase due to toxicological concerns over polynuclear aromatic compounds.

Work on the use of high molecular mass esters in nitrile rubber has compared DINP with DBP and showed that at the 10 phr the nitrile rubber was effectively plasticized with DINP [37].

6. Toxicology and Environmental Aspects

6.1. Toxicity Studies on Plasticizer Esters

Acute Toxicity. The acute toxicity (LD_{50}) of plasticizers is extremely low (>2000 mg/kg). For example, DOP has an oral LD_{50} of >30 000 mg/kg.

In addition to their low acute toxicity many years of practical use coupled with animal tests show that plasticizers do not irritate the skin or mucous membranes.

Numerous long-term feeding trials on plasticizers have been carried out. The majority of these studies have been on di-2-ethylhexyl phthalate (DEHP, commonly called DOP) because it accounts for around 50% of the plasticizer usage in Europe and has been considered as a model for the other phthalates. See also → Phthalic Acid and Derivatives, Section 6.2.5.).

Prior to 1980 such studies showed no adverse effects. However, in 1980 the results of a two-year feeding study carried out as part of the National Toxicology Program/National Cancer Institute (NTP/NCI) Bioassay Program in the United States indicated that DOP causes increased incidence of liver tumors in rats and mice and that di-2-ethylhexyl adipate (DEHA, commonly called DOA) had a similar effect in mice but not rats [38], [39]. In these studies the levels of plasticizers fed were very high, this being only possible because of their low acute toxicity. Their diets contained up to 12 000 ppm of DOP and 25 000 ppm of DOA (this is

comparable with a human consuming 0.5 L of DOA every day).

A large number of more recent investigations [40–43] carried out in both Europe and the United States on a variety of plasticizers and different types of animals clearly show:

1. Plasticizers are not genotoxic.
2. Oral administration of plasticizers, fats, and other chemicals (such as hypolipidaemic drugs) to rodents causes a large increase of microbodies in the liver called peroxisomes. This peroxisome proliferation is considered by some authors to be linked to the formation of liver tumors.
3. The administration of plasticizers, fats, or hypolipidaemic drugs to nonrodent species such as the marmoset (a primate considered to be metabolically closer to humans) does not lead to peroxisome proliferation and liver damage. Some commonly used hypolipidaemic drugs (e.g., clofibrate), which cause peroxisome proliferation in rodents, have been used by humans for many years with no ill effects.
4. These species differences have also been observed in in vitro studies on the liver cells of rats, mice, guinea pigs, marmosets, and humans. Peroxisome proliferation was observed in the rat and mouse cells but not in those of humans, marmosets, or guinea pigs.
5. On the basis of these differences in species response (especially if the extremely high exposure in the animal tests is also taken into consideration) it is concluded that plasticizers pose no significant hazard to humans.

Human Exposure to Plasticizers. Experimental investigations and assessments in the United States and Europe have shown that the average human intake of plasticizers amounts to 2 g per person per year. This is mainly due to traces of DOA migrating from food packaging. The level of exposure is considerably below the dose at which toxic effects are to be expected. The no observed effect level (NOEL) for DOA and DOP is ca. 40 mg per kilogram body weight per day, or higher depending on the kind of effect, i.e., at least 1000 g per year for an average adult. There is thus a 500 fold safety factor between the estimated plasticizer intake of 2 g per person per year and the NOEL. Taking into consideration the difference in response between rodents and primates, the safety factor is in fact even greater.

The Opinion of Official Experts and Legislative Authorities. The IARC of the WHO has classified DOP as "an agent possibly carcinogenic to humans," largely because of the NTP/NCI rodent studies. However, IARC has not classified DOP as a carcinogen for regulatory purposes [44].

The EC Working Group "Classification and Labeling of Dangerous Substances" has examined all the toxicological data and has concluded that DOP should not be labeled as a human carcinogen [45].

In Germany the Advisory Body for Environmentally Relevant Existing Substances (BUA) has summed up the situation in their report No. 4 (1986) as follows [46]:

"Chronic damages have been noticed in rodents exposed to high DOP concentrations (rat: over 40–70 mg per kg bodyweight per day). The rat because of a characteristic feature in its DOP metabolism — different from the human metabolism — is especially sensitive to this substance. Thus, data obtained via tests with these animal species have no relevance for man. Tests with primates — having a metabolism comparable to that of humans — showed that DOP was rather ineffective. According to these findings there is no basis to suspect chronic damages due to DOP exposure at environmentally relevant concentrations."

Similarly the German Health Authority (BGA) has concluded that the carcinogenic effect of DOP in rats and mice is specific to this species and is not relevant to humans.

In the United States the FDA has not introduced any new regulations following the results of the NTP/NCI studies.

6.2. Plasticizers in the Environment

The release of plasticizers to the environment may occur during their production and distribution, during incorporation into PVC, and by loss from the finished article during use or after disposal.

The controlled nature of modern manufacturing processes makes it unlikely that significant loss of plasticizer to the environment

occurs during its production (measurements of total emission from a modern plasticizer plant have given values of less than 0.01 %).

The extremely low solubility of plasticizers in water means that little is lost by leaching from flexible PVC either during use or after disposal. The increasing use of modern incineration techniques to dispose of domestic waste results in complete combustion of plasticizers to carbon dioxide and water.

The main way in which plasticizers enter the environment is therefore by evaporation during processing with PVC. The extent of such losses depends on the process and plasticizer used and has been estimated to vary from 0.02 % for injection molding up to 1 % for coating processes. However, these levels are being continually reduced by the installation of incineration, scrubbing, and filtration systems in processing plants.

Plasticizers can be detected in the environment in the ultratrace (parts per billion) range.

There are no indications of an accumulation of plasticizers in water, soil, or air because they are biologically and photochemically degraded. Degradation is particularly rapid under aerobic conditions to produce carbon dioxide and water as for other organic substances.

The occurrence and effects of phthalates in the environment has been reviewed in detail by ECETOC (European Chemical Industry Ecology and Toxicology Centre) [47]. It is clear from this report that in laboratory tests microorganisms and fish can take up dialkyl phthalates; however, they are rapidly excreted and no toxic effects have been seen. The report concludes that at the levels corresponding to current use and disposal practices, phthalates do not represent a hazard to the environment.

Health Aspects of Flexible PVC. Small quantities of plasticizers may be lost from PVC by evaporation and extraction or by migration into other materials.

Plasticizer Evaporation From Flexible PVC. The use of plasticizers in the production of vinyl wall and floor covering can lead to plasticizer vapor being present in room air. However, the plasticizers used have extremely low vapor pressures and thus at 25 °C the maximum concentration of DOP is only ca. 0.01 mg/m^3. The concentration of the higher molecular mass plasticizers are even lower. Also, given the comparatively slow plasticizer release rate and normal ventilation, then the plasticizer concentration in reality is extremely low. The high concentrations sometimes reported must therefore be attributed to analytical errors. This is demonstrated by the fact that recent measurements of the air in an emission chamber containing 1 m^2 of PVC flooring for 96 h showed no detectable levels of plasticizer; the detection limit was 4 parts per billion.

Flexible PVC Toys. In the United States the Consumer Products Safety Commission (CPSC) has expressed concern that children might ingest plasticizers by sucking teething rings and pacifiers. The estimated intake of plasticizers by infants in this way varies over several orders of magnitude up to a maximum of 0.07 mg kg^{-1} d^{-1}. On the basis of the toxicological evidence this does not represent a health risk. For other toys, such as balls and dolls, the intake of plasticizers is negligible. The use of plasticizers in PVC toys for infants is regulated in some countries.

Medical Uses of Plasticized PVC. Flexible PVC has been established for many years as one of the most important materials used in the manufacture of a wide variety of medical products. The main advantages of PVC are its low toxicity and its flexibility, clarity, and sealing properties. These permit the manufacture of lightweight, breakage-resistant medical devices that can be supplied ready for use in sterile packages.

It is known that low levels of DOP migrate from flexible PVC blood bags into blood. There is published evidence [48] showing that this has a beneficial effect in that it significantly reduces the destruction of red cell walls compared to that which occurs on storage in other plastic or glass systems. DOP is the only plasticizer authorized by the European Pharmacopoeia for use in the manufacture of PVC blood bags.

Plasticized PVC in Food Packaging. Flexible PVC is used to produce food wrap film, cap seals for bottles and jars, and tubing for beverages. DOP, DINP, and DIDP are used in caps and seals, whereas DOA and polymeric adipates are used in the production of food wrap film.

DOA is used in this application because it gives a film with a high degree of cling which remains flexible at low temperatures. It also provides the high permeability to oxygen and water vapor that is necessary to ensure good food storage.

The migration of plasticizer from these packaging materials into foodstuffs has been measured in the UK by the Ministry of Agriculture Fisheries and Food (MAFF) both for domestic and retail packaging of food. These measurements together with a knowledge of the typical diet has enabled MAFF to assess the maximum possible intake of plasticizers as 0.02 mg per person per day of phthalates and 8 mg per person per day of DOA [49]. These estimates are based on a worst case situation, which assumes that all solid foodstuffs are purchased wrapped in cling film and that 50 % of these are subsequently rewrapped in the home.

The UK Committee on Toxicity of Chemicals in Food, Consumer Products, and the Environment (COT) has examined these data together with the relevant toxicological information and has concluded [50]:

"Toxic effects have been demonstrated for some plasticizers, but the safety margins between toxic doses and human intakes are large and we consider it very unlikely that there are any adverse health effects from the current or past use of plasticizers in food packaging materials."

Recent CEFIC studies [51], [52] involving the administration to humans of deuterium-labeled DOA have established the major human urinary metabolites and their excretion rates. This, together with analysis of 24 h urine samples from a limited survey of the UK population, has shown the average DOA intake to be 3 mg per person per day. This is well below the tolerable daily intake of 18 mg per person proposed by the EC Scientific Committee for Food and hence again confirms the suitability of plasticized PVC film for all food contact applications.

Regulations and Provisions. In terms of handling and storage, plasticizers are in general classified as nonhazardous.

In different countries the recommended 8 h TWA limit for occupational exposure varies between 2 and 10 mg/m^3.

These recommended exposure limits have been reviewed by the Health and Safety Authorities in the United Kingdom and Germany, and in the light of recent toxicological findings they have confirmed that the current limits of 5 and 10 mg/m^3, respectively, are satisfactory.

The regulations controlling the use of plasticizers in food contact applications differ from country to country. However, a common feature of the regulations is that plasticizer that migrates into foodstuffs should not have any adverse effects on their taste or smell and in general must not exceed 60 ppm. Because of the large volume of toxicological data indicating that phthalates and adipates pose no health risk to humans, regulatory authorities in most countries allow their use in caps, seals, tubing, and wrapping films.

6.3. Storage and Handling

Plasticizer esters are relatively inert, thermally stable liquids with high flash points and low volatility. Consequently they can be stored safely in mild steel storage tanks or drums for extended periods of time. Exposure to high temperatures for extended periods, as encountered in drums in hot climates, is not recommended since it may lead to a deterioration in product quality with respect to color, odor, and electrical resistance.

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Part 2

Organic Polymers

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Fluoropolymers, Organic

ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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1. Introduction

1.1. History

Researchers of IG-Farbenindustrie in Hoechst/Frankfurt, Germany studied systematically the polymerizations of fluoroethylenes already in the early 1930s; polychlorotrifluoroethylene (PCTFE) and polytetrafluoroethylene (PTFE) including copolymers were prepared and the outstanding properties of these polymers were recognized. The first patent application for a fluoropolymer was filed in October 1934 by SCHLOFFER and SCHERER [7]. During the following years until 1948 there were not many activities anymore within this polymer field in Germany (due to World War II impacts).

Independently polytetrafluoroethylene was discovered by chance by PLUNKETT from DuPont while investigating refrigerants in 1938. The unique properties of PTFE were recognized during the Manhattan Project; there was an urgent need for a material withstanding the highly corrosive substance UF_6. PTFE apparently filled all the needs, spurring the development of processing and production methods for this unique polymer. In 1946, PTFE was commercialized by DuPont under the trademark Teflon. PTFE, PCTFE and all other fluoropolymers with their outstanding chemical, electrical, and surface properties gained immediate acceptance in various markets. During the decades, many fluoropolymers, including fluorothermoplastics and fluoroelastomers, were developed and commercialized. Fluoropolymers serve extremely high demanding applications in respect to performance, longevity, safety, etc., which no other polymer class can provide.

1.2. Monomers

There are only four key C_2-fluoroolefins, which have been polymerized to high molar mass homopolymers of commercial importance: tetrafluoroethylene (TFE), chlorotrifluoroethylene (CTFE), vinylidene fluoride (VDF), and vinyl fluoride (VF).

Most are prepared on industrial scale by pyrolysis of corresponding chlorinated or fluorinated hydrocarbons (→ Fluorine Compounds, Organic). Special care has to be taken in producing and handling TFE due to its high tendency to self-decompose into carbon and tetrafluoromethane.

Other fluorinated or nonfluorinated olefins are used in combination with TFE to generate a large variety of crystalline or amorphous fluoropolymers. The most important monomers for commercial fluoropolymers are listed in Table 1.

1.3. Polymers

Fluoropolymers consist of carbon and fluorine in the polymer backbone. Fluorosilicones and fluoroacrylate polymers are not referred to as fluoropolymers and are not described in this article. Fluoropolymers can be divided into perfluorinated (e.g., PTFE, PFA, FEP, etc.)

Table 1. Monomers used in commercial fluoropolymers

Monomer	CAS registry number	Formula	Abbreviation	*bp*, °C	T_{crit}, °C	p_{crit}, MPa
Ethylene	[74-85-1]	$CH_2 = CH_2$	E	−104	79.6	75.1
Tetrafluoroethylene	[116-14-3]	$CF_2 = CF_2$	TFE	−75.6	33.3	3.7
Chlorotrifluoroethylene	[79-38-9]	$CF_2 = CClF$	CTFE	−28.4	105.8	3.9
Vinylidene fluoride	[79-38-7]	$CF_2 = CH_2$	VDF	−82.0	30.1	4.3
Vinyl fluoride	[75-02-5]	$CFH = CH_2$	VF	−72.2	54.7	5.4
Propene	[115-07-1]	$CH_3CH = CH_2$	P	−47	91.4	4.6
Hexafluoropropene	[116-15-4]	$CF_3CF = CF_2$	HFP	−29.4	86.1	2.8
Perfluoro(methyl vinyl ether)	[1187-93-5]	$CF_3OCF = CF_2$	PMVE	−21.8	96.2	3.4
Perfluoro(propyl vinyl ether)	[1623-05-8]	$CF_3CF_2CF_2OCF = CF_2$	PPVE	36	150.6	1.9

and partially fluorinated (e.g., ETFE, PVDF, etc.) types. A more convenient classification is to divide the fluoroplastics and amorphous fluoropolymers into four categories:

1. High-crystalline, nonmelt-processable PTFEs
2. Semicrystalline (*mp* > 80°C), melt-processable fluorothermoplastics
3. Amorphous fluoropolymers with T_g > 70°C
4. Amorphous, curable fluoroelastomers [9]

Table 2 provides an overview of the most important commercial fluoropolymers. A special group of TFE-copolymers containing sulfonic acids and/or carboxylic acids in side-chains are important polymers to make ion-exchange membranes for the chlorine industry and for fuel cell applications (→ Fluorine Compounds, Organic, Chap. 8.2 Fluorinated Alkanesulfonic Acids).

Table 2. Composition of important fluoropolymers

	Momomer(s)	*mp*, °C
Nonmelt processable PTFE		
PTFE	TFE	327
modified PTFE	TFE PVE (< 1 wt%)	326
Melt processable fluorothermoplastics		
PFA	TFE + PPVE	305
FEP	TFE + HFP	260
ETFE	TFE + E	270
THV	TFE + HFP +VDF	120–220
PVDF	VDF	170
PVF	VF	190
PCTFE	CTFE	210
ECTFE	CTFE + E	240
Amorphous fluoropolymer		T_g, °C
Teflon AF	PDD + TFE	160–240
Hyflon AD	TTD + TFE	90–125
Cytop	PBVE	108
Amorphous, curable fluoropolymer		
FKM	TFE + VDF + HFP + cure package	
TFEP	TFE + P + cure package	
FFKM	TFE + PMVE + funcitional momomer + cure package	

1.4. Production

The principal method for synthesizing fluoropolymers is free-radical polymerization. Due to the electrophilic nature of fluoroolefins, cationic polymerization catalysts are not very effective. Fluoroolefins and epoxides can be polymerized by anionic catalysts, but termination by fluoride ion elimination prevents formation of high molar masses. Coordination catalysts do not effect polymerization of fluoroolefins. The free radical polymerizations are mostly water-based, either as aqueous suspension polymerization or as aqueous emulsion polymerization in the presence of hydrocarbon emulsifiers but preferably in the presence of fluorinated emulsifiers. In previous times, the radical polymerization in fluorinated solvents (e.g., in R113) was widely spread, but due to the high emissions of the fluorinated solvents and due to the Montreal agreement, many polymerization processes were changed to water-based systems. The polymerization in supercritical media (e.g., CO_2), originally introduced as "green" polymerization technology, has not found widespread applicability [10, 11]. Other free-radical polymerization processes, e.g., in gas phase or ionic liquids are only of academic interest.

The polymerization and processing techniques described in this article are described in detail elsewhere (→ Polymerization Processes, 1. Fundamentals).

1.5. Properties

The properties of fluoropolymers vary with the fluorine content and with the distribution of fluorine atoms in the polymer chain. The unique properties of fluoropolymers are due to the strong carbon–carbon bond (ca. −340 kJ/mol) and the stable carbon–fluorine bond (ca. −490 kJ/mol; for comparison: C–H ca. −420 kJ/mol) of the polymer backbone. Substitution of fluorine for hydrogen improves three key physical properties of the polymer:

1. Increased service temperatures and reduced flammability
2. Low surface energy provides nonstick properties, anti-adhesiveness, low coefficient of friction, self-lubricating effects, and lower solubility in hydrocarbons
3. Excellent electrical and optical properties are seen in low high-frequency loss rates and in low refractive indices.

1.6. Uses

The outstanding properties enable applications in almost every industry (Table 3).

2. Fluoroplastics

2.1. Introduction

The family of fluoroplastic polymers (world consumption 2008: 1.8×10^5 t) [12] is headed by the nonmelt processable PTFEs (consumption 2008: 1.05×10^5 t/a). Melt processable fluorothermoplastics include [13]: TFE–HFP (FEP), TFE–PPVE copolymers (PFA), TFE–PMVE (MFA), TFE–ethylene (ETFE) TFE–HFP–VDF (THV), polychlorotrifluoroethylene (PCTFE), CTFE–ethylene (ECTFE), poly (vinylidene fluoride) (PVDF) including copolymers, and poly(vinyl fluoride) (PVF).

The progressing development of the various fluoropolymer grades was mostly triggered by

Table 3. Major applications of fluoropolymers

Industry or application area	Key properties	Typical uses
Chemical processing	chemical resistance good mechanical properties thermal stability cryogenic properties	gaskets, vessel liners, valve and pipe liners, tubing, coatings
Electrical and communications	low dielectric constant high volume and surface resistivity high dielectric breakdown voltage flame resistance, thermal stability low refractive indices	wire and cable insulation, connectors, optical fibers
Automotive and office equipment	low coefficient of friction good mechanical properties cryogenic properties chemical resistance low permeation properties	seals and rings in automotive power steering, transmission, air-conditioning, copier roller and food processing equipment covering, fuel management systems
Houseware	thermal stability low surface energy chemical resistance	cookware coatings
Medical	low surface energy stability excellent mechanical properties chemical resistance	cardiovascular grafts, heart patches, ligament replacement
Architectural fabrics/films	excellent weatherability flame resistance low surface energy	coated fabrics for buildings and roofs; Front/backside films for solar applications
Polymer processing additives	low coefficient of friction flame resistance	polyolefin processing to avoid surface defects, antidripping agents
Semiconductor industry	chemical resistance purity thermal stability	process surfaces, wafer carriers, tubing, valves, pumps, fittings

the trade-off of existing grades or by application needs. The high melt viscosity of PTFE resins prevents processing by conventional extrusion and molding techniques; they are processed by sintering techniques similar to those used in powder metallurgy. Although PTFE can be converted into practically any form (rods, billets, films, fibers, tubing, or coatings) by these techniques, the lack of melt processability is frequently a handicap. Research on melt-processable forms of PTFE began almost immediately after its discovery [14]. The first to be developed was a TFE–HFP copolymer called FEP (fluorinated ethylene–propene) copolymer [15]. The FEP resins, commercialized in 1960, share nearly all the properties of PTFE, but are also processable by extrusion and injection molding. However, the melting point of FEP is ca. 60–70°C lower than that of PTFE; its maximum use temperature is also lower. Further research on TFE copolymers led to the development of perfluoroalkoxy (PFA) resins [16] that were introduced commercially in 1972. These have the same high-temperature properties as PTFE resins and an even lower melt viscosity than FEP resins; they can be processed by extrusion and injection molding. In 1970, ETFE resins were commercialized. They exhibit improved mechanical properties and far better processability than other TFE copolymers. In addition, they can be cross-linked by high-energy radiation. The maximum use temperature, however, is much lower than that of PFA or FEP.

Among the fluoroplastics that contain monomers other than TFE, PCTFE was the first to be commercialized. Extensive development work was carried out on this polymer during World War II in conjunction with the Manhattan Project. Compared to TFE resins, PCTFE is harder, more resistant to creep, and less permeable. It has the lowest permeability to moisture of any plastic. Chlorotrifluoroethylene copolymerized with VDF provides an improved plastic for film manufacture. However, ECTFE is the most important CTFE copolymer [17]. These plastics have similar properties and uses as ETFE copolymers.

Poly(vinyl fluoride) contains the smallest amount of fluorine (41.3%) of any commercial fluoropolymer but possesses many of the properties of more highly fluorinated polymers [18]. It was commercialized in 1961 by DuPont under the trade name Tedlar. It is used mainly in coatings for metal, plastic, paper, and similar substrates to provide resistance to weather, chemicals, staining, and abrasion.

Poly(vinylidene fluoride) (PVDF) shares many of the characteristics of other fluoropolymers, such as thermal and oxidative stability, as well as outstanding weatherability [19]. However, the arrangement of alternate fluorine and hydrogen atoms leads to unusual polarity within the polymer chains, with a dramatic effect on dielectric properties and solubility. An unusual product made from PVDF is a film with piezoelectric properties. Copolymerization of VDF with small amounts (< 15%) of HFP reduces stiffness and improves processability for certain wire coating applications.

A comparison of manufacturing costs is provided in [20]; polymer designations and testing procedures for fluoroplastics are described in EN ISO 12086-1/2 (2006).

2.2. Polytetrafluoroethylene

Polytetrafluoroethylene [9002-84-0] (PTFE) is a straight-chain polymer of tetrafluoroethylene (TFE) of the general formula

$$-(CF_2CF_2-)_n$$

In 2008, the worldwide consumption of PTFE was 1.05×10^5 t/a, and its demand has grown by 2–3% per year over the decades.

Processed PTFE has a high crystalline melting point (327°C), a very high melt viscosity (10×10^9 to 100×10^9 Pa s at 380°C), and a high maximum use temperature (> 260°C). In addition, it exhibits unusual toughness down to very low temperatures (< −200°C); its molar mass is high (10^6–10^8 g/mol). It is insoluble in most known solvents and resists attack by most chemicals. Dielectric loss is low, whereas dielectric strength is high; antistick and antifriction properties are unusual. Although these properties give PTFE great commercial value, they also rule out processing by conventional thermoplastic techniques. Thus, PTFE is also called nonmelt-processable.

High molar mass polytetrafluoroethylene is produced in three different forms. *Granular PTFE* is prepared by aqueous suspension

polymerization. The polymerized product is cut or milled to uniform particle sizes of 20–100 μm and processed by powder metallurgy techniques followed by machining. *Fine powder resins* are prepared by aqueous emulsion polymerization and coagulation of the resulting latices by high-speed agitation or by addition of electrolytes. The fine-powder resin agglomerates (average particle sizes 200–800 μm) consisting of the primary polymerization particles (average particle size 150–300 nm) are mixed with lubricants (e.g., kerosene, hydrocarbons) and processed by a cold extrusion technology called paste-extrusion, and usually after evaporating the lubricant the material is sintered. The third form of PTFE is an *aqueous dispersion*, containing about 40–60% solids and up to 10% nonionic surfactants. The dispersion products are processed by latex processing techniques (e.g., dip coating, spray coating, or roller coating) followed by baking or sintering at high temperatures that causes coalescence of the polymer particles into a continuous film.

Low molar mass ($< 10^6$ g/mol) PTFEs are offered as finely divided powders as so-called fluoro-additives or micropowders for various industries as lubricants or to improve wear-resistance, etc. Due to the reduced molar masses ($\sim 10^4$–16^6 g/mol; melt viscosity $\sim 10^5$ Pa s) these materials have no mechanical strength.

Manufacturers of PTFE include Asahi Glass (Fluon), Daikin (Polyflon), DuPont (Teflon), 3M (Dyneon), Solvay Solexis (Algoflon), and Halopolymer (Ftoroplast). Asian PTFE-producers established large PTFE capacities; the companies are Gujarat, Dongyue, 3F, Meilan, Chenguang, Fuxin, and Juhua.

2.2.1. Production

Polymerization. Tetrafluoroethylene must be stored, handled, and polymerized with great care. Even traces of oxygen can trigger polymerization; to prevent polymerization in storage vessels, inhibitors, such as terpenes or amines are added.

The inhibitors must be carefully removed prior TFE use by distillation, adsorption, e.g., on silica, or washing with sulfuric acid. The purity requirements for polymerization-grade TFE are very demanding (low ppm-range of impurities), because each chain-transfer active species in the TFE is detrimental to achieving the required high molar masses.

TFE also has a high tendency for self-decomposition into carbon and tetrafluoromethane:

$$F_2C = CF_2 \rightarrow C + CF_4 \quad \Delta H \sim -320\,\mathrm{kJ/mol}$$

The generated power of this decomposition is close to that of explosives and can be initiated by so-called hot spots formed during polymerization. Due to the high heat of polymerization (~ -170 kJ/mol) and the excellent insulating properties of PTFE, hot spots can develop if the mixing or agitation and cooling of the aqueous suspension in the vessel are not adequate or if, in the case of aqueous emulsion polymerization, coagulation occurs during polymerization. In the latter case, the hot spots float to the water surface and ignite the TFE gas phase. Consequently, the PTFE manufactures try to polymerize at low temperatures and TFE pressures; it is also recommended to carry out polymerizations under inert gas blankets to avoid explosions [21]. Due to the risk of violent explosions, the whole polymerization equipment as well as transfer lines of TFE-monomers are protected by rupture disks and flame arrestors.

Tetrafluoroethylene is polymerized in aqueous medium by two technologies. Suspension polymerization is the method to produce high molar mass granular resins. In the suspension process, TFE is polymerized without or in the presence of small amounts of emulsifiers (e.g., nontelogenic fluorinated carboxylic acids). Preferred initiators are salts of persulfate, quite often in combination with redox systems (e.g., metal ions or bisulfite) to keep the polymerization temperatures at low levels; $KMnO_4$ is also a widely used low temperature initiator [22]. The vigorous agitation precipitates the initially formed polymer dispersion shortly after the polymerization starts, and most of the polymerization occurs then directly on the precipitated solid particles. Solid contents between 20–40% can be achieved. The irregular shaped polymer particles can show average particle sizes up to 5 mm.

Aqueous emulsion polymerization is used to produce high molar mass fine powder and dispersion PTFE. Significant amounts (up to 15 g/L water) of nontelogenic fluorinated emulsifiers (e.g., fluorinated carboxylic or sulfonic acids with up to 12 carbon atoms) are used. In contrast to suspension polymerization, very mild agitation conditions are applied. Because the PTFE latices are shear sensitive, horizontal reactors with paddle wheels are used. To improve latex stability and to avoid coagulations, paraffin wax is added, which is molten under polymerization conditions. This polymerization method is generating spherical, sometimes rodlike polymer particles with average particle sizes of 50–300 nm.

To fine tune end-use properties, seed polymerization and core-shell polymerizations are employed. The initiator is the same as with the suspension process. The obtained latices with solid contents from 20–40% can be either coagulated to generate fine powder PTFE or are further stabilized by addition of nonionic surfactants and concentrated to solid contents up to 65% PTFE dispersions.

Fluorinated emulsifiers (e.g., perfluorooctanoic acid) are used in aqueous emulsion polymerizations, which is a challenge to recover from downstream processes and products due to environmental and safety concerns.

Granular Resins. The dried as-polymerized PTFE cannot be used as such, because the irregular shaped particles possess a broad particle size distribution and show very high void contents in sintered articles.

During the sintering process, due to the high melt viscosity, fusion of the polymer particles takes place only at the upper surface where particles are in contact. Therefore, the as-polymerized particles must be cut or milled into more uniform and smaller particles. The coarse as polymerized PTFE is processed by wet or dry milling into materials of average particle sizes of 20–100 μm. These materials ensure that after sintering the products have a much lower void content. The polymer particles should also have a good deformability during molding, which can be achieved by polymerizing at lower temperatures. The milled products have poor flow properties and specific bulk densities of 300–500 g/L (specific surface area of 1–4 m^2/g); these materials are often called nonfree-flowing types and cannot be used in automatic or isostatic molding applications.

The fine cut PTFE resins are converted during an agglomeration process into soft agglomerates with good powder flow properties and much higher bulk densities (500–1 000 g/L). The agglomerates comprise of a number of fine cut particles and have average particle sizes of 200–800 μm. Agglomeration can be achieved by dry or wet technologies to get stable free-flowing PTFE resins. The wet process requires the use of mixtures of water and water-insoluble organic liquids (e.g., gasoline). Nonfree-flowing PTFE powder is mixed with such fluids in a stirred vessel to agglomerate the PTFE into free-flowing resins.

Presintered granular PTFE resins are also free-flowing powders of premelted PTFE, predominantly used for ram extrusion applications.

Fine Powder Resins. To modify the processing characteristics (e.g., extrusion pressure) as well as the final end-use properties, core-shell PTFE-polymers are made by aqueous emulsion polymerization. For example, the core of the polymer particle is of high molar mass and the shell is of much lower molar mass; this, for example, reduces the extrusion pressure. In addition, smaller amounts (< 1%) of modifiers, such as HFP, CTFE, or PPVE are used to tailor the properties of fine-powder PTFE. Numerous patent applications describe the benefits of all these modifications [23, 24].

The obtained PTFE-latices are subsequently coagulated to produce fine powders. Usually the latices are diluted and coagulation agents, such as water-soluble organic liquids (e.g., methanol, acetone) or electrolytes (e.g., ammonium carbonate, oxalic acid, hydrochloric acid) are added to cause coagulation under agitation. The primary as-polymerized PTFE-particles (average particle size 50–300 nm) form agglomerates (average particle sizes 300–800 μm, specific surface area 12 m^2/g), which are separated and carefully dried. Fine resin PTFE powder is quite sensitive to shear forces above the transition point (19°C) during work-up and handling processes due to the high tendency to fibrillate.

Aqueous Dispersions. Aqueous dispersions are made by the same polymerization process used to produce fine powder resins. The latices can be polymerized to give different average particle sizes (50–300 nm), which is important for the final applications; also bimodal particle sizes distributions have been recommended [25]. Usually commercial dispersions have average particle sizes of about 200–250 nm. The obtained latices are further stabilized by the addition of nonionic surfactants, such as Triton X-100 or other nonaromatic ethoxylated alcohols. These mixtures are concentrated from 20–40% to 60–65% solids by evaporation under vacuum, by decantation, or by ultrafiltration processes. The pH value, viscosity, etc., of the concentrated dispersion is adjusted to guarantee a high stability during storage, transportation, and in the final applications. The fluorinated emulsifier is recovered by anion exchange technology (→ see Section 4.3).

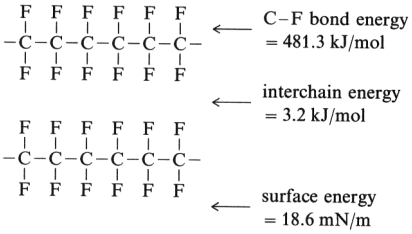
Filled Resins. A variety of fillers are utilized to improve some short-comings of unfilled PTFE [10], such as wear resistance, hardness, cold flow, or creep. These fillers include, for example, glass fibers, carbon, graphite, bronze, molybdenum sulfide, etc. Up to 40% by volume of filler can be added to the PTFE without complete loss of physical properties; the impact of fillers below 5% is low. About one third of granular PTFE is consumed in the form of filled compounds; nonfree-flowing as well as free flowing grades are offered. These PTFE-compounds can be produced by dry blending, alternatively by dry or wet agglomeration technologies of nonfree-flowing granular PTFE and filler.

Micropowders. PTFE micropowders are finely divided low molar mass (10^4–10^6 g/mol) PTFE-additives with small particle sizes (1–20 μm). Due to the low molar masses and reduced melt viscosities (10^2–10^5 Pa s), these materials have measurable melt flow indices, but usually no mechanical strength. Micropowders are almost entirely consumed by industries outside fluoropolymers. Major applications of micropowders include the addition into thermoplastics and elastomers, paints and coatings, printing inks, oils and greases [10]. Micropowders can be prepared by thermal or radiation degradation of high molar mass PTFE (e.g., using off-spec i. e., off-specification PTFE-material or scrap PTFE from processing) followed by milling steps [10]. Alternatively, micropowders can be produced by suspension polymerization or more conveniently by aqueous emulsion polymerization in the presence of chain-transfer agents.

2.2.2. Properties

Physical Properties. The structure of PTFE chains is unusual in that they are completely linear. The branching that occurs during the free-radical polymerization of ethylene cannot take place during the polymerization of TFE because an abstraction of the F-atom is not possible due to the strength of the C−F-bond. Furthermore, PTFE chains are stiffer than polyethylene chains because their fluorine atoms are larger than hydrogen atoms. Steric hindrance prevents a PTFE chain from assuming a planar zigzag structure; instead, it is forced to adopt a zigzag structure with a helical twist along the chain axis. Crystals of PTFE are made up of chains with a 180° twist every 13 to 15 carbon atoms, depending on the temperature. The high melting point of PTFE (327°C) is due to the small entropy change produced during melting, which in turn results from the stiffness of the chains [26].

The chemical bonding forces within the chains, between the chains, and the polymer surface are unusual.



The C−F bond energy is among the highest known. However, the interchain bonding forces are very weak, and the surface energy is very low. The combination of unusually strong and weak forces results in many unique properties.

The melting point of high molar mass, virgin unmelted PTFE is 342°C. Differential scanning calorimetry (DSC) indicates that the 342°C

melting point is irreversible and the subsequent melting point is 327°C. Electron-microscopic studies of dispersion particles indicate that the rodlike crystals in virgin PTFE are fully extended with few defects [27]. The decrease of the melting temperature from 342°C to 327°C is due to the transition of fully extended chains to folded polymer chains. Virgin PTFE particles are 92–98% crystalline. The crystallinity of once-melted PTFE varies with molar mass and the rate of cooling from the melt. Processed commercial grades are usually 45–75% crystalline.

The molar mass of PTFE cannot be determined by the usual methods that require dissolution of the polymer because the solubility in fluorinated solvents is very limited for PTFE below 300°C. Above 300°C PTFE dissolves in fluorinated oligomers and light scattering measurements on lower molar mass PTFE are possible to determine the molar mass and distribution [11, 28]. The number-average molar mass can also be estimated from the determination measurements of end groups. Because the molar mass of PTFE is very high, the concentration of end groups is very low. A quantitative method must be sensitive to less than 1 ppm of end groups. An elegant method tags the end groups with radioactive sulfur in the initiator [29]; the sulfur from the initiator must be retained in the polymer with no loss by hydrolysis. When persulfate is used as initiator, the resulting sulfate end groups are hydrolyzed to carboxylic acid end groups and no radioactive sulfur is detected in the polymer. However, when an iron–bisulfite initiator is used, the sulfur is retained in the polymer because the initiating species (a bisulfite radical, $HOSO_2^{\bullet}$) gives rise to hydrolytically stable sulfonic acid end groups.

A number of PTFE-samples with molar masses of commercial interest where made using the radioactive iron–bisulfite-initiator system. These samples were used to calibrate other methods for measuring the molar mass of PTFE resins, such as the standard specific gravity (SSG) method [29]. Because the rate of crystallization varies inversely with molar mass, samples of high molar mass have a lower SSG than those of low molar mass; typical values for polymers of commercial interest range from 2.14 to 2.20. The SSG method is widely used with PTFE resins. The correlation between number-average molar mass $\overline{M}_n$ and the SSG is given by the following relationship:

$$\mathrm{SSG} = 2.612 - 0.058\, log_{10}\, \overline{M}_n$$

Studies on the melting behavior of virgin PTFE by DSC [31] has led to another method for measuring molar mass. The following relationship was found between number-average molar mass and heat of crystallization (ΔH_c, J/g):

$$\overline{M}_n = 2.1 \times 10^{10} \times \Delta H_c^{-5.16}$$

In addition, rheological tools can be applied to determine molar mass and distribution [32, 33]. A pragmatic approach is to calculate the number-average molar mass of a polymerization batch as:

$$\overline{M}_n = \frac{2 \times M_{TFE}}{I} \times 100$$

where $\overline{M}_{TFE}$ is the number of moles of polymerized TFE, I is the number of moles of consumed initiator.

In addition to its crystalline melting point at 327°C, PTFE has several transition temperatures. Two crystalline transitions, at 19°C and 30°C, have a significant effect on product behavior. Below 19°C, the polymer crystallites are in an almost perfect three-dimensional array. Above 19°C, the triclinic unit cell changes to a hexagonal unit cell. Slight untwisting of the chains is observed in the cell from 13 CF_2 groups to 15 CF_2 groups per 180° twist. The transition at 30°C is only ca. one-tenth as large as that at 19°C. The hexagonal unit cell disappears above 30°C, but the rodlike hexagonal packing of the chains in the lateral direction is retained. Between 19°C and 30°C, the specific volume of PTFE expands by about 1.8%. PTFE has additional several first and second order transition temperatures ranging from −110°C to 140°C. The exact quantity of minor transitions is somewhat dependant on the methods used.

Mechanical Properties. The mechanical properties of PTFE are affected by processing variables, such as preform pressure, sintering

Table 4. Properties of PTFE resins

Property	Granular	Fine Powder	Standard
Standard specific gravity, g/cm^3	2.13–2.18	2.14–2.25	EN ISO 12086
Tensile strength, MPa	> 14	> 19	EN ISO 12086
Elongation, %	> 200	> 200	EN ISO 12086
Flexural modulus, MPa	350–630	280–630	ASTM D 747
Flexural strength, MPa	no break	no break	ASTM D 790
Impact strength, J/m	160		ASTM D 256
Compressive stress at 1% deformation, MPa	4.2		ASTM D 695
Hardness, Shore D	50–65	50–65	ASTM D 1706
Coefficient of thermal expansion, K^{-1}	12×10^{-5}	12×10^{-5}	ASTM D 696

temperature, and cooling rate, as well as by polymer variables, such as molar mass, particle size, and particle-size distribution. The resulting void content and the amorphous content determine some mechanical properties. Void content is determined by measuring gravimetrically the (apparent) density of a specimen and the intrinsic density via its IR-spectroscopically determined amorphous content. The required densities of the amorphous and crystalline phase are assumed to be 1.966 g/cm^3 and 2.340 g/cm^3 [34]. Properties affected are the flex life (the capability of a material to withstand repeated bending without fracture) tensile strength, elongation, permeability, stiffness, resilience, and impact strength. Properties, such as the coefficient of friction, low-temperature flexibility, and thermal stability are relatively unaffected. Typical values for the mechanical properties of granular and fine powder PTFE resins are listed in Table 4. Further data are given in [35].

The volume change caused by the crystalline transition at 19°C must be taken into account when precision parts made from PTFE are designed.

The coefficient of friction of PTFE is unusually low. Static friction decreases with increasing load and is less than the dynamic friction that frees PTFE from stick–slip problems. Because of the low surface energy, only liquids with low surface tension (e.g., fluorinated liquids) can wet a PTFE surface. Surfaces can be made wettable by treatment with alkali-metal compounds (e.g., sodium naphthenate) that, however, also increases the coefficient of friction.

The effect of fillers on the mechanical properties of PTFE is shown in Table 5; tensile strength, elongation are reduced, and the coefficient of friction is not significantly affected. In contrast, wear resistance is dramatically improved (e.g., the wear factor of a bronze-filled material can be reduced by orders of magnitudes compared to that of unfilled PTFE).

Electrical Properties. The very low dielectric constant of PTFE does not change over a wide range of temperature (−40 to 250°C) and frequency (5 Hz to 10 GHz). Such electrical behavior is attributed to PTFE's highly symmetrical structure composed solely of carbon–fluorine bonds, in which all electrical dipoles are exactly balanced. Similarly, the dissipation factor is extremely low and independent of temperature or frequency. Resistivity and dielectric strength, on the other hand, are very high, as is arc resistance; PTFE leaves no carbonized path. The electrical properties of PTFE are given in Table 6.

Table 5. Properties of unfilled and filled PTFE resins

Property	Unfilled resin	Filled resin	
		25% Glass fiber	60% Bronze
Standard specific gravity, g/cm^3	2.16	2.24	3.74
Tensile strength, MPa	28	18	14
Elongation, %	350	250	150
Impact strength, J/m	152	119	
Hardness, Shore D	51	57	70
Wear factor, mPa^{-1}	5 013	26.2	12
Coefficient of friction			
Static, 3.4 MPa load	0.08	0.13	0.10
Dynamic, at PV = 172 kPa m s^{-1}	0.01	0.17	0.15
Thermal conductivity, mW m^{-1} K^{-1}	0.24	0.45	0.46

Table 6. Electrical properties of PTFE resins

Property	Standard	Granular	Fine powder
Dielectric constant, 60 Hz to 2 GHz	ASTM D 150	2.1	2.1
Dissipation factor, 60 Hz to 2 GHz	ASTM D 150	0.0003	0.0001
Volume resistivity, Ω cm	ASTM D 257	$> 10^{18}$	$> 10^{18}$
Surface resistivity, Ω/m^2	ASTM D 257	$> 10^{16}$	$> 10^{16}$
Surface arc resistance, s	ASTM D 495	> 300	> 300
Dielectric strength (2 mm thickness), kV/mm	ASTM D 149	23.60	23.60

Electrical properties can be adversely affected by voids, which may reduce the dielectric strength and corona resistance of fabricated parts. Consequently, voids must be minimized to achieve optimum electrical insulation.

Chemical Resistance. Polytetrafluoroethylene is resistant to attack by most chemicals, including hot fuming nitric acid, hot caustic, gaseous chlorine, chlorosulfonic acid, organic esters, ketones, and alcohols. The only materials known to attack PTFE are molten alkali metals, chlorine trifluoride, and gaseous fluorine at elevated temperature and pressure. Some highly fluorinated oils can swell or dissolve PTFE near its melting point.

Flame Resistance. Polytetrafluoroethylene is one of the most flame-resistant polymers known and does not support combustion in air. It has an extremely high limiting oxygen index (LOI) of 96%, i.e., it burns only in almost pure (96 vol%) oxygen [36].

Weatherability. The weatherability of PTFE is remarkable; it is completely unaffected by all types of weather from dry desert heat to humid jungle conditions. Test films showed no change after 20–30 years of continuous exposure in Florida.

Radiation Resistance. On exposure to a high-energy electron beam or gamma radiation, PTFE undergoes degradation rather than cross-linkage. In the absence of oxygen, stable radicals are produced which slow down the rate of degradation. However, in the presence of air, the radicals react with oxygen that accelerates scission and degradation. On exposure to 10^4 Gy (1 Mrad) of radiation in air, PTFE loses 50% of its original tensile strength. Irradiation also affects its electrical properties: resistivity decreases, whereas the dielectric constant and dissipation factor increase.

Thermal Stability. In both air and nitrogen, PTFE has an extremely high thermal stability. Rates of decomposition are not measurable below ca. 440°C; decomposition rates are high at 540°C. PTFE can be pyrolyzed at about 600°C almost completely back into fluoroolefins, the TFE monomer being the main product [37]; the activation energy is 347 kJ/mol. The melt viscosity decreases during pyrolysis, which probably involves random chain cleavage followed by depolymerization (short kinetic chain length) and termination by disproportionation. In the presence of diverse metals, PTFE reacts violently [38].

2.2.3. Processing

Granular Resins. Moldings are produced from granular resins in three steps: First, the dry powder is placed in a mold and compressed at moderate temperature to produce a preform that is strong enough for handling without breaking. The preform is then placed in an oven at 380°C to allow the particles to coalesce. This operation is called sintering. The final step is controlled cooling to produce the desired crystallinity. Granular resins are available in a number of forms that are optimized for different types of molding. Free-flow resins are used in small and automatic moldings, also for isostatic molding methods. Finely divided resins are preferred for large billet moldings to which they impart superior properties. Presintered resins are easier to handle and are preferred in ram extrusion applications. Most PTFE manufacturers give detailed descriptions of molding equipment and procedures [10].

Automatically molded articles require no further finishing after molding. However, large billets and rods are subsequently skived or machined. Films and sheets are produced by skiving a billet on a lathe. Skiving and machining generate significant scrap rates, only on a

minor portion of which are reused. Precision parts can be machined from ram-extruded rods. Another method, called coining, is used for articles that are too complicated to make by machining. In this operation, a sintered molding is heated to the melting point, quickly pressed into a mold cavity, and held under pressure until it resolidifies. Coined moldings are limited in their upper service temperature. After long periods at high temperature, they can return to their original precoining shape.

Fine Powder Resins. The paste-extrusion process for fine powder resins represented an important advance in PTFE processing. It permits the manufacture of continuous PTFE tubing and continuous PTFE coatings on wires.

In paste extrusion, 15–25 wt% of lubricant (a petroleum fraction, usually kerosene) is mixed with the fine powder resin. The wetted powder is then gently shaped into a preform at low pressure. (Fine powder resins are extremely sensitive to shear; great care must be taken to avoid shearing the powder before extrusion, otherwise processability may be lost.) The preform is forced through a die mounted in the extruder. The high shear exerted at the die fibrillates the powder and confers "green strength" to the extrudate. The lubricant is then evaporated and the extrudate is sintered at 380°C to coalesce the particles. Drying and sintering are performed consecutively by passing the extrudate through a multistage oven located directly after the extruder. Residence time in the oven can vary from a few seconds for thin-walled wire insulation to a few minutes for large-diameter tubing. Extrusion pressure depends on the reduction ratio, which is the ratio of the die diameter to the product diameter, the extrusion rate, the lubricant content, and the extruder characteristics.

Paste extrusion is also used to produce unsintered tape. Lubricant mixing and extrusion are the same as above. The product is extruded into rods, which are calendered on hot rolls to the desired dimensions.

Different fine powder resins have been developed for different applications. Powders that are suitable for high reduction-ratio applications, such as wire coatings, are usually not suitable for medium reduction-ratio applications, such as tubing. Thread sealant tapes are generally produced with other special grades. New types of fine powder resins are constantly developed, leading to both improved and new applications and processing techniques [7, 39].

W. L. GORE developed a unique expansion process to generate small pores in the structure of an article of PTFE; the trademark GoreTex is well known for lightweight and breathable fabrics, filtration membranes, medical implants, sealants, and high tensile fabrics [10, 39]. A good summary about the rheology and processing of PTFE fine powder is provided in [40].

Dispersion Resins. In general, PTFE dispersions are concentrated to 50–60% solids and stabilized by nonionic surfactants and sometimes with ionic surfactants. The dispersions are applied to various substrates (e.g., metal and hard surfaces in cookware applications, etc.) by spraying, flow or roll-coating, dipping, coagulating, or electrodepositing followed by drying and sintering. PTFE-films can be made by casting the aqueous dispersion on a supporting surface, drying, baking, and cooling. If the film is too thick, cracks develop; the maximum film thickness per application is ca. 40 μm. Thicker coatings are made by casting and baking a series of layers.

The most important application of PTFE dispersions is fabric coating. The fabric (e.g., fiberglass) is usually dipped into the dispersion and dried and sintered as in film formation. In some cases, the fiber is coated with the PTFE dispersion before weaving. Dispersions are also used in the production of PTFE fibers [41]. The dispersion is mixed with a matrix-forming medium, such as viscose and spun into fibers through a spinneret and coagulating bath. The fibers are heated to remove the matrix polymer, sintered, and drawn for spinning.

PTFE dispersions are added to other thermoplastic polymers to improve fire performance by suppressing dripping. Fibrillation of PTFE during processing and formation of a structure that retains high viscosity in molten state prevents dripping of the molten host polymer.

Another important application is the coagulation of PTFE-dispersions with fillers (e.g., graphite, bronze, etc.) to manufacture filled bearings.

Table 7. Uses of PTFE resins

Type of resin	Uses
Granular	
Agglomerates	gaskets, packing, seals, bearings, sheet, rod, heavy wall tubing, and tape
Coarse cut	tape, molded shapes for chemical, mechanical, electrical, and nonstick applications
Fine cut	molded sheets, tape, wire, wrapping, tubing, and gasketing
Presintered	rods and tubes
Fine powder	
High reduction ratio*	wire coating and thin-walled tubing
Medium reduction ratio*	tubing, pipe, overbraided hose, and spaghetti tubing
Low reduction ratio*	thread-sealant tape, pipe liners, tubing, and porous structures
Dispersion	
General purpose	impregnation, coating, and packing
Coating	film and coating

* Ratio of extrusion-die diameter to product diameter.

2.2.4. Uses

Overlapping end use designations (see Table 7) make it difficult to segment the markets for the three PTFE-classes. Taking the consumption in the United States as benchmark gives a good general overview [12].

- Granular PTFE is consumed by 45% for mechanical applications (e.g., seals, piston rings, bearings, and cylinder tubes), 35% by chemical processing industries (most PTFE for fluid handling parts as valve and pump linings, dip tubes, expansion bellows, nozzles, valve seats, laboratory apparatus, gaskets), and 20% by electrical applications (e.g., cable connectors, circuit breakers, stand-off insulators, coaxial cores, ribbon cables, skived insulating tapes).
- Fine powder is consumed by 30% in textile laminates (e.g., GoreTex-applications), 28% by the automotive industry (e.g., push-pull cables for throttles, clutches and brakes, hoses for various fluids), 16% by wire and cable (nonautomotive) applications (e.g., direct extrusion into wire and electrical tapes for coaxial cables, hookup wire, and computer wire), 15% by tubing applications (e.g., spaghetti tubing, liners for overbraided tubes, hoses and pipes in chemical processing), and about 11% for other applications including gaskets, pump packing, and thread seal tapes.
- Aqueous dispersions are widely used: about 40% to coat fabrics (e.g., glass-fiber fabrics) for architectural purposes, 15% in consumer and industrial coatings (e.g., cookware coating, manufacturing of conveyor belts, chute liners and rolls), 15% in PTFE-fiber markets (the fibers are used for fabrication of filters, pump packing, gaskets, and bearings), and about 30% in preparations of various items (e.g., metal and graphite parts in heat exchangers and bearings) and coagulations to prepare filled bearings.

2.2.5. New Materials—Modified Granular PTFE

PTFE as an engineering material suffers from three shortcomings (in particular granular PTFE-grades): Low creep resistance (cold flow), difficult weldability, and its insufficiently dense polymer structure (void content).

The reason for these weaknesses is the great tendency of the entirely linear polymer chains to crystallize from the melt. The crystalline phase typically amounts to 50–70% in end-use articles and exhibits a ductile behavior with practically no mechanical strength. Mechanical strength is provided by tie-molecules bridging adjacent lamellae. The entangled tie-molecules make up the amorphous phase. To achieve mechanical strength and toughness, the molar mass of commercial PTFE is required to be in the range of 10^7–10^8 g/mol to partially suppress crystallization and to provide sufficient high tie-chain concentrations. The high molar masses result in high melt viscosities (10^{10}–10^{12} Pa s), which also impairs perfect particle coalescence, and consequently, the processed PTFE shows significant void contents. The intrinsic shortcomings are largely overcome by reducing the molar mass and hence the melt viscosity. Simultaneously, enhanced crystallization is prevented by incorporating bulky side groups into the linear polymer chain [34].

Small amounts (0.01–0.2 mol%) of copolymerized perfluoro(alkyl vinyl ethers), e.g.,

PPVE, are sufficient to reduce the crystallinity of PTFE [42]. Such materials can be polymerized under the conditions described above; the chemical homogeneity and molar mass can be controlled by the mode of feeding the comonomer PPVE. Free-flowing as well as nonfree-flowing grades with different modifier contents are commercially available. Usually the PPVE-content of modified PTFE is in the range of 0.05 mol%; compared to commercial unmodified PTFE-grade, the melt viscosity of modified PTFE can be lower by an order of magnitude. Thus, more efficient particle coalescence during the sinter process is accomplished (also for agglomerated free-flowing grades). The denser polymer texture results in much lower void contents, lower permeability coefficient, higher dielectric strength (in particular for free-flowing grades), and reduced stretch void indices (Table 8).

Modified PTFE shows excellent weldability, revealing the successful establishment of effective chain entanglements, because of the lower melt viscosity and molar mass. The deformation under load is reduced by 50%, and the recovery enhanced by a factor of 2–3. These effects can be attributed to the smaller lamellae size and the increased concentration of tie-molecules that bridge adjacent lamellae.

The modification improves all technical important properties [43, 44]; the dielectrical loss is almost unaffected by the polarizable oxygen atoms of the modifier, and even the thermal stability is identical to unmodified PTFE.

Modified PTFE is processed with the same techniques as conventional PTFE. Due to its lower melt viscosity, modified PTFE is better suited for coined molding, blow molding, and other thermoforming technologies. Because of the reduced cold flow, modified PTFE is specially suited for gaskets.

Increasing the PPVE-modifier content further up to 0.7 mol%, melt processable PTFE-grades are generated with superior properties [9].

Table 8. Properties of modified granular PTFE and unmodified PTFE resins [34]

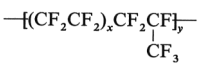
Property	Standard	Modified PTFE 0.1 wt% PPVE		Unmodified PTFE	
		Nonfree-flowing	Free-flowing	Nonfree-flowing	Free-flowing
Standard specific gravity, g/cm^3	EN ISO 12086	2.165	2.165	2.160	2.155
Void content[a], vol‰	EN ISO 12086[a]	2.6	4.0	7.5	8.0
SVI value[b]	EN ISO 12086[b]	85	85	300	300
Dielectric strength (100 μm film), kV/mm	DIN 53481	105	100	105	80
Permeabililty, cm^3 mm m^{-2} d^{-1} bar^{-1}	DIN 53380, 25 °C				
SO_2		200		310	
HCl		210		300	
Cl_2		100		160	
O_2		210		240	
N_2		80		100	
CO_2		540		800	
Water vapor (100 °C), g mm m^{-2} d^{-1}	DIN 53122	2.6		3.8	
Tensile strength, MPa	EN ISO 12086	41	36	41	33
Elongation, %	100 μm film	630	600	450	400
Deformation under 15 MPa, %	ASTM D 621				
	24 h	8	10	16	16
Load	permanent	4	5	11	11
Flexural modulus, MPa	DIN 53457				
23 °C		650	630	600	555
100 °C		290	255	210	210
250 °C		60	60	40	40

[a]Void content is determined by measuring gravimetrically the (apparent) density of a specimen and the intrinsic density via its IR spectroscopically determined amorphous content [42]. The required densities of the amorphous and crystalline phase are assumed to be 1.966 g/cm^3 and 2.340 g/cm^3, respectively.

[b]The stretch void index (SVI) is calculated from the difference of gravimetrically determined densities of the unstretched and stretched specimen until break multiplied by 1 000 (see EN ISO 12086).

2.3. Tetrafluoroethylene–Hexafluoropropene Copolymers

Copolymers of tetrafluoroethylene (TFE) and hexafluoropropene (HFP) are commonly referred to as fluorinated ethylene–propene (FEP) resins [25067-11-2]. They are linear, perfluorinated copolymers:



In 2008, the worldwide consumption in FEP copolymers was about 1.8×10^4 t [12]. There was a great demand for plenum cable and local area network applications during the 1990s. Currently the annual growth is below 2%.

The presence of HFP in the polymer chain reduces the tendency to crystallize. Thus, a copolymer with a much lower molar mass than the corresponding homopolymer PTFE retains toughness adequate for most applications. The molar mass of commercial FEP resins is only ca. 1/100 that of commercial PTFE resins. This results in a ca. 10^6-fold reduction in melt viscosity. Resins made of FEP have melt viscosities in the range of 1×10^3–10×10^3 Pa s at 380°C, which enables standard plastics processing techniques, such as extrusion and injection molding, to be used. In spite of their much lower molar mass, the properties of FEP resins are largely comparable to those of PTFE resins. The FEP resins have outstanding chemical resistance, nonflammability, weatherability, and electrical, antiadhesive, and low-friction properties. The maximum use temperature of 200°C, however, is 60°C below that of PTFE resins.

Most commercial FEP grades have a melting point of 260 ± 20°C and are offered with a wide range of melt viscosities (e.g., MFI 372°C/5 kg from < 1 to > 30 g/10 min) for the different applications and processing technologies. In addition, modified FEP-grades, e.g., modified with PPVE, are available. Aqueous dispersions of FEP with solid contents of 50–60% and nonionic surfactants are also on the market.

FEP resins are offered as melt-pelletized materials, as powders, or as aqueous dispersions by Daikin (Neoflon), DuPont (Teflon), and 3M (Dyneon). Other companies started also to commercialize FEP resins (e.g., Halopolymer, Dongyue, 3F, Juhua).

2.3.1. Production

Copolymerization takes place in aqueous or nonaqueous media. Because it is less reactive than TFE, HFP is present in larger proportions in the mixture. In aqueous media, fluorinated emulsifiers with carboxylic acid groups are normally employed. Persulfate is usually preferred as a free-radical initiator. Aqueous emulsion polymerization conditions are similar to those employed for PTFE fine powder. Standard polymerization equipment can be used; the polymerizations are usually carried out in a temperature range of 50–100°C and within a pressure range of 1.5×10^6–3.0×10^6 Pa. PPVE-modifications (< 2 wt%) are also applied to improve e.g., stress crack resistance and processability.

The obtained latices have particle sizes of 100–250 nm and solid contents of about 30%. Coagulation by addition of electrolytes (e.g., acids) or applying high shear provides a very fine, nonfree-flowing powder, which usually needs to be agglomerated with organic solvents to get free-flowing properties. Persulfate-initiated polymers have many terminal COF- and COO^--endgroups that are easily detected by FT-IR analysis. These carboxylic groups are thermally instable and must be removed, because they cause blistering, discoloration, and corrosion during processing. Various methods are applied to convert the unstable carboxylic groups in more stable CF_2H-group (e.g., by water-heat treatment) or into CF_3-groups by postfluorination [10]. Polymers synthesized in a nonaqueous medium, with fluorinated peroxides or azo compounds as initiators, do not contain unstable end groups [45] and no post-treatments are necessary.

Aqueous dispersions are prepared by adding nonionic surfactants and by removing the applied fluorinated emulsifiers (e.g., by an anionic ion-exchanger); further concentration to 50–60% solids is desirable.

2.3.2. Properties

Physical Properties. The FEP resins are random copolymers of TFE and HFP. The HFP content is usually expressed as an HFP index (HFPI), which is the ratio of IR absorbances at ca. 980 and 2 365 cm^{-1}. Commercial FEP resins

have HFPIs between ca. 3 and 5.5 [15]. The actual HFP content of FEP resins can also be determined by a high-temperature ^{19}F-NMR technique [46]; a typical FEP resin contains about 9 mol% of HFP.

The crystallinity of as-polymerized FEP is lower than that of as-polymerized PTFE (70% vs. 98%). After processing, crystallinity depends on the molar mass and the rate of cooling from the melt. The crystallinity of FEP moldings is usually ca. 50%.

FEP resins are insoluble in most known solvents. Solubility is given in selected perfluorocarbons at higher temperatures [47] and in supercritical media (e.g., CO_2, CHF_3) [48]. This precludes the convenient determination of molar mass by the usual methods. Number-average molar masses have been estimated by measuring the concentration of acid end groups before finishing. Polymerization in aqueous media gives 0.05 to 0.20 mol% acid end groups. A convenient and reliable method to determine molar mass including distribution is based on dynamic rheometry data [49]. The number-average molar masses of commercial grades are between ca. 10^5g/mol and 5×10^5 g/mol. However, molar mass is normally specified in terms of the melt-flow index, measured at 372°C under a load of 5 kg in a melt rheometer of the type used for polyethylene equipped with a corrosion-resistant barrel, piston, and die (ASTM D-2116-02). Melt-flow index values range from ca. < 1 for the high viscosity grade to ca. 35 for the low viscosity grades.

Typical FEP resins have a crystalline melting point from ca. 240 to 280°C, depending on their HFP content and do not exhibit any other crystalline transitions. (An amorphous transition is observed at 90–150°C, depending on frequency of measurement. A second amorphous transition occurs below −150°C [50].

The thermal stability of FEP resins is lower than that of PTFE resins, but is adequate for processing up to at least 380°C. HFP diads (2 adjacent HFP units [10]) are found to be a source for instability but in general, thermal decomposition occurs in two distinct stages. In the first, HFP is preferentially split out of the backbone at a rate that is about four times faster than that found in normal PTFE decomposition. The second stage involves the decomposition of the remaining PTFE backbone, at the same rate as that of PTFE decomposition.

Mechanical Properties. The mechanical properties of FEP are very similar to those of PTFE resins. The absence of the 19°C transition in FEP resins eliminates the volume change observed in PTFE resins at this temperature. The coefficient of friction is slightly higher in FEP resins than in PTFE. However, the static coefficient is lower than the dynamic coefficient, which avoids stick–slip. Typical values of mechanical properties are given in Table 9.

The temperature dependence of the tensile properties of FEP [51] and PTFE resins is similar from ca. −250 to 200°C. However, above 200°C, the FEP properties deteriorate rapidly, whereas the PTFE properties remain satisfactory up to at least 260°C. Thus, the maximum use temperature of FEP is 60°C below that of PTFE resins.

As with PTFE, fillers can be added to FEP resins to increase wear resistance and stiffness and to lower creep. The maximum loading of fillers is controlled by processing considerations. Available compositions include 30% bronze filled, 20% graphite filled, and 10% fiberglass filled. These all have high *PV* (pressure–velocity) values desirable for use as bearings.

The surfaces of FEP can be made wettable by corona discharge or by treatment with sodium naphthenate or with amines in a hot oxidizing atmosphere.

Electrical Properties. The electrical properties of FEP resins (Table 10) and PTFE resins

Table 9. Properties of FEP resins [2]

Property	MFI < 2	MFI 7	Standard
Specific gravity, g/cm^3	2.14–2.17	2.14–2.17	ASTM D 792
Tensile yield, MPa	12		ASTM D 638
Tensile strength, MPa	31	25	ASTM D 1708
Elongation, %	305	325	ASTM D 1708
Flexural modulus, MPa	590	620	ASTM D 790
Compressive strength, MPa	23	21	ASTM D 695
Hardness, Shore D	57	56	ASTM D 2240
Izod impact strength, J/m	no break	no break	ASTM D 256
Coefficient of thermal expansion (0–100 °C), K^{-1}	8×10^{-5}	14×10^{-5}	ASTM D 696

Table 10. Electrical properties of perfluoropolymers [34]

Property	Standard	PFA	MFA	FEP
Volume resistivity (from 23 to 150 °C), Ω cm	ASTM D 257	$> 10^{17}$	$> 10^{17}$	$> 10^{17}$
Surface resistivity, Ω	ASTM D 257	$> 10^{17}$	$> 10^{17}$	$> 10^{17}$
Arc resistance, s	ASTM D 495	> 200	> 200	> 200
Dielectric strength (1 mm thickness), kV/mm	ASTM D 149	30–32	30–32	26–30
Dielectric constant	ASTM D 150			
50 Hz, 23 °C		2.0–2.1	2.0–2.1	2.1
100 kHz, 23 °C		2.0	2.0	2.0
Dissipation factor	ASTM D 150			
50 Hz, 23 °C		3×10^{-4}	3×10^{-4}	3×10^{-4}
100 kHz, 23 °C		5×10^{-4}	5×10^{-4}	5×10^{-4}

(Table 6) are virtually identical. However, the effect of voids on the electrical properties that is observed in PTFE resins is absent in the void-free FEP resins. Because of the stability of FEP in dielectric measurements, the National Bureau of Standards has selected FEP resins as reference standards. The electrical properties of FEP are unaffected by prolonged exposure to water or a temperature of 200°C. Only corona ignition affects the dielectric life of FEP. If the voltage stress is too low to cause corona discharge, dielectric life is infinitely long at any frequency.

Chemical Resistance. FEP resins are inert to practically all chemicals and solvents, with the exception of fluorine at elevated temperature and pressure and molten alkali metals or sodium hydroxide. Adsorption of chemicals is usually less than 1% even after long exposure at an elevated temperature. Adsorption is completely reversible and has no effect on the polymer. Permeation of gas and vapor through FEP is slower than through most other plastics.

Radiation Resistance. The effect of gamma-ray or electron-beam irradiation on FEP and PTFE is largely degradative. In the absence of air, the radiation resistance of FEP is ten times greater than that of PTFE. In the presence of air, however, both degrade at about the same rate. In the absence of air, irradiation at low dose rates at a temperature above the alpha transition (> 150°C) results in cross-linking [52], which is, however, of no practical importance.

Weatherability. FEP resins exhibits an outstanding weatherability. After 15 years' exposure in Florida, the tensile properties and light transmission of a crystal clear FEP film remained unchanged.

Flame Resistance. The flame resistance of FEP is outstanding; it does not support combustion in air and has a LOI of 96%.

2.3.3. Processing

Extrusion and Injection Molding. Conventional methods, such as extrusion and injection molding are employed for processing FEP. However, FEP has a higher melt viscosity and lower critical shear rate than many other thermoplastic materials (e.g., PE, PP, PS), which makes processing more difficult. Molten FEP can corrode the metals used in extruders and injection molding machines. Thus, equipment parts exposed to molten FEP resin should be constructed from more corrosion-resistant materials (e.g., Hastelloy C or Inconel).

Critical shear rates at 380°C, above which melt fracture occurs, are low and range from 20 s^{-1} for FEP with MFI ~ 10 g/10 min to 2 s^{-1} for FEP with MFI < 2 g/10 min. The resulting low production rates preclude the use of pressure-extrusion techniques. Fortunately, FEP resins have a high melt strength and can tolerate high draw-down ratios without fracture. Melt-draw techniques make high production rates possible. In addition, FEP can be extruded into wire coating, tubing, rods, and film of various sizes. It can be extruded over such materials as silicone rubber, poly(vinyl

chloride), glass braid, metal-shielded cables, twisted conductors, and parallel multiconductor cables. Concentrates of any desired color can be blended with standard resins.

Injection molding is best carried out with the low melt viscosity grades (e.g., FEPs with MFI ~ 20). Recommendations for molding equipment, designs, and operating conditions are available from the manufacturers. Bottles, flasks, beakers, and other laboratory ware are typical FEP products that are made by injection molding.

Dispersion Coating. Aqueous FEP dispersions are processed essentially as PTFE dispersions. They are usually coated on the substrate (e.g., glass cloth), and water is evaporated. The coating is then fused by heating above the melting point. Because of the lower melt viscosity of FEP, fusion is quicker than with PTFE resins. In addition, continuous films, free of pinholes, are more readily achieved. Sometimes FEP dispersions are used to provide a final coating on a PTFE coating.

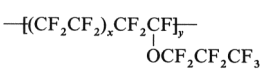
2.3.4. Uses

More than 80% of all FEP resins are used in electrical applications, including hookup wires, computer and thermocouple wires, coaxial cables, etc. The leading market is the production of plenum wire and cables.

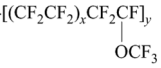
About 6% of FEP is used for film applications, e.g., release film, laminate with polyimide, in solar collectors, etc. Chemical processing industries use FEP-resins, e.g., for tubings in semiconductor industry, linings for fittings, pumps, bellows and valve components, and heat exchangers.

2.4. Tetrafluoroethylene–Perfluoro (Alkyl Vinyl Ether) Copolymers

Copolymers of TFE with perfluoro(propyl vinyl ether) (PPVE) are called propylfluoroalkoxy (PFA) resins [26655-00-5]. They have the following general formula:



Copolymers of TFE and perfluoro(methyl vinyl ether) (PMVE) are called methylfluoroalkoxy copolymer (MFA) and have the following structure [34]:



The worldwide consumption was about 6 000 t in 2008 [12]. Growth rates (1–4%/a) depend on geographic regions.

PFA resins were developed after FEP resins and were designed to overcome the disadvantages of FEP resins in comparison with PTFE resins, i.e., lower thermal stability and poorer mechanical properties at high temperatures. The ether group in the side chain of PFA and MFA resins eliminates steric strain at the branching point, which is responsible for the reduced thermal stability of FEP resins [53]. In addition, the large perfluoropropoxy side group in PFA reduces the crystallinity much more than the trifluoromethyl side group in FEP; it is about five times more effective on a molar basis. The comonomer content of PFA resins is lower than that of FEP resins [34]. The melting point of PFA (305–310°C) is only ca. 20°C below that of PTFE. The thermal stability and maximum use temperature of PFA and PTFE resins are essentially the same. PFA and MFA resins have all the other advantages of PTFE resins: antistick performance, resistance to virtually all chemicals, low coefficient of friction, nonflammability, and excellent electrical properties.

Manufactures for fluoroalkoxy polymers are Daikin (Neoflon), DuPont (Teflon), 3M (Dyneon), Solvay Solexis (Hyflon PFA, MFA).

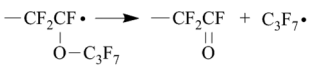
2.4.1. Production

Copolymerization. The copolymerization of TFE and PPVE is either carried out in aqueous [54] or nonaqueous media [55]. The aqueous process resembles the emulsion polymerization used for PTFE fine powders and FEP resins. However, only a small amount of PPVE is present in the PFA reaction mixture. This is because PPVE is ca. five times more reactive than HFP (copolymerization parameter for PPVE is about 5 and for HFP 24, respectively) and a much smaller amount of

comonomer is incorporated into PFA compared to FEP.

To avoid chemical inhomogeneities, PPVE has to be replenished properly according to the copolymerization parameter; the polymerizations are usually done under constant TFE pressure in a range of $1.0 \times 10^6 - 2.5 \times 10^6$ Pa and at temperatures of 40–90°C. Water-soluble initiators, such as persulfates or potassium permanganate are preferred; chain-transfer agents are used to control the molar mass (e.g., H_2, R134, alkanes, alcohols).

A complication of TFE and PPVE copolymerization is the tendency of the growing PPVE radical to terminate by rearrangement:



To avoid this reaction, the polymerization conditions should be below 70°C. This rearrangement reaction occurs to a lesser extent with PMVE.

The polymerization rates can be increased by adding nontelogenic fluorinated solvents or by microemulsion technologies. The aqueous lattices show average particle sizes of about 150–200 nm and 30–40% solids.

Nonaqueous polymerizations in non- or low-telogenic fluorinated solvents use fluorinated peroxides (e.g., bisperfluoro alkanoic peroxides, perfluoro acyl hypofluorides) to generate stable end-groups. Chain transfer agents are used to control the molar mass. Usually high space–time yields are achieved with solid contents of 5–10%; higher solid contents have a gel-like behavior, and polymerizations are hard to control. The polymers are recovered by removing the solvent and unconverted initiator at higher temperatures; the polymer is then compacted for melt-extrusion.

The aqueous lattices are coagulated by shear or addition of electrolytes and are usually agglomerated with e.g., water–gasoline to obtain a free-flowing polymer powder. The polymer powders (in particular from aqueous polymerization) have some unstable end-groups (e.g., COO^-, COF) from initiators, chain transfer agent, or rearrangement reactions. Post-treatments with methanol or ammonia to stabilize the polymer have been recommended [56]. For demanding applications, all the unstable groups are removed by postfluorination with F_2–N_2-mixtures at temperatures up to 250°C [57, 58].

After addition of nonionic surfactants to the aqueous lattices, the fluorinated emulsifiers are removed and the lattices can be concentrated to 50–60% solids PFA-dispersions.

Polymerizations in supercritical CO_2 have been initiated, but did not find widespread applicability [10].

2.4.2. Properties

Physical Properties. PFA resins undergo a single first-order transition at their melting point (305–310°C). They do not display the other first-order transitions present in PTFE resins [59]. Torsion-pendulum measurements revealed three second-order transitions at −100, −30, and 90°C. The crystallinity of as-polymerized dispersion polymer was 65–75%. Samples slowly cooled from the melt had 58% crystallinity.

The number-average molar mass $\overline{M}_n$ for PFA and MFA can be deduced by quantification of the end-groups and weight-average molar mass $\overline{M}_w$ from the extrapolated plateau modulus of the complex viscosity via dynamic melt viscosity. The dynamic rheometry allows also the determination of the molar mass distribution (MWD) [33, 60]. The molar mass is usually in the range of $1–5 \times 10^5$ g/mol.

The amount of incorporated vinyl ethers, the number of polar end-groups, and the amorphous content can be determined by FT-IR-spectroscopy [34]. The melting point is lowered by about 10°C/PPVE mol% (HFP: ~8°C/HFP mol%).

The thermal stability of PFA resins is comparable to that of PTFE resins. Although they can be processed at temperatures up to 425°C [49], degradation occurs on prolonged heating at or above 425°C. Below its melting point, PFA does not decompose. Samples of PFA aged in an air oven at 285°C for years showed no deterioration; in fact, tensile strength, ultimate elongation, and flex life increased.

Some general properties of PFA and MFA are given in Table 11.

Table 11. General properties of PFA polymers and MFA polymers [34]

Property	Standard	PFA	MFA
Specific gravity, g/cm^3	ASTM D 792	2.12–2.17	2.12–2.17
Melting temperature, °C	ASTM D 2116	300–310	280–290
Coefficient of linear thermal expansion, K^{-1}	ASTM E 831	(12–20) × 10^{-5}	(12–20) × 10^{-5}
Specific heat, kJ kg^{-1} K^{-1}		1.0	1.1
Flammability	(UL 94)	V-O	V-O
Oxygen index, %	ASTM D 2863	> 95	> 95
Hardness, Shore D	ASTM D 2240	55–60	55–60
Friction coefficient (on steel)		0.2	0.2
Water absorption, %	ASTM D 570	< 0.03	< 0.03
Upper working temperature, °C		260	230
Refractive index		1.35	1.35

Mechanical Properties. The mechanical properties of PFA resins resemble those of PTFE and FEP resins at room temperature, but above 200°C, PFA resins are superior to FEP resins. The high-temperature mechanical properties of PFA resins are equal or superior to those of PTFE resins. Both PFA and PTFE resins have a maximum use temperature of 260°C. The low-temperature mechanical properties of the two resins are equivalent. Some properties of PFA compared to PTFE are shown in Table 12.

The wear and friction properties of PFA, MFA, and FEP resins are similar. The static coefficient of friction is lower than the dynamic coefficient; consequently, the polymer is free of stick–slip behavior. Fillers, such as fiberglass or bronze powder improve the wear resistance of PFA, FEP, and PTFE resins. Among the partially and perfluorinated thermoplastics PFA, MFA, and FEP exhibit (up to 100°C) the lowest creep resistance; they show much better creep properties above 150°C compared to PVDF, ECTFE, and ETFE [34].

Electrical Properties. The electrical properties of PFA, MFA, and FEP resins are essentially the same [34] (see Table 10).

Flame Resistance. Perfluoroalkoxy resins have the same nonflammability characteristics as PTFE resins. LOI is over 95%. According to Underwriters Laboratories (UL 94), PFA resins are self-extinguishing and classified 94 V-O.

Radiation Resistance. High-energy irradiation affects PFA, MFA, FEP, and PTFE resins similarly. The PFA and MFA resins have about the same rate of degradation as PTFE resins in air, but resist radiation better under vacuum. The main effect of radiation is the reduction of tensile strength and elongation.

Chemical Resistance. Perfluoroalkoxy resins have outstanding resistance to chemicals and solvents, and are unaffected by strong oxidizing acids, bases, halogens, organic acids, aromatic and aliphatic hydrocarbons, alcohols, aldehydes, ketones, ethers, amines, esters, chlorinated compounds, and polymer solvents. Perfluoroalkoxy resins can be attacked by alkali metals and elemental fluorine at elevated temperature and pressure.

Optical Properties. Perfluoroalkoxy films have good optical properties; they are colorless and transparent in thin sections, and are translucent in thicker sections. Light transmission is best in the IR region (87–93%) followed by the visible (80–87%) and UV regions (55–80%). Refractive index is about 1.35.

2.4.3. Processing

High-temperature PFA and MFA melts can be corrosive to conventional stainless steels; more corrosion-resistant metals, such as Hastelloy-C or Inconel are recommended for equipment parts that are exposed to the melts. Processing temperatures of ca. 330–425°C are recommended. Residence times at the upper temperature limit should be kept short (< 10 min) to avoid polymer degradation. PFA and MFA are processed e.g., by extrusion or injection molding techniques; temperatures up to 425°C are required. For these processing techniques, PFA

Table 12. Properties of PFA (3.5 wt% PPVE) and granular nonfree-flowing PTFE resin [34]

Property	Standard	PFA	PTFE
Permeability, cm^3 mm m^{-2} d^{-1} bar^{-1}			
SO_2, 25 °C		190	310
SO_2, 100 °C		1 400	1 600
Cl_2, 25 °C		110	160
Cl_2, 100 °C		900	1 000
O_2, 25 °C	DIN 53380	240	240
O_2, 100 °C		1 400	1 400
N_2, 25 °C		75	100
N_2, 100 °C		700	700
CO_2, 25 °C		600	800
CO_2, 100 °C		2 100	2 100
HCl, 25 °C		180	300
HCl, 100 °C		1 800	1 800
Water vapor, g mm m^{-2} d^{-1}	DIN 53122		
25 °C		0.02	0.03
100 °C		4.5	3.8
Flexural modulus, MPa	DIN 53457		
25 °C		670	600
100 °C		200	210
150 °C		120	80
250 °C		30	40
Deformation (under 15 MPa load), %	ASTM D 621		
24 h		6.7	16
100 h		7.0	17.5
Permanent	permanent	1.6	11
Dielectric strength (100 µm film), kV/mm	DIN 53481	125	105
SVI value	ISO 12086	30	300

and MFA grades of higher MFI values (lower molar masses) are used.

Although perfluoroalkoxy-resins are stable resins, thermal degradation is unavoidable. This is a function of temperature, residence time, and shear rate. Thermal degradation occurs mainly from the end-groups. Chain scission becomes evident at temperatures above 400°C depending on shear rates. As with many other thermoplastics, melt fracture occurs above critical shear rates leading to rough extrudate surfaces [61]. The allowable flow rates are constrained at the low end by the thermal degradation due to longer residence times and at the high end by the melt fracture and chain scissions. Higher extrusion rates can also be achieved by broadening the molar mass distribution.

Transfer molding uses temperatures of 350–380°C and lower shear rates. At these conditions chain scission does not occur. Usually PFA and MFA grades with lower MFI (higher molar masses) are preferred. Transfer molding techniques are typically used for valve and liner applications.

Because of their higher inherent thermal stability, PFA and MFA resins can be processed at a higher temperature than FEP. This results in a further increase in melt-flow index and critical shear rate for PFA and MFA resins. Thus, PFA resins can also be processed at significantly higher rates than FEP (Table 13).

Perfluoroalkoxy resins have sufficient thermal stability for rotocasting and powder coating applications. For both applications, the resins are applied as powder. Rotocasting is used for coating large structures e.g., drums and tanks. During rotocasting operations, the heating cycles

Table 13. Melt-flow index and shear rate of FEP and PFA resins [2]

Teflon grade		MFI (372 °C/5 kg), g/10 min	Critical shear rate, s^{-1}
FEP	PFA		
100		6	20
	340	14	50
140		3	8
	310	6	16
160		1	2
	350	2	6

may range from 90 to 180 min at 350–370°C. During powder coating applications, finely divided powders are used to produce thin layers of PFA or MFA and various substrates. The surfaces to be coated are heated above the melting point of the resins and the powder is sprayed on. The powder melts on the surface, which is then cooled.

Aqueous dispersions are available for coating metals, glass fabrics, and similar substrates. The dispersion can be processed by the techniques used with PTFE dispersions.

2.4.4. Uses

PFA and MFA resins are used to large extent (~ 80%) in chemical processing and semiconductor industry e.g., for wafer carriers, pumps, valves, bellows, pipe and fittings, filtration systems, and tubing; also the lining of storage tanks and processing kettles is an important segment. PFA and MFA films are also produced; these films can be oriented to provide specialized effects. About 20% of the perfluoroalkoxy resins are used in wire and cable applications e.g., in heat trace cable, insulations of hook-up wire cables as well as in appliance, computer, and aerospace wire. MFA has displaced PFA in many wire and cable applications.

2.5. Tetrafluoroethylene–Ethylene Copolymers

Tetrafluoroethylene and ethylene have a strong tendency to alternate during polymerization. Thus, TFE–ethylene copolymers [25038-71-5] (ETFE resins) are composed mainly of alternating sequences of the two monomers and have the following structure:

$$-(CF_2CF_2CH_2CH_2-)_n$$

The world consumption of ETFE resins was about 6 000 t in 2008 [12], with expected growth rates of 1–2%. The alternating comonomer units are responsible for the unique properties of ETFE resins; they have a high tensile strength, moderate stiffness, high flex life, outstanding impact strength, good abrasion resistance, and very high cut-through resistance. Their electrical properties are similar to those of other TFE polymers. The ETFE resins have low dielectric constant, high dielectric strength, excellent resistivity, and a low dissipation factor; they also display good thermal stability and excellent chemical resistance. Unlike other TFE copolymers, ETFE resins have a high resistance to high-energy radiation. They are cross-linked by low doses of electron beam or gamma ray radiation. The cross-linked products have improved high-temperature properties, including resistance to cut-through by a hot soldering iron. The processability of ETFE resins is superior to that of other TFE copolymers (the critical shear rate of ETFE resin is at least a magnitude higher than that of FEP resin). They are particularly well suited to extrusion and injection molding.

Unmodified TFE–ethylene copolymers have poor thermal stress–crack resistance, which severely limits their utility. This problem has been largely overcome by incorporating 1–10 mol% of additional comonomers (modifiers), such as perfluoro(alkyl vinyl ethers), perfluoroalkylethylenes, and HFP in the polymer backbone [62–64]. Commercial ETFE resins are all modified in this way. The thermal stress–crack resistance of modified ETFE resins is a function of the modifier content and the melt viscosity of the resin. Processability (extrusion rate), on the other hand, is mainly a function of the melt viscosity. Lowering the melt viscosity improves processability, but reduces stress–crack resistance. Commercially available modified ETFE resins provide different compromises between processability and thermal stress–crack resistance to meet a variety of use and processing requirements.

ETFE resins are produced by Asahi Glass (Aflon COP), Daikin (Neoflon EP), DuPont (Tefzel), 3M (Dyneon ET), and Solvay Solexis (Halon ET).

2.5.1. Production

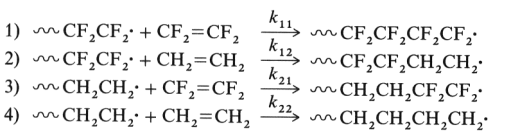
Tetrafluoroethylene and ethylene monomer mixtures can undergo thermal decomposition reactions. The released energy can be even greater than for decomposition of pure TFE. Therefore, great care must be exercised during the copolymerization of these monomers.

Copolymers of TFE and ethylene can be prepared in aqueous, nonaqueous, or mixed systems. Nonaqueous suspension polymerizations are performed in non or low telogenic hydrofluorocarbon solvents (e.g., $CF_3–(CF_2)_{1–8}–H$, $CF_3–(CF_2)_{1–4}–CH_2–CH_3$) [140]. Fluorinated or hydrogenated organic peroxides are used as initiators; in addition, hydrogen or fluorine containing chain-transfer agents are used to control molar mass. The solid contents are usually less than 10 wt% because the viscosity of the polymer slurry gets quite high.

Mixtures of water and fluorinated solvents may also be used [205]; in this case, the polymerization occurs in the organic phase, while the water serves to lower the viscosity of the mixture and to remove the heat of polymerization.

Aqueous emulsion polymerizations use mainly fluorinated emulsifiers (e.g., ammonium perfluoro octanoate). Organic peroxides or manganic salts are used as initiators; inorganic peroxides, such as APS are less preferred because stable sulfate end-groups are generated that might cause discoloration during workup and processing. Solid contents between 20–35% can be achieved. The polymerization temperature is usually in the range of 30°C to 80°C; polymerization pressure is below 2.0×10^6 Pa.

The following four propagation reactions take place in TFE–ethylene copolymerizations:



k = rate constant; reactivity ratio r_1 (C_2F_4) = k_{11}/k_{12}; reactivity ratio r_2 (C_2H_4) = k_{22}/k_{21}.

The reactivity ratios are at 65°C: $r_1 = 0.045$, $r_2 = 0.14$; at −30°C : $r_1 = 0.014$, $r_2 = 0.010$.

These values demonstrate the strong alternation tendencies that decrease with increasing temperature. Calculation show that a 1 : 1 ETFE obtained at −30°C and at 65°C have a 97% and 93% of alternating sequences [2].

Copolymers of ETFE have poor stress crack resistance, even at higher molar masses. To improve stress crack resistance, commercial ETFE grades are modified with 1–10 mol% of additional comonomers, such as perfluoro (vinyl ether) (PPVE, PMVE), HFP, or perfluoro(alkylethylenes).

The copolymers are isolated from the aqueous polymerization medium by coagulating, filtering, washing, and drying. The product is recovered from nonaqueous polymerization by evaporating the fluorinated solvent. Finishing usually includes a melt-compaction step in which the dried powders are converted into extruded pellets.

2.5.2. Properties

Physical Properties. The crystal structure of equimolar ETFE copolymer is determined by X-ray analysis. The unit cell is orthorhombic or monoclinic (a = 0.96 nm, b = 0.925 nm, c = 0.5 nm, μ = 96°), and the calculated crystalline density is 1.9 g/cm^3. The carbon chain is in a planar zigzag orientation.

Adjacent $-CF_2$ groups are on opposite sides of the chain, followed by a similar unit for adjacent $-CH_2$ units. Interpenetration of adjacent chains occurs when electronic interactions cause bulky $-CF_2$ groups of one chain to nestle into the space above smaller $-CH_2$ groups of an adjacent chain. Thus, each molecule has four nearest neighbors, creating an orthorhombic lattice. Therefore, ETFE has exceptionally low creep, high tensile strength, and high modulus among fluoropolymers. Interchain forces hold this matrix until the alpha transition occurs at about 110°C, where the physical properties of ETFE begin to decline and more closely resemble perfluoropolymer properties at the same temperature. Other transitions occur at −120°C (γ) and about −25°C (β).

As the degree of monomer alternation is reduced, the ability of chains to interlock is decreased. Thus, as the ethylene content is either increased or decreased from the 50 : 50 ratio, the crystalline content is reduced. Melting points of equimolar ETFE are higher than predicted based on a linear relationship between polyethylene and PTFE melting points. This positive melting point deviation occurs from 35 : 65 to 65 : 35 mole ratios and has its maximum at 50 : 50 alternating copolymer, which melts about 285°C. Melting points are lowered by incorporating modifiers, but the overall shape of a curve with positive melting point deviation is unaltered. Figure 1A provides a graphical

representation of this phenomenon. Most copolymers of TFE with two or three-carbon alkenes show a linear relationship or a negative deviation when melting point is plotted against polymer composition. Ethylene is the only common monomer that shows a positive deviation. Normally produced ETFE has about 88% alternating sequences, and the melting point is reduced to about 270°C [65–67].

A melting point minimum is reached at about 65–70 mol% TFE. At higher TFE levels, melt processability is lowered and the copolymer behaves increasingly like PTFE as TFE–TFE sequences dominate the properties. Below about 45 mol% TFE, ethylene–ethylene sequences increase exponentially. Properties, such as chemical and oxidation resistance are degraded. Most commercial ETFE grades fall between 50 and 65 mol% TFE. Crystallinity ranges from 40–60%, depending on quench rates.

In addition to the crystalline melting point, ETFE resins exhibit three second-order transitions [68]. At 1 Hz, α-, β-, and γ-relaxations were observed at 110, −25, and −120°C, respectively, in a quenched sample. The α- and γ-relaxations are attributed to motions of long and short segments, respectively, in the amorphous regions. The β-transition appears to occur in the crystalline regions. These transition temperatures depend on frequency. The temperature of the α-transition is 145°C when measured at 100 Hz, and 170°C when measured at 10^5 Hz. The γ-transition occurs at −35°C when measured at 10^5 Hz.

Under ambient conditions, ETFE resins are insoluble in many known solvent. This precludes the measurement of molar mass by the usual methods. However, diisobutyl adipate dissolves ETFE resins above 230°C. A high-temperature laser light-scattering apparatus is used to measure the weight-average molar mass $\overline{M}_w$ of ETFE resin in diisobutyl adipate solution at 240°C [69]. Weight-average molar masses, $\overline{M}_w$, are obtained ranging from 5.6×10^5 to 1.1×10^6, with a polydispersity index $\left(\overline{M}_w/\overline{M}_n\right)$ of ca. 1.4. The correlation between melt viscosity (in Pa s) and $\overline{M}_w$ was shown to be

$$\eta(280°) = 1.99 \times 10^{-16} \times \overline{M}_w^{3.4}$$

The molar mass of ETFE resins is normally specified in terms of melt-flow index (MFI),

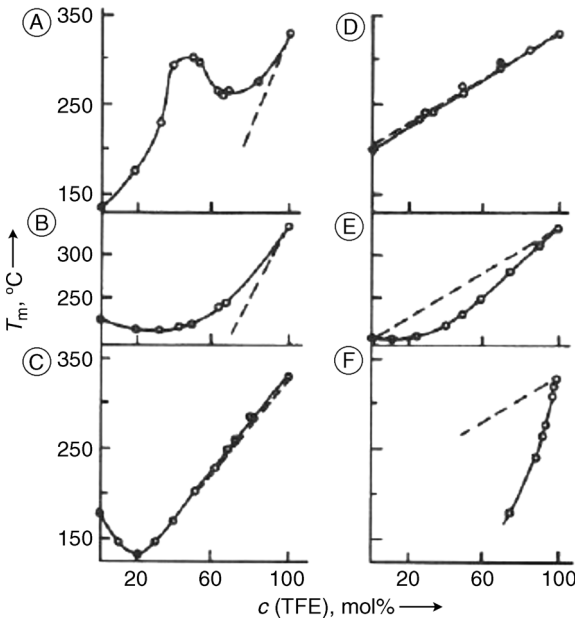


Figure 1. Dependence of melting endotherm maximum on tetrafluoroethylene copolymer composition [34, 67]
A) $CH_2 = CH_2$; B) $CH_2 = CHF$; C) $CH_2 = CF_2$; D) $CF_2 = CHF$; E) $CF_2 = CF_2Cl$; F) $CF_2 = CFCF_3$

Table 14. Properties of ETFE-polymers, FEP, and PTFE [70]

Property	Standard	PTFE	FEP	ETFE*	ETFE (25 wt% glass fiber)*
Specific gravity, g/cm^3	ASTM D 792	2.16	2.14–2.17	1.70	1.86
Melting point, °C	ASTM D 2116	327	260	270	270
Coefficient of linear thermal expansion, K^{-1}	ASTM E 831	12×10^{-5}	9×10^{-5}	9×10^{-5}	3×10^{-5}
Specific heat capacity, kJ kg^{-1} K^{-1}		1.0	1.1	1.9–2.0	
Thermal conductivity at 23 °C, W K^{-1} m^{-1}	ASTM D 696	0.24	0.24	0.24	
Flammability	UL 94	V-O	V-O	V-O	V-O
Oxygen index, %	ASTM D 2863	> 95	> 95	30–32	
Hardness					
Rockwell R	ASTM D 785			R 50	R 74
Durometer D	ASTM D 2240	D 50–65	D 55–57	D 75	
Friction coefficient		0.05–0.08	0.27	0.4	0.3
Water absorption, %	ASTM D 570	< 0.005	< 0.01	0.029	0.022
Upper working temperature, °C		260	200	160	200
Refractive index		1.38	1.344	1.403	

* Values based on ETFE Tefzel grades [2].

measured at 297°C/5 kg in a melt rheometer; values are between 2 and 40 g/10 min (ASTM D 3159-06). General properties are listed in Table 14 [70].

Mechanical Properties. Modified ETFE resins are tougher and stiffer and have higher tensile strength than other TFE polymers, such as PTFE, FEP, or PFA. Typical properties are given in Table 14. As wire insulation, ETFE resins exhibit excellent cut-through and abrasion resistance. It has also excellent impact resistance down to −100°C.

The addition of fillers enhances creep and wear resistance. Unlike other TFE polymers, ETFE can be reinforced by glass fibers. The properties of a 25% glass-reinforced Tefzel ETFE resin are shown in Table 15; it has about twice the tensile strength and heat distortion temperature of the unreinforced resin, and its flexural modulus is also much higher. Its ultimate elongation is low, which is characteristic of reinforced compositions. However, its high toughness is indicated by the high Izod impact values at room temperature as well as at −54°C.

Physical properties, such as modulus, tensile strength, and high-temperature elongation are strongly influenced by the degree of alternation of the comonomers. Room temperature modulus and tensile strength decrease as the ratio of TFE–

Table 15. Properties of ETFE-resins [2]

Property	Standard	ETFE	ETFE (25 wt% glass fiber)
Tensile strength, MPa	ASTM D 638	45	83
Elongation, %	ASTM D 887	200	8
Flexural modulus, MPa	ASTM D 790	1380	6500
Tensile modulus, MPa	ASTM D 638	830	8300
Compressive strength, MPa	ASTM D 695	49	69
Shear strength, MPa		41	45
Izod impact strength, J/m	ASTM D 256		
−54 °C		> 1 070	370
23 °C		no break	490
Deformation under load (13.7 MPa at 50 °C), %		4.1	0.7
Heat deflection temperature, °C	ASTM D 648		
0.45 MPa		104	265
1.8 MPa		74	210
Dielectric constant, kHz	ASTM D 150	2.6	
Dielectric strength (3 mm thickness), kV/mm	ASTM D 149	16–20	
Dissipation factor (1 kHz)	ASTM D 150	8×10^{-4}	
Volume resistivity at 23 °C, Ω cm	ASTM D 256	> 10^{16}	

ethylene is increased. High-temperature elongation is improved; the drop off in tensile strength with increasing temperature is not as great in samples with higher TFE fractions. The operating temperature range of ETFE resins is broad (ca. −100°C to ≥150°C). This upper limit is a conservative estimate based on extensive high-temperature testing. At least half of the original properties are retained after 20 000 h exposure at this temperature. Cross-linking by high-energy radiation or cross-linking agents further enhances its high-temperature mechanical properties [71]. Some radiation-cross-linked ETFE wire constructions have been rated for continuous service at 200°C. Short-term excursions to 240°C are possible for highly cross-linked resins.

Electrical Properties. The ETFE resins serve as excellent insulating materials. Their dielectric constant is low (2.6) and is essentially independent of the frequency. The dielectric strength ranges from 16–20 kV/mm, when measured on 3-mm thick specimens, to 160–200 kV/mm on films 25–75 μm thick [2].

Radiation Resistance. Resistance to gamma and electron beam radiation is excellent. Properties are still useful after exposure to more than 10^6 Gy (100 Mrad). Radiation is more harmful in air than in nitrogen.

Chemical Resistance. Resistance to chemicals and solvents is also excellent [2]. Strong acids and bases, aromatic and aliphatic hydrocarbons, alcohols, ketones, and esters have no effect on ETFE resins. Strong oxidizing acids, organic bases, and sulfonic acids attack ETFE resins to varying degrees at elevated temperatures. Certain high molar mass esters, such as diisobutyl adipate are solvents for ETFE resins above 200°C.

Weatherability. Like other TFE polymers, ETFE resins have outstanding weatherability. Extended exposure in Florida and Arizona had no effect.

Flame Resistance. The ETFE resins are nonflammable in air. Wires insulated with ETFE resins are rated 94V-O by the Underwriters Laboratories, with a LOI of 31%.

2.5.3. Processing

Common techniques such as injection molding, compression molding, blow molding, transfer molding, rotational molding, extrusion, and coating techniques are used for processing ETFE resins. Processing temperatures are usually 280–340°C. Molten ETFE can corrode some steels, and corrosion-resistant steel such as Hastelloy C or Inconel is recommended for equipment parts that come in prolonged contact with molten ETFE resins.

High extrusion rates without melt fracture can be achieved [34]. The critical shear rates for ETFE resins are at about two orders of magnitude greater than for perfluorinated copolymers. Typical values for some ETFE Tefzel grades are reported in Table 16.

ETFE powders can be sprayed electrostatically, followed by baking to coalesce the particles into coatings.

Parts produced from ETFE are easily welded by melt-bonding, such as spin welding, ultrasonic welding, and conventional butt welding using a flame and an ETFE rod. ETFE also bonds well to untreated metal surfaces.

2.5.4. Uses

The largest market for ETFE is for wire and cable applications including automotive wire, computer back panels and back planes, lighting and instrument wiring in mass transit vehicles, heat trace cable, and down hole cables for data transmission during oil exploration. About 30% of ETFE resins are used in chemical processing and architectural applications, including tank, pump, valve and pipe linings, and extruded or molded items, such as tower packings, valve seats, mist eliminators, fittings, pipes, and tubes. Other applications include heat-shrink tubing, wire tie wraps, sockets, connectors, insulators, lithium battery cases, seal glands, and pipe plugs as well as low-permeability multilayer tubing for fuel management systems. Films for architectural applications is a fast growing segment, due to the transparency to UV-light it

Table 16. Melt-flow index and critical shear rate for some ETFE Tefzel grades

Product grade	Melt-flow index (297 °C/5 kg), g/10 min	Critical shear rate, s^{-1}
Tefzel 210	45	12 000
Tefzel 200	8	4 800
Tefzel 280	3	4 500

is used in greenhouses, but also in membrane structures for building.

2.6. Polychlorotrifluoroethylene

Polychlorotrifluoroethylene [9002-83-9] (PCTFE) is a linear, high molar mass polymer with the general formula:



The worldwide consumption of PCTFE including VDF modified polymers was about 5 400 t in 2008. PCTFE is semicrystalline (*mp* ca. 210°C) and can be processed by conventional methods. It has good mechanical properties, chemical inertness, radiation resistance, and low vapor permeability. The introduction of chlorine atom in the polymer structure interrupts the crystallization ability of the polymer chain and results in lower crystallinity, lower melting temperature, better intermolecular interaction, and better mechanical properties compared to PTFE. Manufacturers for PCTFE are Arkema (Voltalef), Daikin (Neoflon), Honeywell (Aclon); Honeywell also produces PCTFE-VDF-copolymers (Aflon).

2.6.1. Production

Polychlorotrifluoroethylene can be polymerized to high molar masses in bulk [72], solution [73], suspension [11], or emulsion systems [74] using free-radical initiators. The emulsion process is carried out at low temperature with a persulfate–bisulfite redox catalyst or organic peroxides. The polymer emulsion is coagulated by freezing or by the addition of salts. The isolated polymer is washed to remove initiator residues and dried.

The dried powders can be stabilized by the addition of phenols or salts of organic acids to help prevent discoloration and bubbling during processing. The tendency for PCTFE to become brittle during use can be reduced by incorporating a small amount (< 5%) of vinylidene fluoride during polymerization; this modification improves also processability.

2.6.2. Properties

The crystallinity of PCTFE ranges from 45% (quick-quenched) to 65% (slow-cooled). The molar mass of PCTFE resin ranges from 1×10^5 g/mol to 5×10^5 g/mol. The useful temperature range is between −200 and 180°C. Other properties are shown in [75–77] and below:

mp, °C	211–216
Second-order transition (amorphous), °C	71–99
Coefficient of thermal expansion, K^{-1}	$(4–7) \times 10^{-5}$
Specific heat, kJ kg^{-1} K^{-1}	0.92
Specific gravity, g/cm^3	2.10–2.18
Specific gravity (amorphous), g/cm^3	2.077
Specific gravity (crystalline), g/cm^3	2.187
Tensile strength at 23°C, MPa	30–40
Elongation at 23°C, %	100–200
Flexural modulus, MPa	1 000–2 000
Hardness, Shore D	80
Dielectric constant at 100 Hz to 1 MHz	2.3–2.7
Dissipation factor at 1 kHz	0.023
Dielectric strength (0.1 mm film), kV/mm	120–150

The α-, β-, μ-relaxations have been determined at various frequencies. Resistance to attack by most chemicals is good. However, chlorinated fluorinated compounds, ketones, and aromatic compounds, such as benzene, toluene, and xylene swell PCTFE resins. They are impermeable to water vapor as well as other gases. They are nonflammable (LOI = 95%) and exhibit outstanding stability to UV and gamma radiation. The coefficient of friction is low; antistick properties are excellent.

CTFE–VDF copolymers have the lowest water vapor transmission of any available transparent plastic. PCTFE displays excellent embrittlement-resistance properties in contact with liquid gases. It also exhibits superior outgasing (barrier) characteristics and is impervious to UV-light and γ-radiation. In addition, the PCTFE-resins show excellent creep resistance at cryogenic temperatures.

2.6.3. Processing

Polychlorotrifluoroethylene resins can be processed by the usual methods for thermoplastic materials, such as extrusion, injection molding, and transfer molding. As with other fluoropolymers, corrosion-resistant materials should be

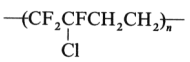
used for equipment parts in contact with the melt. Processing temperatures are in the range of 280–350°C. However, degradation begins at ca. 280°C and thus always accompanies the processing of PCTFE resins. Partial degradation does not seem to affect properties greatly, but severely degraded PCTFE becomes highly crystalline and its mechanical properties suffer. In injection molding, the mold should be heated to 70–130°C. Corrosion-resistant coatings of PCTFE resins can be applied from aqueous dispersions (30–60% solids) by dipping or spraying followed by drying and sintering. Finely divided PCTFE powders (particle size < 150 μm) are used for powder coating.

2.6.4. Uses

Due to the outstanding barrier properties, PCTE resins are widely used as packaging films for drugs and medical products (blister packs for drugs that require oxygen-free storage). Electronics is another large market segment, e.g., for chemical resistant electrical insulation, semiconductor-processing equipment, computer chip production uses PCTFE because of the low moisture absorption properties. PCTFE's toughness in harsh cryogenic environment (e.g., liquid oxygen, nitrogen) for seals and globes is considered useful in the military sector. Low molar mass oils and greases are used as sealants and lubricants.

2.7. Chlorotrifluoroethylene–Ethylene Copolymers

Copolymers of CTFE and ethylene (ECTFE resins) [25101-45-5] are linear, semicrystalline polymers composed of alternating monomer units:



The worldwide consumption was about 2 000 t in 2008. These resins have high tensile strength, moderate stiffness, and good flex life and impact strength. Electrical properties, chemical resistance, weatherability, radiation resistance, and nonflammability are good. The usual processing methods, such as extrusion, injection molding, and transfer molding, are employed. The resins are readily converted into fibers, filaments, films, sheets, and wire and cable insulation. Powder forms are available for the preparation of void-free, low-permeability coatings on metals by electrostatic and fluidized-bed processes. Solvay Solexis is the sole world producer of ECTFE (Halar).

2.7.1. Production

Ethylene and CTFE can be copolymerized by the techniques used for other fluoroolefins. However, to prepare commercially useful products, the copolymerization must be carried out at low temperature (preferably 10°C or below) to reduce the amount of ethylene blocks in the polymer backbone that are susceptible to thermal degradation. Commercial resins with a overall 1 : 1 CTFE : ethylene ratio contain less than 10 mol% of ethylene and CTFE-blocks. A typical polymerization employs a mixture of CTFE and ethylene in water at 10°C, with trichloroacetyl peroxide as catalyst and chloroform as chain-transfer agent [78]. Under these conditions, the copolymerization takes place in the condensed CTFE phase. Water acts as a dispersant and heat-transfer medium. Copolymerization has been carried out at even lower temperatures (between −40 and −80°C), using oxygen-activated trialkylborons as initiators [79]. Modified copolymers with improved thermal stress–crack resistance are prepared similarly [34]. Modifiers include perfluoro(alkyl vinyl ethers), perfluoroalkylethylenes [80], and 2-trifluoromethyl-3,3,3-trifluoroprop-1-ene. Over the course of polymerization, the polymer can agglomerate into spherical beads. Low concentrations of stabilizer additives are added to the dried resins to improve thermal stability. The stabilized powders are melt-pelletized or ground and screened into powder coating grades.

2.7.2. Properties

Physical Properties. The crystallinity of commercial ECTFE resins is in the 50–60% range. X-ray diffraction studies indicate that the unit cell of the alternating copolymer is hexagonal,

with a chain repeat distance of $c = 0.50$ nm [78]. The molecular conformation is an extended zigzag, with an ethylene unit on one chain adjacent to a CTFE unit on another chain.

The melting point of an ECTFE copolymer is a function of the molar ratio and the degree of alternation of the two monomers. Commercial ECTFE resins are 1 : 1 copolymers of CTFE and ethylene, 80–90% alternating. They have melting points in the range of 235–245°C. A 1 : 1 copolymer prepared at −80°C, essentially 100% alternating, melts at 264°C [79]; second-order transitions are observed at 140°C, 90°C, and −65°C. The α- and γ-transitions are associated with the motion of chain segments in the crystalline regions, whereas the β-transition seems to be associated with the amorphous region.

The number-average molar mass ($\overline{M}_n$) of ECTFE resins, determined by osmometry at 150°C, ranges from 1×10^5 g/mol to 5×10^5 g/mol; other properties are shown below:

mp, °C	236–246
Coefficent of thermal expansion, K^{-1}	8×10^{-5}
Specific gravity, g/cm^3	1.63 – 1.73
Tensile strength, MPa	45–55
Elongation, %	200–260
Flexural modulus, MPa	1 800–2 500
Hardness, Shore D	78
Izod impact strength, J/m	
23°C	no break
−40°C	120–60
Dielectric constant (60 Hz to 1 kHz)	2.55–2.60
Dissipation factor (ASTM D 150)	
60 Hz	< 0.005
1 MHz	0.0024
Dielectric strength (0.2 mm film), kV/mm	80–90
Volume resistivity, Ω cm	$> 10^{15}$
Maximum service temperature, °C	150

Mechanical Properties. The ECTFE resins are tough, moderately stiff, and creep resistant. They are usable over a broad temperature range (−100 to 150°C). Abrasion resistance and the heat distortion temperature are good and can be enhanced with fillers. ECTFE-film is the most abrasion resistant fluoropolymer film and has the highest tensile strength.

Chemical Resistance. Both ECTFE and PCTFE resins are similar in chemical resistance. They exhibit good stability toward acids, bases, and halogens. There are no known solvents for these polymers below 120°C, but amines, esters, and ketones can attack ECTFE resins, especially when warm. These resins have excellent barrier properties to water vapor and other gases. In this respect, they are superior to the perfluorinated plastics.

Weatherability and Radiation Resistance. Like most fluoropolymers, ECTFE resins exhibit outstanding weathering resistance. They also resist high-energy gamma and beta emission. The polymer retains useful properties after absorbing more than 10^6 Gy (100 Mrads) of radiation. Cross-linking by exposure to low doses 50–150 kGy (5–15 Mrads) enhances the high-temperature mechanical properties.

Flame Resistance. The ECTFE resins are nonflammable; they burn when exposed to a flame, but are self-extinguishing when the flame is removed. They are nondripping and form a char; LOI is 64%.

2.7.3. Processing

The standard processing methods for thermoplastics, such as extrusion, injection molding, and transfer molding, are employed to process ECTFE. Extrusion is used to manufacture tubing, hose, and wire and cable insulation. Temperatures from 260 to 300°C can be used, but should be kept as low as possible to prevent degradation. Extrusion of ECTFE resins is possible at high rates without degradation. Molten ECTFE resins can be corrosive. A corrosion-resistant steel, such as Hastelloy-C or Inconel is recommended for metal surfaces in contact with the molten polymer. In injection molding of ECTFE resins, the melt temperature should be from 260 to 300°C; for best results, the mold should be heated to 60–100°C. Metals are coated by powders of average particle size below 150 μm using an electrostatic or fluidized-bed process. Coatings of 1 mm or thicker can be obtained free of voids and cracks.

2.7.4. Uses

The principal use of ECTFE resin is in flame-resistant wire and cable insulation [81]. Monofilament made from ECTFE resin is used in the

manufacture of chemical-resistant filters and screens. Other applications include coatings and linings for chemical process equipment. Rotomolded tanks and containers made from ECTFE resins are used to store corrosive chemicals, e.g., nitric and hydrochloric acids. Extruded sheet is used for thermoforming various products, such as battery cases for heart pacemakers. Tubing made from ECTFE resin is used in laboratory and some automotive applications.

The smooth surface of ECTFE reduces the tendency for adhesion of dirt and microorganisms, which is essential for semiconductor and water applications [34].

2.8. Poly(Vinylidene Fluoride)

Poly(vinylidene fluoride) [9002-85-1], poly (1,1-difluoroethylene) (PVDF) is a linear, high molar mass, semicrystalline polymer that can exist in three distinct crystalline forms and has the following structure:

$$-(CH_2CF_2-)_n$$

The worldwide consumption including copolymers was about 2.9×10^4 t in 2008. The alternating CH_2 and CF_2 groups create a dipole that confers solubility in highly polar solvents, such as dimethylformamide and dimethylacetamide. In addition, PVDF has a high dielectric constant and exhibits piezoelectric properties under certain conditions. It has excellent resistance to abrasion, stress fatigue, and cold flow. Like PTFE and TFE copolymers, it has outstanding weatherability. It also exhibits excellent resistance to gamma and beta radiation. The usable temperature range is from ca. −40 to +150°C. The resins are processable by extrusion, injection molding, and other molding techniques. Copolymerization with HFP (< 15%) improves processability, flexibility, and impact strength.

Uses for PVDF resins include durable finishes for exterior metal siding, electrical insulation, and chemical process equipment. Manufacturers for PVDF and copolymers are Arkema (Kynar), Daikin (Neoflon), 3M (Dyneon), Kureha (KF Polymer), and Solvay Solexis (Solef). Chinese fluoropolymer producers have also started PVDF production.

2.8.1. Production

The most common methods for producing PVDF homopolymers and copolymers are emulsion and suspension polymerization. In suspension polymerization, organic peroxides are used as initiators including chain-transfer agents to control molar mass; colloidal dispersants (e.g., cellulose derivatives, polyvinyl alcohol) are often employed. The product is a slurry of suspended particles, which are recovered by filtration. Inorganic peroxides (e.g., persulfates) give polymers with lower thermostability and which are prone to discoloration. In emulsion polymerizations organic peroxides, chain-transfer agents, and mostly fluorinated emulsifiers are also used; due to environmental concerns, nonfluorinated surfactants are nowadays recommended [82–85]. The polymerizations are typically carried out at 70–150°C at pressures up to 7–10^6 Pa.

HFP and CTFE are most commonly employed to prepare PVDF-copolymers (commercial thermoplastic resins contain less than 15 mol% comonomers). To obtain constant compositions, the comonomers have to be adjusted according to their reactivity ratios [34]:

VDF : CTFE	$r_1 = 0.13$	$r_2 = 3.73$
VDF : HFP	$r_1 = 2.45$	$r_2 = 0.00$

2.8.2. Properties

Physical Properties. Poly(vinylidene fluoride) has a highly regular structure, with most VDF units joined head-to-tail and with ca. 5% of the monomer units joined head-to-head. Crystallinity is between 40% and 60%; three different crystalline forms exist.

In phase I (β-form), the polymer crystals are orthorhombic, and the molecules adopt a planar zigzag conformation. In phase II (α-form), the crystals are monoclinic, and the molecules adopt a gauche-trans-gauche-trans conformation. In phase III (γ-form), the crystals are believed to be monoclinic, but the molecules adopt a planar zigzag conformation. Slow or rapid cooling of polymer from the melt yields only phase II. Conditions for converting one form to another have been established [86].

Because of its polymorphism, the melting point of PVDF is not precisely defined (154–184°C). The melting point of the more

Table 17. Properties of PVDF homopolymers and PVDF copolymers [34]

Property	Standard	PVDF homopolymer	PVDF copolymers
Specific gravity, g/cm^3	ASTM D 792	1.75–1.80	1.75–1.79
Melting temperature, °C	ASTM D 34518	160–180	125–170
Refractive index n_D^{25}	ASTM D 542	1.41–1.42	1.40–1.42
Water absorption, %	ASTM D 570	0.01–0.04	0.03–0.09
Tensile strength, MPa	ASTM D 638		
yield		31–57	14–42
break		27–52	15–42
Elongation at break, %	ASTM D 638	50–250	200–500
Tensile modulus, MPa	ASTM D 882	1 030–2 410	480–1040
Flexural modulus, MPa	ASTM D 790	1 130–2 280	240–1180
Izod impact strenghth (25 °C), J/m	ASTM D 256		
notched		110–300	320–NB*
unnotched		800–4 500	3 600–NB*
Hardness, Shore D	ASTM D 2240	75–80	55–75
Abrasion resistance, mg/1 000 cycles	CS-17, 1 000 g	5–9	6–20
Friction coefficient (to steel)		0.14–0.17	
Heat deflection temperature, °C	ASTM D 648		
0.46 MP	a	119–148	
1.82 MPa		84–118	
Thermal conductivity, W K^{-1} m^{-1}	ASTM D 433	0.17–0.19	0.16–0.18
Coefficient of linear expansion (~ RT), K^{-1}	ASTM D 696	$0.7–1.5 \times 10^{-4}$	$1.0–1.5 \times 10^{-4}$
Limiting oxygen index, %	ASTM D 2863	42–80	42– 95

* NB = no break.

common phase II form is ca. 170°C; a glass transition temperature is observed at −40°C. Properties of PVDF resins are shown in Table 17.

PVDF has one of the lowest melting points of commercial fluorothermoplastics, but has the highest heat deflection temperature under load (see Table 18).

PVDF and ETFE are isomeric, but PVDF has a melting point in the range of 150–180°C compared to 260–275°C for ETFE. In both polymers, the alternating units can crystallize with larger CF_2 groups adjacent to smaller CH_2 units of adjacent chains. This penetration increases the moduli for ETFE and PVDF. Perfluoropolymer chains do not have such penetration; thus, they slide past one another, leading to higher creep and lower modulus values.

The high crystallinity and surface tension properties of PVDF provide very low permeation values (see Table 19) compared to other fluoropolymers.

Mechanical Properties. A comparison of mechanical properties of PVDF to those of ETFE and ECTFE at room temperature is provided in Table 20. The tensile modulus is similar but impact strength is lower. Modification with HFP or CTFE lowers the modulus, but increases elongation and impact strength (see Table 17).

Electrical Properties [10]. A high dielectric constant and dissipation factor impair the utility of PVDF as a primary wire and cable insulation. However, these "poor" electrical properties allow the production of PVDF films with their piezoelectric and pyroelectric properties. These films are prepared from extruded films in the phase I (β-form) conformation, obtained by stretching the film as it is extruded; ultrapure polymer is required. Both surfaces of the film are metallized, and it is then subjected to a high voltage, which leaves it permanently polarized. Such films generate a voltage when stretched or compressed (piezoelectricity) or heated (pyroelectricity).

Table 18. Comparison of deflection temperature and *mp* of fluoropolymers (ASTM D 648) [34, 87]

	Deflection temperature, °C		*mp*, °C
	0.5 MPa	1.8 MPa	
PVDF	148	113	178
PCTFE	126	75	218
PTFE	121	56	327
ECTFE	116	77	240
ETFE	104	74	270
PFA	73	48	310
FEP	70	51	270

Table 19. Gas permeability of fluoropolymers[a] [34, 88]

	PTFE	PFA	FEP	ETFE	PCTFE	ECTFE	PVDF	PVF
Water vapor, g m^{-2} d^{-1} bar^{-1}	5	8	1	2	1	2	2	7
Air, cm^3 m^{-2} d^{-1} bar^{-1}	2000	1150	600	175	NA[**]	40	7	50
Oxygen, cm^3 m^{-2} d^{-1} bar^{-1}	1500	NA[**]	2900	350	60	100	20	12
Nitrogen, cm^3 m^{-2} d^{-1} bar^{-1}	500	NA[**]	1200	120	10	40	30	1
Helium, cm^3 m^{-2} d^{-1} bar^{-1}	3500	17 000	18 000	3 700	NA[**]	3 500	600	300
Carbon dioxide, cm^3 m^{-2} d^{-1} bar^{-1}	15 000	7000	47 00	1 300	150	400	100	60

[*] Based on 100 μm film thickness at 23 °C. Gases were measured according to ASTM D 1434-82; Water permeation was measured according to DIN 53122.
[**] NA = not available.

Chemical Resistance. Resistance of PVDF to halogens, most inorganic acids and bases, alcohols, halogenated hydrocarbons, and aromatics is good. PVDF is, however, soluble in polar solvents, such as acetone and ethyl, butyl, and amyl acetate, amines and amides. It is also soluble in supercritical media (e.g., CO_2, CHF_3, CH_2F_2, etc.) [89].

Weather and Radiation Resistance. Resistance of PVDF to UV light is excellent (no effect after 5 000 h exposure in Weather-O-Meter). Tolerance to ionizing radiation is very high. Low radiation doses of 20–150 kGy (2–15 Mrads) cause cross-linking, which enhances the high-temperature modulus of PVDF.

Flame Resistance. When exposed to flame, PVDF is nonflammable and nondripping; it is self-extinguishing after the flame is removed. The LOI is 44%.

2.8.3. Processing

Poly(vinylidene fluoride) can be processed by the usual techniques for thermoplastics, such as extrusion and transfer, injection and compression molding. Metal coatings are applied from organisols (mixtures of resin and solvent) in a process called coil coating. Typically, the organisol is applied to coil stock of steel or aluminum. The film is formed on the metal surface as the solvent evaporates. In extrusion, attention should be paid to the elimination of dead spots where degradation of the polymer can start. The temperature should be between 215 and 270°C. Similarly, in injection molding, the melt temperature should be between 200 and 270°C.

2.8.4. Uses

The largest application for PVDF is within architectural coatings. Typically, PVDF is

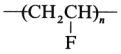
Table 20. Typical physical properties of PVDF, ETFE, and ECTFE

Property	Standard	ETFE	PVDF	ECTFE
Melting temperature, °C	ASTM D 3418	250–275	154–184	236–246
Specific gravity, g/cm^3	ASTM D 792			
Melt		1.3		
Solid		1.72	1.75–1.80	1.7
Tensile strength (23 °C), MPa	ASTM D 638	38–48	36–56	45–60
Elongation (23 °C), %	ASTM D 638	100–350	25–500	150–250
Tensile modulus (23 °C), MPa	ASTM D 638	830	1 340–2 000	
Izod impact strength (23 °C), J/m	ASTM D 256	no break	160–530	no break
Coefficient of thermal expansion	ASTM D 696	9×10^{-5}	$\sim 10^{-4}$	5×10^{-5}
Critical shear rate, s^{-1}		200–10000		
Processing temperature range, °C		300–345	200–300	260–300
Dielectric constant (1 kHz)	ASTM D 150	2.6	7.5–13.2	2.6
Dielectric strength, kV/mm	ASTM D 149	59	260–950	80–90
Dissipation factor (1 kHz)	ASTM D 150	0.0008	0.013–0.019	0.0024
Limiting oxygen index, %	ASTM D 2863	30	44	64

sold as powder for coating metal coils for the production of metallic roofing, window frames, panel siding, and other construction units. It is also used as wire insulation in the aircraft and electronics industries. Heat-shrinkable tubing made from PVDF resin forms solder sleeves that are used in electronic, aerospace, and aircraft industries. It is used on a large scale for solid PVDF pipe and fittings and as a liner for pipes and valves. Piezoelectric PVDF films are very sensitive transducers with various applications [90].

2.9. Poly(Vinyl Fluoride)

Poly(1-fluoroethylene) [24981-14-4], poly (vinyl fluoride) (PVF) is a high molar mass, semicrystalline polymer with a melting point of 180–210°C and the following structure:



It is considered a thermoplastic but cannot be processed by conventional thermoplastic techniques because it is unstable above its melting point. It can be fabricated into films by mixing with latent solvents (i.e., solvents that alone do not dissolve the polymer, but behaves as an active solvent when used in conjunction with an active solvent) and extruding at a temperature below the melting point. (Dissolution in latent solvents takes place at an elevated temperature below the melting point of the PVF.) Films made from PVF have exceptional resistance to sunlight, chemical attack, and water adsorption. They are also extremely tough and have good abrasion resistance. These unusual properties make PVF highly suitable for outdoor coatings or laminates. Films of various tensile modifications and thicknesses are available with adhereable and nonadhereable surfaces. These films are manufactured by DuPont under the Tedlar trade name. DuPont is the sole producer for PVF; the worldwide consumption was about 3 000 t in 2008.

2.9.1. Production

Vinyl fluoride is polymerized by free-radical processes [10]. It is, however, more difficult to polymerize than TFE or VDF and requires higher pressures [91]. Polymerization is carried out in aqueous media between 50°C and 150°C at a pressure of 3.4×10^6–34.4×10^6 Pa. The usual catalysts are peroxides and azo compounds. A continuous process employs water, VF, and catalyst at 100°C and 27.5×10^6 Pa [92]. Polymers have also been prepared at lower temperatures (−30 to 55°C) using oxygen-activated trialkylboron catalysts [93]. The polymerization temperature affects the crystallinity and the melting point of the product; higher temperatures also increase branching.

2.9.2. Properties

Physical and Mechanical Properties. The monomer units in PVF are predominantly head-to-tail, with 12–18% head-to-head [94]. The proportion of head-to-head units decreases with decreasing polymerization temperature. Conversely, randomness increases with increasing polymerization temperature.

The number-average molar mass of PVF resin ranges from 7.6×10^4 g/mol to 2.3×10^5 g/mol, the weight-average molar mass ranges from 1.43×10^5 g/mol to 6.54×10^5 g/mol. The ratio of weight-average to number-average molar mass is 2.5 : 5.6 [95].

The melting point of PVF varies with polymerization temperature but is in the range of 185–210°C. Torsion-pendulum studies indicate that PVF has second-order transitions at 41°C and −20°C. The temperature range for continuous use is −70 to 110°C. The mechanical (ASTM D 882 and 1004) and physical properties of PVF film are shown in [94]:

mp, °C	185–190
Specific gravity, g/cm^3	1.38–1.72
Tensile strength, MPa	~50
Elongation, %	115–250
Tensile modulus, MPa	1 700–2 600
Impact strength, kJ/m	10–22
Tear strength, kJ/m	174–239
Coefficient of thermal expansion, K^{-1}	5×10^{-5}
Dielectric constant, 1 MHz	6.5
Dielectric strength (0.1 mm film), kV/mm	120–140

Chemical Resistance. Poly(vinyl fluoride) is insoluble in ordinary solvents below 100°C. At higher temperature, it is soluble in polar solvents, such as amides, ketones, tetramethylene sulfone, and tetramethylurea.

Films show good resistance to acids and bases at room temperature. The resistance to aliphatic (petroleum), aromatic, and alcoholic liquids is also very good. Warm acetone attacks PVF.

Weather and Radiation Resistance. PVF films have excellent light and weather resistance, showing no change after 10 years outdoor exposure. They are transparent to both UV and visible light. A 25-μm thick film has over 90% transmission between 400 and 1400 nm and over 80% between 230 and 400 nm.

In addition, PVF films show good resistance to high-energy radiation. Usable properties are retained up to 1 MJ/kg exposure to electron beam radiation.

2.9.3. Processing

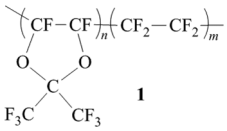
The polymer is dissolved in a latent solvent. Pigments, stabilizers, and plasticizers can be added to the PVF organosol before extrusion. The organosol is extruded into film, and the solvent is evaporated and recovered. The film can be oriented in varying degrees to achieve different levels of tensile and tear strength. Exposure to such treatments as corona discharge or alkali metal in liquid ammonia solution imparts adhesiveness.

2.9.4. Uses

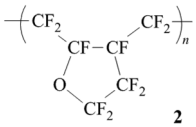
Poly(vinyl fluoride) films are laminated to sheets of metal with special adhesives. The laminates are used for exterior siding on industrial and residential buildings. Pigmented films can be made in any color. Films can also be laminated to hardboard, paper, polystyrene, polyurethane, and other substrates. These laminates are used for wall coverings, aircraft cabin interiors, pipe covering, duct liners, as well as other applications. A weather-resistant PVF barrier is also resistant to abrasion, chemicals, solvents, and staining. Another application for PVF film is as a release sheeting in the molding of phenolic, epoxide, and polyester plastics, and as a release film for bag molding. It does not become brittle and strips easily from the mold. Toughness is maintained at elevated temperatures at all degrees of humidity and in contact with common solvents. The film has been used for photovoltaic applications because of its high transparency and resistance to solar radiation.

2.10. Amorphous Perfluoropolymers

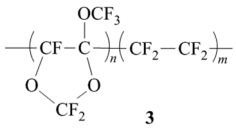
Before 1980, all commercial fluoropolymers were semicrystalline materials, having shortcomings, such as low optical transparency, high creep, or poor solubility. Since mid-1980s, amorphous perfluoropolymers with high glass transition temperatures have been developed and commercialized. These polymers are linear, high molar mass polymers with the general formula:



1



2



3

These polymers retain outstanding chemical, thermal, and surface properties of perfluorinated polymers in addition of having excellent electrical and optical properties. They are also soluble at ambient temperatures in fluorinated solvents.

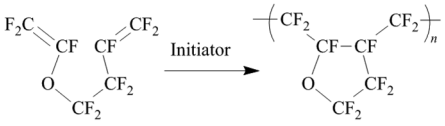
These resins are manufactured by Asahi Glass (Cytop, **2**), DuPont (Teflon AF, **1**), and Solvay Solexis (Hyflon AD, **3**). Current consumption of amorphous fluoropolymers is still very small.

2.10.1. Production

The commercial grades of Teflon AF [37626-13-4] and Hyflon AD [161611-79-6] are copolymers of tetrafluoroethylene and the corresponding dioxole monomers. They are produced by free-radical initiators in nonaqueous media or in aqueous media with a fluorinated emulsifier [96]. Both dioxole monomers form amorphous homopolymers with glass transition temperatures of 335°C for the Teflon AF dioxole-monomer (PDD = perfluoro-2,2-dimethyl-1,3-dioxole) and of 162°C for the Hyflon AD dioxole-

monomer (TTD = 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole) [97]. The PDD-homopolymer is difficult to melt-process because of the narrow processing window below its decomposition temperature. TFE-copolymers with less than 20 mol% PDD are no longer amorphous. At 20 mol% PDD, the T_g of the copolymer is about 80°C. During aqueous polymerization, small amounts of acid fluoride or carboxylic acid groups may be produced by ring opening. These unstable groups are removed and converted to perfluorinated groups by first treating the polymer with ammonia followed by post-fluorination [98].

Cytop [101-182-89-2] is a homopolymer that is synthesized via a unique cyclopolymerization of perfluoro-3-(butenyl vinyl ether) (PBVE) [99, 34].



The glass transition temperature is about 108°C.

2.10.2. Properties

Amorphous perfluoropolymers exhibits good thermal stability with small mass losses at temperatures up to 400°C. In addition, they have excellent chemical resistance, low surface energy, and high LOI.

The mechanical properties differ from those of semicrystalline polymers. Below the glass transition temperature, the tensile module is higher and the creep is generally less and shows less variation with temperature.

These amorphous polymers are soluble at ambient temperature in a variety of fluorinated solvents [34]. The optical properties are outstanding; the optical transmission is greater than 90% throughout most of the UV, visible, and near-IR-spectrum. Teflon AF grades show the lowest refractive indices of any known polymer.

Investigations of Teflon AF grades reveal that the structure is characterized by microvoids; these voids result in a lower than expected polymer specific gravity, low dielectric constant, low refractive index, high gas permeability, and low thermal conductivity. Most likely, the origin of these microvoids is loose chain packing caused by the high energy for rotation and reorientation of the dioxole ring containing polymer chains. The dielectric constant of Teflon AF is the lowest of any know polymer, on the other hand, the gas permeabilities are more than two orders of magnitude higher than, for example, for PTFE [34].

The microstructure of Cytop was also analyzed by positron annihilation lifetime spectroscopy [100]. General properties of amorphous polymers are given in Table 21.

Table 21. Properties of amorphous perfluoropolymers, PFA and PMMA [34]

Property	Cytop	Teflon AF	PFA	PMMA	Remarks
Light transmittance, %	95	95	opaque	93	visible region
Refractive index	1.34	1.29–1.31	1.35	1.49	Abbe's refractometer
Abbe's number	90	92–113		55	Abbe's refractometer
Dielectric constant	2.1 ~ 2.2	1.9	2.1	4	60 Hz–1 MHz
Dissipation factor	7×10^{-4}	12×10^{-4}	$<2 \times 10^{-4}$	0.04	60 Hz
Volume resistivity, Ω cm	$> 10^{17}$		$> 10^{18}$	$> 10^{16}$	RT in air
Dielectric strength, kV/0.1 mm	11	1.9–2.1 [2]	12	2	RT in air
T_g, °C	108	160–240	75	105–120	DSC
mp, °C	not observed	not observed	310	160 (isotactic)	DSC
Specific gravity, g/cm^3	2.03	1.7–1.8	2.12–2.17	1.20	25 °C
Contact angle of water, °C	110	104	115	80	25 °C
Critical surface tension, N/cm	19×10^{-5}	16×10^{-5}	18×10^{-5}	39×10^{-5}	25 °C
Water absorption, %	< 0.01	< 0.01	< 0.01	0.3	60 °C, H_2O
Tensile strength, MPa	39	27	> 28	65–73	
Elongation at break, %	150	> 20	> 280	3–5	
Yield strength, MPa	40		11–15		
Tensile modulus, MPa	1 200	1 600	580	3 000	

2.10.3. Processing

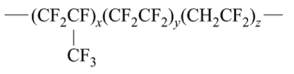
The commercial amorphous perfluoropolymer can be melt-processed by all conventional techniques, such as extrusion, compression, or injection molding. Solutions of amorphous polymers can be used for spin coating, dip coating, spraying, or casting. Spin coating is used to produce very thin and uniform coatings on flat substrates. Dip coating is suitable for nonplanar surfaces. Laser ablation and vacuum pyrolysis techniques are also used.

2.10.4. Uses

Because of their low refractive indexes and excellent optical clarity, amorphous fluoropolymers are used in fiber optics cladding and core applications. Other applications include photolithography, lens covers, antireflective coatings, passivation, and protective coatings for various microwave, radar, optical, and optoelectronic devices in medical, military, aerospace, and industrial markets. Electronic applications include dielectric layers for high density and hybrid integrated circuits, passivation layers, and encapsulation of hybrid and sandwich integrated circuit packaging.

2.11. Semicrystalline Tetrafluoroethylene-Hexafluoropropene-Vinylidene Fluoride Terpolymers

Terpolymers of variable amounts of tetrafluoroethylene (TFE), hexafluoropropene (HFP) and vinylidene fluoride (VDF) [THV resins] are linear, semicrystalline polymers with the following structure:



THV polymers were invented by Hoechst during the late 1980s and commercialized by 3M in 1995. By combining these three monomers, unique properties for THV resins can be achieved, for example, low processing temperatures, bondability, high flexibility, excellent clarity, and low refractive indexes as well as efficient E-beam cross-linking. THV resins are manufactured by 3M; the worldwide consumption was about 1 000 t in 2008.

2.11.1. Production

Based on the Q/e reactivity ratios of the three monomers, most information to design a wide range of THV terpolymer are available; known Q/e value are scattered, but show a common trend: TFE ($Q \sim 0.032$, $e \sim 1.63$), HFP ($Q \sim 0.005$; $e \sim 1.50$), VDF ($Q \sim 0.015$; $e \sim 0.50$) [101]. THV polymers are polymerized in aqueous emulsion in the presence of fluorinated emulsifiers. The preferred initiator is the $KMnO_4$-system for temperature ranges from 30°C up to 80°C; the pressure can go up to 2.0×10^6 Pa. Chain-transfer agents are hydrogen, C_1–C_5-alkanes, or dimethyl ether [102].

The obtained latices have solid contents of about 35 wt%. $KMnO_4$-initiators provide carboxylic and $-CH_2OH$ endgroups, which do not lead to discoloration, whereas persulfate-initiated polymerizations have significant amounts of sulfate endgroups, which cause discoloration during certain processing methods. Hydrocarbon surfactants can also be used to polymerize THV polymers [103]. THV resins are isolated from the aqueous latices by applying high shear forces; agglomerated powders as well as melt-pelletized granules are commercially available. Concentrated dispersions with solid contents up to 50 wt% and stabilized with hydrocarbon surfactants are also offered.

2.11.2. Properties

Depending on the ratio of the three monomers, THV resins can be tailored to have melting points from 120°C up to 230°C (see Fig. 2). Melt viscosity is adjustable over a wide range. THV polymers are well characterized by GPC and rheological measurements. The polymers have usually a linear topography, and MFI values (265°C/5 kg) correlate well with molar mass ($1/\mathrm{MFI} \sim \eta_0 \sim \overline{M}_w^{3.8}$). Molar mass distribution is usually quite narrow $\left(\overline{M}_w/\overline{M}_n \sim 1.7\right)$ [104]. Long chain branched (LCB) THV polymers are prepared by the addition of small amounts of reactive modifiers (e.g., $CF_2 = CHBr$, diolefins) during polymerization; LCB-

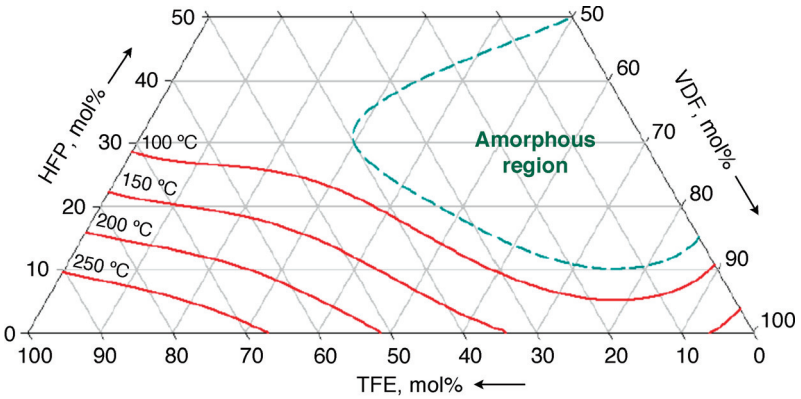


Figure 2. THV melting points versus chemical composition

THVs combine good mechanical properties with high structural viscosity [105, 106].

The low melting grade THV 200 is soluble in common organic solvents. THV 200 and THV 500 have relatively low processing temperatures (220–250°C), which offer new options for coprocessing. Both grades have also low flexural moduli between 8×10^7 Pa and 2.5×10^8 Pa. THV polymers are the most flexible of the melt-processable semicrystalline fluoropolymers. THVs are transparent to a broad band of light energy (UV to IR); the refractive indices are also very low (e.g., 1.355). All THVs retain properties common to other semicrystalline fluoropolymers, such as chemical resistance, weatherability, and low flammability. General properties are provided in Table 22.

2.11.3. Processing

Most THV resins (e.g., THV 200 and THV 500) extrude at lower temperatures (220–250°C) than other semicrystalline fluoropolymers. This provides two benefits:

1. In many cases corrosion-protected equipment is not required to extrude THV
2. It is easier to coprocess THVs with hydrocarbon plastics and elastomers

The low processing temperatures of THV combined with the ability to develop strong chemical bonds to many other materials make THV an ideal candidate for multilayer constructions. For instance, coextruded tubes of THV on

Table 22. Properties of THV-polymers

Property	Standard	THV 200	THV 500	THV 815
Specific gravity, g/cm^3	ASTM D 792	1.95	1.98	2.06
Melting temperature, °C	ASTM D 3418	115–125	160–170	220–230
Thermal decomposition in air*, °C		420	440	460
Limiting oxygen index, %	ASTM D 2863	65	75	80
Tensile strength at break, MPa	ASTM D 638[a]	29	28	30
Elongation at break, %	ASTM D 638[a]	600	500	400
Flexural modulus, MPa	ASTM D 790	80	210	520
Harness, Shore D	ASTM D 2240	44	54	59
Dielectric constant at 23 °C				
100 kHz	ASTM D 149	6.6	5.6	5.1
10 MHz	ASTM D 149	4.6	3.9	3.8
MFI (265°C/5 kg), g/10 min	ASTM D 1238	20	10	12
E-beam cured high temperature resistance, °C		> 150		

* Measured by thermogravimetric analysis.

the inside (for chemical and permeation resistance) with a less expensive plastic on the outside (for strength and protection) can be easily made, or the reverse can be done [34].

THV can also be processed as pure material by the usual techniques for thermoplastics, such as extrusion, blow-, and injection-molding. THV 200 can be applied for solutions in solvents; the aqueous dispersion grades (e.g., THV 340) can be processed like any other fluoropolymer dispersion.

2.11.4. Uses

Most applications of THV are multilayer constructions, where a thin layer of THV provides enhanced barrier properties to other layers. Fuel hoses and fuel management systems are major applications due to the excellent permeation and chemical resistance including high flexibility and ease of processing. Further applications are wire, cable, and protective coatings. THV can also serve as flexible liner for chemical holding tanks. Emerging applications include speciality films for architectural segment solar energy (solar panels) and as safety glass compound.

3. Fluoroelastomers (→ Rubber, 4. Emulsion Rubbers, Chap. 6)

3.1. Introduction

Fluorine-containing elastomers are designed to maintain rubberlike elasticity in extremely severe environments at high and low temperatures as well as in contact with various chemicals. Their primary use is in seals in automotive e.g., as O-rings or shaft seals, where they function to prevent leakage after prolonged compression. The chemical composition determines the balance between e.g., oil resistance and low-temperature characteristics. As fluoroelastomers show compared to hydrocarbon elastomers a rather slow relaxation and recovery from strain, they are rarely subjected to tension and then only at modest elongations. Preferably, they are used in static rather than dynamic applications.

A second application for uncured fluoroelastomers makes use of their ability to enhance processability of polyolefins. As a processing additive, they reduce extrusion related gels, increase throughput, and reduce die build-up [107–109].

Technologically important fluoroelastomers can be divided into organic polymers with carbon–carbon linkages in the backbone and fluoroelastomers with inorganic backbones, such as fluorosilicones, which were developed in the 1950s and the fluoroalkoxyphosphazines introduced in 1975, which represent only a small share of the fluoroelastomer market.

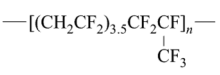
Elastomers have to be flexible and recover from deformation at service temperatures above 0°C. Noncross-linked elastomers are highly viscous, incompressible liquids. To prevent permanent flow deformation under an imposed force and to develop reversible elastic properties, these flexible macromolecules must be cross-linked. The restoring force in a deformed elastomeric network is based on the lower entropy of the extended and hence oriented chains. In general, cross-linking is performed chemically by vulcanization to produce tie points between chains to minimize irreversible flow under stress. However, physical cross-linking by crystallization of hard segments in segmented or grafted copolymers can also provide a network structure in so-called thermoplastic elastomers [110]. The few known thermoplastic fluoroelastomers have a much lower high-temperature service ceiling than thermoset elastomers; nevertheless, they possess certain advantages in processability because they can be reversibly cross-linked. Furthermore, they generally yield less extractable material, because they contain no curatives.

Fluorocarbon elastomers are copolymers made up of two or more major monomer units. One or more monomers give straight chain segments, which tend to crystallize if long enough. A second monomer with a bulky side group is incorporated at intervals to break up the crystallization tendency and produce a substantially amorphous elastomer.

The characteristics of a fluoroelastomer can be tailored by the chemical composition. The monomers VDF, TFE, and E increase the crystallinity, whereas HFP, PMVE, and P have bulky side-groups that hinder crystallization [111]. High solvent resistance and thermal stability in fluorocarbon polymers are important properties of fluoroelastomers but low-

temperature flexibility and high fluorine content are also desirable. These requirements conflict to some extent. TFE increases the chemical resistance, but the crystallinity is also increased, which reduces flexibility.

Copolymerization of VDF and HFP in the molar ratio of 3.5 : 1.0 produces a fluoroelastomer [9011-17-0] with no crystallinity and a T_g of ca. −20°C. This composition (60 wt% VDF) is the basis of the fluorocarbon elastomer industry:



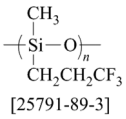
Other combinations of VDF with HFP and TFE, chlorotrifluoroethylene (CTFE), PMVE, or PMVE–TFE also produce substantially amorphous copolymers with glass transition temperatures low enough for practical use. PMVE–VDF-based elastomers have the lowest T_g (−40°C) and are important for the use in aircrafts.

The service temperature range and fluorine and hydrogen content of fluoroelastomers are given in Table 23.

The combinations of TFE with PMVE or other perfluoro(alkoxy alkyl vinyl ethers) with fluorinated cure site monomers lead to perfluoroelastomers with the highest attainable fluid and thermal resistance.

The low-temperature properties of fluorosilicones and fluoroalkoxyphosphazenes (→ Inorganic Polymers, Chap. 4) are superior to those elastomers with carbon backbones substituted by hydrogen, fluorine, chlorine, fluoroalkyl groups, or simple fluoroalkoxy groups. Their outstanding chain flexibility is a result of the alternating oxygen or nitrogen atoms in the backbone. However, fluorosilicones and fluoroalkoxyphosphazenes contain less fluorine than fluorocarbon elastomers; therefore, their solvent resistance and high-temperature stability are inferior.

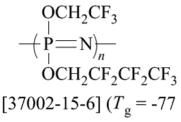
Commercial fluorosilicone elastomers are polydimethylsiloxane homopolymers in which one methyl substituent of each silicon atom is replaced by a 3,3,3-trifluoropropyl group:



[25791-89-3]

Fluorosilicone processing is the same as for standard silicone elastomers and quite different from fluoroelastomer processing.

Fluoroalkoxyphosphazene elastomers have been produced by replacing the chlorine in dichlorophosphazene polymers by fluorocarbon alkoxides [112] but have been withdrawn from the market:



[37002-15-6] (T_g = -77 °C)

Table 23. Service temperature, fluorine content, and hydrogen content of fluoroelastomers

Type	Service temperature*, °C	Fluorine content, %	Hydrogen content, %
VDF–HFP	−18–210	66	1.9
VDF–HFP–TFE	−12–230	66–69.5	1.1–1.9
VDF–PMVE–TFE	−27–230	64–66.5	1.1–1.7
TFE–P	5–200	54	4.3
Perfluorocarbon	0–260	73	0

* Temperature of elastomeric side of glass transition to maximum temperature for continuous service.

3.2. Elastomers Based on Vinylidene Fluoride (FKMs)

Copolymers of 1,1-difluoroethylene and chlorotrifluoroethylene prepared by M. W. KELLOGG were first described in 1955 [113–115]. After vulcanization, this fluoroelastomer (Kel-F) exhibited previously unattainable resistance to heat and solvents. However, it was soon surpassed by an even more stable fluoroelastomer, a copolymer of VDF and HFP, that was described in 1956 and commercialized by DuPont in 1958 as Viton A [116–118]. In 1960, DuPont introduced a TFE-containing terpolymer [25190-89-0] (Viton B) that was even more thermally stable and solvent resistant than Viton A [119, 120]. 3M, who had acquired the fluorocarbon polymer assets of M. W. KELLOGG, introduced a VDF–HFP copolymer named Fluorel in 1958 and continued its manufacture after 1962 under license from DuPont. These products are now sold as Dyneon.

Elastomeric copolymers of VDF and 1-hydropentafluoropropene [32552-63-9] and a TFE-containing terpolymer [29830-35-1] were introduced by Montecatini–Edison during the 1960s [121–123]. However, these polymers, sold as Tecnoflon, lacked the stability of similar HFP compositions, and were replaced by HFP analogs as early patents for poly(VDF–HFP) and poly(VDF–HFP–TFE) expired. In the meanwhile, these products are produced by Solvay-Solexis. Daikin began production of VDF-based fluoroelastomers (Dai-el) under license from DuPont in 1970.

In Russia produced fluoroelastomers are commercialized as Levatherm F by Lanxess. Four Chinese manufacturers (Meilan Shanghai, 3F, Juhua, Chenguang) are also on the market. Trade designations and manufacturers of commercial VDF-based fluoroelastomers are shown in Table 24.

Table 24. Commercial VDF-based elastomers

Copolymer	Trade name	Manufacturer
VDF–HFP	Viton	DuPont
	Dyneon	3M
	Tecnoflon	Solvay-Solexis
	Dai-el	Daikin
	Levatherm F	Lanxess
VDF–HFP–TFE	Viton	DuPont
	Dyneon	3M
	Tecnoflon	Solvay-Solexis
	Dai-el	Daikin
VDF–PMVE–TFE	Viton	DuPont
	Dyneon	3M
	Tecnoflon	Solvay-Solexis
	Dai-el	Daikin

3.2.1. Production

1,1-Difluoroethylene-based elastomers are usually prepared by continuous or semibatch polymerization in aqueous emulsion with free-radical initiators. The monomers are derived from fluorocarbon refrigerants and their intermediates. Since the Montreal Protocol, the raw material base is smaller, due to the phase-out of ozone depleting chlorofluorocarbon compounds.

Fluoroelastomers are produced in an aqueous emulsion polymerization, resulting in polymer latex with particles sizes in the range of 100–1 000 nm. Typical polymerization conditions are at $1 \times 10^6 - 3 \times 10^6$ Pa and 50–120°C for semibatch and $2 \times 10^6 - 7 \times 10^6$ Pa and 60–130°C. Commonly used initiators are inorganic peroxides, such as ammonium persulfate. However, organic peroxides and redox systems are also used, especially at low temperatures where the thermal decomposition of persulfate is slow. Emulsifying agents must be compatible with the highly reactive fluorocarbon radicals of growing polymer chains; salts of fluorocarbon acids are used to prevent chain transfer. Molar mass is regulated by controlling the rate of initiation, rate of polymerization, and termination by chain-transfer agents. Such agents generally have reactive carbon–hydrogen bonds; diethyl malonate [105-53-3] and dimethyl ether [115-10-6] are typically used. Buffers control the pH of the polymerization and stabilize the emulsification system. Molar mass (M_w) ranges from 10^5 to 10^6 g/mol.

In a new approach [124, 125] perfluorinated diiodo compounds are used to increase the iodine content and the architecture of the polymer. In a pseudo-living polymerization, long branches of the polymer can be controlled by using bifunctional molecules that can be very effectively cured by peroxides. The use of perfluoropolyether microemulsions yields high molar mass polymers at good reaction rates.

In semibatch polymerizations, monomers can be added continuously under pressure at rates that correspond to their consumption, providing better control of the copolymer composition.

In a continuous process, water, monomers, initiator, and other components are fed to the reactor while the polymer latex is removed at a corresponding rate. Composition and molar mass can be precisely controlled. Monomers and other reactants of widely ranging reactivities can be used without undue variation in the polymer structure. Unreacted monomers are evaporated from the latex and recycled.

In either process, the latex from the reactor is coagulated by the addition of salts or acids. The polymer crumb is filtered or centrifuged and washed to remove coagulant and water-soluble residues. After being dried, it may be mixed with curing (cross-linking) agents. The finished

Table 25. Physical properties of VDF-based fluoroelastomers

Property	Range	ASTM
Specific gravity, g/cm^3 of raw polymer	1.77–1.91	
Tensile properties		
100% modulus, MPa	2–15	
Tensile strength, MPa	5–20	
Elongation at break, %	50–500	
Hardness, durometer A	60–95	
Compression set*, %		D-395
70 h at 25 °C	10–15	
70 h at 200 °C	10–40	
1 000 h at 200 °C	50–70	
Low-temperature properties		
Clash–Berg torsional-stiffness temperature (69 MPa), °C	−31 to −5	
Retraction temperature (TR-10), °C	−31 to −6	D-1329
Brittle point, °C	−51 to −34	D-746

* Method B, 24.5 × 3.5 mm O-rings.

product is packaged as extruded pellets and lumps or in milled sheets.

3.2.2. Properties

Heat Resistance. 1,1-Difluoroethylene-based copolymers are the largest group of fluoroelastomers in terms of production volume and variety. Their properties are summarized in Table 25. 1,1-Difluoroethylene-based elastomers can be used continuously at temperatures as high as 230°C, depending on polymer type and formulation. Copolymers retain over 50% of their tensile strength for more than one year at 200°C or two months at 260°C. Functionalized hydrocarbon elastomers that are considered resistant to oil, such as nitrile or acrylate rubber, lose 50% of their elongation aging at 150°C for 10 and 25 days, respectively. In comparison, VDF-based fluoroelastomers retain over 95% of their elongation after one year at 200°C [126].

Only VDF–HFP at 60 : 40 wt% is of commercial importance. A wide variety of viscosities and formulations of this composition is sold for different applications. Most of these products are cured with bisphenol.

Fluid and Chemical Resistance. For improved fluid resistance terpolymers with TFE are used. They show higher stabilities with a 30% VDF content without affecting low temperature flexibility. Higher fluorine content increases the chemical resistance. The resistance of VDF–HFP–TFE elastomers to petroleum-based fuels and oils is excellent. Certain lubricants, however, contain additives that disperse sludge and inhibit metal corrosion but are highly basic or decompose to basic products that attack the elastomer. Therefore, the performance of the fluoroelastomer must be evaluated in contact with the particular fluid containing proprietary additives. Formulators of oil additives should examine not only lubricant stabilization and metal protection [127–129] but also the behavior of seals. Fluoroelastomers to be used with hydrocarbon–alcohol fuels (gasohol) must be chosen with care [130]. A VDF–HFP–TFE polymer of 69.5% fluorine content is used in methanol blends to prevent excessive swelling. This polymer is also recommended for certain phosphate ester-based hydraulic fluids. Fluid resistances guides are available [131–133].

In contact with aromatic solvents, polymers with 68% or 69.5% fluorine content give the best performance. Alcohols other than methanol do not greatly swell VDF-based elastomers despite their polar nature, but blends of alcohols and other fluids may act differently. Polar solvents that are only hydrogen bond acceptors, tend to have a high affinity for these elastomers and may dissolve raw polymer or destructively swell vulcanizates. Examples of such solvents are low-boiling ketones and esters (acetone, methyl ethyl ketone, ethyl acetate), amides (*N,N*-dimethylformamide, *N,N*-dimethylacetamide), and ethers (tetrahydrofuran, 2-methoxyethyl ether). Mixtures that contain substantial amounts of these solvents cannot be used with this group of fluoroelastomers.

In addition to the destructive action of highly swelling solvents, the vulcanizate may be attacked chemically. Dehydrofluorination by primary and secondary aliphatic amines occurs readily and is the basis of amine cross-linking. The resulting unsaturated bonds are susceptible to nucleophilic attack, which can lead to cross-linking and embrittlement. With amine-based curing systems, which are seldom used, dehydrofluorination is a controlled process; however, uncontrolled exposure to soluble aliphatic amines and other soluble strong organic bases degrades these vulcanizates and must be

Table 26. Fluid and chemical resistance of VDF-based fluoroelastomers

Outstanding resistance	Good to excellent resistance	Poor resistance
Hydrocarbon solvents	Low-polarity solvents	Strong alkaline solutions
Automotive fuels (free of methanol)	Oxidative environments	Ammonia and amines
Engine oils (free of amine additives)	Aqueous acids	Polar solvents (ketones, methanol)
Nonpolar chlorinated solvents	Dilute aqueous alkaline solutions	Organic acids
Oils and greases	Aromatic solvents	
Halogen oxidizers e.g., chlorine	Water and salt solutions	

avoided. Resistance to aqueous alkali is far greater, but causes surface cracks and failure. Phase-transfer catalysts, such as quaternary ammonium ions accelerate degradation by aqueous alkali. Improvement in base resistance can be achieved by using PMVE instead of HFP. Although these polymers are also attacked by amines, the resulting double bonds are not reactive for further cross-linking. Thus, embrittlement does not occur and service life is significantly extended. Resistance to aqueous acids is generally good, especially if acid acceptors, such as calcium hydroxide, magnesium oxide, or calcium oxide are not present in large amounts. Table 26 gives an overview on fluid resistances of FKMs.

Other Types of Resistance. Ozone resistance and weatherability are excellent [134] and permeability to gases is low. Vulcanizates can be formulated to be self-extinguishing or nonflammable. Abrasion resistance varies. Resistance to β-radiation is moderate and independent of VDF copolymer composition. Radiation doses are cumulative and a total exposure to 10^4–10^5 J/kg produces moderate to severe effects on physical properties. Radiation failure occurs by embrittlement rather than chain cleavage [135].

3.2.3. Processing

Formulation. Elastomer processing generally includes formulation. Optimum conditions must also be selected to provide the properties desired after vulcanization (cross-linking). The composition (in parts per hundred of rubber, phr) of a typical fluorocarbon elastomer is:

Ingredients	Composition, phr
Fluorocarbon elastomer	100
Acid acceptor (inorganic base)	3–15
Filler	0–50
Cross-linker	1–3
Accelerator	0.2–1
Activator	4–6
Processing aids	0–3

Typical acid acceptors for high steam and acid resistance are MgO, ZnO, or PbO. Carbon black, silica, or barium sulfate are often used as filler, and carnauba wax as processing aid acts as a flow lubricant or mold release aid. $Ca(OH)_2$ is used as accelerator, which activates dehydrofluorination. The fluorocarbon elastomer is chosen according to the intended use of the end product.

In O-ring formulations (Table 27), compression-set resistance is of critical importance because sealing can be maintained only if the O-ring can retain some tendency to regain its uncompressed dimensions. Higher molar mass and thus higher viscosity usually display better

Table 27. Fluoroelastomer molding and O-ring compounds

	General-purpose molding	O-ring
material		
Formulation		
Poly(VDF–HFP) [a]	100	
Poly(VDF–HFP) [b]		100
Benzyltriphenylphosphonium chloride	0.25	0.60
Hexafluoroisopropylidenediphenol	1.0	2.0
Calcium hydroxide	6.0	6.0
Magnesium oxide [c]	3.0	3.0
MT carbon black (N-908)	30	30
Compound viscosity [d]	27	35
Vulcanizate properties [e]		
Tensile, 25 °C		
100% Modulus, MPa	2.2	5.3
Tensile strength, MPa	11.2	12.4
Elongation at break, %	360	190
Compression set[f], %	47	16
Hardness, durometer A	66	72

[a] Viton E-45 (DuPont), 100 °C Mooney viscosity, ML-10 = 45.
[b] Viton E-60 (DuPont), 100 °C Mooney viscosity, ML-10 = 100.
[c] Maglite D (Merck & Co).
[d] Mooney scorch minimum viscosity, MS at 121 °C for 30 min.
[e] Press-cured 10 min at 177 °C, postcured 24 h at 232 °C.
[f] ASTM D-395, Method B (O-rings), 70 h at 200 °C.

compression-set resistance. The choice of curing systems is also important because the stability of the cross-links limits the stability of the elastomer network. Bisphenol curing system offers greater compression-set resistance than peroxide curing system and is generally preferred for O-ring and similar sealing applications. However, peroxide-cured stocks usually have better resistance to steam and acids and are often specified in these applications [136].

In formulations for molded articles (Table 27), compression-set resistance is usually sacrificed in favor of elongation. A lower cure state and greater elongation are achieved by using less cross-linking agent or a lower molar mass polymer; this reduces viscosity and increases mold flow. A minimum elongation is required, because many mold designs require substantial elongation of the hot vulcanizate to facilitate removal from the mold. If these processing requirements for elongation have been satisfied, molded articles are not usually used in tension but rather under slight compression although some elongation may occur during installation.

1,1-Difluoroethylene-based elastomers are available in a range of Mooney viscosity values of 0–160 (ML-10, 121°C) (Mooney viscosity is a measure of polymer plasticity), that correspond to molar masses of 1×10^4–1.5×10^5 g/mol. The choice of fillers and acid acceptor in fluoroelastomers has a major effect on viscosity and, therefore, influences processability and properties after vulcanization [137, 138].

Specialized polymers can be compounded for exceptional resistance to fluids and low-temperature flexibility (Table 28). The PMVE polymer exhibits the best low-temperature properties of any commercial fluorocarbon elastomer. Excellent resistance to methanol and methanol–fuel blends is characteristic of compounds based on a polymer containing 69.5% fluorine [138]. Higher fluorine containing elastomers based on TFE and special vinyl ethers guarantee low solvent swelling combined with lowest T_g (−40°C) [141, 142].

Mixing. Standard rubber compounding equipment and techniques are used to mix VDF-based fluoroelastomer stocks. Rubber mills are suitable for most viscosity grades, although some reduction in molar mass may occur when high-viscosity polymers are cold milled, and the clearance between rolls is small. Banbury and other internal mixers are also suited for preparing precompounds that contain fillers, inorganic acid acceptors, and processing aids. Detailed mixing procedures are given in a processing guide for fluoroelastomers [143]. Producers commonly supply precompounds that are fully compounded by a custom-mixing firm or by the molder.

Molding. Compression molding is the oldest and simplest way of vulcanization. In this process, a piece of uncured rubber is placed in the mold cavity and cured under pressure. Compression molding has several advantages: Loss of expensive material is minimized, flexibility for small series, and low equipment cost. Disadvantages are the high labor cost and variability of quality. Usually products with high molar mass are processed by compression molding, which give parts with excellent mechanical properties and environmental resistance [144].

In transfer molding, lower viscosities are required, because the compound needs to flow easily. Bisphenol-curable compounds are suitable for transfer molding because premature vulcanization during processing is low.

Injection molding requires a higher capital investment but is less labor intensive. Its use has increased and is justified in large-scale production where labor savings offset equipment costs and increased waste from mold filling channels. Injection molding provides the maximum product consistency and shortest cycle times compared to other molding processes. Compound formulation is critical for injection molding, because high flow rates and compound safety are required. Injection molding of thermoset elastomers is much more demanding than of thermoplastics or thermoplastic elastomers, because the former case entails irreversible chemical reactions that increase viscosity and creates cross-links during hot flow; in the latter case, the polymer flows easily in the melt and is simply cooled or crystallized in the mold.

Molding cycles are usually 1–5 min at 160–200°C and depend on the article size

Table 28. Specialty compounds for increased fluid resistance and low-temperature flexibility

	Terpolymers			Standard copolymer
	Methanol resistant	Standard	Low-temperature resistant	
Formulation				
Poly(VDF–HFP–TFE)[a], 69.5% F	100			
Poly(VDF–HFP–TFE)[b], 68.5% F		100		
Poly(VDF–PMVE–TFE)[c]			100	
Poly(VDF–HFP)[d], 65% F				100
Triallylisocyanurate	3		4	
Organic peroxide[e]	3		4	
Sublimed litharge	3			
MT black (N-908)	30	30	30	30
Calcium hydroxide		3	4	6
Magnesium oxide[f]		3		3
Benzyltriphenylphosphonium chloride		1.0		0.6
Hexafluoroisopropylidenediphenol		2.0		2.0
Compound viscosity[g]	40	72	32	35
Vulcanizate properties [h]				
100% modulus at 25 °C, MPa	5.4	7.0	5.3	5.3
Tensile strength, MPa				
25 °C	17.6	15.0	13.8	12.4
−30 °C			37.4	45.5
−40 °C			39.9	28.4
Elongation at break, %				
25 °C	210	210	200	190
−30 °C			160	60
−40 °C			60	20
Brittle point (1.91 mm thick)[i], °C	−45	−42	−51	−34
Clash–Berg torsional-stiffness temperature (69 MPa), °C	−5	−12	−31	−17
Compression set[j], %	38	30	30	16
Hardness, durometer A	76	80	67	72
Volume swell, 24 °C for 7 d, %				
Toluene	4	13		
Reference fuel C[k]	3	6		
Methanol	3	22		
Reference fuel C/methanol (85/15)	9	20		
Phosphate ester hydraulic fluid[l], 121 °C	45	127		
Reference fuel C/ethanol (85/15), 100 °C	18	24		
Permeability to automotive fuel[m], g				
Reference fuel C	1	3		6
Reference fuel C/ethanol (85/15)	11	19		28
Reference fuel C/methanol (85/15)	17	57		125

[a] Viton GF, contains peroxide-sensitive cure site (DuPont).
[b] Viton B (Du Pont).
[c] Viton GLT, contains peroxide-sensitive cure site (DuPont).
[d] Viton E-60 (DuPont).
[e] Luperco 101-XL (Pennwalt Corp.).
[f] Maglite D (Merck & Co.).
[g] Mooney scorch minimum viscosity, MS at 121 °C for 30 min.
[h] Press-cured 10 min at 177 °C, postcured 24 h at 232 °C.
[i] ASTM D-2137.
[j] ASTM D-395, Method B (O-rings), 70 h at 200 °C.
[k] 50% toluene, 50% isooctane.
[l] Skydrol 500-B (Monsanto Co.).
[m] ASTM E-96, 0.45 mm membrane, 24 °C.

due to heat transfer limitations. In injection molding, however, frictional or shear heating, produced by high flow rates through small mold orifices, raises the temperature in the mold significantly. In large moldings produced by compression or injection molding, the heat of reaction of vulcanization must also be considered.

Extrusion. Fluorocarbon elastomers can be shaped by extrusion. Elastomer fed to the extruder is moved through the barrel by a screw to a die to get the desired extrudate cross-section. Because elastomers are essentially amorphous, viscous liquids, melting is not required. Extrusion of compounds must be carried out at temperatures below 120°C to avoid premature curing. The continuous extrudate, which may be hose or tubing, rod stock for spliced O-rings, or profile stock for cut gaskets, is rolled up or otherwise placed in a steam autoclave, where curing takes place at ca. 160°C. Extruded stock is also used to cut preforms for subsequent curing by compression or transfer molding.

Vulcanization Chemistry. Bisphenol curing (Fig. 3) is the most widely used curing system for VDF–HFP and VDF–HFP–TFE fluoroelastomers. It has the advantage of excellent processing safety, fast cures, excellent final properties, and high temperature compression set resistance in seals. Preferred cross-linker is bisphenol AF.

The chemical reactions that result in formation of networks in bisphenol-cured fluoroelastomers involve dehydrofluorination of HFP–VDF–HFP or HFP–VDF–TFE sites forming $-C(CF_3) = CH-$ double bonds. Fluoride ions catalyze a shift of the double bond to form $-CH = CF-$. The resulting double bonds are susceptible to nucleophilic attack because of their electron-deficient character. Addition of a nucleophile and subsequent elimination of a fluoride leads to a new double bond, which in turn is attacked by an intermediate phenolate accelerated by quaternary phosphonium or ammonium phenolate [136, 145, 146]. Because fluoride ions are formed in the curing reaction, a fluoride scavenger is needed.

Peroxide-initiated cross-linking of bromine or iodine containing fluoroelastomers in the presence of radical traps, such as triallyl isocyanurate (TAIC) [1025-15-6] starts by the attack of a radical at the allyl functions of TAIC. The propagating TAIC radicals abstract bromine or iodine atoms from the fluoroelastomer, and the resulting fluorocarbon radicals attack intact TAIC double bonds. The driving force for this reaction is the addition of an electron-deficient free radical to an electron-rich double bond. Propagation reactions may involve redistribution of the free-radical intermediates from fluoroelastomer radical addition to a double bond of the partially polymerized radical trap [136, 147] (Fig. 4).

Diamine cure is nowadays restricted to applications where FDA compliance is needed.

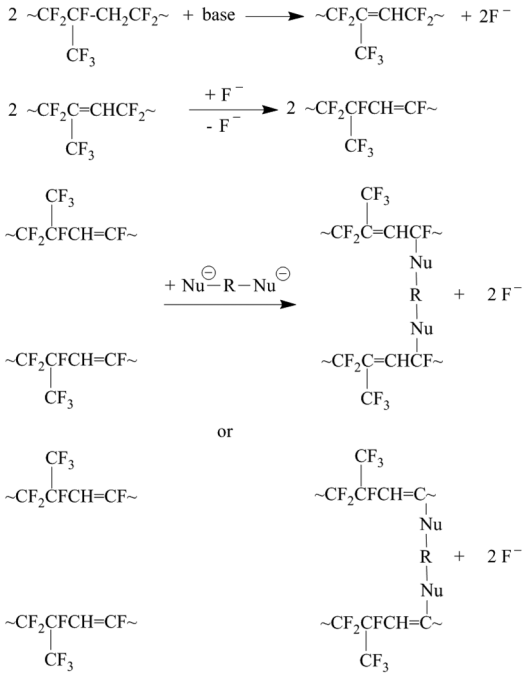


Figure 3. Bisphenol curing mechanism [34, p.79]

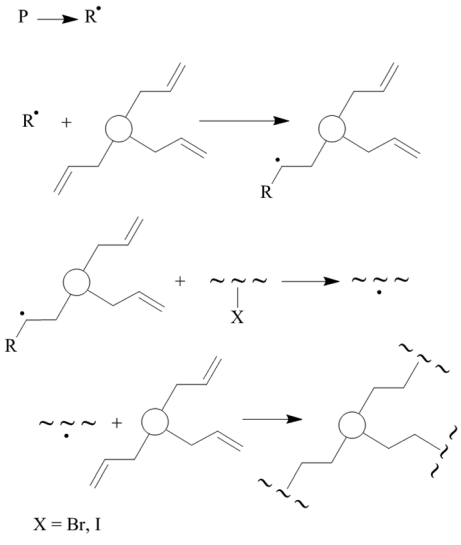


Figure 4. Mechanism of peroxide cure [34, p. 80]

Postcuring. The curing chemistry has to be designed such that during the processing of the elastomer, at temperatures of 120–130°C, no change in the viscosity occurs, but during the curing step at 170–180°C a high cure state is reached within 5 min. To develop optimum physical properties, such as compression-set resistance and tensile strength, fluorocarbon elastomers are usually postcured [148]. The postcure cycle subjects a press-cured article to circulating air at atmospheric pressure at 200–260°C for 12–24 h. Small amounts of volatile substances are removed, and slight shrinkage occurs. Typical bisphenol-curable stocks undergo a 0.3% mass loss on press curing and a further 1.2% loss on postcuring [149, 150]. Postcuring is believed to complete the vulcanization and deactivate remaining intermediates. The conditions for a postcure cycle are established arbitrarily, because each elastomer-curing system has a point at which heating a vulcanizate in air gives optimum properties, beyond which further heating or heating at a higher temperature affects physical properties undesirably with the onset of heat aging.

3.2.4. Uses

1,1-Difluoroethylene-based elastomers are used widely in vehicle construction because of their excellent resistance to heat and oil. Important fluoroelastomer parts are engine oil seals of both the rotating and reciprocating types, drive-train seals, and fuel-handling components, such as gaskets, O-rings, valve seals, and hoses. Other applications are hydraulic and pneumatic seals, hoses and seals for chemical industry, flue-duct expansion joints for power plants, pollution control equipment, and fuser rolls for copying machines. The aircraft industry uses more fluorosilicone than fluorocarbon elastomers because of the extreme low-temperature requirements of high-altitude flight [151].

3.3. Elastomers Based on Tetrafluoroethylene—Perfluoro(Methyl Vinyl Ether) Copolymers (FFKM)

Despite the vast improvement that VDF-based elastomers offer over conventional hydrocarbon elastomers in thermooxidative stability and oil resistance, even more stable elastomers are required for critical industrial and military applications. In response to this need, perfluorinated materials were developed at DuPont in the 1960s. The goal was an elastomer with the inertness and solubility characteristics of PTFE or FEP.

To create such a stable elastomer, a comonomer was required that interrupted TFE crystallinity and imparted good low-temperature properties. At this time, the epoxidation of HFP was developed and the resulting hexafluoropropene oxide (2,2,3-trifluoro-3-(trifluoromethyl) oxirane) [428-59-1] used to produce perfluoro (methyl vinyl ether) (PMVE) (→ Fluorine Compounds, Organic, Section 6.2). Perfluorovinyl Ethers).

Copolymerization of PMVE with TFE results in an elastomer [26425-79-6] whose thermal, oxidative, and chemical stability before cross-linking approach that of perfluorocarbon plastics [152]. However, the inertness of this base elastomer and the absence of cure sites prevented cross-linking, and most of the effort to develop a practical elastomer went into cure site monomers [153–158]. Several types of curing systems were developed, and articles made from them were commercialized by DuPont in the mid-1970s as Kalrez Perfluorocarbon Elastomer Part. Due to the great difficulties in processing and curing, only finished Kalrez parts are sold. Raw perfluoroelastomer gum, based on triazine or peroxide curing, is sold by Daikin, 3M, and Solvay Solexis [159].

3.3.1. Production

Copolymerization of TFE–PMVE and cure-site monomers is conducted in an aqueous emulsion like that used with VDF–HFP-based systems (see Section 3.2.1). Polymerization rates in continuous reactors are about one-tenth of those of VDF–HFP-based systems at temperatures that give useful molar masses. An important difference between the polymerization of VDF–HFP and TFE–PMVE is that the latter requires a surfactant. Hydrocarbon-based surfactants cannot be used because of chain-transfer reactions with the highly reactive perfluorocarbon chain radicals; salts of C_8–C_{12} perfluorocarbon acids are satisfactory. For the different curing systems (peroxide, bisphenol, or nitrile), different cure site monomers have to be incorporated (Table 29).

Table 29. Heat aging* and fluid swell of perfluoro-vulcanizates [163]

Cure site	-R_fCN	-H	-R_fBr
Curative	Ph_4Sn	bisphenol	TAIC
Probable cure site monomer	8-CNVE	VDF	BTFB
Heat aging, %			
225 °C		−3	−11
250 °C		−24	−54
275 °C		−45	−80
290 °C	24	−36	
Fluid resistance (swell after 70 h exposure), %			
Concentrated nitric acid, 85 °C	3	8	9
Glacial acetic acid, 100 °C	3	32	16
Butyraldehyde, 70 °C	13	10	14
Methyl ethyl ketone, 70 °C	6	4	4
Toluene, 100 °C	7	7	7
Water, 225 °C	10	60	7

* Change in T_B (tensile strength at break) after aging ten days in air.

The polymer latex is coagulated by addition of polyvalent metal salt solutions. The polymer crumb is filtered or centrifuged, washed to remove coagulant, initiator, and surfactant, and dried [156].

3.3.2. Properties

Heat Resistance. The mass loss of a TFE–PMVE copolymer in air is 6.5% at 316°C over seven days; an uncured terpolymer that contains the proprietary perfluoro(phenoxy ether)-based cure-site monomer loses 12% under the same conditions [156]. The higher loss of a perfluoroelastomer is because the cure site has a more complex structure than the backbone and is more prone to degradation under these extreme conditions. Degradation of the cure site leads to some local degradation of the main chain.

Cured perfluoroelastomer specimens are also exceptionally stable and are differentiated by the stability of their cross-links. A perfluoroelastomer with a perfluorocarbon nitrile group as cure site retains physical properties best under extreme heat conditions. The triazine cross-links are formed by trimerization of the nitrile functions, catalyzed by tetraphenyltin and are sufficiently stable to prevent any change from the original postcured properties with respect to 100% modulus, tensile strength, and elongation at break in air at 288°C over 18 days. Even at 316°C, useful properties are maintained: 100% modulus is reduced by less than 20%, tensile strength by less than 40%, and elongation at break is unchanged. Other cross-link reactions, avoiding tetraphenyltin and resulting in comparable stabilities, have been developed by 3M [160, 161].

Although perfluoroelastomers cross-linked by perfluorophenoxy groups are less stable to heat, they are still far more stable than hydrofluoroelastomers: After 20 days at 288°C in air, 100% modulus is reduced by less than 25% and tensile strength by less than 15%; elongation at break is increased by 120%. Table 29 gives some properties of FFKM for heat aging and fluid swell.

Fluid and Chemical Resistance. The chemical resistance of perfluoroelastomers depends on the cure system [162–164]. Uncured TFE–PMVE-based perfluoroelastomers are insoluble in most solvents except certain perfluorocarbons and chlorofluorocarbons.

Typical physical properties of a K_2–AF-cured vulcanizate loaded with carbon black follow [157]:

100% modulus, MPa	9
Tensile strength, MPa	16
Elongation at break, %	160
Hardness, Shore A	75
Compression set B (O-rings), %	
70 h at 121°C	23
70 h at 288°C	45
Clash–Berg torsional-stiffness temperature (66.9 MPa), °C	−2
Brittle point, °C	−38
Retraction temperature, °C	
TR-10	−1
TR-50	+8
Specific gravity, g/cm^3	2.05

3.3.3. Processing and Uses

Perfluoroelastomers based on TFE–PMVE are difficult to process because of the stiffness of the fully fluorinated chains. Because the polymer is also difficult to cross-link and expensive to produce, these materials are available as finished articles (Kalrez Perfluorocarbon Elastomer Parts). A substantial market was found for O-rings, flat and lathe-cut gaskets, rotating and reciprocating shaft seals, and diaphragms. Other products include coated fabrics, hose linings, tubing, industrial gloves, and extruded articles, such as autoclave and oven seals. The high cost of these products is justified in applications where no other material is equally resistant to oxidative, thermal, fluid, and chemical exposure. They are used in the manufacturing, aerospace, and automobile industries.

3.4. Elastomers Based on Tetrafluoroethylene–Propene Copolymers

In the 1960s, DuPont [165] and Asahi Glass [166–168] established independently that TFE and propene (P) undergo a nearly alternating polymerization. The resultant TFE–P fluoroelastomer [27029-05-6] exhibits very good thermal and chemical resistance, but has a high glass transition temperature (−2°C) despite its low fluorine content (54%). Although resistance to swelling by aromatic hydrocarbons is inadequate, these elastomers offer excellent resistance to certain polar solvents. An unusual property of TFE–P fluoroelastomers is their exceptional resistance to dehydrofluorination by organic bases.

Due to the high stability against dehydrofluorination, high temperatures (300–360°C, 2–4 h) are needed to introduce double bonds, which are accessible for peroxide cure [169]. Alternatively, a specific cure site is used [170, 171].

Asahi Glass introduced TFE–P polymers in the mid-1970s as Aflas. Compared to VDF–HFP–TFE fluoroelastomers, TFE–P vulcanizates have poorer low-temperature characteristics and resistance to compression set. Because of the excellent electrical properties, TFE–P has been used for wire and cable coating applications.

To make TFE–P polymers susceptible to bisphenol curing TFE–P–VDF polymers have been developed [172–175]. These polymers show significantly better resistance to lubricating oil than VDF–HFP containing polymers and show better processing and curing characteristics than TFE–P copolymers, but base resistance is significantly compromised by the presence of a large fraction of VDF units. In the late 1990s, workers at DuPont Dow Elastomers reinvestigated the TFE–P elastomer family to develop fully base resistant products with better processing and curing characteristics. Certain cure-site monomers, such as trifluoropropene incorporated into TFE–P makes the elastomer susceptible to bisphenol curing [176]. These terpolymers have better base resistance than VDF-containing TFE–P elastomers and have better hydrocarbon fluid resistance than TFE–P copolymers [177].

3.4.1. Production

Tetrafluoroethylene–propene elastomers are prepared in aqueous emulsion with a perfluorocarbon surfactant. Batch copolymerization at 70–80°C, using a conventional ammonium persulfate–sodium sulfite redox catalyst, produces elastomers of relatively low molar mass ($\overline{M}_w = 70\,000$ g/mol) due to chain transfer. To minimize transfer reactions, more active redox initiators were developed [139]. With these catalysts, combinations of ammonium persulfate, ferrous sulfate, ethylenediaminetetraacetic acid, and sodium hydroxymethanesulfinate, efficient batch polymerization to a $\overline{M}_w$ of 150 000 g/mol can be carried out at 25–35°C.

The polymer latex is coagulated by addition of solutions of polyvalent salts, and the coagulated crumb is washed and dried.

3.4.2. Properties

Typical properties of a TFE–P elastomer vulcanized by a peroxide–radical trap curing system (press-cured at 160°C for 30 min, postcured at 200°C for 2 h) [168] are given below:

Raw polymer	
Specific gravity, g/cm^3	1.55
Mooney viscosity (ML-10, 100°C)	85
Appearance	dark brown
Formulation, phr	
Poly(TFE–P)	100
α,α'-Bis(*t*-butylperoxy)diisopropylbenzene	2
Triallylisocyanurate	3
MT carbon black (N-908)	30
Vulcanizate properties	
Specific gravity, g/cm^3	1.60
Tensile properties at 25°C	
100% modulus, MPa	3
Tensile strength, MPa	20
Elongation at break, %	300
Compression set at 200°C, %	
1 d	40
30 d	65
Hardness, Durometer A	72
Brittle point, °C	−40
Retraction temperature (TR-10), °C	3
Volume increase after immersion, %	
95% H_2SO_4, 100°C, 3 d	4.4
Water, 150°C, 3 d	8.7
Steam, 160°C, 3 d	4.6
Fuel oil B, 25°C, 7 d	59
Benzene, 25°C, 7 d	40
Methanol, 25°C, 7 d	0.2
Ethyl acetate, 25°C, 7 d	88

3.4.3. Processing

The isolated tetrafluoroethylene–propene copolymer is subjected to a heat treatment to generate enough unsaturation to allow peroxide curing [176]. Dialkyl peroxides are used together with radical traps, such as polyallyl or polyvinyl compounds or *N*,*N*′-*m*-phenenedimaleimide for curing. An inorganic acid acceptor, such as calcium hydroxide or magnesium oxide is also present. Fillers, such as silicas can be used, but carbon blacks are usually chosen for reinforcement [168].

VDF-containing TFE–P elastomers show a similar curing behavior with bisphenol as the standard VDF–HFP polymers [178].

Tetrafluoroethylene–propene elastomers process less smoothly on conventional rubber processing equipment than VDF–HFP-based fluoroelastomers. Processing aids, such as carnauba wax or sodium stearate are widely employed. Similarly, longer press-cure cycles are used to develop optimum properties: Press-cured vulcanizates are usually postcured at 200°C for 16 h [179, 180].

3.4.4. Uses

The TFE–P fluoroelastomers are used where high temperatures and destructive media are encountered. Applications are similar to those described for VDF–HFP-based polymers (Section 3.2.4), but the choice may depend on specific requirements. Thus, TFE–P is recommended for exposure to strong organic bases and certain highly polar solvents, but not for maximum oil resistance and low-temperature properties.

3.5. Fluoroelastomers containing Ethylene

3.5.1. TFE–E–PMVE Polymers

In 1986, DuPont introduced fluoroelastomers based on TFE, E, and PMVE. Peroxide curing is possible by using bromine cure sites [181]. They can be used in severe environments, such as oilfield applications, where the seals are exposed to high temperatures, H_2S, and amine based corrosion inhibitors. They show better low temperature properties than TFE–PMVE and TFE–P elastomers and have better fluid resistance against hydrocarbons than the latter.

3.5.2. TFE–VDF–HFP–E Polymers

Solvay-Solexis developed a polymer based on TFE–VDF–HFP–E [182]. The polymer contains about 5% ethylene, which shields the vinylidene fluoride hydrogens, making the polymer less susceptible to base attack. Peroxide cure is possible due to bromine containing cure site monomers. Polymerization rate can be increased by a special microemulsion polymerization technique [183].

3.6. Thermoplastic Elastomers (→Thermoplastic Elastomers)

Thermoplastic elastomers combine elastomeric properties with standard thermoplastic processing. They are either polymer blends of a thermoplastic polymer and an elastomer or A-B-A block copolymers of hard (A) and soft (B) (elastomeric) segments. During processing,

the polymer is completely molten, when cooled, the hard segments cocrystallize, thus forming physical cross-links between the soft segments. This gives the polymer elastomeric properties [34].

Daikin offers fluorinated TPEs commercially as Dai-el. To tailor block copolymers the "living" polymerization technology is used. In a first step, the elastomeric block is polymerized, consisting of VDF–HFP–TFE that has two iodine end-groups. In a second step, a thermoplastic polymer consisting of TFE–E–HFP is polymerized starting from the iodine end-groups to produce the A–B–A structure. The melting point is about 230°C; dimensional stability is good up to 120°C. The high temperature properties can be improved by either chemical or radiation curing. Typical applications include tubing, sheet, O-rings, and molded parts.

3.7. Vinyl Ether Copolymers

A new class of fluorinated coatings was developed by Asahi Glass Co. Ltd. under the trade name Lumiflon [184, 185].

The base polymer is a fluoroethylene-vinyl ether (FE–VE) copolymer, which comprises an alternating sequence of a fluorinated ethylene, normally CTFE, and different vinyl ether units.

FE–VE polymers are the first solvent-soluble fluoropolymers for coatings, which can be cured at room temperature conditions. The polymers are completely amorphous. The polymers combine various characteristics, such as solubility in organic solvents, film-forming ability, and transparency of the resulting film, which make them good base polymers for paints. FE–VE based coatings maintain excellent appearances (gloss, color) of buildings and bridges, where on-site coating is required, for more than twenty years. The coatings protect steel or concrete from sunshine, wind, rain, and corrosion, thereby reducing the total maintenance cost, such as repainting or cleaning.

In addition, FE–VE polymers that can be applied as emulsion or powder have been developed [186].

The molecular design of FE–VE gives some possibilities to tailor the resin applicable to different coating purposes (Fig. 5).

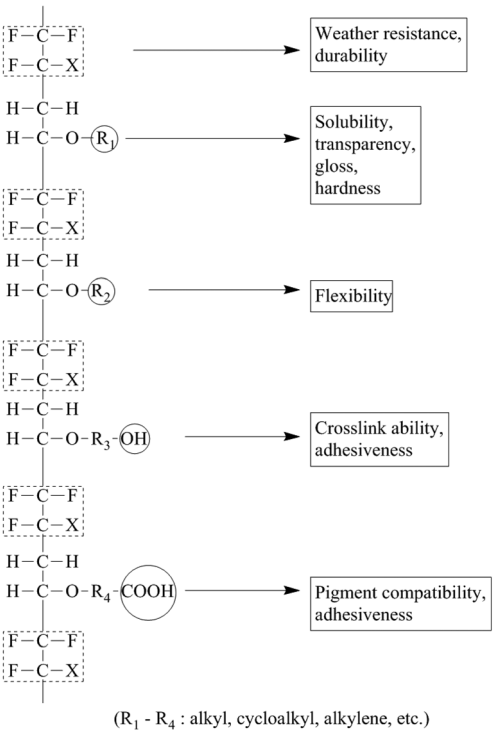


Figure 5. Molecular design of FE-VE polymers [34, p. 560]

CTFE as the fluorinated olefin improves the solubility of the polymer compared to TFE. The FE and VE components are highly alternating, which protects the rather unstable VE units in the backbone, adding excellent weather resistance to the resin. Several different VE compounds are used in the polymerization. Alkyl, cycloalkyl, or alkylene substituted VE are responsible for the solubility and the glass transition temperature. Introducing hydroxyl groups in the side chain enables the molecule to be cured with isocyanate to urethane polymers. Compatibility with pigments is achieved by partial carboxylation of hydroxyl groups. Copolymers with a higher COOH content are soluble in an aqueous medium.

The great advantage of FE–VE paints is their ability to cure at room temperature. PVDF, which is also used for protective coating, has to be baked at > 250°C, to form a continuous film. Due to the fluorinated backbone, FE–VE based paints show a much higher weathering stability, compared to fluorinated acrylic based coatings.

Some fundamental properties of a FE–VE polymer [34, 187] are:

Fluorine content, wt%	25–30
OH value, mg KOH/g	47–52
COOH value, mg KOH/g	0–5
Number-average molar mass $\overline{M}_n$, g/mol	$0.8–6 \times 10^4$
Weight-average molar mass $\overline{M}_w$, g/mol	$1–15 \times 10^4$
Specific gravity, g/cm^3	1.4–1.5
T_g, °C	20–70
Decomposition temperature, °C	240–250
Solubility parameter	8.8 (calc.)

4. Toxicology and Occupational Health

All commercial fluoropolymers are low in toxicity and safe under normal conditions. They are physiologically inert and some have been approved by the FDA for use in contact with food or for human implants. Incineration of fluoropolymers should be avoided because the combustion products include hydrogen fluoride, a toxic and corrosive gas.

4.1. Fluoroplastics

Polytetrafluoroethylene resins are subjected to prolonged heating at 380°C during sintering. Because a small quantity of toxic fumes can be emitted during this process, adequate ventilation should be provided to prevent inhalation of the fumes, which can cause a condition known as polymer fume fever. This temporary flulike disorder occurs several hours after exposure and lasts for 36–48 h. The effect is not cumulative. It is often caused by smoking tobacco contaminated with PTFE powder. Therefore, smoking and tobacco should be forbidden in areas where PTFE is processed. Safe handling practice must be observed during processing [188]. Enormous quantities of PTFE resins have been manufactured, processed, and used without causing any known cases of serious illness or death.

The same precautions should be followed with all TFE-containing polymers. In the extrusion or molding of TFE copolymers, the resin is heated above 300°C (to 425°C in the case of PFA resins). Exhaust hoods should be used over the die and feed hopper to remove any toxic fumes that may be evolved.

The main hazard associated with the processing of PVDF, ECTFE, and PVF resins is the evolution of hydrogen fluoride; this is prevented by avoiding overheating. Exhaust hoods should be used over the feed and die sections of the extruder or molding machine to remove hydrogen fluoride.

4.2. Fluoroelastomers

Fluorocarbon elastomers are nontoxic and nonirritating when handled in accordance with manufacturers' recommendations. Detailed literature on safety is available from the manufacturers; the following general principles should be observed:

1. Adequate ventilation of compounding, extrusion, curing, and postcuring areas should be provided
2. Dispersion of finely divided active metals or high concentrations of active dehydrofluorinating agents (e.g., aliphatic amines and combinations of phase-transfer catalysts with metal oxides or hydroxides) should be avoided
3. Fluoroelastomers should not be heated to or above their decomposition temperature
4. Incineration should not be used as a waste disposal method because of the attendant evolution of hydrogen fluoride.

Certain compounding ingredients may pose specific hazards, and manufacturers' or suppliers' recommendations should be followed.

Certain fluoroelastomers have been approved for contact with foods under the Code of Federal Regulations, 21, Food and Drugs, Part 177.2600.

4.3. Environmental Aspects

Presently, no overall and sustainable concepts for the recycling of fluoropolymers from processors or postconsumer waste are available. Only limited amounts from processor waste streams get recycled, the rest including postconsumer waste is uncontrolled incinerated or landfilled. In future, legislation will change this situation,

e.g., forcing manufacturer and processors to develop concepts to reuse or recycle fluoropolymer waste, e.g., pyrolyzing perfluorinated polymers to TFE, HFP or to incinerate fluoropolymer in a controlled way [187, 189–191]. Europe and Japan will certainly be the front runners to handle scrap and waste streams of fluoropolymers in a sustainable manner.

In the late 1990s, attention became focused on ammonium perfluorooctanoate (APFO), a perfluorinated emulsifier used in aqueous emulsion polymerizations of fluoropolymers [12]. Use of a nontelogenic emulsifier in aqueous emulsion polymerization is essential, both to stabilize the final fluoropolymer latices and as process safety measure to control the exothermic polymerizations. APFO has been widely used by all fluoropolymer manufactures since the 1950s. However, evidence of wide spread distribution and persistence of APFO in the environment, its biopersistence in humans, and its toxicity in laboratory animal studies have raised serious concerns about its continued use [192–194]. The fluoropolymer industry developed and implemented containment technologies to recover and reuse APFO from off-gas stream, from aqueous wastestreams, and from products (e.g., aqueous dispersions) and closed the manufacturing loops [195–197].

Nevertheless, in 2006 the U.S. Environmental Protection Agency (EPA) announced a stewardship program challenging fluoropolymer manufacturers to eliminated APFO and related chemicals from emissions and products by 2015. As a result, considerable efforts have been made to reduce the use of APFO and to develop safer alternatives. Meanwhile a variety of nontelogenic, highly fluorinated, oxygen-containing carboxylic acid [198] have been developed as APFO substitute; these alternatives have superior EHS profiles compared to APFO [199]. Containment technologies, developed for APFO can be applied for the new generation of fluorinated emulsifiers to recover and reuse these materials [200–203].

5. Economic Aspects

Fluoroplastics. In 2008, world consumption of fluoropolymers reached 182 000 t and exceeded 3.0×10^9 $ [12]. World production capacity was more than 260 000 t/a. Annual growth of consumption is expected to be in the range of 3–6%. China has added huge PTFE production capacities and is the world's largest producer of PTFE with 30%. The landscape of fluoropolymer producers has changed by mergers and acquisitions since the late 1990s. Major producers include Asahi Glass (JP), Arkema (EU), Daikin (JP), DuPont (U. S.), 3M (U.S.), Honeywell (U.S.), Solvay Solexis (EU), Halopolymer (Russia), Gujarat (IN), 3F (CN), Meilan (CN), Dongyue (CN), Juhua (CN), Chenguang (CN), Fuxin (CN), and Kureha (JP).

Fluoroelastomers. In 2009, world consumption of fluorocarbon elastomers (FKM incl. FFKM) reached 19 500 t; the global demand for fluorosilicones (FSR) was about 1 700 t; the total market value is estimated to about 1.1×10^9 $ [204]. Based on sales volumes, the United States accounted for 26% of world consumption, Europe for 29%, and Asia for 42% in 2009. Total demand for fluoroelastomers (FKM, FFKM, FSR) is forecast to grow at about $5 - 6\%$/a. Included in FKM demand is their use as polymer processing acids (PPA) e. g., for the polyolefin industry. Currently there is a large overcapacity of FKM in China, which has a production capacity of 10 000 t. The landscape of producers changed during the last decade; major FKM- and FFKM-producers include: Asahi Glass (JP), Daikin (JP), DuPont (U.S.), 3M (U.S.), Halopolymer (Russia), Solvay Solexis (EU), Meilan (CN), Shanghai 3F (CN), Juhua (CN), Chenguang (CN), Dongyue (CN).

Abbreviations used in this article:

APFO	ammonium perfluorooctanoate
CTFE	chlorotrifluoroethylene
DSC	differential scanning calorimetry
ECTFE	ethylene–chlorotrifluoroethylene copolymer
E	ethylene
ETFE	ethylene–tetrafluoroethylene copolymer
FE	fluoroethylene
FEP	fluorinated ethylene–propene copolymer

FFKM	perfluoroelastomer
FKM	fluorohydrocarbon elastomer
FSR	fluorosilicones
HFP	hexafluoropropene
HFPI	hexafluoropropene index
IR	infrared
LCB	long chain branched
LOI	limiting oxygen index
MFA	methylfluoroalkoxy copolymer
MFI	melt-flow index
MWD	molar mass distribution
P	propene
PBVE	perfluoro-(3-butenyl vinyl ether)
PCTFE	polychlorotrifluoroethylene
PDD	perfluoro-2,2-dimethyl-1,3-dioxole
PE	polyethylene
PFA	perfluoroalkoxy copolymer
phr	parts per hundred of rubber
PMVE	perfluoro(methyl vinyl ether)
PP	polypropylene
PPA	polymer processing acids
PPVE	perfluoro(propyl vinyl ether)
PS	polystyrene
PTFE	polytetrafluoroethylene
PV	pressure–velocity
PVC	poly(vinyl chloride)
PVDF	poly(vinylidene fluoride)
PVF	poly(vinyl fluoride)
SSG	standard specific gravity
SVI	stretch void index
TAIC	triallyl isocyanurate
TFE	tetrafluoroethylene
TFEP	tetrafluoroethylene–propene rubber
THV	tetrafluoroethylene–hexafluoropropene–vinylidene fluoride polymer
TTD	2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole
VDF	vinylidene fluoride
VE	vinyl ether
VF	vinyl fluoride

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Polyacrylamides and Poly(Acrylic Acids)

ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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1. Introduction

It is difficult to imagine an aspect of our modern world not touched by polyacrylamides and poly (acrylic acids). These hydrophilic polymers, their copolymers with other hydrophilic monomers, and their metallic salts are utilized in many applications. Polyacrylamides are used in applications, such as mining, water treatment, sewage treatment, papermaking, oil well drilling, oil production, and agriculture. Poly(acrylic acids) are used in boiler-water additives, superabsorbent diapers, paints, detergents, industrial coatings, cosmetics, ceramics, textiles, ion-exchange resins, industrial adhesives, cements, and drug delivery [1]. The term polyacrylamide is used for homopolymers as well as for copolymers of acrylamide. Common comonomers for acrylamide are acrylic acid and its salts ("anionic polyacrylamide") as well as cationic ester of acrylic acid ("cationic acrylamide").

The utility of these polymers is directly related to their chemical structure, functionality, and molecular mass. The acid and amide functions are highly solvated by water, and are responsible for the solubility of the polymers in aqueous solutions. When cross-linked, the polymers swell in water without dissolving. The properties of polymers containing acrylic or methacrylic acid are dependent on the pH of the aqueous solution in contact with the polymer. Because the metal ion salt interacts with more water molecules than the unneutralized acid group, higher viscosity or higher swelling is observed at elevated pH, which is useful in thickeners or absorbent polymers. The proximity of the carboxyl groups to one another in poly(acrylic acid) gives rise to chelating properties with di- and trivalent metal ions, which is exploited in boiler-scale control and detergent builders. The high polymerizability of the monomers allows the preparation of high molecular mass polymers, which are useful as flocculants and thickeners. When the molecular mass is reduced, the polymers can be used as dispersants and scale inhibitors. The reactivity of the amide and acid groups allows simple chemical modifications that change the polymer properties and amplify the number of applications.

2. Raw Materials

Some useful physical properties of the water-soluble monomers used in the production of polyacrylamides, poly(acrylic acid), and poly

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(methacrylic acid) are listed in Table 1. All the monomers are toxic and should be handled with great care. Contact with the skin, eyes, and mucous membranes should be avoided. Breathing of vapors should also be avoided; operations should be conducted in vessels vented to scrubbers or in laboratory fume hoods. The monomers are quite reactive; their contamination can lead to uncontrolled polymerization and must be avoided. Dedicated storage vessels are used for the monomer. Manufacturers' data should be consulted for the safe handling and use of the products, e.g., [2, 3]. The best sources are material safety data sheets of the raw material producers, which are updated if new information is available.

Acrylic acid is described in detail elsewhere (→ Acrylic Acid and Derivatives). It is manufactured via oxidation of propene and has the largest production volume of the hydrophilic monomers. Significant progress has been made towards bio-based acrylic acid [4]. 3-Hydroxypropionic acid (3-HP) is the most likely precursor in a fermentation process. Acrylic acid is very corrosive to the skin and eyes, and its vapors are irritating to the eyes and lungs. Personal protective equipment, such as rubber gloves, goggles, impervious body coverings, and an organic vapor respirator should be used in the case of possible contact with acrylic acid. Commercial acrylic acid is normally inhibited against polymerization with 4-methoxyphenol (methyl ether hydroquinone, MEHQ). As this inhibitor requires oxygen for long-term effectiveness, air should be added to storage containers. The monomer should not be allowed to freeze because this causes the inhibitor to separate from the monomer by fractional crystallization. The resulting uninhibited acrylic acid is hazardous due to the significantly increased potential for uncontrolled polymerization.

Runaway polymerizations have occurred. A rail car of acrylic acid exploded in Teesside (UK) in 1976 as a result of too rapid thawing of frozen acid. The highly exothermic, adiabatic vinyl polymerization can become so hot that decarboxylation of the polymer occurs, with concomitant production of large volumes of carbon dioxide. A less violent, unplanned, runaway polymerization has been described [5].

Table 1. Properties of monomers used in the production of polyacrylamides, poly(acrylic acids), and their copolymers

Name	CAS registry number	Molecular formula	M_r	*mp*, °C	*bp*, °C	Density, g/cm^3	Flash point, °C	Heat of polymerization, kJ/mol	Oral (rat) LD_{50}, mg/kg
Acrylamide	[79-06-1]	C_3H_5NO	71.08	84.5	136 (3.33 kPa)	1.122 (30°C)		81.5	124
2-Acrylamido-2-methylpropanesulfonic acid	[15214-89-8]	$C_7H_{13}NSO_4$	207.21	185			160	92.0	1 410
Acrylic acid	[79-10-7]	$C_3H_4O_2$	72.06	13.5	141 (101.3 kPa)	1.040 (30°C)	50	77.5	340
N,N-Dimethylacrylamide	[2680-03-7]	C_5H_9NO	99.15	−40	81 (2.80 kPa)	0.926 (25°C)	70		700
N-Isopropylacrylamide	[2210-25-5]	$C_6H_{11}NO$	113.16	64					
Methacrylic acid	[79-41-4]	$C_4H_6O_2$	86.10	16	163	1.015	76	56.3	1 600 (mouse)
Methacrylamide	[79-39-0]	C_4H_7NO	85.12	110				56.0	459
N,N'-Methylene-bisacrylamide	[110-26-9]	$C_7H_{10}N_2O_2$	154.17	300		1.24 (30°C)		82.7	390

Here the major product of the vigorous reaction was polyester, which is formed in a Michael-type reaction between molecules of acrylic acid. In 2012 an explosion occurred at the Nippon Shokubai Himeji Plant. The explosion and subsequent fire in an acrylic acid intermediate tank killed one person and injured 36 [6].

Methacrylic acid is similar to acrylic acid in most regards and should be handled accordingly. For a detailed description of this compound, see →Methacrylic Acid and Derivatives.

Acrylamide is described elsewhere (→Acrylic Acid and Derivatives). It has toxic effects on the nervous system. A low-dose, long-term exposure study in rats showed an increased incidence of tumors. For a review on the toxicity of acrylamide see [7]. At higher doses, laboratory animals experienced reproductive deficiencies [2]. Contact with the monomer should be strictly avoided. Solid acrylamide sublimes readily so that contact with the vapor is a likely route for exposure. Therefore, acrylamide is supplied commercially as an aqueous solution to make handling simpler and to reduce potential exposure to vapors. Nowadays, most of the acrylamide monomer is produced by a biological process. Acrylonitrile is enzymatically hydrolyzed to acrylamide [8]. This process is cheaper and more selective than the copper-catalyzed hydrolysis of acrylonitrile. As with acrylic acid, oxygen is critical for inhibition of polymerization and dissolved oxygen should be present during storage because MEHQ is used as a free-radical scavenger. Acrylamide monomer is readily absorbed through the skin so that rubber gloves and impervious body clothing are required when contact with the aqueous solution is likely.

N,N-*Dimethylacrylamide.* At elevated temperatures and at high pH acrylamide can be hydrolyzed to acrylic acid. Therefore, in some special applications, acrylamide is replaced by the more stable *N,N*-dimethylacrylamide. However, this monomer is more expensive and used only in niche applications [9].

3. Production

3.1. Free-Radical Polymerization

Kinetics. An understanding of the polymerization kinetics of the monomers is essential for the control of polymer production. The molecular mass and molecular mass distribution of the polymers are key determinants of their physical properties and are influenced strongly by polymerization kinetics.

Advanced physical methods and modeling give a deeper insight to the kinetics, i.e., initiation, propagation, and termination [10]. Polymerization kinetics have been studied extensively for acrylic acid, its salts, and acrylamide. Less extensive data are available for the other monomers although some are available for methacrylic acid [11].

The kinetics of free-radical polymerization of acrylic acid, methacrylic acid, acrylamide, and methacrylamide have been investigated in water, dimethyl sulfoxide, tetrahydrofuran, and formamide at 30–60°C with azobisisobutyronitrile as initiator [12]. The polymerization rate is proportional to the monomer concentration and to the square root of the initiator concentration. The acrylics react faster than the methacrylics under identical conditions. The polymerization rate depends on the nature of the solvent; values of the kinetic constants for each monomer in each solvent were determined [12].

The polymerization kinetics for the acid monomers become complicated as the pH of the system changes. At constant overall monomer concentrations, the polymerization rate initially falls as the pH is increased from 2 to 7, then rises slowly from pH 7 to 12 [13, 14]. This has been attributed to a change in the propagation rate constant as the degree of ionization increases [15]. At pH 7 to 12, rates increase with an increase in the ionic strength of the medium [16]. This is accomplished either by adding simple monovalent salts or by increasing the ionized monomer concentration. Methacrylic acid shows a similar behavior [17]

Initiators play a complex role in polymerization kinetics, and initiator fragments can be important in the subsequent use of the polymer: For example, solution properties can deteriorate with time, depending on impurities [18]. Thermal initiators (e.g., azo compounds and

Table 2. Reactivity ratio as a function of pH [30]

pH	Acrylic acid	Acrylamide	Methacrylic acid	Acrylamide
	r_1	r_2	r_1	r_2
4	0.32 ± 0.046	0.57 ± 0.067	2.80 ± 0.44	0.20 ± 0.069
6	0.33 ± 0.20	0.85 ± 0.62	0.19 ± 0.08	0.55 ± 0.078
8	0.63 ± 0.004	0.12 ± 0.004	0.32 ± 0.004	0.53 ± 0.003

peroxides) produce free radicals in a homolytic scission reaction. The reaction, producing a pair of radicals, is characterized by the temperature at which the specific initiator is half consumed in 10 h. With those initiators the polymerization rate generally depends on the monomer concentration and the square root of the initiator concentration [19, 20]. The monomer may react with the initiator prior to the reaction of the free radical with monomer, and induce the decomposition of the initiator. In such cases (e.g., acrylic acid and sodium persulfate), the polymerization rate depends on the 1.5 power of monomer concentration and the square root of the initiator concentration [15, 16, 21]. Redox initiators produce free radicals in a reaction between a reducing agent and an oxidizing agent. Examples include the persulfate–thiosulfate reaction [22] and the manganic ion (Mn^{3+})-isobutyric acid reaction [23]. For redox initiators not involving metal ions, the polymerization rate usually depends on the first power of the monomer concentration. The rate also depends on the concentration of oxidant and reductant, the stoichiometry of their reaction, and the extent to which the initiators (usually the reductant) participate in radical termination reactions [22, 24–26]. When metal ions are involved in the redox reaction, the kinetics are more complex because the metal ion also participates in the termination step of the polymerization [23, 27, 28].

Copolymerization. See also→Polymerization Processes. The monomers listed in Table 1 are frequently copolymerized with one another and with other monomers. The relative reactivities of the monomers affect the microstructure and thus the physical properties of the polymer. When a comonomer is more reactive than its partner, it tends to be used up earlier in the reaction. The final product then has a distribution of composition as well as a distribution of molecular masses.

Reactivity ratios are derived from measurements of polymer composition as a function of conversion. Data from the entire conversion range of the copolymerization of acrylamide (AAm) and acrylic acid (AA) were utilized to calculate the following reactivity ratios [29]:

$$r_1(\mathrm{AA}) = 1.45 \pm 0.33,\ r_2(\mathrm{AAm}) = 0.57 \pm 0.04$$

Reactivity ratios for acrylic or methacrylic acid copolymerized with acrylamide have also been determined as a function of pH [30]. and the copolymerization has been studied [31]. Selected data are given in Table 2. Reactivity ratios for these and many other potential comonomers have been tabulated [32].

3.2. Polymerization Processes

The techniques described in this section are described in detail elsewhere (→Polymerization Processes).

3.2.1. Solution Polymerization

Batch Polymerization. The batch polymerization of the water-soluble monomers in solution is straightforward. The monomers are dissolved in water (or another solvent for both the monomer and polymer) at a desired concentration (usually 10–70%). Although acrylamide and acrylic acid have been polymerized in various organic solvents [12], water is used in industrial processes more or less exclusively. One of the very few exceptions is the polymerization of acrylic acid in 2-propanol, which introduces besides the carboxylic function additional functional groups into the molecule by acting as chain transfer agent [33].

The monomer solution is deoxygenated by bubbling an inert gas through the solution or by a series of evacuations and repressurization with an inert gas. The desired free-radical initiator is then added and the temperature, usually 40–80°C depending on the specific initiator used, is brought to the appropriate point for polymerization to begin.

The initial monomer concentration is limited because polymerization of the undiluted monomers is extremely dangerous due to the high heat of polymerization and rapid polymerization kinetics [34]. The concentration is also limited by the capacity of the equipment for removing the heat of polymerization and by the molecular mass of the desired polymer. If no heat can be removed from the reactor, the adiabatic temperature rise can be calculated for a given monomer concentration [35]. A suitable monomer concentration can then be calculated, based on the desired initial and final temperatures [36]. To have a better temperature control semibatch polymerizations are used: Part of the monomer solution is charged and the rest of the monomer solution is fed over a period of time [37]. The viscosity of the reaction mass is also important with regard to the equipment available for pumping the product. Higher molecular mass products generally dictate a lower monomer concentration because of their high viscosities, whereas low molecular mass products allow higher monomer concentrations.

Low molecular mass, water-soluble polymers are often desired, and several processes have been developed to produce them industrially. In one such process, sodium hydrogensulfite is added continuously to an aqueous monomer solution in a stirred tank while introducing fine air bubbles; polymerization occurs below 80°C [38]. The sulfite acts as a chain-transfer agent to lower the molecular mass. Sodium hypophosphite and 2-mercaptoethanol are commonly used for the same reason [39–41]. In another industrial process, poly(acrylic acid) of molecular mass 1 000–20 000 is prepared at 55 wt% concentration by polymerization with hydrogen peroxide and transition-metal activators, such as copper, iron, or manganese [42].

For some applications solid, dried products are preferred, e.g., powder detergents. The water may be evaporated using hot, rotating drum dryers or continuous belt, hot-air ovens, spray drying, or granulation devices. The dry flakes or lumps are then milled to the desired particle size and packaged in bags ranging in size from 22 to 1 000 kg. Depending on the process conditions, spray drying leads directly to powders or granules without further treatment [43]. Granules are more and more preferred over powders because of the much lower dust level.

Continuous Polymerization. Polymers can often be produced more efficiently by using a continuous polymerizer. An aqueous solution of monomers, initiators, and other additives is fed into one end of the polymerizer, and the polymeric product removed from the other. Low molecular mass copolymers of acrylic acid and acrylamide of controlled molecular mass (10 000 to 100 000) were produced in a packed-tube reactor operating at elevated pressure [44].

When a higher molecular mass is needed the aqueous monomer solution rapidly forms a gel after low conversions. This polymer gel is transformed by cutting, drying, and grinding into a powder. These powders contain up to 90 mass% of polymer. Such products can be used directly as powders (e.g., superabsorbents in diapers) or they are dissolved in water and used as diluted solutions (e.g., as flocculant in sewage plants). The production of superabsorbents is described elsewhere (→ Superabsorbents, Chap. 4). In principle the same processes can be used for the production of polyacrylamides [45]. Common are endless belt and tubelike reactors. If the molecular mass is less than 10^6 the gel is sticky after polymerization and not processable. Therefore, a minimum molecular mass is needed for gel polymerization.

A more flexible process is based on so-called smart scale production (SSP). It has a modular design and setup, and product switches can be handled in a shorter time frame [46]. In another process, 30–40 wt% aqueous monomer solution is pumped onto a continuous moving belt. Angled rollers at the edges of the belt cause a trough to be formed over a section of the belt. The trough holds the liquid monomers. As polymerization proceeds, a gel is formed from the reagents. The belt section flattens after it passes the final set of rollers, and the gel is

released from the belt and is finally discharged from the end of the conveyor. Superabsorbent polyacrylates are prepared industrially in this manner [45]. Another process for superabsorbent polymers is based on kneader technology. The monomer solution is fed at one end into a twin shaft reactor and discharged at the other end [47]. A quite different process, the so-called drop polymerization is currently under development. A droplet generator at the top of a reaction chamber releases droplets of a monomer solution into a gaseous atmosphere [48].

3.2.2. Inverse Emulsion Polymerization

In inverse emulsion polymerization, tiny droplets of aqueous monomer solution are dispersed in a continuous organic phase (usually aromatic or aliphatic hydrocarbons) prior to polymerization. The droplets are stabilized by surfactants. Free-radical polymerization of the monomers is conducted similarly to that described for solution polymerization (Section 3.2.1) [49, 50].

An obvious reason for using this technique instead of solution polymerization is to simplify the handling of the polymer product. The low-viscosity dispersion of monomer and polymer droplets is easy to agitate and pump and allows more efficient heat removal during polymerization. In addition, the particle size of the product is more easily controlled because it depends on the nature and amount of the emulsifier used to form the droplets prior to polymerization. Droplet size is typically 0.1–10μm. However, the process is more complicated; several more ingredients need to be controlled and recycled, especially the hydrocarbon phase (unless the product is sold in emulsion form). It is less efficient on a volumetric basis compared to a powder product, due to the presence of the continuous organic phase. However, it is possible to make such inverse emulsions with a high active content. For a cationic polyacrylamide it is possible to use up to 70 wt% of aqueous monomer phase that itself has a monomer concentration of 30–70 wt% [50]. The overall content of the polymer can reach nearly 50 mass%.

It is possible to increase the active content by removing the volatile byproducts and water [51]. Such products are more expensive due to the distillation step and are used for special applications, such as personal care and pharmaceutical formulations [52].

Modern inverse emulsion products are self-inverting. The monomer emulsion is made using a water-in-oil emulsifier (HLB 3.5–7.5). After polymerization a second emulsifier with higher HLB is added (9 to 14), which acts as an oil-in-water emulsifier [53]. If the product is added to a large amount of water, the oil is emulsified in the water, and the polymer is released. This process is very rapid, and the polymer is dissolved completely within a very short time so that inline dosage is feasible. This is an advantage of inverse emulsions over powder products.

Inverse emulsions can be converted into a powder by a spray-drying process [54]. However, this process causes additional costs and is, if at all, used for niche applications.

3.2.3. Suspension Polymerization

In suspension polymerization, small droplets of aqueous monomer solution are dispersed in a hydrocarbon phase, generally with the aid of water-in-oil emulsifier or other polymers [55, 56]. Poly(acrylic acid) (linear and cross-linked) and polyacrylamides can be made by this process. Free-radical polymerization of the monomers is then conducted in a manner similar to that described for emulsion systems (see Section 3.2.2). After the polymerization, the polymer is dried by boiling off the water. The beads are filtered from the organic phase using a centrifugal or other industrial filter. The residual organic phase is then evaporated from the beads using an explosion-proof dryer. The droplet size is controlled by the amount of dispersant used; more dispersant generally yields smaller particle size. Larger polymer particles can be obtained than with emulsion processes. Typically, 15–500 μm spherical beads are formed. Cellulose esters or cellulose ethers are used as protective colloids in the suspension polymerization of sodium acrylate, acrylamide, 2-acrylamido-2-methylpropanesulfonic acid, or sodium styrenesulfonate [57]. A mixed suspending agent for water-soluble monomers consisting of hydrophobic

fumed silica and a copolymer of acrylic acid and lauryl methacrylate yields a controlled particle size distribution [58]. A copolymer of cetostearyl methacrylate and methacrylic acid is beneficial for the polymerization of cationic polyacrylamide [59].

3.2.4. Precipitation Polymerization

In precipitation polymerization, the monomer is polymerized in a medium which is a solvent for the monomer but a nonsolvent for the polymer. As the polymer forms, it precipitates from the monomer phase. With the proper choice of medium, polymer isolation and purification is simplified. For example, cross-linked polymers can be produced by copolymerizing acrylic or methacrylic acid with small amounts of an allyl phosphate or phosphite with free-radical initiators in a solvent, such as benzene, hexane, acetone, or chloroethane at ca. 20–90°C [60]. This technology is the basis for the process used industrially to produce Carbopol poly(acrylic acid) resins. The precipitating polymerization of poly(acrylic acid) has been accomplished in methyl ethyl ketone [61].

3.2.5. Polymer-Analogous Reactions

The term polymer-analogous reactions denotes reactions that are used to modify the functional groups of polymers. Such reactions are complex from a practical perspective because of the high viscosities of polymer solutions and the changing solubilities of the polymers as they are converted to a different functionality. Polymers of acrylate esters can be hydrolyzed to the corresponding acid polymers and their salts. Polyacrylate esters can also be reacted with amines to yield polyacrylamide or polymethacrylamide derivatives. Polyacrylonitrile can be saponified to a copolymer of acrylic acid salt and acrylamide.

Poly(acrylic acid) undergoes reactions typical of other organic carboxylic acids. It has been reacted with diazomethane to yield poly (methyl acrylate) and with thionyl chloride to yield the acid chloride, which has increased reactivity in acylation reactions, such as amidation. A direct amidation of polyacids is carried out in water at elevated temperature to obtain partially sulfonated polymers [62, 63]. Poly(acrylic acid) can also be dehydrated above 200°C to yield a polyanhydride. The polyacids are generally reacted with neutralizing agents, e.g., alkali-metal hydroxides, carbonates, or amines, to yield the salt. Esterifications and transesterifications have been carried out in organic media using enzymes as catalyst [64]. Polyacrylamides can also be chemically derivatized [65]. Polyacrylamide reacts with formaldehyde in aqueous solution to yield a partially hydroxymethylated polymer. It is also readily hydrolyzed with aqueous sodium hydroxide or sodium carbonate solution to give a polymer with a maximum of ca. 86% acrylic acid moieties [66]. Main issue for this process is the large amount of ammonia that is released. Amide groups are converted to amine groups via the Hofmann reaction [67]; the amide is reacted with sodium hydroxide and hypochlorite to yield the amine. Amine groups can also be introduced into polyacrylamide by the Mannich reaction. Polyacrylamide is reacted with formaldehyde and an amine to produce an *N*-aminomethylated polymer. Intramolecular imidization occurs when polyacrylamide is heated with a strong acid catalyst.

Due to the processing difficulties encountered in conducting polymer-analogous reactions, such reactions are not typically used to convert a polymer to one with different functional groups. Nevertheless, the technique is used widely for cross-linking polyacrylamides and poly(acrylic acids). Polyacrylamide is cross-linked by reaction of its amido groups with glyoxal (→ Glyoxal). Alternatively, a reactive monomer can be synthesized from acrylamide and glyoxylic acid, copolymerized with acrylamide, and used as a reactive site for subsequent cross-linking (→ Glyoxylic Acid). Poly(acrylic acid) is cross-linked by reaction of its carboxylic acid groups with glycols; this technique is used industrially to cross-link the surface of superabsorbent polymers (→ (Superabsorbents, Chap. 4)).

3.2.6. Residual Monomer Scavenging

An important part of the production of these polymers is the reduction of residual monomers, especially residual acrylamide as it is

carcinogenic. Depending on the application, different types of polyacrylamides are available. For drinking water application, special grades are offered with very low residual acrylamide.

The residual monomer content can be reduced by sulfite solution or gaseous sulfur dioxide [68, 69]. The principle is the Michael addition of a scavenger to the double bound of the residual monomer [70]. Another option is the use of initiator combinations containing one component that reacts at later stage of the production process, e.g., a UV initiator is activated in the drying by irradiation [71].

For solution polymers and inverse emulsions a reshoot with additional polymerization initiator is possible. Simple distillation [72] and solvent extraction [73] have also been employed.

4. Properties

The properties of the polymers as solids and in solution (particularly aqueous solution) determine their applications. Their hydrophilic nature and molecular mass are key determinants of the usefulness of the polymers for specific applications. The molecular mass and the molecular mass distribution can be measured by light scattering, osmometry, and ultracentrifugation. Intrinsic viscosity is the most useful and widely used method of correlation between molecular mass and viscosity: Appropriate equations are given below for individual polymers. Molecular masses are also correlated to the radius of gyration of the molecules in solution by gel permeation chromatography (size-exclusion chromatography) or hydrodynamic chromatography. Very high molecular mass polymers are susceptible to degradation by high shear [74], oxidation [75], and conformational changes [76], which can be induced by impurities introduced as polymerization modifiers. The above methods are useful for measuring the extent of such changes.

Analysis of the polymers and determination of their content of comonomer residues are of practical importance. These can be determined by infrared spectroscopy [77] and nuclear magnetic resonance (NMR) spectrometry [78]. The tacticity of the polymers is also measured by NMR spectrometry [79]. Thermal transitions and polymer chemistry are investigated with differential scanning calorimetry, thermogravimetric analysis (TGA), and TGA-mass spectrometry.

Poly(acrylic acid) [9003-01-4] is soluble in many polar and usually hydrogen-bonded solvents such as water, methanol, ethanol, dioxane, dimethylformamide, 2-propanol, formamide, ethylene glycol, and acetic acid. The value of the glass transition temperature (T_g) is still in dispute because it is difficult to obtain a solventfree sample. T_g has been reported at 106°C [80], at 118°C [81], and at 126°C [82]. Mark–Houwink–Sakurada relationships for determining the weight-average molecular mass M_W from the intrinsic viscosity $[\eta]$ have been determined in many solvents but the following two are widely used:

$[\eta] = 0.085\ M_W^{0.5}$ mL/g	dioxane, 30°C [83]
$[\eta] = 0.1062\ M_W^{0.5}$ mL/g	0.2 mol/L HCl, 14°C [84]

The exponents of 0.5 indicate theta conditions for the polymer. Under theta conditions, a given polymer–solvent pair behaves as if it were an ideal solution. This is because the attraction between polymer chain segments just equals the loss of entropy brought about by interpenetration of polymer molecules. If conditions for solvation are made any poorer than those at the theta condition, the polymer precipitates. For poly(acrylic acid), lowering the temperature from the upper critical solution temperature, UCST, causes phase separation. Poly(acrylic acid) is stable in acid or base solution. The solid polymer slowly liberates water upon heating above 100°C, forming the anhydride. The polymer decomposes slowly above 250°C, liberating carbon dioxide.

The simple alkali-metal salts have been characterized extensively, especially poly(sodium acrylate) [9003-04-7]. Poly(potassium acrylate) [25608-12-2] and poly(ammonium acrylate) [9003-03-6] are also known. These polymers are soluble in water and in aqueous salt solutions. Small amounts of organic solvents dissolved in water are sometimes tolerated. The fully neutralized sodium salt has a glass

transition temperature at about 250°C [81]. Obtaining an accurate value is difficult because of the hygroscopic nature of the polymer. Mark–Houwink–Sakurada relationships have been determined in many aqueous solutions; for example

$[\eta] = 1.24 \times 10^{-3} M_W^{0.5}$ mL/g — 1.5 mol/L NaBr, 15°C [85]
$[\eta] = 0.146 \times 10^{-3} M_V^{0.80}$ mL/g — 0.1 mol/L NaCl, 25°C [86]

Poly(acrylic acid) salts are more stable to heat than the acid polymer. Anhydride formation is not observed above 50 mol% neutralization of acid groups and up to 250°C, where carbon dioxide evolution is observed.

Polyacrylamide [9003-05-8] is soluble in polar, hydrogen-bonded solvents, such as water, aqueous salt solutions, ethylene glycol, formamide, ethanolamine, dimethyl sulfoxide, and morpholine. For cationic and anionic copolymers, water is the main solvent. The glass transition temperature is again difficult to determine, because it is difficult to prepare a solvent-free sample; T_g is reported as 170°C [87] and 188°C [82]. The density of the polymer is 1.302 g/cm^3 [88]. The diffusion coefficient D and the sedimentation coefficient S_0 have been determined as a function of molecular mass [89]:

$D = 1.24 \times 10^{-4} M_W^{-0.53}$ cm^2/s
$S_0 = 1.07 \times 10^{-15} M_W^{0.48}$ svedberg

Mark–Houwink–Sakurada relationships have been determined in many solvents [90]:

$[\eta] = 9.33 \times 10^{-3} M_W^{0.75}$ mL/g — water
$[\eta] = 7.19 \times 10^{-3} M_W^{0.77}$ mL/g — 0.5 mol/L NaCl
$[\eta] = 1.36 \times 10^{-1} M_W^{0.51}$ mL/g — ethylene glycol

A theta condition has been established in a 2 : 3 ratio of methanol : water at 20°C [91], and has been estimated at −38°C in aqueous solution.

Solutions of polyacrylamide in strong acid gradually become turbid due to imide formation from amide groups. The amide groups hydrolyze to ammonia and carboxylic acid above pH 9. The solid polymer is stable below 210°C, but the amide groups decompose to ammonia above 210°C.

The determination of the molecular mass is quite difficult as most of the polymer have a molecular mass above the exclusion of GPC. Field-flow fractionation has been established as a method to evaluate molecular masses [91]. Very important for the characterization of polyacrylamides are rheological methods [92].

Poly(methacrylic acid) [25087-26-7] is soluble in ethanol, methanol, water, dimethylformamide, dioxane, and 2-ethoxyethanol. The polymer and its sodium salt [54193-36-1] have been characterized because of curiosity about the conformational change that occurs upon neutralization of the acid polymer to about 30 mol%. The glass transition temperature occurs at 185°C [93]. Mark–Houwink–Sakurada relationships are:

$[\eta] = 22.4 \times 10^{-3} M_W^{0.679}$ mL/g — methanol, 25°C [94]
$[\eta] = 6.6 \times 10^{-3} M_W^{0.5}$ mL/g — 0.002 mol/L HCl, 30°C [95]

The above theta condition at 30°C in dilute hydrochloric acid is questionable in light of experiments that show phase separation in poly(methacrylic acid) solutions when the temperature is raised to 56°C [84].

The stability of poly(methacrylic acid) and its salts to acids and bases is similar to that of poly(acrylic acid). The solid polymer evolves water above 180°C, forming an anhydride.

Polymethacrylamide [25014-12-4] is soluble in methanol, water, ethylene, glycol, and mixtures of acetone and water. A Mark–Houwink–Sakurada relationship has been established as

$[\eta] = 2.1 \times 10^{-3} M_W^{0.76}$ mL/g — water [96]

Stability of polymethacrylamide, either in solution or as dry solid, has not been reported.

The major copolymers are those of acrylic acid and acrylamide, prepared either by partial hydrolysis of polyacrylamide [97] (hydrolyzed, sodium salt [25987-30-8] and hydrolyzed, potassium salt [31212-13-2]) or by copolymerization of the respective monomers [82]. The properties of the copolymers depend on the mole fractions of the two monomer residues [98] and on the distribution of molecular masses of the sample [99]. The intrinsic

viscosity (and the second virial coefficient) of the copolymers shows a maximum at 33 mol% acrylic acid residues [98]. Flocculation rate increases with molecular mass; maximum activity was observed with a 70 mol% acrylate copolymer [100]. Solution characteristics of heterodisperse copolymers were determined at various compositions in salt solutions by viscometry, light scattering, and gel permeation chromatography. Mark–Houwink–Sakurada relationships have been determined over the entire composition range with corrections for heterodispersity [99]. Copolymers of methacrylic acid and acrylamide have been similarly characterized as a function of pH [101]. The sudden increase in intrinsic viscosity observed at pH 4–5.5 has been attributed to a sudden unfolding of the chains when the electrostatic repulsion of the ionic groups is just sufficient to overcome the hydrophobic bonding of the α-methyl groups.

Poly(N-isopropylacrylamide) [25189-55-3] is of interest because of a lower critical solution temperature (LCST) of just 31°C in aqueous solution [102]. Dissolved poly(*N*-isopropylacrylamide) precipitates and its cross-linked gels deswell when the temperature is raised above the LCST. It is soluble in water, methanol, and tetrahydrofuran. The glass transition temperature has been measured at 130°C [103]. A Mark–Houwink–Sakurada relationship has been determined:

$[\eta] = 0.112\, M_W^{0.51}$ mL/g — water, 20°C [104]

Poly(N,N-dimethylacrylamide) [26793-34-0] is soluble in water, methanol, 2-methoxyethanol, methyl ethyl ketone, diethyl ether, toluene, chloroform, and dioxane. It has a low glass transition temperature (89°C) [105]. The polymer has been extensively characterized only in methanol and water. The Mark–Houwink–Sakurada relationships are [106]:

$[\eta] = 17.5 \times 10^{-3}\, M_W^{0.68}$ mL/g — methanol, 25°C
$[\eta] = 23.2 \times 10^{-3}\, M_W^{0.81}$ mL/g — water, 25°C

Poly(2-acrylamido-2-methylpropanesulfonic acid) [27119-07-9] is soluble in water, aqueous salt solutions, and dimethylformamide. The sodium salt is soluble in aqueous solution. Mark–Houwink–Sakurada relationships for the homopolymer and its sodium salt are [107]:

$[\eta] = 2.11 \times 10^{-3}\, M_W^{0.8}$ mL/g — H^+ form, 5 mol/L NaCl
$[\eta] = 1.95 \times 10^{-3}\, M_W^{0.85}$ mL/g — Na^+ salt in 0.5 mol/L NaCl

Solution properties of carboxylated and sulfonated copolymers have been compared [108].

5. Uses

The molecular mass of a polymer is a key factor in determining its usefulness for a particular application. Polymers of molecular mass less than 20 000 are used as sequestrants and scale inhibitors. Polymers of molecular mass between 20 000 and 80 000 are useful as pigment dispersing agents. Polymers with molecular mass between 10^5 and 10^6 are used as textile finishing agents and retention aids for papermaking. Molecular masses exceeding 10^6 are necessary for flocculants and thickening agents [109]. High molecular mass, cross-linked polymers are used as fluid absorbents. Uses of functional polymers in general and in particular of poly(acrylic acids) and polyacrylamides have been described [1]. The ionic character of the polymer is another important factor in determining its applications. Choices range from nonionic polyacrylamides to partially hydrolyzed polyacrylamides or copolymers of acrylic acid and acrylamide and finally to the salts of poly (acrylic acid). The appropriate choice of ionic content depends on the pH, ionic strength, surface charge of any substrate with which the polymer interacts, and other conditions specific to the application.

The polymers are supplied as solutions, emulsions, and powders. Low molecular mass polymers are typically supplied as viscous, aqueous solutions containing 20–50 wt% polymer. Above a molecular mass of 2×10^5, the high viscosity of such solutions makes them too difficult to meter into processes and mix well; they are supplied as powders packaged in 22 kg bags. The powders are difficult to dissolve in water because the particles hydrate

exceedingly fast, forming gelatinous clumps. Special mechanical dispersers are available from the suppliers to aid dissolution [110]. High molecular mass polymers are also supplied as inverse emulsions; micrometer-sized polymer particles are dispersed in a liquid hydrocarbon with the aid of surfactants. These emulsions are of relatively low viscosity and readily pumped and metered. When the emulsion is added to water the emulsion inverts and the small polymer particles quickly dissolve. Emulsion products are supplied in drums or tank trucks. Cross-linked polymers, such as superabsorbents are supplied as granules in 1-t sacks that empty from the bottom to make addition of the polymer into hoppers easier.

5.1. Poly(Acrylic Acids) and Their Salts

Water-soluble poly(acrylic acid) and its neutralized salts with a molecular mass of 2 000–5 000 are used as scale inhibitors, sludge (mud, silt, clay) dispersants in cooling water systems, and as dispersants for preparing $CaCO_3$ or clay slurries as fillers, pigments, or paper-coating materials [111].

Homo- or copolymers of acrylic acid and methacrylic acid and mixtures with up to 10 wt % alkyl acrylate comonomers prevent soil redeposition in liquid detergent formulations [112]. The polymer, neutralized or not, has a molecular mass of 10^5–10^6. Relatively small amounts of polymer prevent soil redeposition, improve cleaning performance and viscosity control.

Copolymers having small amounts of pendant hydrophobic groups are also useful as hydraulic fracturing fluids for oil well drilling [113]. The fluids are readily formulated to give an initial viscosity that is retained for long periods at high temperatures and under high shear rates; this is due to hydrophobic bonding between the pendant groups. The polymer molecular mass can be below 10^6 and yet provide high viscosity in solution because the associating hydrophobic groups create a high pseudomolecular mass.

Cross-linked poly(sodium acrylate) is used as an absorbent in baby diapers [114–116]. Other applications include adult incontinent products [117], feminine hygiene products [118], absorbents in transmission cables [119], and agricultural mulches [120]. Cross-linked polymers of acrylic or methacrylic acid, neutralized to greater than 50 mol%, may also be used to provide high water retention capacity and high viscosity in plaster [121]. A cross-linked, water-absorbent acrylic acid polymer can be used in formulations for sustained-release tablets for oral administration [122]. A blend of water-swellable particles of anionic polymer of acrylic acid or methacrylic acid and their soluble salts and cationic polymers of amino acrylate and aminoalkyl acrylamide is used in prepasted wall-covering adhesive [123] to reduce water absorption. Cross-linked poly(acrylic acid) is also used as a weakly acidic, cation-exchange resin (→ Ion Exchangers).

5.2. Polyacrylamides and Hydrolyzed Polyacrylamides

Polyacrylamides are typically high molecular mass products ($>10^6$) made by gel polymerization or inverse emulsion polymerization. Less common products are inverse suspension polymers, which are used in some special applications.

Slightly hydrolyzed polyacrylamide with molecular mass $(1–5)\times10^5$ is useful as a strengthening agent in finished paper. Polymers with molecular masses up to 10^6 add wet strength in paper production. Polyacrylamides with molecular masses of $(1–2)\times10^6$ are used as retention aids in papermaking. The polymer binds the smaller fibers and any filler particles to the larger fibers.

Polyacrylamides and molecular masses of $(1–2)\times10^6$ are used as retention aids in papermaking. The polymer binds the smaller fibers and any filler particles to the larger fibers.

Polyacrylamides and hydrolyzed polyacrylamides having molecular masses of $(2–20)\times10^6$ are used in applications involving flocculation or to increase the viscosity of aqueous systems. Flocculation is the major use for polyacrylamides [124](→Water, 4. Treatment by Flocculation and Filtration)) and (→Acrylic Acid and Derivatives)). Flocculant applications include clarification of water used in industrial processes (e.g., as pretreatment of boiler water), in treatment of

effluent from paper mills, and in sewage treatment. In sewage treatment, polyacrylamides increase the removal of solids in the primary settling step, improve clarification of the discharged water, aid in sludge thickening, improve clarity in the supernatant from digesters, and increase water removal during sludge dewatering [125]. Molecular mass and and mole fraction of ionic groups are optimized to obtain maximum performance. Copolymers of acrylamide and acrylic acid of different compositions were prepared and their flocculation activity toward kaolin clay suspensions studied [100]. Flocculation rate increased with molecular mass, maximum flocculation activity are observed with 70 mol% acrylate copolymer.

In the exploration and production of mineral oil, there are several applications for polyacrylamides. They are used as rheology modifier for aqueous drilling fluids (water-based muds) and shale inhibitors in drilling of boreholes [126]. The water-based mud is used to power and cool the drill bit and to stabilize the formation. Additionally, the water-based mud transports the cuttings to the surface. To be most efficient a complex rheology is necessary. Low molecular polyelectrolytes are used as fluid loss control agents. These products prevent the loss of water from the drilling into the formation. The same principle applies to the cementing of the borehole in which similar products are employed.

During the life-cycle of an oil field the enhancement of the gas or oil-flow might be necessary. This process is called stimulation. If the permeability of the reservoir rock is too low, a so-called fracturing might be applied. During this operation, aqueous solutions are pressed under very high pressure into the formation, which induces fractures. To minimize energy losses during pumping, so-called friction reducers (drag reducers) are used. Liquid inverse emulsions of anionic polyacrylamides are frequently used in this application. If the aquifer of the oil reservoir is too close to the producing well, high amounts of water are pumped with the oil. To reduce the amount of produced water, aqueous solutions of polyacrylamides are pumped with gelling agents through the production well into the formation. Common gelling agents are chromium and zirconium salts. This operation is called water shut-off.

With maturity of an oil field, the reservoir pressure is maintained by injection of water from the sides of the reservoir (secondary oil recovery). During this operation, water channels through the oil banks and thus increases the fraction of water in the produced fluid (mixture of oil and water). To reduce the channeling, the viscosity of the injection fluid is increased to that of the oil by the addition of polymers (tertiary oil recovery). Anionic polyacrylamides are used nearly exclusively for this application. For high salinity or high temperature oil fields sulfonated and/or hydrophobically modified polymers are used.

Some superabsorbents containing acrylamide as comonomer are used in special applications, such as soil conditioning or cable insulation (→ Superabsorbents, Chap. 6). Dust is controlled on roads, in mines, and particularly on surfaces of pulverized coal and mineral piles within open transit cars or trucks by applying oil- continuous emulsions of highly branched, cross-linked, water-swellable polymers of acrylamide and acrylic acid [127]. The polymers are in the form of microgelatinous particles ($\leq$ 1 mm diameter) that swell dramatically in water and then bind dust particles.

5.3. Other Polymers

The polymers described in this section are generally experimental products, some of which are available in developmental quantities.

Lightly cross-linked poly(*N*-isopropylacrylamide) hydrogels have a phase transition at 31°C. This property has been suggested to be useful in separations, such as concentration of soy protein from aqueous extracts [128] or in controlled drugs release [129].

The good balance of hydrophobic and hydrophilic groups in poly(*N,N*-dimethylacrylamide) and copolymers of *N,N*-dimethylacrylamide with other water-soluble monomers makes these materials soluble in a wide range of solvents. This suggests utility as thickeners in formulations with high concentrations of organic chemicals. The homopolymer is mutually soluble with poly(vinyl acetate), poly(methyl methacrylate), and polystyrene. Appropriate copolymers may serve as polymer compatibilizers [130]. The homopolymers of

2-acrylamido-2-methylpropanesulfonic acid and copolymers with acrylamide [131] and the corresponding alkali-metal salts have been used in applications where the chelation tendencies of carboxylate copolymers toward di- and trivalent ions are detrimental, and for thickening aqueous solutions of strong acids [132] (e.g., in the acidification of oil wells [133]).

6. Economic Aspects

The homo- and copolymers of acrylic acid, its salts, and acrylamide make up the majority of the production volume of these polymers. Manufacturers and trade names are listed in Table 3. In 2008, worldwide production of poly(acrylic acid) and polyacrylamide amounted to 1.58×10^9 kg and 750×10^6 kg, respectively.

The market for poly(acrylic acid) was divided as follows: 69.6% as superabsorbent polymers, 10.5% as detergent additives, 11.7% as industrial dispersants, 4.6% as water treatment chemicals (primarily sequestrants and scale inhibitors), and 3.8% as coatings components and drilling muds. The polyacrylamide market was divided as follows: 37% for water treatment (primarily flocculants, 22% for municipal and 15% for industrial water treatment), 25% for additives in pulp and paper, 20% for oil recovery, 10% for mineral processing, and 8% other. Geographically, 48.2% of the poly(acrylic acid) was used in the United States and Canada, 31.3% in Western Europe and 20.5% in Japan. For polyacrylamide the breakdown was 28% United States and Canada, 27% Europe, and 45% Asia.

Annual growth for all segments of the polyacrylamide market was expected to be 5–7% in 2008. The poly(acrylic acid) market is dominated by the superabsorbent polymers which is expected to grow by 3 to 4 % in 2006. For the other polymer a slightly lower growth is expected (around 3%)

Table 3. Manufacturers and trade names of poly(acrylic acids) and polyacrylamides

Company	Trade name	Type*
Poly(acrylic acids)		
Akzo Nobel	Alcosperse	b
BASF SE	Dispex	b
	Sokalan	b
	Hysor	a
BF Goodrich	Carbopol	d
Dow Chemical	Acusol	b
Evonik	Favor	a
Nippon Shokubai K.K.	Aqualic	a
Sanyo Chemical Industries	Sanwet	a
Polyacrylamides		
Alco Chemical	Aquatreat	b
BASF SE	Magnafloc, Zetag	c
	Percol	c, d
	Alcoflood	d
Beijing Hengiu	Hengfloc	c
Kemira	Superfloc	c
	Fennopol	e
Mitsubishi Rayon Co, Ltd.	Diafloc	c
Nalco	Ultimer	c, d, e
SNF Floerger	Aquasorb	a
	Flopam	c
	Floret	e
Solenis	Praestol	c, d
	Praestaret	e

* a = superabsorbent; b = dispersant, scale inhibitor; c = flocculant; d = thickener; e = retention aid.

7. Toxicology, Occupational Health, and Environmental Aspects

Polyacrylamides, hydrolyzed polyacrylamides, poly(acrylic acids) and their salts are relatively nontoxic materials. Care should be taken in the finishing of the polymers to strictly limit the content of any unreacted monomers because they are toxic [135]. Handling of the monomers is described in Chapter 2.

Poly(acrylic acid) showed low toxicity in acute screening tests indicated by an LD_{50} of 5 000 mg/kg (rat, oral) and 3 000 mg/kg (rabbit, dermal) [109, 136]. Screening tests for toxicity to aquatic wildlife showed that the LC_{50} was greater than 1 000 ppm for daphnia, sunfish, and trout [137]. Neutralized products of high alkalinity can be irritating to the eyes and skin.

The toxicity of polyacrylamide and hydrolyzed (anionic) polyacrylamide containing only 500–800 ppm residual monomers has been evaluated in rats, dogs, and fish [138]. Low toxicity is indicated by the single oral dose LD_{50} which is greater than 4 000 mg/kg in rats. The results from two-year feeding studies in rats showed no effect at 1% dietary concentration and a slight retardation in growth at the 5% dietary level. Dogs were unaffected by

feeding diets containing up to 6% of these polymers. Fathead minnows, bluegills, and rainbow trout were unaffected by up to 100 ppm of these polymers in the water for 90 days. Minnows were all killed by a solution of 2 500 ppm of hydrolyzed polyacrylamide; the fish had extreme difficulty swimming due to the high viscosity of this test solution. Cationic derivatives of polyacrylamides can kill fish and should not be allowed into natural waterways. Polyacrylamide, cationic- and anionic-modified polyacrylamides, and poly(acrylic acid) and its salts strongly adsorb to many solids. They are thereby effectively removed from sewage in a waste treatment plant as a component of the sludge. Polyacrylamides showe no evidence of toxicity at a dosage of 10^4 mg/kg in rabbits [65]. The fate of polyacrylamides in hydrosystems is reviewed in [139]

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Polyacrylates

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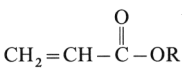
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1. Introduction

Acrylic acid and acrylate esters have been known since the middle of the nineteenth century. A systematic investigation of acrylate esters was published in 1901 by H. von Pechmann and O. Röhm [12]. A process for the industrial production of acrylate esters was developed in 1928 by H. Bauer [13] of Röhm & Haas. Solution polymers have been produced from methyl methacrylate since 1927 by Röhm & Haas (Darmstadt, Germany). Emulsion polymers were first developed on an industrial scale in 1929/30 by H. Fikentscher [14, 15], and were introduced onto the market by BASF as a polymer dispersion named "Corialgrund" for the surface finishing of leather.

The use of polyacrylates in many fields of application increased rapidly with the development of new methods for producing acrylic acid and acrylate esters (e.g., the process described by W. Reppe in 1953 [16]).

Acrylate esters are compounds of the general formula



where R is an alkyl group.

Methyl, ethyl, *n*-butyl, and 2-ethylhexyl acrylate are produced on a large scale. Other acrylate esters such as *tert*-butyl, isobutyl, or lauryl acrylate are also produced industrially, but have not yet become quantitatively important.

Homopolymers of acrylate esters are suitable only for a few areas of application, whereas their copolymers have numerous potential applications. Methacrylates (particularly methyl methacrylate), styrene, acrylonitrile, vinyl acetate, vinyl chloride, vinylidene chloride, and butadiene are used as comonomers to obtain the desired copolymer properties.

In addition, auxiliary monomers are frequently incorporated in polyacrylates to obtain specific technical properties in dispersions. Although these auxiliary monomers are only present in low concentration in the polymer, they have a substantial influence on the colloid chemistry and other properties of polymer dispersions. Commonly used auxiliary monomers include acrylic acid, methacrylic acid, acrylamide, methacrylamide, and other monomers with functional groups.

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Polyacrylates can be produced by various processes, emulsion polymerization being the most important industrial method. Solution polymerization is also of practical importance. Bulk polymerization is only performed on a small scale, but will presumably become more important in the future; printing plates are produced by this process. Radiation-curable paints also undergo bulk polymerization. In contrast to the methacrylates, suspension polymerization is of no technical importance.

2. Raw Materials

The production and properties of acrylic acid and its esters are described elsewhere, → Acrylic Acid and Derivatives [17]. Acrylates produced industrially by esterification of acrylic acid are available with a purity of 99–99.5%. Special acrylates may have a somewhat lower purity. Acrylate esters are clear, colorless liquids, which are normally stabilized with 15 ± 5 ppm of hydroquinone monomethyl ether. These small amounts of stabilizer do not affect polymerization. Hydroquinone monomethyl ether does not cause discoloration during polymerization and is therefore preferred to hydroquinone. Since the stabilizer is effective only in the presence of oxygen, the monomers must be stored under air and not under an inert gas. In exceptional cases (e.g., overseas dispatch or in special acrylates), a higher amount of stabilizer is used (≥ 100 ppm).

Unstabilized monomeric acrylates can be stored for only a few weeks at temperatures below 10 °C. The stabilized monomers are generally stored below 20 °C. Acrylic acid and methacrylic acid should not, however, be stored below 18 °C because they crystallize and spontaneously polymerize at this temperature.

Some physical properties of acrylates, comonomers, and auxiliary monomers are summarized in Table 1. Further data on the industrially most important acrylate esters are listed in Table 2. Guidelines for analyzing acrylates to determine their purity, acid number, water content, and stabilizer content [17] can be obtained from the technical data sheets of the manufacturers [18].

Acrylates with appropriate substituents can be copolymerized to obtain copolymers with special properties such as low flammability, antistatic behavior, cross-linkability, elasticity, solubility or insolubility in certain solvents, hydrophilicity, or hydrophobicity [22]. Such substituents include halogens, hydroxyl, epoxy, or *N*-methylol groups. Hydrophilicity is achieved by incorporating acrylic acid, acrylamide, or hydroxy-functional monomers (e.g., hydroxypropyl or hydroxyethyl acrylate). Incorporation of relatively large amounts of acrylic acid can increase hydrophilicity to such an extent that the emulsion polymers dissolve completely in water as a result of salt formation, to form a clear solution at pH 6–8 [23].

Compatibility with cationic auxiliaries is achieved by incorporating cationic monomers such as dimethylaminoethyl methacrylate or diethylaminoethyl acrylate.

Physical properties of selected acrylates and methacrylates with reactive groups are listed in Table 3 [17].

3. Production

Acrylates can be polymerized extremely easily because their carbonyl groups are adjacent to a vinyl group. Polyacrylates are produced almost exclusively by radical polymerization; conventional radical formers (e.g., peroxides and other per compounds) or azo starters are used as initiators. Polymerization can also be initiated photochemically, by γ-rays, or by electron beams. Although ionic (particularly anionic) polymerization [24] is possible, this process is not used industrially. Ordered (i.e., cis or trans) polymers can be produced by this polymerization process. The heat of reaction in the exothermic polymerization of acrylates is ca. 60–80 kJ/mol, and must be removed if the process is to be controlled effectively [25, 26]. The kinetics of radical polymerization and copolymerization are described in detail elsewhere (→ Polymerization Processes, 1. Fundamentals, → Polymerization Processes). The reactivity ratios r_1 and r_2 for industrially important acrylates and comonomers are summarized in Table 4.

3.1. Emulsion Polymerization

Emulsion polymerization is the most important industrial process for producing polyacrylates and their copolymers [47–50]. Polymers with

Table 1. Physical properties of monomeric acrylates and other comonomers [18]

Monomers	CAS registry no.	M_r	*fp*, °C	*bp* (101.3 kPa), °C	d_4^{25}	n_D^{25}	Solubility in water, g/100 cm^3	
							25 °C	80 °C
Acrylates								
Methyl acrylate	[*96-33-3*]	86	−74	80	0.951	1.4010	5.2	5.3
Ethyl acrylate	[*140-88-5*]	100	−69	99	0.917	1.4037	1.6	1.8
n-Propyl acrylate	[*925-60-0*]	114	−65	119	0.904	1.4100	1.5	1.6
n-Butyl acrylate	[*141-32-2*]	128	−61	148	0.895	1.4160	0.15	0.20
Isobutyl acrylate	[*106-63-8*]	128	−60	135	0.885	1.4122	0.18	0.22
sec-Butyl acrylate	[*2998-08-5*]	128	−63	131	0.887	1.4110	0.21	0.22
tert-Butyl acrylate	[*1663-39-4*]	128	−68	120	0.879	1.4080	0.15	0.15
n-Hexyl acrylate	[*2499-95-8*]	156	−46	89[a]	0.879	1.4247	0.04	0.08
2-Ethylhexyl acrylate	[*103-11-7*]	184		217	0.880	1.4332	0.04	0.04
Lauryl acrylate	[*2156-97-0*]	240	−8	129[b]	0.870	1.4437	<0.001	<0.001
Comonomers								
Methyl methacrylate	[*80-62-6*]	100	−48	101	0.939	1.4119	1.5	1.6
Ethyl methacrylate	[*97-63-2*]	114	−76	118	0.909	1.4138	0.54	0.70
n-Butyl methacrylate	[*97-88-1*]	142		163	0.889	1.4220	0.08	0.15
Isobutyl methacrylate	[*97-86-9*]	142	−35	155	0.879	1.4172	0.13	0.19
tert-Butyl methacrylate	[*585-07-9*]	142	−47	144	0.873	1.4120	0.10	0.16
n-Hexyl methacrylate	[*142-09-6*]	170	−65	207	0.894	1.4290	<0.03	0.03
Acrylonitrile	[*107-13-1*]	53	−82	78	0.805	1.3888	8.3	9.7
Methacrylonitrile	[*126-98-7*]	67	−36	90	0.795	1.3977	2.6	3.0
Styrene	[*100-42-5*]	104	−31	145	0.905	1.5455	0.02	0.06
1,3-Butadiene	[*106-99-0*]	54	−109	−4	0.615	1.4220[c]	0.081	
1,2-Butadiene	[*590-19-2*]	54	−136	19	0.645	1.4200		
Vinyl acetate	[*108-05-4*]	86	−97	73	0.933	1.3959	2.9	2.9
Vinyl propionate	[*105-38-4*]	100	−81	95	0.917	1.4042	0.67	0.68
Vinyl chloride	[*75-01-4*]	62	−154	−13	0.911	1.398[d]	0.11	
Vinylidene chloride	[*75-35-4*]	97	−123	32	1.208	1.4237	0.25	
Auxiliary monomers								
Acrylic acid	[*79-10-7*]	72	14	141	1.044	1.4185	∞	∞
Methacrylic acid	[*79-41-4*]	86	17	161	1.015	1.4288	∞	∞
Acrylamide	[*79-06-1*]	72	87	125[a]	1.122		76	∞
Methacrylamide	[*79-39-0*]	85	112				27	

[a] 2.5 kPa.
[b] 3.8 kPa.
[c] −6 °C.
[d] Calculated.

Table 2. Further properties of industrially important acrylates

Property	Methyl acrylate	Ethyl acrylate	Butyl acrylate	2-Ethylhexyl acrylate
Vapor pressure, kPa				
0 °C	4.2	1.2	0.14	
25 °C	13	4.9	0.68	0.03
50 °C	36	17	2.8	0.16
75 °C	83	44	8.2	0.63
100 °C			22	2.1
125 °C			52	5.8
Heat of vaporization at boiling point, kJ/g	0.39	0.35	0.28	0.26
Specific heat (liquid), J g^{-1} °C^{-1}	2.00	1.967	1.925	1.88
Heat of polymerization, kJ/g	0.915	0.777	0.605	0.424
Rate constant of chain growth, L mol^{-1} s^{-1}	1000 (50 °C) [19]	800 (50 °C) [20]	679 (30 °C) [21]	155 (50 °C) [20]
Rate constant of chain termination $k_t \times 10^{-6}$, L mol^{-1} s^{-1}	3.55 (50 °C) [19]	1.76 (50 °C) [20]	6.4 (30 °C) [21]	0.233 (50 °C) [20]

Table 3. Acrylates and methacrylates with functional groups

Monomers	Formula	CAS registry no.	M_r	*fp*, °C	*bp*, °C (kPa)[a]	d_4^{25}	n_D^{25}	Solubility in water at 25 °C, g/100 cm³
Carboxyl								
Fumaric acid	HOOCCH=CHCOOH	[*110-17-8*]	116	286	165 (0.17)	1.625		0.7
Maleic acid	HOOCCH=CHCOOH	[*110-16-7*]	116	130		1.609	1.544[b]	78.8
Crotonic acid	$CH_3CH=CHCOOH$	[*3724-65-0*]	86	16	169 (101)	1.026	1.442[c]	
Itaconic acid	$CH_2=C(CH_2COOH)COOH$	[*97-65-4*]	130	175	decomp.	1.573	1.512[b]	9.1
Di- and triacrylates								
Ethylene glycol diacrylate	$CH_2=CHCOOCH_2CH_2OCOCH=CH_2$	[*2274-11-5*]	170		70 (0.13)		1.453[c]	
Diethylene glycol diacrylate	$H_2C=CHCOO(CH_2CH_2O)_2COCH=CH_2$	[*4074-88-8*]	224		94 (0.03)		1.457[c]	
Triethylene glycol diacrylate	$H_2C=CHCOO(CH_2CH_2O)_3COCH=CH_2$	[*1680-21-3*]	258		120 (0.02)	1.108	1.462[c]	5.0
Tetraethylene glycol diacrylate	$H_2C=CHCOO(CH_2CH_2O)_4COCH=CH_2$	[*17831-71-9*]	302	−53	328 (101)	1.078	1.463	9.1
Butanediol diacrylate	$CH_2=CHCOO(CH_2)_4OOCCH=CH_2$	[*1070-70-8*]	198	−5	120 (1.3)	1.049	1.455[c]	0.6
Hexanediol acrylate	$CH_2=CHCOO(CH_2)_6OOCCH=CH_2$	[*13048-33-4*]	226	9	107 (0.03)	1.015	1.458	0.12
Neopentyl glycol diacrylate	$CH_2=CHCOOCH_2C(CH_3)_2CH_2OOCCH=CH_2$	[*2223-82-7*]	212		101 (0.4)	1.024	1.451	0.9
Trimethylolpropane triacrylate	$(CH_2=CHCOOCH_2)_3CCH_2CH_3$	[*15625-89-5*]	296	−22	126 (0.03)	1.102	1.474	0.09
Tripropylene glycol diacrylate	$CH_2=CHCOO(CHCH_3CH_2O)_3OCCH=CH_2$	[*42978-66-5*]	300	−60	109 (0.03)	1.036		
Di-(meth)acrylamides								
N,N'-Methylene bisacrylamide	$CH_2=CHCONHCH_2HNCOCH=CH_2$	[*110-26-9*]	154	188				3.5
N,N'-Methylene bismethacrylamide	$CH_2=C(CH_3)CONHCH_2HNCOC(CH_3)=CH_2$	[*2359-15-1*]	182	164				
Hydroxyl								
2-Hydroxyethyl acrylate	$CH_2=CHCOOCH_2CH_2OH$	[*818-61-1*]	116	< −60	60 (0.13)	1.114[c]	1.451[c]	∞
2-Hydroxyethyl methacrylate	$CH_2=CCOOCH_2CH_2OH$ (CH₃)	[*868-77-9*]	130	−12	95 (1.3)	1.06[c]	1.450	∞
Hydroxypropyl acrylate	$CH_2=CHCOO(CH_2)_3OH$	[*25584-83-2*]	130		63 (0.13)	1.06[c]	1.448[c]	∞
Propylene glycol methacrylate	$CH_2=CCOOCH_2CHCH_3$ (CH₃, OH)	[*2761-09-3*]	144		96 (1.3)	1.024	1.446	13.0
Butanediol monoacrylate	$CH_2=CHCOO(CH_2)_4OH$	[*2478-10-6*]	144		130 (2.7)	1.039	1.453[c]	∞
Ethers								
Ethyldiglycol acrylate	$CH_2=CHCO(OC_2H_4)_2OC_2H_5$	[*32002-24-7*]	188	−66	99 (0.5)	1.006	1.438[c]	14.0
Amines								
Dimethylaminoethyl acrylate	$CH_2=CHCOO(CH_2)_2N(CH_3)_2$	[*2439-35-2*]	143	−92	70 (2.9)	0.936[c]	1.437[c]	∞
Dimethylaminoethyl methacrylate	$CH_2=CCOO(CH_2)_2N(CH_3)_2$ (CH₃)	[*2867-47-2*]	157	−30	68 (1.3)	0.921	1.438	∞

N-(3-Dimethylaminopropyl)-methacrylamide	$CH_2=C(CH_3)CONH(CH_2)_3N(CH_3)_2$	[*5205-93-6*]	182		92 (0.005)		1.479[c]	
Diethylaminoethyl acrylate	$CH_2=CHCOO(CH_2)_2N(C_2H_5)_2$	[*2426-54-2*]	171	−100	97 (3.6)	0.925[c]	1.443[c]	10.7
tert-Butylaminoethyl methacrylate	$CH_2=C(CH_3)COO(CH_2)_2NHC(CH_3)_3$	[*3775-90-4*]	185	< −70	105 (1.6)	0.914	1.440	11.5
Halogen								
2-Chloroacrylonitrile	$CH_2=CClCN$	[*920-37-6*]	88	−65	89 (101)	1.085	1.428	1
N-Hydroxymethyl								
N-Hydroxymethyl acrylamide	$CH_2=CHCONHCH_2OH$	[*924-42-5*]	101	79				∞
N-Hydroxymethyl methacrylamide	$CH_2=C(CH_3)CONHCH_2OH$	[*923-02-4*]	115	54		1.145		∞
Sulfonic acid								
2-Sulfoethyl methacrylate	$CH_2=C(CH_3)COOCH_2CH_2SO_3H$	[*10595-80-9*]	194		decomp.	1.325		∞
2-Acrylamido-2-methylpropanesulfonic acid	$CH_2=CHCONHC(CH_3)_2CH_2SO_3H$	[*15214-89-8*]	207	185		1.401	1.560[b]	150
Polyfunctional								
Glycidyl methacrylate	$CH_2=C(CH_3)COOCH_2CH(O)CH_2$	[*106-91-2*]	142		75 (1.3)	1.073	1.448	3.0
Diacetone acrylamide	$CH_2=CHCONHC(CH_3)_2CH_2COCH_3$	[*2873-97-4*]	169	57	107 (0.03)			>100
Diacetone methacrylamide	$CH_2=C(CH_3)CONHC(CH_3)_2CH_2COCH_3$	[*22029-67-0*]	183		138 (1.5)			
Acrylamidoglycolic acid	$CH_2=CHCONHCH(OH)COOH$	[*6737-24-2*]	145	95				13
Methylacrylamidoglycol methyl ether	$CH_2=CHCONHCH(OCH_3)COOCH_3$	[*77402-03-0*]	173	73				18

[a] To convert kPa to mm Hg, multiply by 7.5; to convert to mbar, multiply by 10. [b] Calculated from refractive index. [c] 20 °C.

Table 4. Copolymerization parameters r_1 and r_2* [27]

Monomer 1	Monomer 2	r_1	r_2	Reference
Methyl acrylate	acrylonitrile	0.844	1.540	[28]
$Q = 0.45$	butadiene	0.070	1.090	[29]
$e = 0.64$ [46]	methyl methacrylate	0.400	2.150	[30]
	styrene	0.168	0.722	[28]
	vinyl acetate	6.300	0.030	[31]
	vinyl chloride	4.400	0.093	[28]
	vinylidene chloride	1.000	1.000	[32]
Ethyl acrylate	acrylonitrile	0.810	1.160	[33]
$Q = 0.41$	methyl methacrylate	0.280	2.000	[34]
$e = 0.55$ [46]	styrene	0.152	0.787	[35]
	vinylidene chloride	0.720	0.580	[36]
Butyl acrylate	acrylonitrile	0.820	1.080	[37]
$Q = 0.38$	butadiene	0.074	1.040	[29]
$e = 0.85$ [46]	methylmethacrylate	0.430	1.880	[38]
	styrene	0.180	0.840	[39]
	vinyl acetate	3.480	0.018	[40]
	vinyl chloride	4.400	0.070	[41]
	vinylidene chloride	0.873	0.934	[42]
2-Ethylhexyl acrylate	styrene	0.310	0.960	[43]
$Q = 0.37$	vinyl acetate	7.500	0.040	[44]
$e = 0.24$ [46]	vinyl chloride	4.150	0.160	[45]

* For definitions, see → Polymerization Processes, 1. Fundamentals.

high molecular masses are obtained at high polymerization rates; polymerization times are consequently short. Since the viscosity is generally low, the heat of polymerization can easily be removed via the aqueous phase. Emulsion polymers with solids contents of up to 60 wt% and molecular masses of 10^5–10^6 can be produced. These represent advantages compared with solution polymerization, and in addition there is no safety hazard due to flammable solvents.

3.1.1. Starting Materials

The most important starting materials for emulsion polymerization are water, monomers, emulsifiers, initiators, and, if necessary, modifiers.

Water. The water should preferably be distilled or completely demineralized because electrolytes can affect emulsion stability.

Monomers. The monomer composition is governed by the properties required by the relevant area of application.

Emulsifiers. Anionic, nonionic, and, less often, cationic or amphoteric compounds are normally used for emulsification. A combination of ionic and nonionic emulsifiers can considerably improve the stability of the dispersions.

Anionic Emulsifiers include sodium, potassium, or ammonium salts of fatty acids and sulfonic acids; alkali salts of C_{12-16}-alkyl sulfates; ethoxylated and sulfated or sulfonated fatty alcohols; alkyl phenols; and sulfodicarboxylate esters. The emulsifiers are used at concentrations of 0.2–5 wt%, based on monomers.

Nonionic Emulsifiers include ethoxylated fatty alcohols and alkyl phenols with 2–150 ethylene oxide units per molecule.

Cationic Emulsifiers include ammonium, phosphonium, and sulfonium compounds with a hydrophobic moiety that contains at least one long aliphatic hydrocarbon chain.

Many companies offer very large ranges of emulsifiers and emulsifier mixtures that vary in terms of chemical structure. The emulsifier has several functions in emulsion polymerization. It is required for the preparation of the monomer emulsion, and later stabilizes the final dispersion. The particle size (diameter) of the dispersion can be adjusted in the range 50–1000 nm by the choice of emulsifier, its amount, and the mode of addition.

Protective colloids such as cellulose derivatives, starch, or poly(vinyl alcohol) can also be used to stabilize the dispersions. Protective colloids are, however, less suitable for initiating particle formation.

Initiators. Water-soluble peroxo compounds (e.g., alkali persulfates, ammonium persulfate, or hydrogen peroxide) are used as initiators with a polymerization temperature between 50 and 85 °C. The initiators are used in amounts of 0.05–1 wt% (usually 0.2–0.5 wt%) based on monomer. Higher initiator concentrations may adversely affect the stability of the dispersion (electrolyte content) or improve it (additional stabilization); they also lower the molecular mass of the product.

If redox systems are used for initiation [51–53], polymerization can be performed below 50 °C. Oxidizing agents include hydrogen peroxide and alkali persulfates. Iron(II) sulfate, sodium bisulfite, sodium thiosulfate, or sodium formaldehyde sulfoxylate can be used as reducing agent. Iron(II) salts can also be added in small amounts as catalysts. The optimal quantitative ratio of oxidizing agent to reducing agent has to be determined experimentally.

Alkali persulfate cannot be used as an initiator in the preparation of cationic dispersions due to salt formation; water-soluble organic peroxides or hyrogen peroxide are more suitable. Polymerization is generally performed in the pH range 2–7.

Modifiers. The molecular mass of the polymer can be reduced by adding modifiers with the result that the polymers become more tacky. Common modifiers include halogen-containing compounds (e.g., carbon tetrachloride, carbon tetrabromide, bromoform, benzyl bromide, bromotrichloromethane), or thiols (e.g., butyl or dodecyl thiol).

3.1.2. Production Processes

Emulsion polymers are produced from acrylates in batch and semibatch (continuous emulsion or monomer feed) processes. All processes should be performed under nitrogen since oxygen inhibits polymerization.

Batch Process. The monomer emulsion is added to the cooled reaction vessel (<15 °C). The redox initiator is then added, generally as an aqueous solution. Polymerization begins and the temperature rises over the course of 0.5–1 h and then falls due to constant cooling and removal of the heat of reaction. The polymerization rate can sometimes be controlled by appropriate metering of the initiator.

The advantage of the batch procedure is the larger space–time yield. Disadvantages include the poor utilization of the cooling capacity, as well as poor reproducibility of the procedure and product properties.

If cooling is insufficient to prevent the reaction going out of control, the batch can be split into two or more partial batches. If monomers and initiator solution are added in an infinite number of small steps, this is referred to as a continuous feed (semibatch) process [54]. Accurate temperature control is easier with the semibatch (continuous feed) process. Mixed batch and semibatch procedures are used in practice.

Semibatch Procedure. In the *semibatch procedure with emulsion feed* [55, 56], the reaction vessel contains some water and is heated to the desired reaction temperature. Part (5–10%) of the monomer emulsion and initiator solution is then added as an initial batch to the reactor.

Alternatively, some of the emulsifier and the water is added, the remaining emulsifier is then used to prepare the monomer emulsion. The initial batch is polymerized for 15–30 min. The number of particles and the particle size of the polymer dispersion are determined in this starting phase (batch).

Product properties can be modified by adjusting the proportion of emulsifier in the initial batch and the feed. Instead of an initial batch, a finely particulate dispersion can also be used as "seed". The monomer emulsion and initiator solution are then added from separate tanks over 2–3 h.

In the *semibatch procedure with monomer feed* the water and emulsifiers are first added to the reactor. The monomer mixture, initiator solution, and the solution of auxiliaries are then fed in continuously.

In semibatch processes specific product properties can be selectively adjusted by small

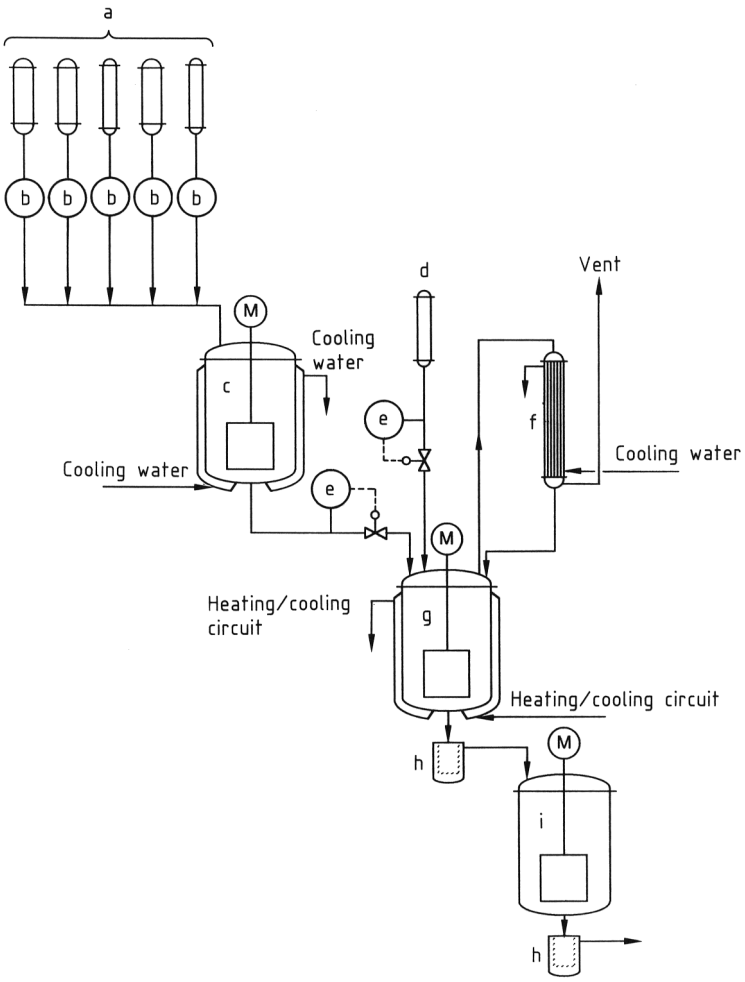


Figure 1. Production of polyacrylates by emulsion and solution polymerization
a) Storage tanks for monomers, distilled water, emulsifiers; b) Flow meter; c) Mixing tank; d) Storage tank for initiator; e) Flow registration control; f) Cooler; g) Polymerization reactor; h) Filter; i) Product storage tank

changes (e.g., of temperature, pH, and delayed addition of certain monomers) [57]. If polymerization is performed under specified conditions, the properties of the resulting dispersions remain virtually constant from batch to batch. These advantages have to be offset, however, by increased complexity, for example as regards temperature control and feed regulation.

Many "specialty" chemicals are produced by batch or semibatch processes. Continuous emulsion polymerization is mainly used on an industrial scale in the production of styrene–butadiene rubber [58–61]. No bulk polyacrylates have so far been produced by a continuous process.

Equipment. Figure 1 shows a production plant for batch and semibatch operation. Water, monomers, emulsifiers, and additives are contained in storage tanks (a) and fed via metering devices (b) to the mixing tank (c), in which the monomer emulsion is produced. The mixing tank is made of stainless steel (V2A, V4A) and equipped with a stirrer and cooling jacket. The shape of the stirrer and stirring rate are chosen to ensure thorough emulsification of the monomers. The mixing tank is, however, unnecessary if the individual components are accurately metered and an in-line mixer is used to prepare the monomer emulsion, or a monomer feed procedure is employed.

The monomer emulsion is usually added to the polymerization reaction batchwise or continuously over a period of minutes or hours. The reactor may be connected to further feed vessels for initiator and other additives, and usually has connections for flushing with inert gas. The internal reactor temperature can be regulated by wall cooling or evaporative cooling.

Vessels, stirrers, and all parts that come into contact with the product are made of stainless steel. The interior wall of the reactor should be as smooth as possible to prevent the deposition of wall scale. The polymerization reactor may have a capacity of 30 m^3 or more. The design, size, and power of the stirrer depend on the batch size and viscosity of the dispersion. High stirring rates (shear rate) may lead to coagulation, while low stirring rates may result in insufficient mixing.

After the end of the feed stage the dispersion is maintained for a further 1–2 h at the reaction temperature to reduce the residual monomer content before being cooled. The dispersion is discharged through a filter (h) and pumped to a storage tank (i). In the storage tank the solids content and pH value are often adjusted and formulations are prepared. Stabilizers and microbiocides are also added.

The dispersions are transported to the consumer or customer in polyethylene-lined metal drums, polyethylene vessels, or tank cars. The purchase of dispersions in barrels is being superseded by delivery in large-capacity containers for economic reasons.

3.2. Solution Polymerization

See also→ Polymerization Processes, 1. Fundamentals. Acrylates are polymerized as solutions in organic solvents [25, 62–64] if the user wishes to exploit specific properties of polymers in dissolved form (e.g., low molecular mass, good flow behavior, and homogeneous film formation after drying in paints or adhesives). As a result of growing environmental awareness (solvent disposal), solution polymerization of acrylates will probably not expand to the anticipated level.

Aromatic hydrocarbons such as benzene and toluene can be used as solvents for the polymerization of acrylates of long-chain alcohols; esters and ketones can be used for acrylates of short-chain alcohols.

Table 5. Transfer constants of various solvents

Monomer	Solvent	$k_u \times 10^4$	Temperature, °C	Reference
Methyl acrylate	acetone	0.622	80	[65]
	benzene	0.326	80	[65]
	2-butanone	3.238	80	[65]
	n-butanol	2.747	80	[65]
	carbon tetrachloride	1.25	80	[66]
	chloroform	2.10	80	[67]
	cyclohexane	0.027	80	[65]
	2-butanol	2.496	80	[65]
	toluene	1.775	80	[65]
Ethyl acrylate	acetone	1.10	80	[68]
	benzene	0.525	80	[68]
	n-butanol	5.85	80	[68]
	sec-butanol	22.20	80	[68]
	carbon tetrachloride	1.55	80	[68]
	chloroform	1.49	80	[68]
	cyclohexane	1.22	80	[68]
	ethyl acetate	0.89	80	[68]
	hexane	0.97	80	[68]
	2-propanol	21		[69]
	methanol	0.32	60	[70]
	toluene	2.60	80	[68]
Butyl acrylate	ethanol	4.28	80	[71]
	methanol	0.47	80	[71]
	propanol	3.78	80	[71]
	2-propanol	14.12	80	[71]
2-Ethylhexyl acrylate	toluene	2.13	80	[20]

If the solvent boils at the temperature used for polymerization, a large proportion of the heat of polymerization can be removed by evaporative cooling.

Solvents may act as modifiers in solution polymerization. This should be kept in mind when choosing the solvent [65–71]. Some transfer constants of solvents are summarized in Table 5. The lower the transfer constant, the higher will be the molecular mass of the polymer. The viscosity of the solution increases with the molecular mass of the polymer. This has an adverse effect on the mixing of the reactor contents and the removal of the heat of polymerization [72]; it its therefore essential to choose an optimum polymer concentration for a given molecular mass.

The molecular mass can be controlled by adding modifiers (e.g., halogenated aliphatic hydrocarbons and thiols [73]) or by adjusting the initiator concentration (increasing initiator concentrations lower the molecular mass).

Soluble azo compounds, peroxides, or hydroperoxides are used as initiators at a concentration of 0.01–2 wt% relative to the

Table 6. Half-lives of organic peroxides and azo compounds used as initiators (0.1 mol/L in benzene)

Compound	Temperature for a half-life of 1 h, °C	Half-life, h					
		20 °C	40 °C	60 °C	80 °C	100 °C	120 °C
Acetylcyclohexanesulfonyl peroxide	46	57	2.4	0.1			
Diisopropylperoxy dicarbonate	61	400	18	1.2			
tert-Butylperoxy pivalate	74		92	5.7	0.5		
Dilauroyl peroxide	80			12	1.0		
Diacetyl peroxide	87			35	2.4		
Dibenzoyl peroxide	91			48	3.8	0.4	
tert-Butylperoxy 2-ethylhexanoate	92				6	0.4	
tert-Butylperoxy isobutyrate	96				6.7	0.6	
tert-Butylperoxy benzoate	124					18	1.6
Dicumyl peroxide	136						5.7
Di-*tert*-butyl peroxide	146						18
tert-Butyl hydroperoxide	200						
2,2′-Azobis(2,4-dimethylvaleronitrile)	64		25	1.8	0.17	0.021	
Azobis(isobutyronitrile)	82			15	1.2	0.12	

monomer. Some common peroxides and azo compounds together with their half-lifes are given in Table 6 [74, 75].

An initiator should be chosen with a half-life that guarantees a sufficient level of initiator throughout the feed time. Radical formation may be influenced by the solvent [76]. Azo compounds, e.g., 2,2′-azobis(isobutyronitrile), are often used as initiators in polymerization in organic solvents; 0.01–2% of initiator is used depending on the desired product properties.

Solution polymerization can also be initiated with UV light ($\lambda < 360$ nm) or γ-radiation (see Section 5.1). However, gels are often formed due to cross-linking reactions.

As with emulsion polymerization, solution polymers can be produced by batch or semibatch processes (see Section 3.1.2).

Semibatch processes can be efficiently controlled as regards temperature. Part of the solvent and monomer mixture (or all of the solvent with part or all of the initiator) is charged to the reactor. The remaining monomer–solvent mixture (or monomers) is added continuously over the course of 1–4 h. The monomers can also be added in portions. The batch is fully polymerized after 2–24 h.

The apparatus used in solution polymerization is similar to that for emulsion polymerization (Fig. 1). The monomers and solvents are fed into a stirred mixing tank or directly into a polymerization reactor via an in-line mixer.

In addition to the main feed line, the polymerization reactor has inlets for the initiator and modifier solutions. It is equipped with a heating/cooling jacket and an evaporative cooler. Most of the heat is generally removed by evaporative cooling. The initial batch is first heated by the heating jacket. Cooling is generally only necessary to control the reaction in the event of disorders.

The polymer solution should not be subjected to large temperature changes during storage. At elevated temperature there is a danger of solvent loss, while at low temperature the viscosity rises sharply and the polymer solution can no longer be pumped. Storage facilities (e.g., tank cars) should therefore be temperature controlled.

3.3. Elimination of Residual Monomers

Although polymerization proceeds almost quantitatively, residual monomers sometimes have to be removed.

After emulsion polymerization is complete, the dispersion is heated for a short period at 95–98 °C, if necessary under reduced pressure, and the residual monomers are expelled. Foaming can be suppressed by adding antifoaming agents.

Continuous removal of the residual monomers is, however, more effective. Steam is blown into the dispersion, which is under vacuum and begins to foam strongly. The rising dispersion foam is destroyed mechanically and the dispersion returned to the reactor; the monomers are condensed in a cooling device [77]. This process is used on an industrial scale.

Table 7. Toxicity of the most important acrylate esters

Parameter	Methyl acrylate	Ethyl acrylate	Butyl acrylate	2-Ethylhexyl acrylate
OSHA				
PEL[a] (skin)	10 ppm or 35 mg/m^3	5 ppm or 20 mg/m^3	10 ppm or 55 mg/m^3	not regulated
STEL[b] (skin)		25 ppm or 100 mg/m^3		
Irritation data[78]				
rabbit eye	100 mg/24 h, moderate	1204 ppm/7 h	500 mg/24 h, mild	500 mg/24 h, mild
rabbit skin	10 mg/24 h open, mild	500 mg/open, mild	500 mg/open, mild	500 mg/open, mild
Toxicity data[78]				
LD_{50} rat, oral, mg/kg	277	800	900	5660
LC_{50} rat, inhalation, 4 h, ppm	1350	2180	2730	
LD_{50} rabbit, dermal, mg/kg	1243	1834	2000	8480
MAK	5 ppm or 18 mg/m^3	5 ppm or 20 mg/m^3	10 ppm or 55 mg/m^3	
IARC Group[c]	3	2	3	

[a] Permissible environmental limit (8 h TWA).
[b] Short term exposure limit (15 min TWA).
[c] International Agency for Research on Cancer (1987).

In some cases the residual monomer content is lowered by adding small amounts of suitable initiators at the end of the polymerization.

3.4. Toxicology and Environmental Aspects

Polyacrylates, being high molecular mass compounds, are not toxic. Films and coatings produced from acrylate dispersions are permitted for food packaging in Germany [Recommendation XIV Plastics Dispersions (Empfehlung XIV Kunststoff Dispersionen) of the Federal Ministry of Health] and in the United States (21 CFR 176.189 Components of paper and paperboard in contact with dry food, FDA). Auxiliary substances also have to be taken into consideration in food legislation. The toxicology of polyacrylates is determined not by the polymers themselves, but by their auxiliaries (e.g., initiator residues, emulsifiers) and residual monomer content. Table 7 contains toxicity data for the most important acrylate esters. The residual monomer content of polymer dispersions is usually reduced to less than 300 ppm by the methods described in Section 3.3.

With solution polymers there are additional difficulties as regards toxicity, safety, and environmental pollution due to the use of organic solvents. This can be improved by choosing a suitable solvent. In most cases, however, solution polymers are not as environmentally safe as aqueous polymer dispersions; they are treated as combustible mixtures if the solvents are flammable.

4. Properties

4.1. Polymer Solutions and Dispersions

4.1.1. Polymer Solutions

The flow properties of polymer solutions and their formulations are of great importance as regards processability. The temperature dependence of these properties determines the temperature range in which the solution polymer can be handled.

The viscosity of polymer solutions depends on the molecular mass, molecular structure, temperature, and thermodynamic behavior of the solvent [72]. Information on polymer molecular mass, coil dimensions, interaction between solvents and polymers, and the thermodynamic behavior of a solvent are usually obtained from measurements on dilute solutions (light scattering, osmometry, sedimentation, viscosimetry), see also → Plastics, Analysis.

Interactions between the polymer molecules increase with rising concentration. Temporary polymer–polymer contacts are formed that finally lead to the formation of undesirable gels that do not flow and cannot be processed.

4.1.2. Polymer Dispersions

Dispersions consist of two phases, and are therefore more complicated systems than polymer solutions; they often also contain

polyelectrolytes. Almost all investigations are carried out on dilute systems.

The most important properties of polymer dispersions are appearance, concentration, pH, surface tension [79], residual monomer content, particle size, particle size distribution, viscosity, and stability.

Residual Monomer Content. Residual monomers are determined by chromatography. The volatile monomers can be quantitatively determined by gas chromatography using calibration and addition of an internal standard (e.g., toluene or methyl ethyl ketone [80]). An accuracy of ca. 1 ppm can be achieved.

The content of water-soluble, nonvolatile monomers (e.g., acrylic acid) is determined by high-pressure liquid chromatography [81].

Particle Size and Particle Size Distribution. The particle size and particle size distribution of emulsion polymers influence other properties (e.g., the viscosity of dispersions with a high solids content). At the same concentration and with the same auxiliary system, coarse dispersions generally have a lower viscosity than fine dispersions due to electrostatic effects or, in the case of dispersions with protective colloids, to steric effects.

Particle size and particle size distribution can be determined by *electron microscopy* (measurement range: 1–1000 nm) [82].

A simple method for determining the mean particle size is to measure the *light transmission* of a highly dilute sample. The relationship between the turbidity and particle radius of spheres is described by Mie's theory [83]. The particle diameter is shown as a function of the light transmission in Figure 2. An important parameter is m, the ratio of the refractive index of the polymer to that of water. The approximate refractive index of copolymers can be calculated with the following formula:

$$n = w_1 n_1 + w_2 n_2 + w_3 n_3 + \ldots$$

where the mass fractions $w_1+w_2+w_3 \ldots = 1$ and n_1, n_2 are the refractive indices of the homopolymers.

A mean particle size can also be determined from *static light scattering* (measurement range: 300–1500 nm). Hydrodynamic diameters can be accurately measured by *quasielastic light scattering* (QELS); measurement range: 10–3000 nm) [84–88].

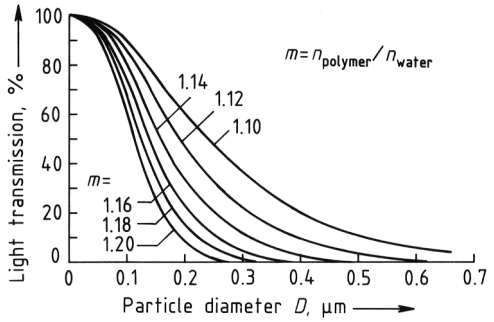


Figure 2. Relationship between light transmission and particle size for 0.01 wt% polymer dispersion (path length 2.5 cm, λ 546 nm)

The particle size distribution can be determined with the *ultracentrifuge* (measuring range: 10–20 000 nm in a gravity field of 20–200 000 g) [89]. The particles must be spherical.

The surface areas of latex (dispersion) particles are determined by *soap titration*, from which the particle size can be calculated [90–93]. Soap titration is simple and quick to perform, and yields reasonable values with homologous polymer dispersion series. Care should be taken, however, when evaluating latex surfaces of different hydrophilicity.

Viscosity. Dispersions with solids contents of 40–60 wt% exhibit a broad spectrum of rheological behavior [94], [95] that depends on the volume fraction, temperature, particle size, particle size distribution, and auxiliary system. Dispersions may be highly liquid to pasty, and may exhibit a Newtonian to viscoelastic flow behavior [96]. In dispersions structural viscosity ("shear thinning") is frequently observed; dilatancy is observed less often; thixotropy and rheopexy are rarely encountered.

Stability. Dispersions must have a certain degree of mechanical (shear) stability if coagulation is not to occur during pumping, stirring, or spraying. Mechanical stability is checked by determining the amount of coagulate after a stirring test; the stirrer, temperature, shear velocity, time, and other parameters should correspond to possible stresses occurring during use.

Thermal stability is checked by subjecting the dispersions to the anticipated service

temperature conditions. A freeze–thaw test with five cycles is widely used. However, the results depend on the container size and temperature control so that the correlation between laboratory results and frost stability under relevant weathering conditions is generally unsatisfactory.

The polymer dispersion must be stable to electrolytes when diluted with hard water and when formulating products such as paints or adhesives. The stability is therefore tested by adding salts.

Minimum Film-Forming Temperature. Whether a dispersion forms a coherent film after evaporation of the water or whether a brittle, pulverizable layer is formed depends on the glass transition temperature of the polymer, residual water content, and temperature at which the film is formed. The lowest temperature at which a coherent film can still form from the copolymer dispersion is called the minimum film-forming temperature (MFT). The MFT is measured with a metal plate that has a temperature gradient [97, 98]. The temperature at which the film begins to crack or the so-called white point, at which the turbid film starts to become clear, is measured [99].

The MFT depends on the copolymer composition, as well as the particle size and polarity of the comonomers [100–102]. It is usually comparable to the glass transition temperature, but may be substantially lower, probably because the emulsifier and water act as a plasticizer.

4.2. Properties of the Polymers

Glass Transition Temperature. The glass transition temperatures (T_g) of polyacrylates and homopolymers of monomers that are frequently used in acrylate copolymers are summarized in Table 8. The values were determined by differential thermoanalysis on dispersion films (heating rate 20 °C/min, midpoint), the films being repeatedly heated until reproducible values were obtained. Other factors that influence the glass transition temperature (e.g., molecular mass, [103, 104]) are discussed elsewhere [105, 106].

The glass transition temperature of most copolymers can be accurately calculated with the nonlinear equation of GORDON and TAYLOR [107] given below. Other nonlinear equations are discussed elsewhere [108].

$$T_g = \frac{T_{gA} w_A + c T_{gB} w_B}{w_A + c w_B}$$

where w_A and w_B are the mass fractions of the monomers A and B, and T_{gA} and T_{gB} are the absolute glass transition temperatures of the corresponding homopolymers ($T_{gA} < T_{gB}$). The constant c takes into account the expansion coefficients of the melt and glass state of the two homopolymers. Its value is generally between 0.5 and 2.0.

With the exception of *tert*-butyl acrylate, most acrylate homopolymers have extremely

Table 8. Properties of homopolymers

Monomer	CAS registry no. of polymer	T_g [a], °C	d_4^{25}	n_D^{25}
Methyl acrylate	[*9003-21-8*]	22	1.20	1.479
Ethyl acrylate	[*9003-32-1*]	−8	1.13	1.464
n-Propyl acrylate	[*24979-82-6*]	−25	1.10	1.462[b]
n-Butyl acrylate	[*9003-49-0*]	−43	1.06	1.474
Isobutyl acrylate	[*26335-74-0*]	−17	1.05	1.464[b]
sec-Butyl acrylate	[*30347-35-4*]	−6	1.06	1.462[b]
tert-Butyl acrylate	[*25232-27-3*]	55	1.03	1.468
n-Hexyl acrylate	[*27103-47-5*]	−51	0.98	1.468[b]
2-Ethylhexyl acrylate	[*9003-77-4*]	−58	0.99	1.433[b]
Lauryl acrylate	[*26246-92-4*]	−17	0.99[c]	1.468[b]
Methyl methacrylate	[*9011-14-7*]	105	1.19	1.488
Ethyl methacrylate	[*9003-42-3*]	67	1.12	1.483
n-Butyl methacrylate	[*9003-63-8*]	32	1.06	1.483
Isobutyl methacrylate	[*9011-15-8*]	64	1.05	1.475
tert-Butyl methacrylate	[*25189-00-8*]	102	1.02	1.460
n-Hexyl methacrylate	[*25087-17-6*]	−14	1.01	1.479
Acrylonitrile	[*25014-41-9*]	105	1.18	1.519
Methacrylonitrile	[*25067-61-2*]	112	1.18	1.545[b]
Styrene	[*9003-53-6*]	107	1.05[d]	1.591[d]
trans-1,4-Butadiene	[*40022-02-4*]	−107	0.97	1.518
cis-1,4-Butadiene	[*40022-03-5*]	−102	1.01	1.52
Vinyl acetate	[*9003-20-7*]	42	1.19	1.463
Vinyl propionate	[*25035-84-1*]	8	1.14	1.465[b]
Vinyl chloride	[*9002-86-2*]	77[e]	1.40	1.545
Vinylidene chloride	[*9002-85-1*]	−18[f]	1.84[g]	1.618[b,g]
Acrylic acid	[*9003-01-4*]	130[h]	1.54[c]	1.544[b]
Methacrylic acid	[*25087-26-7*]	162[h]	1.45[c]	1.563[b]
Acrylamide	[*9003-05-8*]	220[h]	1.44[c]	1.603[b]
Methacrylamide	[*25014-12-4*]	243[h]	1.40[c]	1.616[b]

[a] Emulsion polymers or aqueous solution polymers, differential scanning calorimetry, 20 °C/min, midpoint.
[b] From the refractive increment.
[c] From the specific volume.
[d] Atactic.
[e] Polymerization temperature 90 °C.
[f] Amorphous.
[g] Crystalline.
[h] After repeated heating.

Table 9. Determination of the molecular mass according to the Staudinger equation (intrinsic viscosity in cm^3/g)

Polymer	Tetrahydrofuran, 25 °C [109]		Acetone, 20 °C		Chloroform, 20 °C [110]	
	$K \times 10^3$, cm^3/g	a	$K \times 10^3$, cm^3/g	a	$K \times 10^3$, cm^3/g	a
Poly(methyl acrylate)	10.0	0.73	5.6 [110]	0.75	3.0	0.85
Poly(ethyl acrylate)	8.9	0.75	8.8 [110]	0.72	7.3	0.78
Poly(*n*-propyl acrylate)	11.9	0.72				
Poly(*n*-butyl acrylate	7.4	0.75	5.2 [110]	0.73	13.1	0.69
Poly(isobutyl acrylate)	12.7	0.71				
Poly(*tert*-butyl acrylate)	43.4	0.60	4.7 (25 °C) [111]	0.75		
Poly(*n*-hexyl acrylate)	5.5	0.76				
Poly(2-ethylhexyl acrylate)	11.1	0.68				
Poly(*n*-lauryl acrylate)	27.3	0.58				

low glass transition temperatures. They are therefore too soft, too tacky, or have too high an elongation and insufficient strength for many areas of application. Polymers for specific applications can be produced by copolymerization with monomers whose homopolymers have high glass transition temperatures (e.g., styrene, acrylonitrile, methyl methacrylate, ethyl methacrylate).

Molecular Mass. See also → Plastics, Analysis, Chap. 5. The molecular mass can be calculated from the intrinsic viscosity [η] and a knowledge of the two constants K and a:

$$[\eta] = K \cdot M^a$$

Values for K and a in various solvents are listed in Table 9.

Molecular mass determination does not generally present any difficulties with solution polymers. With acrylate emulsion polymers, however, cross-linking of the dispersed particles may cause problems. In this case it is impossible to produce a molecular-disperse solution. Before the molecular mass is determined it must therefore be checked whether a true dilute solution exists.

Mechanical Properties of Polymer Films. The temperature dependence of mechanical moduli [112, 113] provides detailed information about the mechanical behavior and structure of polymer films. Stress–strain diagrams of polymer films [114] are plotted with conventional apparatus; rupture strength and elongation at break are thus obtained. The values exhibit a relatively high degree of scatter with dispersion films, however, due to film defects. It is therefore often more appropriate to use the force required for a specific elongation, or the elongation that occurs when a defined force is applied as a measure of the stress–strain behavior. Mechanical moduli can be accurately measured by performing tensile tests with small extensions.

Poly(methyl acrylate) films have a relatively low elongation at break and an extremely high rupture strength at room temperature. The elongation of poly(ethyl acrylate) films is greater and the rupture strength is considerably lower. Poly(ethyl acrylate) is elastic and almost rubberlike. The elongation of poly(butyl acrylate) is extremely high and the rupture strength very low; the films are not elastic, but exhibit viscous flow even at small elongations and cannot be freely handled. Poly(ethylhexyl acrylate) has an even higher elongation and the films have no strength.

Tackiness. Poly(methyl acrylate) is not tacky at room temperature, poly(ethyl acrylate) is only slightly tacky. Poly(butyl acrylate) and poly (ethylhexyl acrylate) are, however, extremely tacky.

Tackiness depends on the molecular mass: tacky films can be produced from poly(methyl acrylate) with a very low molecular mass, whereas tack-free films can be produced from poly(butyl acrylate) of very high molecular mass. Increasing chain length of the alcohol residue ($>C_8$) causes the tackiness to fall. The polyacrylates become increasingly "dry" and elongation at break decreases due to crystallization of the *n*-alkyl chain. For example, poly(*n*-hexadecyl acrylate) is waxy and rigid at room temperature.

Electrical and Optical Properties. The electrical and optical properties of acrylate homo- and copolymers are similar to those of the polymethacrylates. Polyacrylates hardly yellow under direct sunlight, because they only absorb UV radition below 290 nm. If UV stabilizers are added, their properties do not change at all under the action of light. This is an important advantage of polyacrylates.

Solubility. Polyacrylates with short side chains are relatively polar and thus soluble in polar solvents, aromatic hydrocarbons, and chlorinated hydrocarbons. Common solvents include tetrahydrofuran, dimethylformamide, acetone, butanone, ethyl acetate, and chloroform. Precipitating agents include water, methanol, ethanol, diethyl ether, and aliphatic hydrocarbons.

The solubility parameters for different polyacrylates calculated according to SMALL [115, 116] vary only slightly. The values for polymethyl, polyethyl, and polybutyl acrylate and for the corresponding polymethacrylates are 21.3–18 $(MPa)^{0.5}$ and 10.4–8.8 $(cal/cm^3)^{0.5}$, respectively. Solubility in a certain solvent can be expected if the solubility parameters of the solvent and substance to be dissolved are comparable [117].

Chemical Stability. Polyacrylates are extremely resistant to oxygen, and only decompose very slowly under extreme conditions such as high temperature and in an oxygen-rich atmosphere. When heated, polyacrylates depolymerize to monomers much less readily than the corresponding polymethacrylates. Poly (methyl acrylate) decomposes at 292–399 °C to produce mainly methanol and carbon dioxide [118]. Volatile decomposition products of poly (ethyl acrylate) at 300–500 °C are ethylene, ethanol, and carbon dioxide. Butene, butanol, and carbon dioxide are formed from poly(butyl acrylate) in the same temperature range. Volatile decomposition products of poly(2-ethylhexyl acrylate) are 2-ethylhexene, ethylhexanol, and carbon dioxide [119]. Polyacrylates are largely resistant to acid and alkaline hydrolysis. The longer the alkyl radical, the greater the resistance to hydrolysis [120].

Cross-Linking of Polyacrylate Films. Solubility and tackiness are reduced by cross-linking, the rupture strength increases, whereas the elongation at break decreases. Emulsion polymers and, in special cases, solution polymers are cross-linked by incorporation (copolymerization) of monomers with groups that react with one another under certain conditions (e.g., change in pH or temperature) or in the presence of additives. Such monomers include *N*-methylolacrylamide, *N*-methylolmethacrylamide, and the corresponding ethers. The methylol groups react in the acid pH range at elevated temperature to form methylene bisacrylamide linkages with elimination of formaldehyde. Reviews of cross-linking systems are given in [121–128]. Environmentally friendly systems are preferred that cross-link at room temperature and do not lead to the release of toxic substances such as formaldehyde [128, 129]; an example is cross-linking of acrylic acid via formation of metal salts.

Cross-linking and cross-linking density can be determined by measuring the solvent uptake of the polyacrylate film. Suitable solvents are tetrahydrofuran or dimethylformamide, in which the noncross-linked polyacrylates are completely soluble. The relationship between swelling and cross-linking density can be derived from a model used to describe rubber elasticity [130–134]. Measurement of the cross-linking density from the temperature dependence of the modulus of elasticity [135–138] or modulus of torsion is somewhat more time-consuming.

5. Uses

Many important physical properties of polyacrylates and their copolymers can be varied within wide limits by a suitable choice of comonomers, auxiliaries, and polymerization process to give a large number of products for a wide variety of applications. The most important areas of application are concerned with protection, binding, and adhesion.

5.1. Paints and Coatings

See also → Paints and Coatings, 1. Introduction.

Architectural Paints. Good pigmentability, processability, and film properties are important

for the use of a polymer dispersion as a paint binder [139]. Vinyl ester copolymer dispersions mostly contain protective colloids, are coarsely particulate, and have favorable rheological properties for coating materials. However, vinyl acetate hydrolyzes on strongly basic substrates and the high water absorption of the dispersion films is also a disadvantage [140].

Acrylate copolymer dispersions usually contain emulsifiers and are finely particulate; they can therefore be highly extended with pigments [141, 142], but auxiliaries are necessary to adjust rheology. The low water absorption of the dispersion films is also an advantage. Emulsion paints based on these dispersions are stable to hydrolysis and are largely weather-resistant [143–145].

Copolymers with very high styrene contents tend to yellow in UV light and are therefore only used for interior paints. Coats with a matt, silk, or high-gloss finish can be formulated. Acrylate ester–methacrylate ester copolymers ("pure acrylates") have outstanding light stability, even in UV light, and are resistant to hydrolysis. They are therefore commonly used as binders for transparent and low-pigment coatings [146]. Specially selected pure acrylate dispersions with wet adhesion on alkyd substrates are used in gloss paints.

Vinyl ester, vinyl ester–acrylate ester, and acrylate ester–methacrylate ester copolymers are widely available in the United States. Styrene acrylics and pure acrylates are becoming increasingly important in Europe.

Trade names include Acronal, Propiofan, Luhydran (BASF); Uramul (DSM); Crilat (Montedison); Mowilith (Hoechst); Walpol (Reichhold Chemie); Primal, Rhoplex (Rohm and Haas); Revacryl (Revertex); Plextol (Röhm); Rhodopas (Rhône-Poulenc); Synthacryl (Synthopol); Ucecryl (UCB); Vinacryl and Vinamul (Vinyl Products); Vinnapas (Wacker).

Coatings and Lacquers. Metals are often coated with a waterborne priming coat and a solvent-containing topcoat. The trend is toward topcoats with high polymer concentrations to reduce solvent emissions. In cases where stringent requirements do not have to be satisfied as regards weather resistance and corrosion protection, the trend is toward waterborne topcoats [147–151].

In the automobile industry three coats are generally applied:

1. A waterborne priming coat, which is mainly responsible for corrosion protection
2. An intermediate coat (filler) which compensates for any unevenness of the substrate
3. A pigmented topcoat

In metallic-effect coatings the topcoat consists of an aluminum-pigmented, colored metallic basecoat and a clearcoat.

The primers may be waterborne polyacrylate systems. Waterborne or low-solvent systems are increasingly used in fillers and metallic basecoats. Acrylic resins with hydroxyl groups, which are reacted with melamine resins or isocyanates, are used in the clearcoat; solution polymers offer advantages as regards application, gloss, and weather resistance.

Trade names include Acronal, Larodur, Luhydran, Lumitol, Luprenal (BASF); Desmophen A (Bayer); Synocryl (Cray Valley); Degalan (Degussa); Elvacite, Lucite (Du Pont); Macrynal, Synthacryl (Hoechst); Joncryl (Johnson); Neocryl (Polyvinyl Chemie); Acryloid, Paraloid (Rohm and Haas); Plexigum (Röhm); Setalux (Synthex); Synthalat (Synthopol Chemie).

Radiation-Curable Systems. Coating methods in which monomers and oligomers are cured (hardened) by exposure to radiation (usually UV light but also electron beams) are experiencing considerable growth (see → Paints and Coatings, 1. Introduction). Advantages of these methods include low emission of volatile organic compounds (VOCs), energy savings, high production rates, and excellent gloss of the coating. However, radiation curing can only be employed on flat surfaces, and cannot therefore be used in the automobile industry. Unsaturated polyester resins (mainly acrylate and methacrylate esters of epoxides), polyesters, oligoethers, urethanes, and polyhydric alcohols are used as binders. Reactive species (radicals) are formed after exposure of photoinitiators to UV light [152–158]. In electron-beam curing, free radicals are generated by interaction of accelerated electrons with organic compounds.

The main areas of use include the coating of wood (doors, furniture, parquet floors), paper

(printing lacquers for record sleeves, postcards), and plastics (PVC coverings).

5.2. Paper Industry [159]

High-quality papers are coated with pigments to improve their printability, appearance, gloss, and other properties [160, 161]. Natural products (e.g., starch and casein) were first used as binders. One of the first acrylate-based dispersions, Acronal 500 D, was introduced on the market in the 1950s. Acrylate-based substitution products (cobinders) also became available for casein and starch [162]. The first fully synthetic binders that could be used without cobinders were introduced in the 1960s [163]. Various dispersions with different polymer hardnesses are available for different types of paper and printing methods [164]. Vinyl esters, acrylonitrile, or styrene are used as comonomers for acrylates; styrene gives good adhesion.

In the United States, acrylate dispersions are of minor importance as binders in coating compositions for paper, butadiene copolymer dispersions are used instead. These products are becoming increasingly important in Europe.

Polyacrylate cationic dispersions [165], and dispersions containing protective colloids are used as sizing agents in paper production.

Trade names include Acronal, Acrosol, Basoplast, Styronal (BASF); Primal, Rhoplex (Rohm and Haas).

5.3. Adhesives and Sealing Compounds [166–169]

Laminating adhesives, pressure-sensitive adhesives, building construction adhesives, and sealing compounds are produced from polyacrylates; see also → Adhesives, 1. General. Homopolymers and copolymers with a low glass transition temperature (usually based on 2-ethylhexyl acrylate and butyl acrylate) are used to obtain the desired tackiness. The glass transition temperature can be adapted for individual applications by copolymerization with acrylonitrile, styrene, vinyl acetate, or methyl methacrylate. Products with a balanced adhesion–cohesion ratio can thus be obtained.

Tackiness is extremely important in emulsion adhesives and adhesives based on solution polymers. The higher the glass transition temperature, the lower has the molecular mass to be in order to obtain the necessary tackiness. The higher the molecular mass, the better is the cohesion of the film. Cohesion often has to be improved by additional cross-linking. Depending on the molecular mass, solution polymer concentrations of up to 50% can be produced. Solvent naphtha, aromatic compounds, ethyl acetate, and alcohols are used as solvents. However, solution polymers are being replaced by aqueous dispersions.

Dispersions and solution polymers are used as industrial laminating adhesives (e.g., high-gloss foil laminating, automobile industry). Laminating adhesives for food and cosmetic packaging must be solvent free. Good adhesion to the substrate is important in this area of application, and can be achieved by using monomers with reactive groups (e.g., carboxyl or amide) or special additives.

Polyacrylates are replacing natural products in pressure-sensitive adhesives (e.g., label adhesives, pressure-sensitive sheets, adhesive tapes, adhesive plasters); glyoxal derivatives are used as cross-linking agents (→ Glyoxal, Chap. 5.). The advantages of polyacrylates compared with natural rubber, for example, are their better resistance to aging and temperature. Both solution polymers and dispersions are used [170–172]; solution polymers have a better water resistance than dispersion adhesives [173].

Structural adhesives (adhesives for floor coverings and tiles) are mainly dispersions [174]. Adhesives for floor coverings are formulated with tack-imparting resins and incorporate organic solvents. Developments in this field include the use of solvent-free systems, i.e., addition of solvent-free resins (e.g., aqueous tackifier dispersions). Tile adhesives are solvent free and are generally mixed with cement; dry powder adhesives will be of particular interest in the future.

Sealing compounds are based on dispersions and must be tack-free in the dry state. One-component polyacrylate systems offer economic advantages compared with silicones. Disadvantages are their water sensitivity and poor adhesion to glass and ceramics.

Trade names include Coldac (Allied Colloids); Airflex, Flexbond, Flexcryl (Air Products); Acronal, Lutonal, Propiofan (BASF); Lacstar, Voncoat (Dai Nippon); Emultex

(Harco); Litex (Hüls); Revertex (Revertex); Rhodopas (Rhône–Poulenc); Texicryl (Scott Bader); Ucecryl, Ucefix (UCB); Vinnapas (Wacker).

5.4. Textile Industry

In the textile industry polyacrylates are used almost exclusively as emulsion polymers (e.g., as binders for pigment dyeing or printing) [175–180]. In almost all areas of application apart from bonding and laminating, soft, nontacky films are desired. The treated textiles generally have to be resistant to washing and drycleaning; this is achieved by cross-linking the polyacrylates after film formation. Drycleaning resistance can be improved by copolymerization with polar monomers such as acrylonitrile, but the handle and feel are then hard.

Polyacrylates are also used as binders for textile flocking to produce velvety surfaces. In addition, fabrics may be coated with water-resistant dispersions (e.g., wax cloth and umbrella material).

Polyacrylates are of minor importance in high-grade finishes [181] that are used to improve textile properties such as handle, feel, abrasion resistance, and crease resistance. A further field of application of polyacrylate dispersions is the consolidation of nonwoven fabrics [182–186] for uses such as interlinings [187], filter materials, and carrier materials for leather imitates [188]. Thermosensitive dispersions that coagulate at a specific temperature during the drying process are also used in the production of nonwovens (→ Nonwoven Fabrics, Section 2.2.).

Trade names include Acronal, Helizarin-binder, Perapret (BASF); Acramin (Bayer); Imperon (Hoechst); Primal (Rohm and Haas).

5.5. Leather Industry [189, 190]

The surface of leather is treated to make it hydrophobic while retaining its natural character, in particular appearance. Highly reversible stretching and good cohesion of the dispersion film are important for the use properties; the leather finish must not crack or tear after repeated folding and bending and should have a low tackiness [191–194]. See also → Leather, Chap. 9.. The first synthetic polymer dispersion for industrial use was "Corialgrund" developed by BASF [193].

Trade names include Corialgrund, Corial Binder (BASF); Euderm (Bayer); Hycar (Goodrich); Fondocryl (Henkel); Melio Resin A (K. J. Quinn); Revertex (Revertex); Primal (Rohm and Haas); Resin RA (Stahl Chemical Ind. B.V.).

5.6. Miscellaneous Uses

Polyacrylates, mainly emulsion polymers, are used in many minor areas: for example, as sizes in the production of textile and glass fibers [195–197]; as polishes for floor coverings, automobiles and shoes; and as additives for hydraulic binders. Polyacrylates are used as additives in mortar and concrete, as well as in agriculture for seed protection and spraying with fertilizers (→ Fertilizers, 3. Synthetic Soil Conditioners, Chap. 4.). They are also employed as matrices for ion exchangers cross-linked with divinylbenzene (→ Ion Exchangers, Section 2.1.).

6. Economic Aspects

Detailed production figures for acrylates are only available for the United States [198], and not for Western Europe and Japan. According to estimates for 1982 and 1984, the United States produced ca. 50%, Western Europe ca. 35%, and Japan ca. 15% of all acrylate esters. These figures have probably not changed substantially. Production figures for acrylate esters from 1969 to 1987 are given in Table 10. Total production has increased in the United States and presumably in Europe, whereas in Japan it has remained constant. The percentage proportions of methyl and 2-ethylhexyl acrylates have remained virtually unchanged. Butyl acrylate showed average annual growth rates of 7.3% between 1969 and 1984, while ethyl acrylate experienced a downturn of 0.6%. The consumption of acrylate esters for 1989 and various fields of application is given in Table 11 [198].

Most polyacrylates are produced by emulsion polymerization. In the United States the proportion of solution polymers is 12%; relevant figures are not available for Europe.

Table 10. Production of acrylates (10^3 t/a)[198]

Year	Methyl acrylate	Ethyl acrylate	*n*-Butyl acrylate	2-Ethylhexyl acrylate	Other acrylates	Total
United States						
1969	14	91	29	15	4	153
1975	20	109	81	15	9	234
1980	29	122	157	31	17	356
1984	28	139	193	39	27	426
1987		147	234			
Western Europe[a]						
1984	60–75	60–75	105	45–60	6	300
Japan[b]						
1975						67
1980						111
1984						106

[a]Chemical Economics Handbook (CEH) estimated values.
[b]Excluding Asahi Chemical.

Although the proportion of solution polymers (which are largely used for coatings and adhesives) may well fall, they will not be completely replaced by emulsion polymers. The use of polyacrylates in the adhesives and paper industries is substantially higher in Europe than in the United States. Methyl acrylate is used almost exclusively in the polymerization of acrylonitrile for fibers to improve dyeability. The mean annual growth rate in the consumption of polyacrylates for 1984–1989 is estimated to be 3.3% for the United States and 2.8% for Europe [198]; specialty fields have the highest growth rates.

Table 11. Estimated consumption of polyacrylates in 1989 expressed in 10^3 t/a (%) [198]

Area of use	United States	Western Europe	Japan[a]
Dispersions			
Surface coatings	124 (32)	103 (36)	38 (33.4)
Adhesives	27 (7)	48 (17)	
Textiles	68 (17.5)	33 (11)	37 (34.9)
Leather	7 (2)	33 (11)	37 (34.9)
Paper	18 (4.5)	49 (17)	
Polishes	13 (3)		
Miscellaneous uses	18 (4.5)		13 (11.9)
Other polymers			
Acrylonitrile fibers	14 (3.5)	26 (9)	15 (13.9)
Solution polymers for surface coatings	45 (12)	28 (10)	
Miscellaneous uses	53 (14)		7 (6.7)
Total	387 (100)	287 (100)	110 (100)

[a]1984 excluding Asahi Chemicals.

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Polyamides

ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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1. Introduction

Polyamides are a versatile family of thermoplastics that have properties that vary broadly from relative flexibility to significant stiffness, strength, and toughness. The term "nylon" is generic and is equivalent to "polyamide". A key characteristic of nylons is their resistance to oils, greases, lubricants, hydrocarbons, and most chemicals. Phenols, strong mineral acids, and oxidizing agents attack them.

Polyamides are synthetic polymers that contain multiple amide −CONH− groups as a recurring part of the chain. The most important commercial nylons are the semicrystalline materials, which account for over 90 % of global usage. There is another significant class of nylons that are referred to as being "amorphous". These typically contain a ring structure. There is an almost unlimited range of nylon materials that can be made by using different monomers.

The first publications describing polycondensation were [1, 2]—the basic principles of nylon synthesis were in 1929. Synthesis of poly (hexamethylene adipamide), the original "nylon",

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was carried out by WALLACE H. CAROTHERS in a DuPont laboratory in 1935 and provided a material whose properties were judged to be appropriate for apparel use. This invention culminated in the first patent for the production of synthetic polyamides in 1937 [3], and their subsequent commercial introduction in 1938. The other principal commercially important polyamide, nylon 6, based on polycaprolactam, was first made at IG Farbenindustrie in Germany by P. SCHLACK in 1938, who was issued a patent in 1941 [4]. The history of these nylons and those made from 11-aminoundecanoic acid and dodecanolactam were reviewed in 1986 [5–7].

The intellectual achievement of creating nylon was a major breakthrough in the science of synthetic polymer chemistry. This development provided incontrovertible evidence for the Staudinger thesis [8] that polymers are high molecular mass species and not aggregated entities. Materials with new types of physical properties were achievable, and could be tailored to various end uses by adjusting parameters such as molecular mass, viscosity, backbone chemistry, additives, etc. CAROTHERS' classic 1931 review [9] of polymerization and his first definitions of the terminology of polycondensation are still valid today. Polycondensation polymerization is a type of step-growth or step polymerization [10] (see Chap. 3). The initial success of nylon led to the numerous scientific and engineering innovations that were required to commercially develop and extend polymer usage. Routes to starting materials were necessary, as was the development of polymerization equipment to manufacture the polymer, and analytical techniques to measure the materials.

Mechanical and physical properties, rate and equilibrium constants, thermal and oxidative stability, resistance to hydrolysis and solvents, and other chemical behavior depend on the specific nylon polymer, but the basic chemistry discussed herein applies to all of these polyamides. Even though nylon was initially used as a fiber, its application as a plastic for a variety of purposes such as brush filaments, wire coating, coil forms, gears, and a variety of parts occurred very soon thereafter. The focus of this article is on the polyamides used as plastics. The technology has evolved to the point where nylons, especially reinforced compositions, are widely used in place of metals, even in under-the-hood applications in automobiles (see Chap. 8). For a discussion of polyamides used as fibers, see → Fibers, 4. Polyamide Fibers.

2. Nomenclature

In current terminology the word "nylon" is a generic term reserved for aliphatic and semiaromatic polyamides. The fully aromatic polyamides are called "aramids" (see → High-Performance Fibers). The origin of the word nylon is uncertain but there is reasonable speculation that it is a mutation of the word "norun" from nylon's first use in hosiery [11, p. 3], [12]. Although nylons can be prepared from various reactive derivatives of carboxylic acids and amines, in general, especially in commercial manufacture, nylons are prepared directly from dicarboxylic acids and diamines [Eq. (1)], ω-aminoacids [Eq. (2)], or lactams [Eq. (3)]:

$$n\,H_2N(CH_2)_xNH_2 + n\,HOOC(CH_2)_{y-2}COOH \rightleftharpoons H[NH(CH_2)_xNHCO(CH_2)_{y-2}CO]_nOH + (2n-1)H_2O \quad (1)$$

$$n\,H_2N(CH_2)_{x-1}COOH \rightleftharpoons H[NH(CH_2)_{x-1}CO]_nOH + (n-1)H_2O \quad (2)$$

$$n\,HN(CH_2)_{x-1}C{=}O + H_2O \rightleftharpoons H[NH(CH_2)_{x-1}CO]_nOH \quad (3)$$

Equation (3) represents the hydrolytic polymerization of a lactam. It is described in detail in Section 3.2. Two basic monomer types are possible.

1. AB type monomer; both the acid and amine functionalities are contained in the same molecule.
2. AABB type monomer; two monomers are required for polymerization, one monomer contains the amine functionality and the other the carboxylic moiety.

A and B stand for the functional groups NH_2 and COOH, respectively. Lactams are considered AB type monomers as these are derivatives of amino acids, which, by virtue of their structures, have a strong driving force for cyclization (lactam formation). In current practice, AABB and AB may describe products that do not involve polymerization via amine and acid ends but can be visualized as if so made. This is realistic because under conditions of fabrication and processing, moisture is always present.

Reaction of the polyamide with moisture under these conditions (hydrolysis), regardless of the starting monomers used in their preparation, would generate the corresponding amino acid or the acid and amine monomers. The AABB types are regarded as homopolymers because of the absolute requirement for alternation of both reactants to form a polymeric chain that includes both moieties in the repeating structure (see Chap. 3). This is consistent with IUPAC recommendations [13]. Copolymers result from simultaneous polymerization of AABB and AB types or use of more than one AA, BB, or AB type. They are common and were used as early as 1940 [6].

In the early development of nylons, the monomers used were most often linear aliphatic compounds. A simple system of nomenclature that is still used today is to designate these polyamides by the number of carbon atoms in the monomers. The polyamides (PA) or nylons are identified by numbers corresponding to the number of carbon atoms in the monomers (diamine first for the AABB type). Thus, two numbers represent an AABB polyamide; the first number refers to the diamine and the second number to the carboxyl monomer. An AB type is represented by a single number. Table 1 provides a list of the common names of the commercial nylon homopolymers, their numerical designations, their CAS registry numbers, and their CAS names. The monomers TMD in TMDT and PACM in PACMT are mixtures of isomers and TMDT and PACMT are in fact copolymers. The systematic IUPAC naming of polyamides [14] is awkward and is rarely encountered in commercial literature. The CAS names are largely in accord with IUPAC practice, but examination of Table 1 reveals some inconsistencies. Many of the IUPAC rules for nomenclature are conveniently assembled in a polymer handbook [15] wherein, however, older versions of the IUPAC names for PA 66 and 6 are used [16]: poly(iminoadipoyliminohexamethylene) and poly [imino(1-oxohexamethylene)].

Table 2 lists some of the most common monomers. As shown in the tables, numerical symbols are simple, convenient, and unambiguous only for linear aliphatic monomers. This system of nomenclature is inadequate and it is often necessary to use letters instead of numbers for

Table 1. Commercial polyamides or nylons

Common name	*xy* or *x* *	CAS name, CAS registry no.
Poly(tetramethylene adipamide)	46	poly[imino(1,4-dioxo-1,4-butanediyl)imino-1,6-hexanediyl] [24936-71-8]
Poly(hexamethylene adipamide)	66	poly[imino(1,6-dioxo-1,6-hexanediyl)imino-1,6-hexanediyl] [32131-17-2]
Poly(hexamethylene azelaamide)	69	poly[imino-1,6-hexanediylimino(1,9-dioxo-1,9-nonanediyl)] [28757-63-3]
Poly(hexamethylene sebacamide)	610	poly[imino-1,6-hexanediylimino(1,10-dioxo-1,10-decanediyl)] [9008-66-6]
Poly(hexamethylene dodecanoamide)	612	poly[imino-1,6-hexanediyliminо(1,12-dioxo-1,12-dodecanediyl)] [24936-74-1]
Poly(*m*-xylylene adipamide)	MXD 6	poly[iminomethylene-1,3-phenylene-methyleneimino(1,6-dioxo-1,6-hexanediyl)] [25805-74-7]
Poly(trimethylhexamethylene terephthalamide)	TMDT	1,4-benzenedicarboxylic acid, polymer with 2,2,4-trimethyl-1,6-hexanediamine and 2,4,4-trimethyl-1,6-hexanediamine [25497-66-9]
Poly(11-aminoundecanoamide)	11	poly[imino(1-oxo-1,11-undecanediyl)] [25035-04-5]
Polycaprolactam or polycaproamide	6	poly[imino(1-oxo-1,6-hexanediyl)] [25038-54-4]
Polydodecanolactam or polylaurolactam or polydodecanoamide	12	poly[imino(1-oxo-1,12-dodecanediyl)] [24937-16-4]
Hexamethyleneadipamide-hexamethyleneterephthalamide copolyamide	6T/66	1,4-benzenedicarboxylic acid, polymer with 1,6-hexanediamine and hexanedioic acid [25776-72-1]
-Caprolactam-hexamethyleneterephthalamide copolyamide	6T/6	1,4-benzenedicarboxylic acid, polymer with hexahydro-2*H*-axepine-2-one and 1,6-hexanediamine [25086-53-7]
Bis(4-aminocyclohexyl)methane-terephthalic acid copolymer	PACMT	1,4-Benzenedicarboxylic acid, polymer with 4,4′-methylenebis(cyclohexanamine) [117092-07-6]

* *xy* and *x* refer to the number of carbon atoms according to Equations (1)–(3).

Table 2. Monomers for polyamides

Common and (CAS) name	CAS registry no.	*x* or *y* *	Source	Properties and synthesis
Adipic acid (hexanedioic acid)	[124-04-9]	6	benzene, toluene	→ Adipic Acid
Azelaic acid (nonanedioic acid)	[123-99-9]	9	oleic acid	→ Dicarboxylic Acids, Aliphatic, Section 2.4.7.
Sebacic acid (decanedioic acid)	[111-20-6]	10	castor oil	→ Dicarboxylic Acids, Aliphatic, Section 2.4.8.
Dodecanedioic acid	[693-23-2]	12	butadiene	→ Dicarboxylic Acids, Aliphatic
Dimer acid (fatty acids, dimers)	[61788-89-4]	36	oleic and linoleic acids	→ Dicarboxylic Acids, Aliphatic, Section 3.4.2.
Isophthalic acid (1,3-benzenedicarboxylic acid)	[121-91-5]	I	*m*-xylene	→ Carboxylic Acids, Aromatic → Terephthalic Acid, Dimethyl Terephthalate, and Isophthalic Acid
Terephthalic acid (1,4-benzenedicarboxylic acid)	[100-21-0]	T	*p*-xylene	→ Terephthalic Acid, Dimethyl Terephthalate, and Isophthalic Acid
Tetramethylenediamine, 1,4-diaminobutane (1,4-butanediamine)	[110-60-1]	4	acrylonitrile and HCN propene	→ Amines, Aliphatic, Section 8.1.3.
Hexamethylenediamine, 1,6-diaminohexane (1,6-hexanediamine)	[124-09-4]	6	butadiene, propene	→ Hexamethylenediamine
2-Methylpentamethylenediamine (1,5-pentanediamine, 2-methyl)	[15520-10-2]	MPMD	butadiene butadiene	
4,4′-Diaminodicyclohexylmethane (cyclohexaneamine, 4,4′-methylenebis-)	[1761-71-3]	PACM	aniline and formaldehyde	
m-Xylylenediamine (1,3-benzenedimethaneamine)	[1477-55-0]	MXD	*m*-xylene	
2,2,4-Trimethylenehexamethylenediamine 2,4,4-Trimethylenehexamethylenediamine	[3236-53-1] [3236-54-1]	ND IND	acetone acetone	
Dodecamethylenediamine, 1,12-diaminododecane (1,12-dodecanediamine)	[2783-17-7]	12	butadiene butadiene	→ Amines, Aliphatic, Section 8.1.3.
11-Aminoundecanoic acid (undecanoic acid, 11-amino-)	[2432-99-7]	11	castor oil castor oil	
ε-Caprolactam (2 *H*-azepin-2-one, hexahydro)	[105-60-2]	6	benzene, toluene	→ Caprolactam
Laurolactam, dodecanolactam, (azocyclotridecane-2-one)	[947-04-6]	12	butadiene	→ Cyclododecanol, Cyclododecanone, and Laurolactam

* *x*, *y* = number of carbon atoms according to Equations (1)–(3).

monomers of more complex structures. The absence of unifying rules to deal with monomers other than linear, aliphatic monomers has led to different symbols for the same monomer. More recently ISO 1874-1 has been established and gives recommended symbols for some monomers; however, it fell short of establishing rules for assigning letter designation for complex monomers. Notice the new designation for the isomers of TMD wherein the two positional isomers are given designations of ND for the 2,2,4-trimethylhexamethylenediamine and IND for the 2,4,4-trimethylhexamethylenediamine. However, no distinct symbols were assigned to the *cis–cis, cis–trans*, and *trans–trans* isomers of PACM. Another aspect still not addressed by ISO 1874-1 is the configurational isomerism with polyamides of nonsymmetrical monomers such as ND, IND, and MPMD. These diamines can produce head-to-head, head-to-tail, and tail-to-tail isomerism in their polymers.

The ISO recommendation for polyamides is to use the symbol PA for polyamide followed by the monomer symbol. Pronunciation is in accord with the monomers so that the homopolymer from hexamethylenediamine and adipic acid, which is represented by PA 66, is pronounced PA six-six not sixty-six, PA 612 is PA six-twelve, PA 11 is PA eleven, etc. Often the space between PA and the monomer symbol is eliminated as in PA66, PA612, PA11. Copolymers are designated by "PA" followed by the polyamide symbols separated by a slash. For example, a copolymer of PA 6 and PA 66 is represented as PA 6/66, and a copolymer of PA 66 and PA 610 is PA 66/610. No provisions for polyamide blends have been established. Kohan [11, p. 5] designates blends by separating the component polyamides with a slash. For example a blend of PA 6 and PA 66 is represented as PA 6/PA 66 to distinguish it from the copolymer PA 6/66.

3. General Considerations in Polyamidation

Carothers [1] proposed the term "polycondensation" for polymerization reactions wherein two functional groups react to form a covalent bond with the elimination of a simple molecule as a byproduct in accordance with the definition of condensation reactions in organic chemistry. In this type of polymerization, chain growth involves the stepwise reaction of the functional groups. Step-growth polymerization, a broader term that encompasses all polycondensation polymerizations, was first used by Lenz [10]. Detailed coverage of step-growth polymerization is given in Polymerization Processes, 1. Fundamentals [17].

The basic concepts of equilibria and kinetics in polyamidation are in large measure owing to Flory and are summarized in his classic text [18]. Derivations of the following important expressions are to be found in many places, e.g., [17–20], and will not be developed here.

3.1. Molecular Mass

The extent of reaction, p, is the fraction of possible reactions that has occurred. The number-average degree of polymerization, $\bar{P}_n$ (IUPAC recommends $\bar{X}_n$), is the number of monomer units in the average polymer chain and is $2n$ for the AABB type nylon and n for the AB type where n is as shown in Equations (1)–(3). The typical polymer consists of molecules of varying molecular masses, so it is necessary to talk of average values. The number-average molecular mass, $\bar{M}_n$, is the product of $\bar{P}_n$ and the average molecular mass of the units in the polymer (see also → Plastics, Analysis, Chap. 5.). This ignores the contribution of end groups, which is unimportant at usefully high molecular masses. $\bar{M}_n$ is, precisely, the sum over all species of the number fraction of each molecular mass species multiplied by its molecular mass. The relation between $\bar{P}_n$ and p is:

$$\bar{P}_n = \frac{1}{1-p} \tag{4}$$

This equation applies strictly to equilibrium conditions but is well suited to commercial polyamides. For PA 6 or PA 66, the average mass per amide is 113. Thus, $\bar{P}_n$ is 100 for an $\bar{M}_n$ of 11 300 and p is 0.990. This is at the low end of the range of useful $\bar{M}_n$ values. For a more typical value of about 20 000, p is 0.994. The need for pure monomers and clean, essentially complete reactions is clear. $\bar{M}_n$ for most commercial nylons is in the range 11 000–34 000. Physical

properties depend on $\bar{M}_n$ which can be conveniently determined by end group analysis.

The weight-average molecular mass, $\bar{M}_w$, is given by $\bar{M}_w = \sum M_i + \sum_i (M_e)_i$ i.e., the sum of the products of the weight fraction w_i of each of the molecular mass species i and its molecular mass M_i plus the contributions of end groups. Melt viscosity, important in processing, varies with $\bar{M}_w^{3.4}$ [21–23]. $\bar{M}_w$ is available from light scattering or equilibrium ultracentrifugation. Solution viscosity is often used to approximate molecular mass and corresponds more nearly to $\bar{M}_w$. Both $\bar{M}_n$ and $\bar{M}_w$ can be obtained by chromatographic techniques [24–27]. $\bar{M}_w$ relates to p as shown:

$$\bar{M}_w = (1 + p)/(1 - p) \tag{5}$$

The distribution of molecular masses is important. A much-used index of the distribution is the ratio, $\bar{M}_w/\bar{M}_n$. Dividing Equation 5 by Equation 4 yields

$$\bar{M}_w/\bar{M}_n = 1 + p \tag{6}$$

At useful molecular masses where p nearly equals 1, $\bar{M}_w/\bar{M}_n$ is almost exactly 2. This was defined by FLORY as "the most probable distribution" of molecular masses. In such a distribution, which applies closely to almost all commercial nylons, the number fraction of any species decreases with increasing molecular mass. The weight fraction versus molecular mass curve goes through a maximum, the position of which is equal to $\bar{P}_n$ [18, 28].

The most convenient analytical technique is solution viscometry, which delivers a so-called viscosity-average molecular mass, $\bar{M}_v$. Solution viscosity can be used to estimate both $\bar{M}_n$ and $\bar{M}_w$ as long as their ratio is known and remains the same. Formic acid is a convenient solvent for PA 6, PA 46, and PA 66, but *m*-cresol or sulfuric acid must be used for nylons with fewer amide groups. Details of the technique and expressions relating viscosity and molecular mass can be found in [19].

Added or adventitious reactants with more than two reacting groups per reactant molecule (or just two alike in the case of AB types) will lead to branching and, in turn, will change the equilibrium distribution of molecular masses [18, 29]:

$$\bar{M}_n = 2/[N_e - (f - 2)b] \tag{7}$$

$$\bar{M}_w = 4/[N_e - f(f - 2)b] \tag{8}$$

where

N_e = number of ends
f = functionality (number of reactive groups in a monomer molecule)
b = number of branch points

At onset of gelation, where $\bar{M}_w$ goes to infinity, the number of branch points is

$$b_{gel} = N_e/f(f - 2) \tag{9}$$

Since the number of moles is $1/\bar{M}_n$, b' the number of branch points per mole, is $b\bar{M}_n$. At the gel point

$$b' = 2\, b_{gel}/[N_e - (f - 2)b_{gel}] \tag{10}$$

For $f = 3$, $b_{gel} = N_e/3$, and $b'_{gel} = 2\, b_{gel}/(N_e - b_{gel}) = 1$. That is, it takes only one branch point per polymer molecule to cause gelation if a trifunctional reactant such as trimesic acid [554-95-0] (1,3,5-benzenetricarboxylic acid), or bishexamethylenetriamine [143-23-7] [*N*-(6-aminohexyl)-1,6-hexanediamine] is present. The latter compound can be formed by intermolecular reaction of two amine ends of 1,6-hexamethylenediamine with loss of ammonia.

Star-type branching occurs when AB monomers react with a polyfunctional reactant that contains only A or B groups and not both kinds. In this special situation [30] gelation cannot occur. Broad distributions occur for low p values and narrow distributions for p approximating unity in which case $\bar{M}_w/\bar{M}_n = 1 + f^{-1}$. Branched polyamides were introduced commercially in the late 1990 [31–34] (see Section 6.2).

The effect of mixing two polymers of different molecular masses is often questioned. In the case of $(\bar{M}_w)_1/(\bar{M}_n)_1 = (\bar{M}_w)_2/(\bar{M}_n)_2 \approx 2$, which most often applies to nylons [19]:

$$(\bar{M}_w/\bar{M}_n)_{blend} = 2 + [2\, F_1 F_2 (R - 1)^2/R] \tag{11}$$

where F is the weight fraction of components 1 or 2 and R the ratio of number-average

molecular masses of components 1 and 2. Thus, for $F_1 = F_2 = 0.5$ and $R = (\bar{M}_n)_2/(\bar{M}_n)_1 = 2$, an extreme case for nylons, $\bar{M}_w/\bar{M}_n = 2.25$. This type of blending, therefore, has little effect on the molecular mass ratio and the changes observed are due to the changes in $\bar{M}_w$ and $\bar{M}_n$.

The reaction of amine and acid to form an amide is described by the following equilibrium expression:

$$K_{eq} = \frac{[CONH][H_2O]}{[COOH][NH_2]} \tag{12}$$

At high molecular masses [CONH] is essentially constant and depends only on the average molecular mass per monomeric unit. For PA 6 or PA 66 this becomes 1/113. For numerical convenience the units of ends and other concentrations are often expressed as the number of moles (or equivalents) per 10^6 g so that [CONH] is 8850.

The product of end group concentrations, [COOH] $[NH_2]$ = P, is determined by the temperature and moisture content. The molecular mass depends on the number of ends, which is minimized (and the molecular mass maximized) for a fixed P when the concentration of amine and acid ends is the same, i.e., balanced. An imbalance may be imposed on purpose to limit the molecular mass by adding an excess of one kind of monomer or a chain-terminating reactant that contains only one functional group.

Addition of AA or BB in the polymerization of AB yields a polymer that at high extents of reaction (p very close to unity) has essentially only one kind of end group and belongs to the class of star-type products mentioned above. In this case the distribution of molecular masses represented by $\bar{M}_w/\bar{M}_n$ no longer approximates to 2 and, because the functionality is 2, is about 1.5. The addition of monofunctional acids or amines in the polymerization of AB or AABB and the addition of excess diacid or diamine in the polymerization of AABB does not alter the distribution and can be treated in a general way. If n is the amount of additive expressed as the mole fraction of AB or either AA or BB, and not the sum of AA and BB, then $\bar{P}_n$ is simply $1/n$ in the case of the AB polymer and $2/n$ for the AABB polymer. The factor of 2 is due to the fact that reaction of a difunctional monomer yields two amide groups. Including the contribution of the additive requires adding 1 to $\bar{P}_n$.

A problem in AABB polymerization lies in the fact that the imbalance of ends often results from loss of diamine during polymerization because its volatility is significantly higher than that of the diacid. It cannot, therefore, be anticipated but must be determined by analysis of the product. Assume N_A and N_B are the numbers of amine and acid ends found in the product in convenient units such as equivalents per 10^6 g. Assume also that a monofunctional acid has been added in an amount equal to n defined as in the above paragraph. Assume further that the average of the molecular masses of AA and BB less the 2 mol of water eliminated by polymerization is M so that the concentration of amide functions in the polymer, in the same units, is $10^6/M$. The total number of ends, N_T, in the polymer is $N_A + N_B + n\ 10^6/2\ M$. Because the polymer is linear, the number of amide groups per polymer molecule, that is $\bar{P}_n$, is $2 \times 10^6/MN_T$. By way of example, if N_A, N_B, and n are 70, 30, and 0.01, respectively for PA 66, N_T is $100 + 0.01 \times 4425$ and $\bar{P}_n$ is $2 \times 10^6/(113 \times 144) = 123$.

A related question is the implication of imbalanced ends for the equilibrium moisture content where it is desired to achieve or maintain a given molecular mass, i.e., have the same sum of ends. $P_{bal} = N_e^2/4$ if the ends are balanced, i.e., the amine and acid ends are equal in number and add up to N_e. For imbalanced ends and the same N_e, let $P_{imb} = N_A N_B$ where N_A and N_B are the new concentrations of amine and acid ends. For excess acid ends, define $r = (N_B - N_A)/N_e$. Since $N_e = N_B + N_A$, it is readily shown that $1 - r^2$ is $4\ N_A N_B/\ N_e^2$. Thus,

$$P_{imb} = (N_e^2/4)(1 - r^2) = P_{bal}(1 - r^2) \tag{13}$$

Because the equilibrium moisture content varies directly with the product of ends,

$$[H_2O]_{imb} = [H_2O]_{bal}(1 - r^2) \tag{14}$$

where $[H_2O]_{imb}$ is the equilibrium moisture content in the case of imbalanced ends. Thus, if $r = 0.5$, which corresponds to a ratio of unreacted amine ends to unreacted acid ends (or vice versa) of 3/1 and is rather large, $[H_2O]_{imb}$ is 0.75 $[H_2O]_{bal}$. Polymerization to a

higher molecular mass or hydrolysis to a lower one occurs depending on whether the water content is above or below the equilibrium value. The significance for the drying of resin and melt processing is clear.

3.2. Equilibrium and Rate Constants

The equilibrium constant for the polycondensations corresponding to Equations (1) and (2) is defined in Equation 12. Few data exist for such polycondensations. Many equilibrium and rate studies have been concerned with the so-called hydrolytic polymerization of ϵ-caprolactam in the presence of water. A comprehensive coverage of lactam-based polyamides is given in [35]. This polymerization is not as simple as Equation (3) indicates. Three reactions in the hydrolytic polymerization of caprolactam are of prime concern:

1. Hydrolysis of the lactam by water to yield the amino acid (Eq. 3 with $n = 1$)
2. Condensation as in Equation (2)
3. Lactam addition to the amine end of the growing chain (Eq. 15):

$$n\,\underbrace{HN(CH_2)_5C{=}O} + H[NH(CH_2)_5CO]_mOH \rightleftharpoons H[NH(CH_2)_5CO]_{m+1}OH \quad (15)$$

Also contributing to the complexity is the formation of cyclic oligomers corresponding to the following formula [36]:

$$\left[\begin{array}{l} NH(CH_2)_5CO \\ \\ [CO(CH_2)_5NH]_n \end{array}\right] \qquad n \geqq 1$$

Structures with n up to 7 have been reported [37]. The amount of lactam monomer ($n = 0$) at equilibrium depends on the temperature (Fig. 1), [19, 38, 39]; the monomer comprises about 75 % of the extractable material, i.e., monomer and cyclic oligomers [40]. Residual lactam monomer and its cyclic oligomers are relatively volatile and tend to vaporize and condense on cool surfaces during melt processing unless provision for their removal has been made. Cyclic

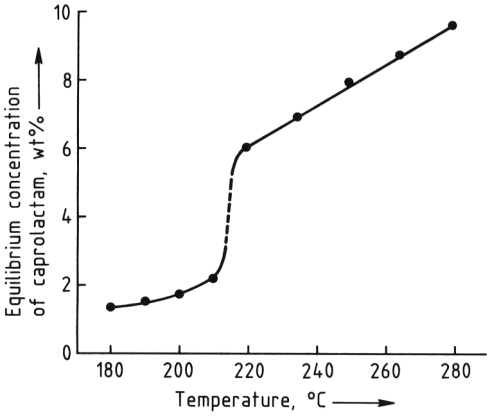


Figure 1. Dependence of monomer on temperature in polycaprolactam (data from [19, 38, 39])

oligomers exist not only in the higher AB-type nylons such as PA 11 and PA 12 but also in AABB types such as PA 66 and PA 610 [27, 28, 41–43]. However, the concentrations are much lower, and the extractable fractions are usually below 2 wt % [44–48] so that separation is not required as it is for PA 6.

There are further complications. The amine and acid end groups may exist as ammonium and carboxylate ions; this raises the possibility of alternative reactions involving condensation reactions between ions or between an unionized end and an ion. Degree of hydration is another question. Also a concern is the use of concentrations instead of the theoretically correct activity coefficients. The dependence of conventionally calculated equilibrium constants K_{eq} on water content, which can affect ionization, hydration, and activities, has been observed many times [49–53]; these K_{eq} values are thus apparent equilibrium constants. GIORI and HAYES [54] showed for PA 6 that the apparent equilibrium constant for polycondensation increased with water content up to about 2 wt% and decreased thereafter (Fig. 2). They used vapor–liquid equilibria, which showed a negative deviation from Raoult's law, to obtain activities [55]. K_{eq} (their K_{III}) showed much less deviation with percent water when using activity coefficients instead of concentrations (Fig. 3). Their K_{eq} at 2 wt % water (using concentrations) is about 600 at 240 °C and 450–500 at 270 °C. Values of 519 and 377

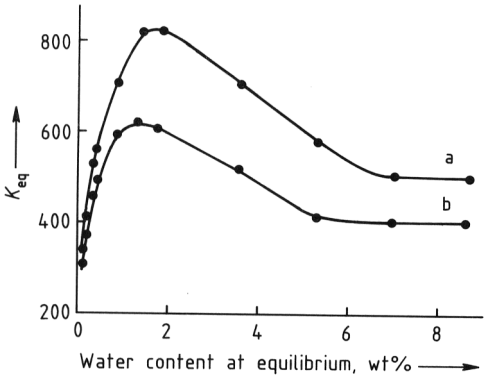


Figure 2. Apparent equilibrium constants for polycondensation versus equilibrium water content a) 240 °C; b) 260 °C
(reproduced with permission of John Wiley and Sons from Figure 1 in [54])

for comparable conditions can be calculated from the data of TAI and coworkers [56]. These variations are typical of the data available on the hydrolytic polymerization of caprolactam, most of which have been generated at water contents much higher than practical for melt processing.

Nylons are typically sold with about ≤ 0.2 wt % water. Extrapolation of data obtained at 0.2 wt% water at 240 and 260 °C by GIORI and HAYES [54] gives $K_{eq} = 280$ at 280 °C. TAI's data [56] yield $K_{eq} = 410$ at 280 °C at the lowest water content studied (0.42 mol/kg or 0.76 wt %). ZIMMERMAN [57] used a reported moisture content of 0.16 wt%, an end product of 3000,

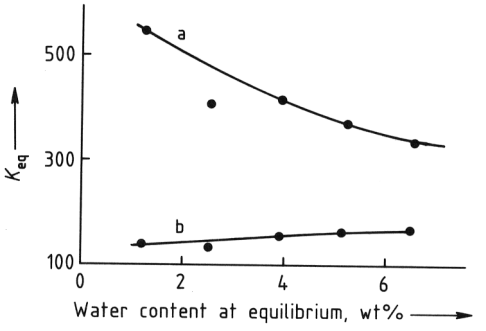


Figure 3. Equilibrium constants for nylon 6 polycondensation versus equilibrium water content at 270 °C
a) Apparent equilibrium constants; b) Equilibrium constants corrected for the water activity coefficient
(reproduced with permission of John Wiley and Sons from Figure 8 in [54])

and an amide concentration of 8850 g equivalents/10^6 g at 101.3 kPa steam for PA 66 at 280 °C to calculate a K_{eq} of 260. The effect of moisture on processing requirements is best resolved by examining its significance for the stability of melt viscosity at the temperatures of concern as long as excessive holdup times and temperatures leading to thermal degradation are not involved [19].

Kinetic and thermodynamic constants for the polymerization of caprolactam have been summarized ([56], Table 3) and have been said to correlate with manufacturing experience with a deviation of less than 12 wt% [58]. The data in Table 3 are averaged for initial water contents of 0.82 and 1.18 mol/kg (1.48 and 2.12 wt%). Examination of the original data, which also included an initial water content of 0.42 mol/kg, indicates modest changes in the various constants except in the case of the temperature-independent constant, A^c_2 for catalyzed polycondensation which increased by a factor of 20.4 over the 2.8 increase in water content. Enhanced ionization and catalysis are thus indicated to be more important than reduced concentration of unionized species. Both second- and third-order kinetics (uncatalyzed and acid-catalyzed) for all three processes (Eqs. 2, 3 with $n = 1$, and 15) have been observed. For illustration the appropriate expressions for the polycondensation reactions are shown below:

$$-\mathrm{d[end]}/\mathrm{d}t = k^o_2[\mathrm{NH_2}][\mathrm{COOH}] \quad (16)$$

$$-\mathrm{d[end]}/\mathrm{d}t = k^c_2[\mathrm{NH_2}][\mathrm{COOH}]^2 \quad (17)$$

Amidation is reversible so that the contribution of hydrolysis cannot be ignored. The rate constant for hydrolysis is k/K_{eq} where K_{eq} is defined as in Equation 12 and k is the rate constant for amidation. At low water contents and high extents of reaction, as in the case of commercial nylons, third-order kinetics apply. The optimum water concentration for polymerization varies with conversion—high initially to promote opening of the ring and low in the later stages to promote high conversion. Figures 4 and 5 illustrate this effect of water content.

The amidation constants corresponding to Equations (1) and (2) are generally applicable because of the postulate that end group activity is independent of chain length [18], but overall

Table 3. Kinetic and thermodynamic constants in the hydrolytic polymerization of caprolactam*

i	A^0_i, kg mol^{-1} h^{-1}	E^0_i, cal/mol	A^c_i, kg^2 mol^{-2} h^{-1}	E^c_i, cal/mol	ΔS_i, e.u.	ΔH_i, cal/mol
1	5.9874×10^5	1.9880×10^4	4.3075×10^7	1.8806×10^4	− 7.8846	1.9180×10^3
2	1.8942×10^{10}	2.3271×10^4	1.2114×10^{10}	2.0670×10^4	0.94374	-5.9458×10^3
3	2.8558×10^9	2.2845×10^4	1.6377×10^{10}	2.0107×10^4	− 6.9457	-4.0438×10^3

* Average of data obtained with initial water contents of 0.82 and 1.18 mol/kg (1.48 and 2.12 wt%, respectively). A_i = pre-exponential factor and E_i = activation energy from $k_i = A_i \exp(-E_i/RT)$; ΔS_i = entropy; ΔH_i = enthalpy; $i = 1$, ring opening (hydrolysis of lactam to aminocaproic acid); $i = 2$, polycondensation (of aminocaproic acid); $i = 3$, polyaddition (addition polymerization of ϵ-caprolactam). Reproduced with permission of John Wiley and Sons from Table II in [56].

reaction rates and ring-chain equilibria vary because of differences in ring stability. Rings with 5, 6, 12, or 13 members are more stable than the 7-membered caprolactam. The larger rings are also, however, more difficult to form. This accounts for the use of catalysts in synthesizing PA 12 and for its lower equilibrium concentration of extractables. An excellent review of the properties of lactams has been provided by Sekiguchi [52].

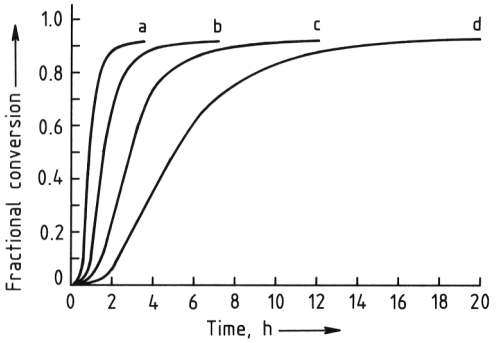


Figure 4. Effect of initial mass fraction of water (W_o) on rate and extent of conversion ($T = 265$ °C)
a) $W_o = 0.08$; b) $W_o = 0.04$; c) $W_o = 0.02$; d) $W_o = 0.01$
(reproduced with permission of John Wiley and Sons from Figure 8 in [51])

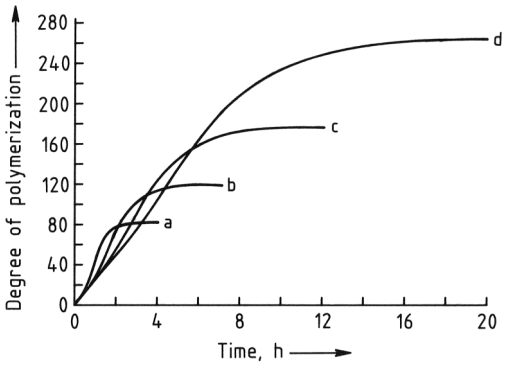


Figure 5. Effect of initial mass fraction of water (W_o) on rate and degree of polymerization
a) $W_o = 0.08$; b) $W_o = 0.04$; c) $W_o = 0.02$; d) $W_o = 0.01$
(reproduced with permission of John Wiley and Sons from Figure 10 in [51])

Catalysts for amidation are not used for PA 6 or PA 66, although a small amount of aminocaproic acid or diammonium carboxylate such as the salt used to make PA 66 can be added to the caprolactam–water mix to eliminate the induction time required for lactam hydrolysis. Reported catalysts for amidation include metal oxides and carbonates or acidic materials [59], strong acids [60], lead monoxide [61], terephthalate esters [62], acid mixtures [63], titanium alkoxides or carboxylates [64], and phosphorus compounds [65–67].

3.3. Effects of Monomer Structure

The ability of monomers to participate in polyamidation is markedly influenced by their tendency to form cyclic structures and the stability of those structures once formed. Carothers [1] showed that it is difficult to form high molecular mass polymers when the formation of cyclic structures is favored. This principle affects the formation of both AB and AABB-type polymers, but in different ways. Lactams with five or six members are more stable than the seven-membered caprolactam rings, and their formation is favored over chain growth. The stability of the 5-membered ring lactam is so high that melt polymerization of pyrrolidone to PA 4 results only in low molecular mass polymers. Polymers of useful molecular mass have been obtained from these monomers only by using mild conditions such as solid-phase polymerization or anionic polymerization [68], and under

these conditions the monomer will be regenerated when the polymer is heated (Section 3.2). The 12- and 13- membered lactams are less reactive than caprolactam and require the use of catalysts for polymerization. Despite its enhanced reactivity, caprolactam has an equilibrium concentration of 8 % in the presence of its polymer. The equilibrium concentrations of 12- and 13-membered lactams in their polymerizations are less than 0.5 % because the reformation of these large rings is entropically unfavorable.

Ring formation can also lead to byproducts and chain-termination reactions in AABB polymerization. Succinic and glutaric acids, for example, produce only low molecular mass polymer under melt polyamidation conditions due to formation of the favored five- and six-membered cyclic imides derived from a reaction with the diamine comonomer. Although adipic acid has very little tendency to form its seven-membered cyclic imide, under typical polymerization conditions it does cyclize to the five-membered cyclopentanone by the elimination of carbon dioxide. The formation of pyrrolidine from 1,4-diaminobutane was reported by Roerdink et al. [69, 70] in the manufacture of PA 46. The pyrrolidine formation and the instability of adipic acid preclude the attainment of high molecular mass in the melt polymerization of PA 46 (see Section 5.1).

3.4. Amide Interchange

Amide interchange (transamidation) is the interchange of amide groups between various polymer molecules or segments thereof. It is a factor when blending polyamides different molecular masses and/or different polymers. As noted above (Eq. 11), the effect of transamidation on molecular mass distribution is minor. Furthermore, there is rapid approach to an equilibrium value [53, 71]. The degree of interchange necessary for producing a random copolymer is slow enough, however, that block polymers are feasible [53, 72], although high conversion of the mix results in block lengths significantly smaller than the original chain lengths [73]. A study of the interchange reaction involving polymerization of sebacamide and *N*,*N*′-diacetylhexamethylenediamine suggested that the rate increased with water concentration and was proportional to $[COOH]^{1/2}$ [53]. Miller studied the reaction of model compounds with each other and with PA 66 [73]. The primary reaction was acidolysis; aminolysis was acid catalyzed and did not occur in the absence of acid.

3.5. Structure-Property Considerations

Polyamides are valued as a plastic due to their good mechanical properties, excellent chemical resistance, and their ability to resist high temperatures. These qualities are due to their crystallinity and high melting points (see Chap. 6). Data that have been accumulated from the wide range of polyamides that have been studied have led to some generalizations on the effects of structure on their properties.

A large body of evidence has demonstrated that the underlying characteristic of polyamides that influences their properties is their ability to form strong hydrogen bonds. Any structural changes that affect the hydrogen bonding ability will have a very large effect on the properties. The dependence of the melting point, T_m, on the crystal heat of fusion, ΔH_u, and entropy of fusion, ΔS_u, is defined by:

$$T_m = \frac{\Delta H_u}{\Delta S_u}$$

The high melting points of polyamides are attributed to their low liquid-state entropy of fusion due to possible retention of hydrogen bonding in the melt and some stiffening of the amide group due to resonance [74]. The increase in melting point that goes with increased ability to form hydrogen bond is exemplified by PA 66 and PA 46. The latter has an increased ratio of CONH to CH_2 groups, which means more hydrogen bonding, and a increased melting point (see Chap. 6). On the other hand, lateral substituents on either the carbon chain or amide nitrogen or the presence of comonomers result in lower crystallinity and melting points. More drastic effects are exhibited when the substituent is bulky and/or on the nitrogen atom. The T_m for PA 66 is 265 °C but the polymer from *N*,*N*-dimethylhexamethylenediamine and adipic acid is amorphous and rubbery. A more detailed discussion of this topic is covered in [75].

4. Other Polymerization Techniques

4.1. Variants of Hydrolytic Polymerization

This category includes the use of acid derivatives or precursors instead of the acid itself [76] in high-temperature reactions. Examples are esters [77, 78]; acid halides [79]; amides [80]; and nitriles [81–85]. Another variant is the use of high-boiling, stable liquids that may or may not be a solvent for the nylon, e.g., selected phenols or white oil [86], glycols [87], and polar solvents such as *N*-methyl-2-pyrrolidone or sulfolane [88]. The use of amine derivatives is limited. The reaction of an aromatic diisocyanate with a dibasic acid is an example [89]; an appropriate choice of solvent and catalyst is necessary to avoid side reactions. A special case involves the use of the relatively reactive oxalate esters that react with diamines at ordinary temperatures.

4.2. Interfacial and Solution Polymerization

These are low-temperature methods for the preparation of polyamides whose stability and/or viscosity prevent melt polymerization. The reaction of an amine and acid chloride to yield aramid-type products is typically involved. The classic text on the subject is that of MORGAN [90]. Reference to the technique can also be found in [91]. (See also, → High-Performance Fibers, Section 2.2.1.. Aramid Fibers and → Polymerization Processes, 1. Fundamentals.)

4.3. Ionic Polymerization

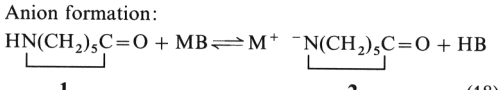
Both anionic and cationic polymerization of anhydrous lactams have been demonstrated. Cationic methods have, however, failed to yield useful polymers because of side reactions that limit attainable molecular mass. Reviews of ionic polymerization have been provided [35, 51, 52].

The anhydrous, *anionic polymerization* of caprolactam has been of interest because the monomer is converted to polymer in minutes. This not only eliminates the need for costly polymerization facilities but also allows for use of inexpensive molds of complex design. It makes low-volume production feasible but is not economical for mass production of small parts. Unless modified, this method yields a polymer with properties somewhat different from hydrolytically polymerized PA 6 because of higher molecular mass and higher crystallinity [92].

Preferred techniques involve the use of the lactam anion, which is made in situ by reaction with a base (catalyst), and a lactam with an electrophilic substituent on the nitrogen atom (the cocatalyst). A very large number of publications and patents deal with the choice of catalyst and cocatalyst and their implication for advantages in process or properties. Examples of catalysts are metal hydrides, oxides, alkoxides, amides, carbonates, and Grignard reagents; cocatalysts are *N*-acyl caprolactams or compounds that form such derivatives in situ, e.g., anhydrides and isocyanates. Patents in the 1980s (e.g., [93–102]) have focused more on fillers, toughening agents, applications, and process variants than on novel catalyst systems.

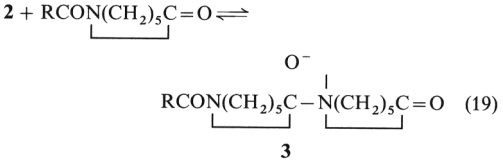
The mechanism of anionic polymerization is depicted below (M = metal, B = base, R = alkyl or aryl):

Anion formation:

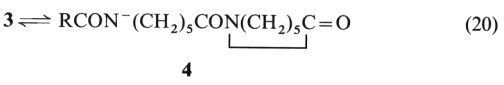


(18)

Initiation:

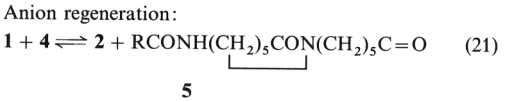


(19)



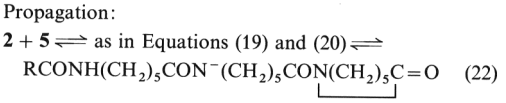
(20)

Anion regeneration:



(21)

Propagation:



(22)

SEKIGUCHI [52] prefers a mechanism that requires reaction of with to yield and . As

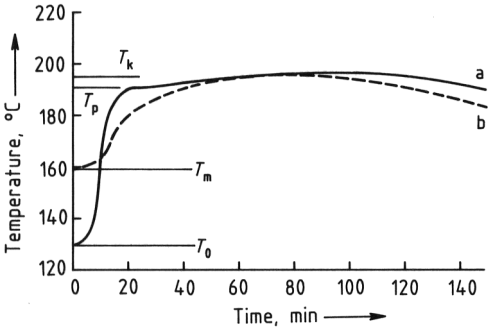


Figure 6. Temperature as a function of time in a typical cast polymerization of nylon 6 [92]
a) Temperature at center of large casting; b) Temperature of mold
T_o = initial temperature of polymerization (melt); T_p = final temperature of polymerization; T_k = maximum temperature; T_m = initial temperature of mold

he points out, there are many possible reaction pathways and side reactions, some of which arise from the increased probability of mid-chain ion formation as polymerization proceeds and the ratio of polymeric chain to lactam monomer increases.

Sample temperature is plotted versus time and density versus temperature for cocatalyzed, anionic polymerization of caprolactam in Figures 6 and 7, respectively. The polymer crystallizes during the polymerization since the maximum temperature of the system is lower than the melting temperature of the polymer. The maximum temperature of the system is caused by the heat of polymerization and the heat of crystallization, and is thus higher than the polymerization

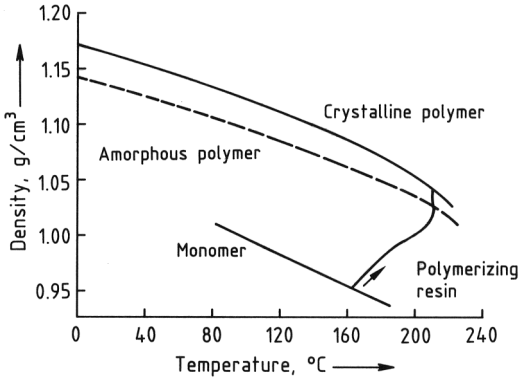


Figure 7. Density of caprolactam monomer and polymer as a function of temperature [92]

temperature which can be calculated from the heat of polymerization under adiabatic conditions. Anionically polymerized polycaprolactams are more crystalline than hydrolytically polymerized ones, and thus have higher densities (1.16 versus 1.14 g/cm^3).

A toughened, anionically polymerized caprolactam adaptable to reaction injection molding (RIM) technology was developed by Monsanto. Reaction of a bislactam with a soft polyether terminated by hydroxyl groups, e.g., a poly(propylene oxide), in the presence of caprolactam and a magnesium Grignard reagent yields a bisacylated prepolymer which, on further reaction with lactam, yields the polymeric product [103–105].

PA 12 has been made by cocatalyzed, anionic polymerization [106]. Other nylons (e.g., PA 4, PA 5, and PA 7) have been similarly prepared but have not been commercialized. Successful polymerization of PA 4 and PA 5 has, however, been of considerable theoretical interest because these nylons are not otherwise available. PA 4 has received a great deal of attention and has been commercialized in fiber applications. However, its thermal instability makes it unsatisfactory for molding and extrusion applications [35, Vol. II, pp. 74–117]. The best technique for the synthesis of PA 4 involves the use of carbon dioxide in place of an electrophilically substituted lactam, but it has been argued that this is not a cocatalyzed polymerization because the carbon dioxide cannot be found in the polymer [52].

4.4. Solid-Phase Polymerization

Solid-phase or solid-state polymerization (SPP or SSP) was first applied to low molecular mass polyamides by Flory [107]. Applicability to a variety of polyamides with melting points ranging from about 190 to 290 °C was indicated. SPP of diamine–diacid salts has been discussed [108–110] but has not yet been commercialized. Highly crystalline PA 11 has been made in the laboratory by SPP of 11-aminoundecanoic acid [111]. Monroe [112] described a fluidized-bed process for increasing the molecular mass of polyamide particles not over 10 mm in diameter from an initial 1000 to 15 000 to over 15 000. Beaton [113] claimed a procedure which avoided agglomeration and permitted higher

temperatures in a nonagitated bed of polymer. The rate of polymerization depends on particle size, temperature, and exposure to an inert gas maintained at a low relative humidity. As noted in [114], only the polycondensation reaction has been studied. SPP yielded higher molecular masses at equilibrium than expected for the water vapor pressure present [115]. This can be explained on the basis that the end groups and the absorbed water exist outside the crystalline regions. A broader than normal molecular mass distribution was also observed. Similarly, a transient distribution had been noted after the SPP of PA 12 wherein return to the equilibrium value ($\bar{M}_w/\bar{M}_n \approx 2$) occurred with a lowering of the weight-average molecular mass (but not of the degree of conversion) when the SPP product was melted [116]. The SPP of powdery 6-prepolymer was said to depend on the diffusion of acid ends and the initial molecular mass [117]. It is of interest that the number of bonds needed for the reported increases in molecular mass in both [112] and [117] is roughly proportional to the time required. Prior removal of oligomers facilitates SPP of PA 6 [118, 119].

The most significant application of SPP is in the synthesis of PA 46. A product with a narrow molecular mass distribution was obtained by SPP of 46-salt at 290 °C [120]. Prepolymerization in the presence of water followed by SPP yields a commercial quality product [121, 122]. Second-order kinetics are said to apply [121]. Special technique is required for PA 46 to control the tendency of the tetramethylenediamine to form a pyrrolidine ring which then acts as a monofunctional chain stopper. The utility of SPP in PA 46 is ascribed to the higher equilibrium constant for amidation at the lower temperature and to the higher activation energy for ring formation than for polymerization, 137 versus 83 kJ/mol [53, 69]. For a comprehensive coverage of SPP refer to [123].

5. Commercial Processes

The primary raw material sources of the monomers used to prepare commercial nylons have been listed in Table 2. Commentary on most monomer syntheses can be found in [5–7, 19]. The diamine for PA 46 is made via the addition of hydrogen cyanide to acrylonitrile [124]. For convenience, certain basic parameters of the commercial nylons have been assembled in Table 4.

5.1. PA 46

The 46-salt can be converted into prepolymer at 180–240 °C under steam pressure [122, 125]. SPP is carried out at 220–275 °C. Variations include a continuous polymerization method involving short exposure at 293 °C [125], water extraction of prepolymer to improve its color [126], a two-stage heat treatment to make prepolymer [127], control of temperature and steam pressure to yield high molecular mass [128], and polymerization with some of the adipic acid replaced by terephthalic acid to give a PA 46/4T copolymer [129].

Table 4. Basic parameters of commercial nylons

PA	CH_2/CONH[a]	M_u [b]	[CONH], $10^6/M_u$ [c]	T_m [d], °C	Density, g/cm^3
46	4	99.13	10 088	295	1.18
66	5	113.16	8 837	269	1.14
69	6.5	134.20	7 452	215	1.08
610	7	141.21	7 082	225	1.08
612	8	155.24	6 442	220	1.07
MXD 6		123.15	8 120	243	1.21
TMDT		144.20	6 935		1.12
11	10	183.30	5 456	190	1.05
6	5	113.16	8 837	228	1.14
12	11	197.30	5 068	180	1.02

[a] Ratio of methylene to amide groups per repeating unit (or average monomer unit).
[b] M_u is the average molecular mass per amide group.
[c] [CONH] is the concentration of amide groups.
[d] The melting temperatures (points) are as determined by the disappearance of the last vestige of birefringence on a hot stage and correspond to the minimum fabricating temperature. Estimates were made where such data were not available.

5.2. PA 66

The first step is preparation of pure, balanced salt in aqueous solution. Stoichiometric equivalence is determined by pH measurement. Some excess diamine is normally added to compensate for losses due to its relative volatility. The equivalence pH for the aliphatic salts approximates 7.6 [130, 131]. Charcoal decolorization of the salt solution is required unless the diamine has been carefully refined and, in particular, is free of *cis*-1,2-diaminocyclohexane [132]. Purging a charcoal bed with inert gas increases its life [133]. Treatment with diacid followed by removal of acid with diamine before use with salt solution avoids initial losses in molecular mass [134]. A two-stage, recycling method of salt preparation is used in a continuous process [135]. Two-step addition to diamine with intermediate evaporation of water yields a concentrated salt solution [136]. Ways of mixing molten acid and diamine have been patented [137–139]. To avoid precipitation when stored at about 25 °C a 50% aqueous salt solution is normally prepared.

5.2.1. Batch Production

The stored salt solution is concentrated under pressure to 65–80% before charging to an autoclave. A typical cycle is shown in Figure 8 [140]. The essential features are heating to 210 °C under autogeneous pressure to reach a pressure of 1.75 MPa, gradually increasing the temperature to about 275 °C while releasing steam at a rate which maintains the pressure, reducing the pressure at a rate that avoids cooling and finally holding the batch at atmospheric or reduced pressure to obtain the target molecular mass before extruding the polymer under inert gas pressure. This procedure is designed to assure that there is enough water present to avoid freezing of the batch before the melting point has been reached. Water also minimizes excessive loss of diamine. Stirred autoclaves are used but are normally unnecessary. The extrudate is a wide ribbon that is quenched with water that is subsequently removed by jet blowers. The ribbon is cut into chips which are blended and packaged [141, 142]. Hermetically sealed containers are used to avoid absorption of moisture that can hydrolyze polymers to lower molecular masses during subsequent melt processing. The containers vary from 10 kg bags to 500 kg or larger cartons. Nylon molders and extruders have drying equipment to contend with situations where the moisture content of as-received or reprocessed material requires adjustment.

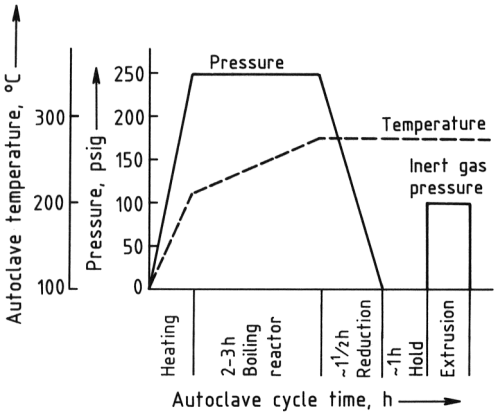


Figure 8. A typical autoclave cycle useful for batch preparation of nylon 66
(DuPont Technical Laboratory, Seaford, Delaware, reproduced with permission of John Wiley and Sons from Figure 8 in [140])

5.2.2. Continuous Production

The same concerns for control of the rate of removal of water and loss of diamine exist as in batch polymerization, but the situation is complicated by the needs of a continuous process. Typically, a first stage involves evaporation/reaction with controlled loss of water to form a prepolymer and minimize loss of diamine (Fig. 9). Further reaction occurs in subsequent stages with controlled evaporation in devices known as "separators" and "flashers". The desired molecular mass and water content are obtained in a "finisher". A large patent literature exists that claims improvement in each of these devices or combinations thereof for process simplification (see the review [140]). An early process that includes an additive port for delusterant is shown in Figure 9 [143]. A modification thereof (Fig. 10) includes a separator after the flash tubes to provide an essentially steam-free melt to the finisher [144]. Further improvements include the addition of a cage structure at the top of the screw section for better flow and reduced gel formation [145], insertion of static mixers in the flash tubes [146], putting holes in

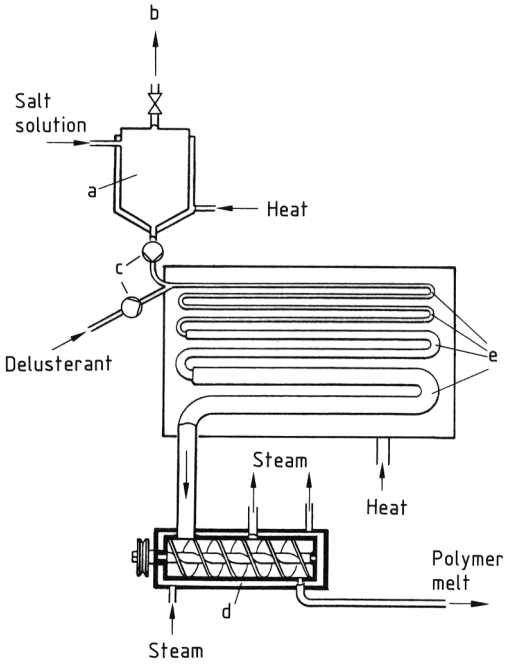


Figure 9. Continuous polymerizer for PA 66 [143]
a) Evaporator/reactor; b) Vent; c) Pump; d) Finisher; e) Flash tubes

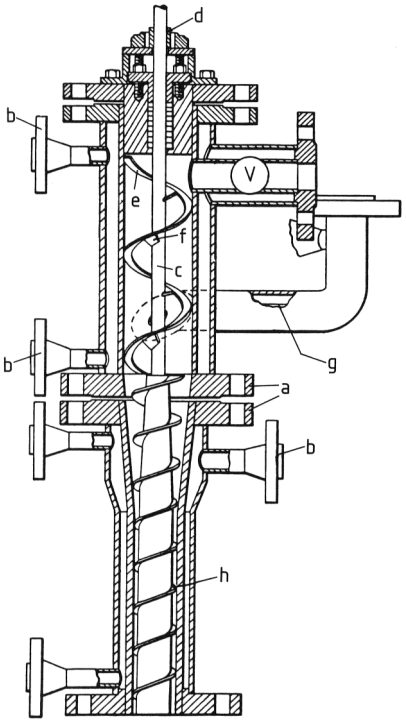


Figure 10. Two-part separator for polymerizer depicted in Figure 9 [144]
a) Flanges joining upper and lower members; b) Part of heating system; c) Shaft; d) Journal bearing; e) Ribbon flight; f) Spokes attaching ribbon to shaft; g) Feed from flash tubes; h) Transfer screw feeding melt to finisher

the ribbon flight in the separator [147], and providing flow splitters in the flash tubes [148]. A modification between the flash tubes and the separator significantly increases steam release and achievable molecular mass [149]. Dimensions, time, temperature, and pressure vary somewhat with specific design, but the same basic needs outlined above always apply in order to obtain a molten, high molecular mass product of low water content that can be fed to spinners or granulators. Severe constraints such as holdup spots and exposure to oxygen must always be avoided in continuously operated, high-temperature equipment such as polymerizers, extruders, or injection molding machines.

Another design (Fig. 11) involves essentially adiabatic evaporation in a second zone by directing the flow from an initial evaporator/reactor through a perforated ring nozzle against a heat exchanger with a surface of high thermal conductivity [150]. Another device emphasizing adiabatic evaporation makes use of the observation that the presence of low molecular mass polymer in salt solution decreases the tendency of the salt to precipitate [151], and another resorts to a multiplicity of zones [152]. Other procedures include rectification columns in the first zone, e. g., [153, 154]; a one-stage process with a long, narrow, coiled tube emptying into a stirred melt pool [155]; modified screw finishers [156–158]; designs to provide thin films of melt [159–161]; an apparatus that uses a dry salt charge [162]; and a dispersion technique for high-viscosity polymers involving cyclic monomers [163].

5.3. Other AABB Polyamides

The polymerizations yielding PA 69, PA 610 and PA 612 are subject to the same concerns as that yielding PA 66. These polyamides are made in much the same way with differences due to different melt viscosities and melting points. The choice between continuous or batch process depends mostly on production volume. Because

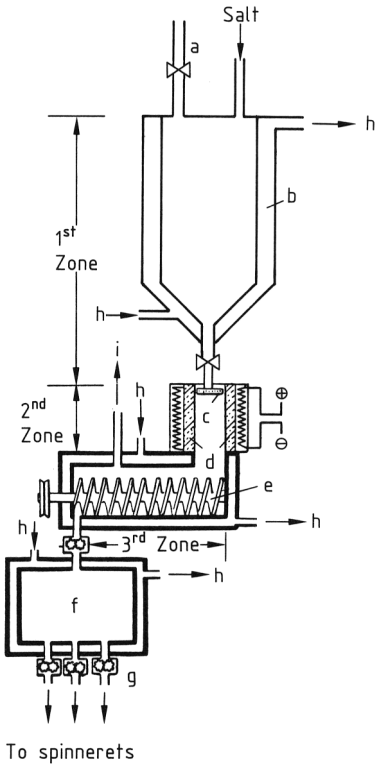


Figure 11. Polymerizer with essentially adiabatic evaporation in second zone [150]
a) Pressurized vent; b) Evaporator/reactor; c) Ring nozzle; d) Heat exchanger with surface of high thermal conductivity; e) Finisher; f) Heat exchanger; g) Gear pumps; h) Heat exchanger fluid; i) Exit tube to atmospheric vent or vacuum

of smaller sales volume, the batch method is favored for these specialty nylons.

The AABB principles described above can easily be extended to monomers containing an aromatic or cycloaliphatic moiety in the AA, the BB, or both portions of the molecule. Because of the presence of these structures these polyamides present special problems due in part to their high viscosity and/or stability at the high processing temperatures. An example is PA MXD6, a polyamide prepared from *m*-xylylenediamine (MXD) and adipic acid. Careful control of steam pressure in the early stage of polymerization of MXD6 is required to minimize decomposition of the aromatic diamine [164]. In the production of TMDT polymer, the salt is precipitated from an aqueous solution with isopropyl alcohol, partially condensed in a stirred reactor, and finally polymerized to a number-average molecular mass of about 20 000 in an extruder [165].

Polyphthalamides (PPAs), also known as high temperature nylons (HTNs) are high-melting semiaromatic nylons resulting from the addition of an aromatic ring to the polymer backbone. The high polymerization temperatures required for their manufacture necessitates either a short residence time in the melt by using an extruder or polymerization below their melting points (see Section 4.4) [166, 167].

5.4. PA 6

Continuous processes are used by the major manufacturers of PA 6. The so-called VK tube (Vereinfacht Kontinuierlich = simplified continuous) was developed in Germany. It is a vertical tube operated at atmospheric pressure wherein heating and prepolymerization take place in the upper part and polymer is formed in the lower section [168]. Problems of initial stoichiometry and ingredient volatilization, inherent with AABB polymerization as already discussed, do not apply; however, the need to free the product of its equilibrium content of monomer and oligomers presents a different kind of problem. A schematic of the BASF process [6] shows a VK tube feeding a pelletizer followed by a water extraction unit (Fig. 12). A process [169] involving vacuum extraction is shown in Figure 13. Claim is made that controlling initial conversion to 45 % yields a product with less than 2 % of cyclic oligomers with a vacuum finish that does not require prolonged heating at less than 665 Pa [170]. Improved processes include a baffled hydrolyzer operating in plug flow and at a carefully controlled temperature [171] and a two-stage hydrolyzer [172].

The simulation and optimization of the hydrolytic polymerization of caprolactam have been attempted [58, 173, 174]. Lack of detailed manufacturing data has been indicated to prevent confirmation of the analysis.

Polymerization in an extruder has also been discussed [175]. Numerous publications and patents continue to appear that deal with the anionic polymerization of caprolactam. No large-scale applications exist as yet although modified systems in reaction injection molding (RIM) for the production of block copolyesteramides and

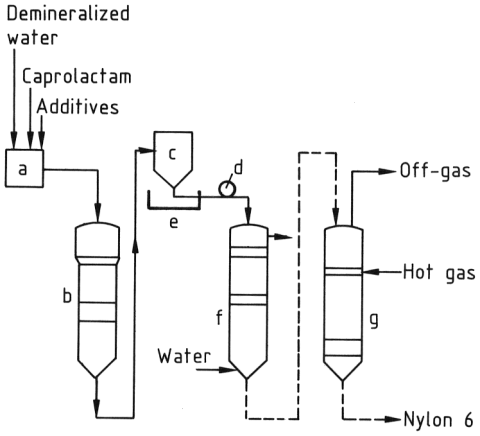


Figure 12. Production of nylon 6 by BASF
a) Feed tank; b) VK tube; c) Pourer; d) Pelletizer; e) Water bath; f) Extractor; g) Dryer
(reproduced with permission of Elsevier Science from Figure 5 in [6])

copolyetheramides have been developed by several companies [35]. Some details on recommended RIM procedures such as separation of feed streams, mold design, and temperature have been published [176, 177].

5.5. PA 11

PA 11 is made in a continuous process that is operated under inert gas at atmospheric pressure [178]. The monomer (11-aminoundecanoic acid, which is made from castor beans) is suspended in water and mixed with the desired additives (antioxidants, etc.) before charging to a three-zone, upright converter. The monomer is melted, water eliminated, and the polymerization begun in the top section. Near completion of the condensation occurs in the middle zone. Adjustment to the target molecular mass takes place in the bottom section which provides a melt pool for uniform discharge of product. The good thermal stability of the polymer and the low tendency of the monomer for cyclization simplify the process design.

Phosphoric acid catalyzes the polymerization as does hypophosphoric acid. The latter can, however, make the product insoluble if used in excess with prolonged heating [179].

5.6. PA 12

Polylaurolactam, PA 12, is made by heating dodecanolactam (which is made from butadiene) with an acid catalyst such as phosphoric acid in the presence of water to effect conversion to a prepolymer, then evaporating the water, and finally heating in an inert atmosphere to complete the polymerization [35, 180]. Temperatures up to 350 °C may be used to effect completion [181, 182]. Confirmation of the independence of reaction rate on molecular

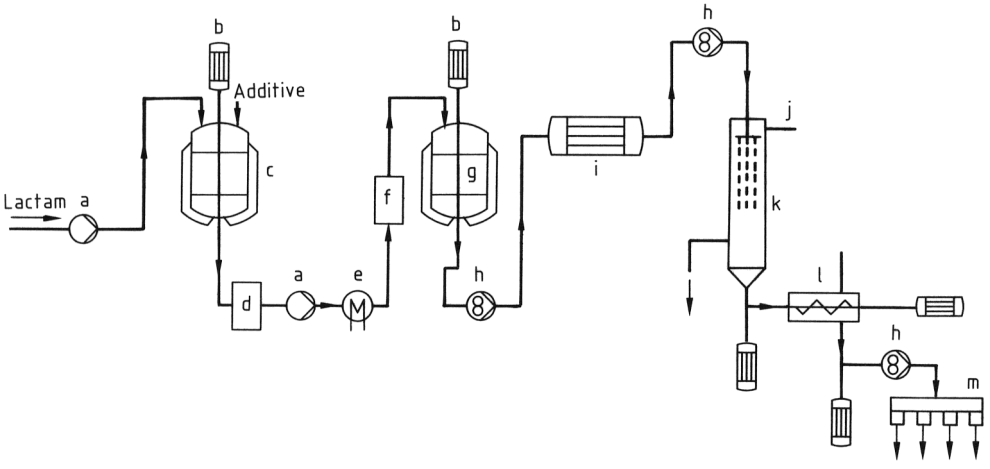


Figure 13. Production of nylon 6 by Allied Chemical [169]
a) Pump; b) Stirrer; c) Holding tank; d) Filter; e) Flowmeter; f) Preheater; g) Hydrolyzer; h) Metering pump; i) Polyaddition reactor; j) Vent; k) Vacuum flasher; l) Finisher; m) Spinning heads

mass and of a most probable molecular mass distribution together with an expression relating degree of polymerization to viscosity in *m*-cresol are provided in [183].

6. Properties

The enduring utility of nylons rests upon their combination of properties and upon their susceptibility to modification. Key properties are resistance to oils and solvents; toughness; fatigue and abrasion resistance; low friction and creep; high strength; stability at elevated temperatures; fire resistance; drawability; good appearance; and good processibility.

Polyamides are readily modified in order to achieve desired changes in processing behavior or properties. This characteristic has allowed them to sustain their growth in spite of the advent of challenging new materials. However, modifications to enhance some specific properties can have negative effects on other properties. Basic modifications can be accomplished through changes in the polymer molecule itself and/or the incorporation of additives. Alternative techniques of modification include use of branching agents (see Section 6.2) and post-polymerization treatments such as annealing, conditioning to a specific moisture level, dyeing, metallizing, painting, irradiation, or chemical reaction such as alkoxyalkylation.

6.1. Properties of Unmodified Polyamides

A problem common to most polymers is the lack of adequate and comparable data. Nylons are no exception; however, the increasing global acceptance of ISO protocols in measuring properties has alleviated the situation. A limited comparison of unmodified nylon resins is provided in Table 5. Even these data are not unambiguous because the molecular masses are not specified. The table is self-evident and reflects the differences in amide group concentration and crystallinity. Information on literally hundreds of nylon compositions can be obtained from various web sites maintained by the suppliers and in the Campus database [184]. Additional information is also available from the *Plastics Technology Handbook* and *Modern Plastics Encyclopedia*, which are both issued annually.

This introductory section, however, is concerned with those features of neat polyamides that determine their properties and account for differences between individual nylons. The most distinguishing feature is the amide group,

Table 5. Properties of unmodified polyamides*

Property	ASTM	66		6		612		11		12	
		Dry	50% R.H.	Dry	50% R.H.	Dry	50% R.H.	Dry	50% R.H.	Dry	50% R.H.
Tensile strength, MPa	D 638	83	77	81	69	61	61	57	54	49	47
Yield strength, MPa	D 638	83	59	81	44	61	51			49	40
Ultimate elongation, %	D 638	60	≥ 300	200	300	15	30	120	300	250	250
Elongation at yield, %	D 638	5	25	9		7	40			10	20
Flexural modulus, MPa	D 790	2830	1210	2700	970	2030	1240	1170	1030	1410	1030
Izod impact strength, J/m	D 256	53	112	58	215	53	75	40		58	64
Water absorption, %	D 570										
24 h		1.5		1.6		0.4		0.25		0.25	
50% R.H.		2.5		2.7		1.3		0.8		0.7	
100% R.H.		8.5		9.5		3.0		ca. 2.4		ca. 2.0	
Heat deflection temperature, °C	D 638										
455 kPa		235		185		180		150		150	
1820 kPa		90		65		90		55		52	
Dielectric constant	D 150 (1 kHz)	3.9	7.0	3.8		4.0	5.3	3.7		3.6	
Flammability	UL 94	V 2		HB		HB		HB		HB	

* Data assembled from publications of various manufacturers for standard injection molding grades. Variations in molecular mass contribute to differences in properties.

which is responsible for strong hydrogen bonding between adjacent chains. Melting point increases with increasing ratio of CONH groups to CH_2 groups in the chain and the increased opportunity for hydrogen bonding, but not regularly because whether the number of CH_2 groups between the CONH groups is odd or even is important as well as the ratio of CH_2 to CONH. The odd number of CH_2 groups between the amide groups in PA 6 allows complete hydrogen bonding when the amides in adjacent chains have an opposed or antiparallel orientation but not when they have the same or parallel orientation (Fig. 14). Changing from a parallel to an antiparallel array requires inverting the entire molecular chain in this odd-numbered case, but only a one-segment lateral movement is needed if there is an even number of CH_2 groups, as in the case of PA 66 with its intervening number of 4 and 6 CH_2 groups. It is believed that this odd/even feature accounts for the lower melting point and percent crystallinity

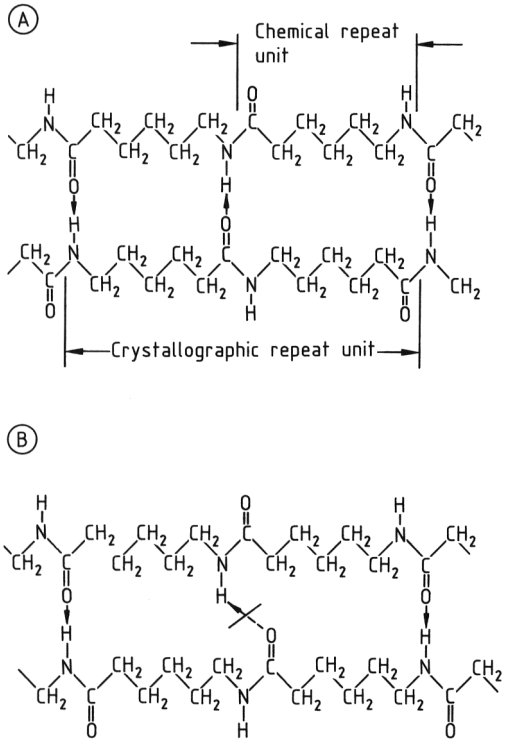


Figure 14. Schematic of a hydrogen bonded sheet of PA 6 with antiparallel (A) and parallel (B) orientation of amide groups

of PA 6 versus PA 66. It is the reason in general why PA-odd and PA-odd/even have lower melting points than comparable or similar PA-even/even, such as PA 6 versus PA 7.

Increasing crystallinity results in higher stiffness, density, tensile and yield stress, chemical and abrasion resistance, and better dimensional stability. It decreases elongation, impact resistance, thermal expansion, and permeability. Crystallinity is responsible for the development of microscopically observable structures, known as spherulites, that scatter light and make nylons opalescent unless very thin. The transparent nylons are amorphous and are made so by appropriate copolymerization involving at least in part aromatic or cycloaliphatic AB, AA, or BB monomers in order to have acceptable stiffness.

Orientation [5, p. 300] contributes importantly to properties not only in film, fiber, and strapping but also in injection-molded articles. The resulting anisotropy means that properties vary with the direction of stress and must be considered in rationalizing resin behavior.

Water absorption is characteristic of nylons. Unless compensated for by increased crystallinity, a higher proportion of amide groups leads to higher water adsorption. Increased water content has an effect analogous to that of increased temperature, i.e., enhanced segmental mobility with, for example, concomitant loss in stiffness and tensile strength, gain in toughness, and growth in dimensions (elongation). At very low temperatures, however, water stiffens the nylon. Thus, the brittleness temperature (ASTM D 746) of PA 66 is − 80 °C if dry and −65 °C if conditioned to 50% relative humidity. Properties are frequently reported in the "dry", as-molded, condition corresponding to about 0.2% water or less, and after equilibration to a specified relative humidity such as 50 or 65%, and occasionally to 100%. The greatest change occurs in the vicinity of the glass transition temperature (T_g) so that a useful aid in understanding behavior is a knowledge of the effect of humidity on T_g. This is complicated because of variation with the method of calculation or measurement (Table 6), but it is generally true that nylons with fewer CONH groups and lower water adsorption have a lower dry T_g but show less change of T_g with relative humidity [19, 121, 185–190].

Table 6. Glass transition temperatures (T_g, °C) of polyamides at various relative humidities (R.H.)*

	Dry				50% R.H.			100% R.H.	
PA	A	B	C	D	C	D		C	D
46	102	78	78						
66	82	65	80, 78, 66	48	35	15	− 15	− 37	35
6 (extracted)	56	65	75, 65	41	20	3	− 22	− 32	20
610	56	46	67, 70	42	40	10			
612	52	40	60	45	40	20		20	
11	36	29	53	43					
12	29	25	54	42				42	
MXD 6	71		68						
TMDT			150						

* A) Estimated from melting temperatures using $T_g = (2/3)\ T_m$ [185]; B) Calculated from group contributions [186]; C) Dynamic measurements with torsion pendulum [121, 187–189]; D) Static measurements by differential thermal analysis or inflection point in curve of modulus of elasticity as a function of temperature [19, 190].

Little change in sensitivity to aliphatic hydrocarbons occurs with a change in polyamide type, but aromatic hydrocarbons are more strongly absorbed by polyamides with fewer amide groups. For example, PA 66 and PA 6 absorb 1 % toluene; PA 610, PA 3, and PA 11 absorb 6.8 %.

With this background now in place, a comparison of the properties of various nylons can be made, moving from the least aliphatic, to the most aliphatic, and then to semiaromatic nylons.

PA 46 is structurally similar to PA 66, and is produced from 1,4-diaminobutane and adipic acid. This nylon has the highest amide-to-methylene group ratio and the highest crystallinity of the commercial nylons. The high amide concentration accounts for the high moisture absorption of the polymer. Its melting point is 290 °C.

PA 66, which has one amide group for every 4 or 6 (with an average of 5) methylenes, has a high melting point of 269 °C, good strength and creep resistance, and excellent gas barrier properties. These qualities have led to its widespread use in automotive mechanical and electrical and electronic applications.

PA 6 also has an amide to methylene ratio of 1:5, but the odd number of methylene units retards crystallization and results in a more amorphous polymer with a lower melting point of 228 °C. These characteristics can be desirable for extruded film and wire and cable jacketing, but make PA 6 somewhat more sensitive to moisture and chemicals and limits its resistance to temperature spikes.

PA 69, 610 and 612 are all produced from hexamethylenediamine plus azelaic, sebacic, or dodecanedioic acids, respectively. PA 612 is intermediate between 6/66 and 11/12 with an average amide to methylene group ratio of 1:8, and provides an excellent compromise between PA 66 and higher nylons, with its excellent dimensional stability, reasonably high melting point (212 °C), strength, creep resistance, and barrier properties. This balance leads to widespread use in toothbrush filaments, battery components, and parts that are exposed to hot aqueous environments.

Higher nylons, like PA 11 and 12, have much lower amide to methylene group ratios (1:10 and 1:11 respectively), which results in more polyethylene-like materials that have excellent dimensional stability, low-temperature toughness, and stress-crack resistance at the expense of lower melting point and strength. They are readily plasticized for use in flexible, chemically-resistant tubing that has high burst pressures. The long aliphatic chains impart a low affinity for moisture. In addition, PA 11 is available in powder grades that may be applied by electrostatic spray or in fluidized beds for coating metallic parts.

Semiaromatic nylons are generally copolymers that are commonly made using terephthalic acid and/or isophthalic acid as comonomers often with an aliphatic or alicyclic acid. Common semiaromatic nylons will contain units derived from hexamethylenediamine and adipic acid or caprolactam. They typically have high melting points (295–325 °C for

commercial grades) and exhibit a significant decrease in moisture absorption when compared to purely aliphatic nylons. The aromatic groups in the polymer backbone make them less mobile than linear aliphatic nylons and contribute to their high stiffness and good strength, creep resistance, and dimensional stability. Biaxially oriented films made from semiaromatic polymers provide excellent gas and oxygen barrier properties allowing for use in packaging materials and bottles.

Control of Rheological Properties. Control of melt rheology is very important for nylon processing (see Chap. 7). Low viscosity is desired for molding application for easy mold-filling. On the other hand, a high viscosity and melt strength are desired in extrusion and blow-molding applications. Control of molecular mass is the most convenient method for controlling rheological properties. Most polyamides have number-average molecular masses in the range of 11 000 to 34 000. Toughness increases with increasing molecular mass, but the effect is a moderate one. The major practical reason to change the molecular mass of a polyamide is to obtain a desired level of melt viscosity, which can range from less than 1000 Pa · s for injection molding to over 4000 Pa · s for shaped extrusion.

Another technique used to modify rheological properties is to change the molecular architecture. Introduction of low-level branching results in more non-Newtonian behavior, especially at low shear rates where an increase in melt strength and melt viscosity is obtained. Star nylons (see Section 3.1), although known for a number of years, are a new class of commercially available semicrystalline polyamides that exhibit a quasi-Newtonian rheological behavior and enhanced flow properties during processing [191]. The polymer is a modified PA 6 and has a star-like structure that is based on proprietary polymerization techniques. Polymerization catalysts and chemicals incorporated into the polymerization cycle produce a nylon with controlled branches. These materials can be compounded with large amounts of glass fibers or mineral fillers and molded with increased melt flow under normal processing conditions. The enhanced flow characteristics promote an excellent surface finish and aesthetic appearance. Commercial uses now include automotive engine covers, air-intake manifolds and trim parts, fishing reels, and appliance doors [192].

6.2. Copolymerization

Copolymerization to modify the properties of polyamides has long been practiced. This technique allows one to obtain varied properties without resorting to developing new polyamides from new monomers. Copolymerization increases the disorder in the polymer molecules and interferes with the ability of the molecules to pack and form hydrogen bonds. As a consequence, copolymers in general are characterized by a lower degree of crystallinity and a slower rate of crystallization, greater transparency, a lower modulus and strength, and greater solubility than the respective homopolymers. In a PA 66/6 copolyamide, for example, the melting point minimum is about 180 °C at 40 wt% of caprolactam units. PA 66/6 copolymers with about 40–65 wt% caprolactam units become soluble in hot methanol whereas the homopolymers PA 6 and PA 66 are insoluble in this solvent [19, 193, 194]. Terpolymers such as PA 66/6/610 are designed to further enhance solubility for use as binders [19, 195]. Transparency with good retention of properties is achieved by use of alicyclic or aromatic comonomers as has been noted for PA TMDT. A review of transparent polyamides that includes a comparison with other transparent engineering plastics is given in [196, 11, pp. 377–387].

There are quite a number of pairs of monomers, however, that have comparable distances between their functional groups and that yield copolymers in which the amide moieties can assume the proper orientation for hydrogen bonding. These molecular characteristics permit the comonomers to crystallize in the same morphology [197–199]. Instead of being depressed, the melting points of these isomorphous copolymers are weighted averages of the melting points of the component homopolymers. Some examples of isomorphous pairs of monomers are adipic and terephthalic acids; *p*-benzenedipropionic and sebacic acids; and *p*-xylylenediamine and *m*-xylylenediamine. For a more extensive discussion refer to [11, pp. 370–372].

6.3. Modification by Additives

Additives are materials used in small amounts (less than 5 wt% and usually less than 1 wt%) to affect various aspects of polymer processing, polymer properties, and/or appearance. Additives used to alter properties or appearance include antioxidants, antistatic agents, biodegradative agents, biopreservatives, blowing agents, colorants, fragrances, and stabilizers against hydrolysis, thermal degradation, or UV degradation. Processing additives include coloration inhibitors, lubricants, mold-release agents, nucleating agents, and viscosity thickeners or reducers. They have little effect on the physical properties except in the instance of nucleating agents, which not only increase the rate of crystallization and the degree of crystallinity, but impart reduced mold shrinkage and increased tensile and flexural properties. Enhanced crystallization may be desired to shorten molding cycles, and also to modify mechanical properties.

Modifiers are used in larger amounts, usually more than 5 wt%, in order to achieve desired changes in properties. Modifiers include mineral fillers, glass or carbon fibers, lubricants to improve wear and friction, plasticizers, fire retardants, electrically conductive materials, and/or blends with other polymers to toughen or otherwise affect the nylon. A broad discussion of additives is given in [11, pp. 361–448], [200].

6.3.1. Filled and Reinforced Polyamides

Fillers and reinforcing agents have contributed significantly to the sustained growth in the use of nylons. Particulate mineral fillers (e.g., aluminum or calcium silicates) always increase the modulus of elasticity and often the tensile strength whereas elongation always decreases. Impact strength as measured by the notched Izod test may or may not improve; it depends on the choice of filler and matrix. Temperature resistance is increased.

Reinforcement with glass and carbon fibers has similar but larger effects with consistently improved Izod impact strengths because of the fiber acicularity. Warpage can be a factor in some applications. This again relates to fiber acicularity and is, accordingly, less in the typical mineral-filled compositions. Mixtures of fillers and reinforcing agents are used, therefore, to cope with such situations. Important factors are the efficacy of the bonding agent used to promote adhesion between the filler or the reinforcing agent and the polyamide matrix and the length to diameter ratio of the fiber in the final product. The properties in Table 7 were chosen to illustrate these effects but because of the number of variables involved they should not be construed as limiting.

Long glass fibers are used in polyamide compositions with the attendant implications for properties and processing [201, 202]. Most of these compositions are produced by a pultrusion process [203, 204]. The continuous glass fibers are pulled through an impregnation line where they are coated with nylon resin. Upon cooling, the resin is chopped into long pellets that contain reinforcing fibers equal in length to the pellet. Traditional extrusion compounding of glass into nylon yields much shorter fibers, and hence less stiffness and worse transverse mechanical properties. The balance of properties makes long-fiber reinforced compositions ideal for the replacement of metals such as die-cast aluminum in many parts. In specialty applications, long fibers of carbon, aramids, and steel are used in addition to glass [205].

Table 7. Selected properties of dry, filled/reinforced PA 66[*]

Property	Neat	40 % Mineral[**]	33 % Glass fiber	Mineral and glass fiber	30 % Carbon fiber
Tensile strength, MPa (ASTM D 638)	83	89	186	130	241
Ultimate elongation, % (ASTM D 638)	60	17	3	12	
Flexural modulus, MPa (ASTM D 790)	2830	5240	8960	6900	20 000
Izod impact strength, J/m (ASTM D 256)	53	70	117	48	80
Heat deflection temperature, °C (ASTM D 638)					
at 455 kPa	235	230	260	257	
at 1820 kPa	90	185	255	239	257
Density, g/cm^3	1.14	1.51	1.38	1.45	1.28

[*] Data from publications of various manufacturers.
[**] "Mineral" as found in the nylon literature normally refers to various silicates and carbonates.

Nanocomposites are emerging with increased acceptance of the properties that they offer. They can improve strength, stiffness, heat deflection temperature, dimensional stability, gas barrier, flame retardancy, and electrical conductivity. Nanoparticle platelets are only 1 nm thick with an aspect ratio (*L/D*) sufficiently high that relatively low loadings (generally 2 to 6 wt%) provide significant property advantages. These clay-based additives have been used with PA 6, PA 612, and PA MXD 6 to improve stiffness heat resistance, oxygen barrier and gloss, but confer a disproportional loss of toughness. In 2000 these nylon compositions were first commercialized for container and packaging applications [206–208]. A more detailed discussion of the many aspects of nanotechnology is given in [209].

6.3.2. Blends and Alloys

Blends of nylon (and polymers in general) are mixtures that contain at least one other polymer or copolymer. The properties of the blends can be additive, averaged, synergistic, or antagonistic. An alloy is an immiscible polymer blend having a modified interface between both components and/or morphology. While positive synergism of the components is most desired, a weighted averaging of properties based on the volume component of resins is usually the rule. Nature rarely provides something for nothing so there are often tradeoffs of properties and for every advantage obtained by a resin blend, there are often disadvantages as well. The disadvantages are often so significant that the resulting material is unusable. The primary reason for the negative results is that most polymer pairs are immiscible because of high interfacial tension, which results in phase-separated components. A brief list of some common property tradeoffs is:

Stiffness, strength (e.g., glass, mineral)	vs.	toughness, ductility
Melt flow	vs.	toughness, elongation
Fire retardance	vs.	environmental considerations, toughness, melt stability
Solvent resistance (i.e. crystallinity)	vs.	mold shrinkage
Cycle time	vs.	shrinkage
Softness	vs.	creep, stiffness
Product complexity	vs.	compounding yield, speed, cost

The successful use of blending to tailor-make materials for specific end use applications depends on the type of resins used, their morphologies, the relative levels of the resins, and the property tradeoffs that are acceptable [210–212].

Some of the polymers, that have been successfully blended with polyamides include polypropylene (PP), high impact polystyrene (HIPS), styrene-acrylonitrile (SAN) and acrylonitrile-butadiene- styrene (ABS) copolymers, poly(methyl methacrylate) (PMMA), styrene-maleic anhydride (SMA) copolymer, EPDM elastomers, polycarbonate (PC), and poly(phenylene ether) (PPE) [213].

For all blends, it is essential to develop processes that control the morphology and the interfaces of the phase-separated components. Interfaces can be modified by the addition of reactive and nonreactive compatiblizers, as well as by reactive extrusion to assure a controlled chemical reaction between the components and thus compatibilize the blend in situ [214].

The broad utility of nylons was restricted for many years by their notch sensitivity and loss of toughness at very low temperatures. For example, the impact strength of PA 66 at 23 °C and 50% humidity is 37 J/m with a notch radius of 0.05 mm, 112 J/m with a 0.25 mm radius (the Izod specification of ASTM D 256), and 366 J/m with a 0.75 mm radius. At −40 °C with the standard radius of 0.25 mm, it is 27 J/m. Some improvements were made, but no major breakthrough occurred until suitably defined elastomeric modifiers were used [215]. This work yielded compositions that were ductile and exhibited Izod impact strengths over 534 J/m even when dry. Independence of notch radius down to 0.0025 mm; insensitivity to part thickness, orientation, proximity to the molding gate or rate of loading; and improvement down to about −20 °C were demonstrated [216]. One requirement in this work was a sufficiently small particle size of the dispersed elastomeric phase. Ductile behavior independent of part thickness has been shown for a PA 6–ABS blend (about 50/50 weight ratio) with a cocontinuous phase morphology [217]. Another variant of toughener involves a core – shell structure in the dispersed phase [218]. The effect of orientation, position in the molded part, rate of loading and temperature has not yet been shown for these alternative materials. Many studies on toughening nylons from both industrial laboratories and

academia have appeared. Morphology, type of toughener, testing with sophisticated instrumentation, and analysis of the mechanism of toughening have been studied. It is, however, beyond the scope of this report to delve into this broad and complex subject.

The number of impacts to failure of toughened PA 66 increases, as would be expected, as the impact energy is lowered below that required for failure in a single blow [219]. Noteworthy, however, is the resistance to repeated impact of neat PA 66 [219, 220].

Mineral-filled and glass-reinforced nylons have also been toughened. For example, a dry, mineral-filled product with a tensile strength (TS) of 89 MPa, a flexural modulus (FM) of 5300 MPa, and a notched Izod impact strength (Iz) of 69 J/m was toughened to yield one with corresponding values of 79 MPa, 4600 MPa, and 130 J/m [221]. Similarly, a dry, glass-reinforced PA 66 with a TS of 200 MPa, a FM of 8960 MPa, and an Iz of 100 J/m was toughened to yield a TS of 140 MPa, a FM of 7000 MPa and an Iz of 250 J/m [221]. These examples illustrate the feasability of the wide spread practice combining various additives and modifiers to meet the demands of specific applications.

6.3.3. Flame-Retardant Polyamides

Many nylons are rated UL 94 V-2, and fire-retardant grades with a UL 94 rating of V-0 in thin sections are available. For a discussion of UL ratings, see →High-Performance Fibers. Common flame retardants are highly-halogenated organic compounds and polymers such as brominated polystyrenes, poly(dibromostyrenes), or dechlorane [222, 223]. These are often used in combination with a synergist such as an antimony oxide. Red phosphorus is also used as a flame retardant [224]. Concerns about the toxic fumes released when these materials are heated [225] and the hazards involved in handling red phosphorus have led to the development of halogen- and elemental-phosphorus-free flame retardants based on melamine cyanurates that function by generating molecular nitrogen upon decomposition, which smothers the flame [226, 227]. More recently, flame retardants comprising a mixture of phosphinates and melamine cyanurates or melamine phosphates have been introduced [228].

Flame-retardant polyamides have many automotive, electrical, and electronics applications. One survey discusses control of tracking (formation of a conducting path on the polymer surface) [229]. Another review addresses properties of glass-reinforced thermoplastics including PA 6, PA 66, and PA 610 [230]. Colorants can increase flammability [231]. Safety is increasingly stressed and is generating even greater concern for smoke suppression and the toxicity of gases formed during combustion as well as the inhibition of ignition and flame support [225].

6.3.4. Conductive Polyamides

The burgeoning market for electronics has led to a great demand for electrically conductive polymers. Electronic devices generate radio frequency radiation during operation, and to prevent the consequent electromagnetic interference (EMI) with other devices, it is necessary to shield the source with an electrically conductive material. Since polyamides are not intrinsically conductive, EMI shielding of nylon parts can be accomplished in either a two-step process that involves coating the plastic with a conductive material, or, preferably, filling it with a conductive additive, such as carbon fibers, metal-coated carbon or glass fibers, metal fibers, carbon black, or graphitic carbon fibrils [232, 233].

It should be noted that neat and glass-reinforced nylons have also been successfully used for some time in electrical power engineering and electronics [234]. A variety of plastics containing metal fillers or carbon to make them electrically conductive, including PA 66, were exposed to an aqueous detergent solution at 25 and 80 °C and to isopropyl alcohol; the effect on EMI shielding was assessed [235]. The compositions with carbon generally outperformed those with metal fillers. The only PA 66 evaluated contained carbon fibers, and its retention of shielding was equivalent to that of the other materials tested.

Unadulterated polyamides are *thermal insulators*, but when combined with heat-conductive additives such as graphite fibers or ceramics like boron nitride and aluminum nitride, they can be used in heat-removal applications that include heat sinks for electronics and electrical applications [236].

6.3.5. Other Formulations

The amount of polyamide used and the nature of its dispersion in a blend with other polymers may be such that it is properly defined as the modifier rather than the base resin. One commercial example is a blend of nylon and poly (2,6-dimethyl-*p*-phenylene oxide). Allusion has been made to a blend with poly(phenylene sulfide) as the major ingredient [237]. Another composition presumably involves mostly ABS and some nylon [238]. A developmental material is a glass-reinforced blend of polycarbonate and nylon [239]. The literature on blends is voluminous. Brief reviews of all commercial blends including some commentary on their processing are given in [237–239]. A recent text focuses specifically on commercial blends and alloys [240]. It may reflect success in finding a compatibilizing agent for essentially incompatible polymers.

A different kind of product in which nylon is the principal component arises from reaction during molding of pellets that differ in chemical constitution; at least one component is caused to form a cross-linked structure. In one commercial case a pseudo- or semi-interpenetrating network (SIPN) results which physically binds a silicone modifier to a nylon matrix [241].

With the appropriate additives, polyamides can be used in a variety of specialized applications. For example, polyamides can be combined with magnetic materials such as neodymium-iron-boron alloy powders, permitting the injection molding of magnetic parts [242].

High-density polyamide formulations can be obtained by compounding with metal fillers and powders such as aluminum, zinc, steel, tungsten, or lead. The densities of the materials can be fine-tuned by using metals of different densities and varying their loadings. Addition levels of up to 95 wt% have been achieved. However, the polymer can still comprise 40–70% of the volume, which permits these compositions to be processed using standard equipment. Wear and abrasion on extruder barrels, screws, and molds is an issue and hardened steel tooling is recommended. These polyamide metal materials can serve as substitutes for metal in both practical (such as for X-ray and radiation shielding applications, fishing-line sinkers, and bullets) and aesthetic applications. In the former, the substitution of moldable plastics for metal parts permits a greater degree of design freedom. In the latter, the added heft and metallic feel given to the plastics creates a perception of greater value [243–245].

Rigid parts made from polyamides can be given soft coatings by overmolding them with thermoplastic elastomers. Suitable elastomers include polypropylene-EPDM thermoplastic vulcanizates that contain small amounts of polyamide block copolymer to serve as a compatibilizer. Such "soft-touch" materials have a variety of applications in consumer goods [246, 247]. Alternatively, block copolymers of polyethers and polyamides have elastomeric properties and their hardness can be tuned over a wide range. These materials can be overmolded onto other materials for a variety of consumer, industrial, automotive, and adhesive applications [248] (→Thermoplastic Elastomers).

The amount of polyamide used and the nature of its dispersion in a blend with other polymers may be such that it is properly defined as the modifier rather than the base resin. One commercial example is a blend of nylon and poly (2, 6-dimethyl-p-phenylene oxide). Allusion has been made to a blend with poly(phenylene sulfide) as the major ingredient [194]. Another composition presumably involves mostly ABS and some nylon [195]. A developmental material is a glass-reinforced blend of polycarbonate and nylon [196]. The literature on blends is voluminous. Brief reviews of commercial blends including some commentary on their processing are given in [194–196]. A recent text focuses specifically on commercial blends and alloys [197]. Blends in which there is some level of bonding between matrix and modifier, whether due to likeness of solubility parameters, hydrogen bonding, or some other factor are sometimes termed alloys.

7. Processing

Nylons are processed into useful articles by a variety of techniques—injection molding, extrusion, blow molding, monomer casting, solution coating, fluidized-bed or electrostatic coating, or forming [19]. The major fraction of the annual polyamide volume is processed by

injection molding, extrusion, and blow molding. Each of these melt processes requires different melt viscosities for optimum processing. Whereas injection molding requires the lowest melt viscosity, for extrusion and blow molding a high melt strength is needed, which by necessity requires a high melt viscosity. Molecular mass can be altered to meet the viscosity required for the desired process. In addition, modifying molecular architecture is sometimes used to alter the rheological properties (see Section 6.2).

Equation 12 governs the dynamics of the amidation/hydrolysis equilibrium in polyamides. The polyamide molecular mass will either increase or decrease, and consequently the melt viscosity, as well, depending on whether the moisture content is higher or lower, respectively, than the equilibrium moisture content. Thus, moisture control in polyamide melt processing is extremely important and because of the ubiquitous nature of moisture it is often the most difficult to control. Most problems in nylon processing could be attributed to poor control of moisture. These problems can manifest themselves in mechanical properties, appearance, and processibility.

Good flow and fast set-up make nylons relatively easy to process. Standard three-stage screws with or without mixing heads, corotating twin screws, and barrier screws with or without venting are all used. Most reciprocating screws in injection molding are of standard type. Moisture content should be somewhat lower for extrusion than for injection molding because the absence of high die pressure facilitates volatilization. Control of moisture to avoid hydrolysis or polymerization is always a concern. Processors use dehumidifiers to control the moisture present in molding materials especially when using regrind or while operating under hot, humid conditions. Failure to compensate for changes in molecular mass during measurement of melt viscosity because of failure to control moisture content adequately, e.g., by over drying has resulted in questionable estimates of the activation energy of viscous flow. Thermal degradation can also be a problem if the melt is held too long at too high a temperature. Thus, one study preferred to use a capillary mounted on an injection molding machine rather than an Instron capillary rheometer in part because of shorter hold-up times [249]. Values of 42–63 kJ/mol for the activation energy of viscous flow appear reasonable rather than those of 71–92 kJ/mol as have sometimes been reported [19, 250]. Master curves that are based on only the T_g and melt flow index (MFI) per ASTM D 1238 have been proposed for a number of polymers including nylons [251]. These curves plot the product of viscosity and MFI against shear rate divided by MFI. The sample curves in Figure 15, mostly at 280 °C, were taken from [252–255]. As shown in the figure, the apparent melt viscosity of the linear, aliphatic nylons starts to decrease rapidly at a shear stress of ca. 50 MPa.

Filled and reinforced nylons have higher melt viscosities than their neat analogues, but the differences become smaller as the level of shear increases [256, 257]. Processing variables affect the ultimate fiber size in the blend and can accordingly affect the properties of the molded product [258, 259]. Compounding studies indicated that the major fiber degradation occurs in the melting region [260]. A subsequent study came to the same conclusion and showed fiber fracture to be independent of fiber concentration and dispersion and to arise from fiber interaction with shear in the matrix [261].

Toughened nylons also tend to have higher melt viscosities than their neat counterparts. There is again diminution of the difference as shear increases. The lower modulus implies

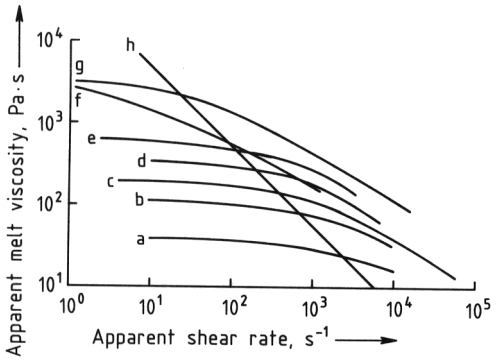


Figure 15. Dependence of apparent melt viscosity on apparent shear rate for various nylons at 280 °C (adapted from [19])
a) Nylon 610 [254]; b) Nylon copolymer [254]; c) Nylon 66, M_n ca. 18 000 [253, 254]; d) Nylon 6, M_n ca. 20 000 [253]; e) Nylon 6, M_n 19 100 at 203 °C [252]; f) TMDT at 250 °C [255]; g) Nylon 66, M_n ca. 34 000 [253, 254]; h) Line of constant shear stress of 50 MPa.

longer molding cycles, but in at least one case the toughener induced nucleation which made for fast molding [216].

8. Uses

Nylons are used in many and diverse ways. They are found in appliances, business equipment, consumer products, electrical/electronic devices, furniture, hardware, industrial/machinery, packaging, and automotive and truck. This diversity makes classification and analysis difficult as shown in Table 8, which shows the pattern of consumption in the major regions and globally [262].

Automotive and truck is the largest market for nylons. The good performance of nylon at high temperatures and pressures, as well as its chemical resistance and compatibility with many automotive fluids, along with the design flexibility available with plastics, paved the way for the adoption of polyamides in many under-the-hood applications. The introduction of high-performance mineral reinforced and glass reinforced versions of nylon greatly increased the ability to tailor properties for individual engine components. When government regulations required automobile manufactures to install pollution-control devices, designers turned to these proven materials for critical air and fuel system control components because of the polymer's performance and the relative ease of part manufacture. Utilizing nylon in the engine compartment reduces weight, which can improve fuel efficiency without sacrificing engine performance. Key developments were pioneered in Europe where smaller cars, higher gasoline costs, and emission control mandates drove innovation. Soon, commercial applications of nylons in air intake manifolds, brake fluid reservoirs, power steering reservoirs, radiator end tanks, and oil pans were introduced. These developments gained footholds in Europe and spread to other regions. Unreinforced resins are used in electrical connectors, wire jackets, windshield wiper and speedometer gears, and emission canisters. The softer nylons are used in fuel lines, air brake hoses, and spline shaft coatings. Glass reinforced nylons are used in engine fans, radiator headers and grilles, brake and power steering fluid reservoirs, valve covers, air intake manifolds, wheel caps, air brake contacts and head-rest shells. Applications for nylons combining tougheners and reinforcement include brackets, steering wheels, and accelerator and clutch pedals. Mineral-filled resins are used in wheel caps, radiator grilles, and mirror housings. Nylons containing both glass fibers and minerals are used in exterior parts such as fender extensions. Toughened nylons are found in stone shields and trim clips.

Electrical and electronic applications comprise a major market for nylons, albeit more so in Northeast Asia and Western Europe than in North America. Flame-retardant materials are particularly important in this area. Uses include color-coded components, plugs, connectors, coil forms, wiring devices, terminal blocks, antenna mounting devices, and harness ties. A review of nylon in electrical power engineering and electronics has already been cited [234]. Wire and cable jacketing is used mostly over primary insulation because of the solvent, wear, and abrasion resistance of nylons. Relays, fittings, and contact makers constitute a partial list of applications in telecommunications.

Industrial/machinery applications are attracted to the excellent fatigue resistance and repeated impact strength of nylons. Examples are hammer

Table 8. Pattern of nylon consumption globally and regionally in 2012; data sourced and used with permission of IHS Chemical [262]

Nylon Engineering Resin End-Use Demand	North America	South America	Greater Europe	Asia and rest of world	Global
Automotive and truck, %	49.9	58.0	36.9	29.1	35.9
Electrical and electronic, %	5.3	5.0	14.1	13.0	11.8
Appliances, %	2.5	4.0	6.2	11.1	7.9
Film, coating, cable, %	20.6	11.0	18.5	13.2	15.9
Consumer, %	11.5	5.0	8.3	10.7	9.8
Industrial/machinery, %	5.8	8.0	11.0	16.9	13.0
Others, %	4.5	9.0	5.1	6.1	5.6
Total, 10^3 t	399	100	810	1266	2575

handles and moving machine parts. The mechanical strength accounts for use in gears, bearings, antifriction parts, snap fits, and detents. Food- and textile-processing equipment, pumps, valves, agricultural and printing devices, and business and vending machines comprise a partial list of other industrial uses.

Consumer products exploit the toughness of nylons in ski boots, ice and roller skate supports, racquet equipment, and bicycle wheels. Kitchen utensils, toys, photographic equipment, brush bristles, fishing line, sewing thread, and lawn and garden equipment show that the breadth of utility of nylon also includes consumer products.

Appliances and power tools make use of the impact strength of nylons. Glass-reinforced resins, which combine stiffness at high temperatures with toughness and grease resistance, are used in handles, housings, and parts in contact with hot metal. Sewing machines, laundry equipment and dishwashers are examples of other appliances that have utilized nylons.

Film and coating applications have grown in importance because of the use of nylons in coextruded, composite films for food packaging. Polyamides are also used in cook-in bags and pouches. Another development involves dispersion of nylon platelets in a polyolefin matrix to combine both hydrocarbon and moisture barrier properties in blow molded containers [263, 264].

Other Applications. The soft polymer-modified, anionically polymerized caprolactam has been used via RIM to make machine housings, grain buckets, and fuel tanks [266]. Blow molding compositions [267], PA 46 and MXD 6, have extended the utility in the market [268–270]. Products with improved processing characteristics, high- and low-temperature performance, and new property profiles obtained via the use of new modifications and combinations thereof have been introduced [271, 272]. A PA 6 with reduced moisture sensitivity has been demonstrated [269], as has the use of block copolymers as thermoplastic elastomers [248].

The adaptability of nylon to be changed to even obtain diametrically opposite results is shown in Figure 16, which gives some examples of the applications involved. Nylons with qualified approval in the United States in 2002 for processing, handling, and/or packaging food are PA 66, 610, 66/610, 6/66, 11, 6, 6T/66, 612, 12, MXD6 and impact-modified MXD6, 12/AI (A = bis(4-amino-3-methylcyclohexyl)methane [6864-37-5]), 6I/6T, 6/69, 46, and TMDT [273].

9. Ecological Aspects and Toxicology

9.1. Recycling

Polyamides are quite stable, and are used primarily in durable applications that are not major contributors to the waste stream. Scrap and trim are generally reused during processing, further minimizing waste. Some consumer applications such as bristles, strapping, and composite film for packaging do involve routine disposal, but the total is well below 0.05 wt% of all collected refuse. As a result, commercial nylon recycling processes are not as well developed as they are for other thermoplastics. However, it is far more energy efficient to recycle nylon than to burn it [274], and European directives in 2001 that phase in a requirement that almost all plastics used in automobiles be recycled over the subsequent two decades will continue to spur development in the recycling of mixed thermoplastics. Several commercial initiatives to recycle readily-available PA 6 and PA 66 carpet fibers were conducted in the United States and Europe, but were only partly successful because of the low demand and the difficulties of efficiently and economically collecting raw materials [275–278].

Difficulties involved in recycling postconsumer polyamides include the fact that they are often used compounded with a wide variety of additives (see Section 6.3) that need to be removed and the fact that the properties of polyamides generally suffer strongly upon multiple reheatings, as the polymers tend to degrade and lose molecular mass. Most of the current commercial recycling processes involve the depolymerization of the polymer chains and isolation of the monomers, which are then used as feedstocks to make near-virgin polyamides. PA 6 can be depolymerized to caprolactam by heating the polymer in the presence of

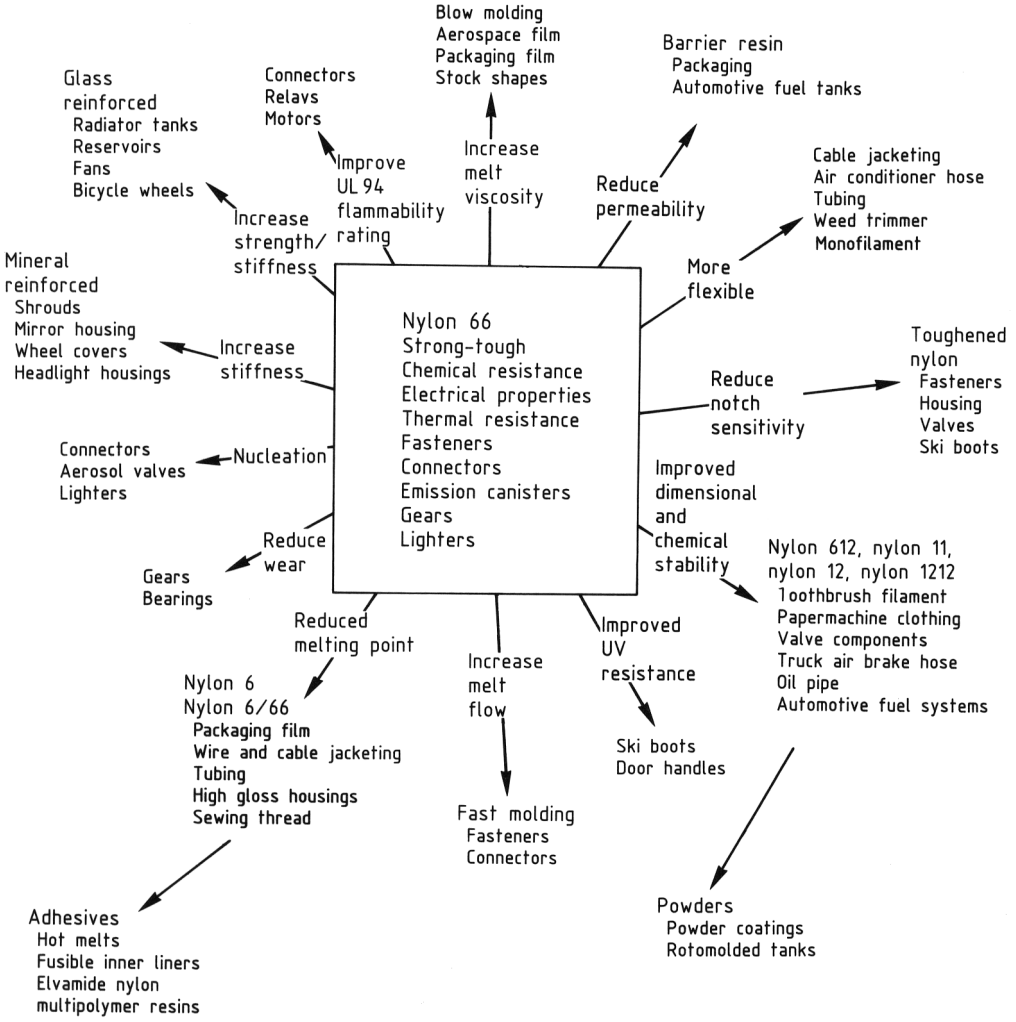


Figure 16. Nylon readily tailored to market needs

superheated steam and an acid catalyst such as phosphoric acid and collecting the monomer by distillation [279, 280]. PA 66 or PA 6 can be depolymerized by ammonolysis, which involves heating the polymer with ammonia at elevated pressures in the presence of a Lewis acid catalyst to yield hexamethylenediamine (HMD) or caprolactam and a series of nitriles and amides, some of which can be hydrogenated to yield HMD or caprolactam precursors [281, 282]. Other methods exist that convert PA 66 or PA 6 to adipic acid by treating the polymers with an aliphatic acid at elevated temperatures and oxidizing the resulting alkylamides and bisalkyamides [283].

Depolymerization followed by repolymerization is an expensive process, however, and mechanical recycling of polyamides, which involves grinding or crushing the resin, followed by pelletizing, is also used, although the resulting resins are of lower quality and have limited uses. A solution-based polyamide recovery process has been developed in which the polymer is dissolved in an anhydrous polyol or aliphatic carboxylic acid at elevated temperatures, insoluble fillers are removed by filtration, and more solvent at a sufficiently low temperature to cause the polyamide to precipitate is added quickly [284]. As a result of the rapid quenching, this process leads to relatively

little degradation of the polymer, which can be then be reused. A disadvantage of this process, however, is that the resulting solutions are quite viscous, which makes filtration through fine filters, and hence the removal of submicron particles, such as titanium dioxide (which is often used in polyamide fiber applications) difficult. To address this problem, a process was developed to partially depolymerize a polyamide dissolved in methanol or ethanol to achieve a viscosity suitable for filtration, separate the insoluble material, and then repolymerize the recovered low molecular polymer by solid-phase or melt polymerization [285].

9.2. Polyamide Monomers

Most polyamide monomers come from petroleum-based feedstocks, although two commercially important monomers, sebacic acid (decanedioic acid) and 11-aminoundecanoic acid, are derived from castor beans. The processes for preparing many common monomers often use ingredients that can generate byproducts and thus must be handled carefully. For example, adipic acid is generally produced by oxidizing a mixture of cyclohexanone and cyclohexanol with nitric acid, generating nitrous oxide, which is believed to be a greenhouse gas, as a byproduct. These byproducts are contained under rigorous manufacturing controls and abated and not released into the environment. A variety of research projects have addressed these issues. A process has been developed that oxidizes benzene to phenol with nitrous oxide. The phenol is converted to cyclohexanone, which is oxidized to adipic acid with nitric oxide, and the resulting nitrous oxide byproduct is recycled back into the process [286, 287]. Recently a method has been reported to directly oxidize hexane to adipic acid in the presence of air using molecular sieves containing cobalt(III) ions [288]. A method has been developed to oxidize *p*-xylene to terephthalic acid using a heterogeneous catalyst in supercritical water [291].

9.3. Other Aspects

Polyamides degrade slowly in sunlight with the evolution of organic acids, aldehydes, and oxides of carbon. These are assimilated with other natural decomposition products. Resistance to attack by bacteria and fungi makes for very slow decomposition when buried in the soil. Nylons are normally inert, nonleaching, and well compacted in sanitary landfills so they pose no danger to subsurface water. Normal incineration in air at 800 °C yields the same gaseous products as do naturally occurring, proteinaceous materials such as wool, silk, hair, and leather, i.e., mainly carbon dioxide and carbon monoxide with small amounts of ammonia and hydrogen cyanide. Silk generates more of these products than does PA 66 under the indicated conditions of incineration.

Most polyamides are biologically inert and offer no toxicological problems except, possibly, in the instance of additives or some low molecular mass fragments. Caprolactam monomer has been reported to be a convulsant poison in sufficient doses although aminocaproic acid is not [290]. The same comment is applicable to the dermatological situation—no problem with the polymer but caution with respect to additives and caprolactam. Polyamides have been widely used as a suture material and many are approved for food uses. The use of wood fiber as a lightweight reinforcing agent in polyamides that comes from a renewable resource and leaves no ash upon incineration has also been investigated [292]. Polyamides can contribute to decreased emissions and fuel consumption when they replace heavier metals in automotive applications and can replace toxic metals in certain applications (see Section 6.3.5).

10. Economic Aspects

The following discussion is based on data sourced from and used with permission of IHS Chemical [262]. Global consumption of polyamides in engineering polymers applications has grown from 800 000 t/a in 1990 to 1700 000 t/a in 2000 to 2500 000 t/a in 2011. Even with the impact of the recession of 2008, the average annual compounded growth rate from 1990 to 2010 was 5.6%. Recovery to pre-2008 recession consumption levels is expected by 2012.

The largest polyamide consumption regions are Northeast Asia, Western Europe, and North

Table 9. Major producers of polyamides

Company	PA 6	PA 66	Other	Trade names
Asahi Kasei		x		Leona
Arkema	x	x	11, 12	Rilsan, Orgamid, Cristamid, Platamid
Ascend Performances Materials		x		Vydyne
BASF	x	x	610	Ultramid
Lanxess	x	x		Durethan
DSM	x	x	46, 610	Akulon, Stanyl
DuPont	x	x	612, phthalamides, amorphous	Zytel, Minlon
EMS-Grivory	x		12, amorphous	Grilon, Grilamid, Grivory
Evonik			12, amorphous	Vestamid, Trogamid
Invista		x		Torzen
Mitsubishi Gas			MXD6	Reny
Mitsubishi Petrochemicals			phthalamides	Arlen
Nilit		x		
Radici	x	x	610	
Rhodia	x	x	610	Technyl
PingMei Shenma		x		
Solvay			MXD 6, phthalamides	Ixef, Amodel
Toray	x	x	610, 12	Amilan
Ube	x	x	12	Ube
Unitika	x			Unitika

America with 38%, 29%, and 15% of global demand for polyamides respectively. Polyamide consumption in Northeast Asia grew from 100 000 t/a in 1990 to 900 000 t/a in 2010 with an average annual compounded growth rate from 1990 to 2010 of 12%. In the more developed markets, polyamide consumption in West Europe has grown from 275 000 t/a in 1990 to 690 000 t/a in 2010, which corresponds to an average annual compounded growth rate of about 3%. In North America, consumption of polyamides has grown from 290 000 t/a in 1990 to 360 000 t/a in 2010, corresponding to an average annual compounded growth rate of 1%. The impact of the recession in 2008 can be seen by comparing the polyamide consumption in North America of 430 000 t/a in 2006 to the 360 000 t/a consumption in 2010.

Major market segments worldwide for injection-molded polyamides are appliances, consumer products, electrical and electronic, and automotive and truck applications. Globally, automotive and truck and electrical and electronic applications are the fastest growing segments and are expected to grow at higher rates than the global demand in polyamides. In Northeast Asia the average annual compounded growth from 2006 to 2011 for the automotive and truck, electrical and electronic appliances, and film and coating segments was 7% for automotive and more than 3% for the others. In Western Europe and North America the average annual compounded growth from 2006 to 2011 dropped for most segments because of the recession in 2008.

Producers of polyamides with their products and trade names are listed in Table 9.

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Polyaspartates and Polysuccinimide

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Polysuccinimide is an intermediate in the production process of polyaspartates and may be easily isolated in a dry state. Tablets of polysuccinimide are formed which release traces of polyaspartate over a long period of time under neutral to slight alkaline pH conditions. Those tablets are mainly used for the treatment of waters. Applications of polysuccinimide are based on its hydrolyzation properties or on its reaction with nucleophiles such as amines and sulfides.

1. Introduction

Mineral formation and scaling, widely occurring problems in various industrial processes, are currently solved by the use of inhibitors and dispersants such as polycarboxylate homo- and copolymers. Most of these compounds are ultimately released to wastewater but they are usually poorly biologically degradable, if at all [1].

In nature, the control of inorganic crystallization is vital to almost all organisms. Inorganic crystals, for example, modified by association with organic components are constituents of skeletons, shells, and teeth. The study of such composite materials and the ways in which they are formed and modified is inherent in the more general field of biomineralization, which has been the subject of numerous publications [2–5].

A multitude of organic molecules from biological systems potentially interact with and modify inorganic crystallization. Key among these is a class of polyanionic proteins. The main constituents of these proteins are aspartic acid and phosphoserine, together accounting for roughly 60 mol % of the total composition of amino acids [6–8].

In aqueous solution, these polyanionic proteins can inhibit crystal nucleation and growth by altering the morphology of microscopically small crystals. Studies using modern analytical methods, e.g., atomic force microscopy [9], and

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molecular modeling methods [10] have been carried out in order to understand these interaction phenomena. In the 1980s, the first attempts were made to utilize this principle of action in industrial applications. Starting with natural proteins from, e.g., crustacea (biodesign), led to a new class of polypeptide-mimicking polyamides, the "polyaspartates". These can be used to solve industrial scale or dispersion problems, e.g., the stabilization of weakly soluble salts such as alkaline-earth carbonates, sulfates, or phosphates in aqueous solution, or the dispersion of inorganic and organic particles. These polymers, which are functional equivalents of the currently used inhibitors and dispersants are biodegradable and therefore might be a new and more environmentally acceptable alternative to the existing products (see → Disperse Systems and Dispersants, → Laundry Detergents).

Polyaspartates can be used in many applications such as laundry detergents, dishwasher chemicals, chemicals for the treatment of cooling and process water, dispersants for organic and inorganic solids, and as a basis for absorbent and gelling materials. (see Section 5.2)

Polyaspartates manufactured by using thermal processes (see Chapter 2) represent a group of acidic polyamides which have been known for a long time [12]. By the end of the nineteenth century, SCHIFF [13] already had polymerized aspartic acid. Fox [14], HARADA [15], and KOVACS [16] later continued this work during investigation of the formation of proteinoid structures under prebiotic conditions.

While the polyaspartic subunits in naturally occurring polyamino acids contain only α-moieties, poly(aspartic acids) obtained by thermal polymerization processes contain a mixture of α- and β-moieties:

2. Synthesis and Production of Polyaspartates

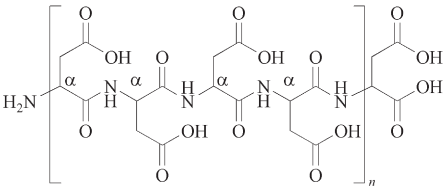
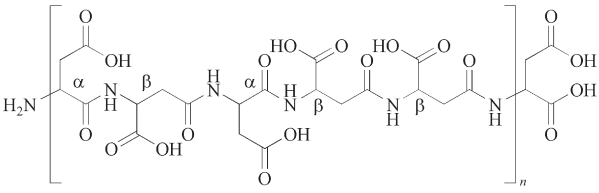
During the past decades, numerous methods for the synthesis of polyaspartates have been developed. It was found that the synthetic method used strongly influences the structure and properties of the resulting product. Because of their interesting properties, polyaspartates could be used on a large scale in different applications. Therefore, the production of polyaspartates has been the focus of extensive research.

Peptide Synthesis. Like other peptides, polyaspartates can be synthesized using an automated, solid-phase peptide synthesizer. A family of polyaspartates ranging in size from ASP_5 to ASP_{60} were prepared by this method and studied in the control of the crystallization of $CaCO_3$ [17].

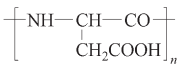
Polymerization of Protected Aspartic Acids. In small scale, polyaspartates of well-defined structure can also be synthesized by

1. the polymerization of the *N*-carboxyanhydride of L-aspartic acid β-benzylester [12, 18, 19] or
2. the anionic polymerization of L-aspartic acid β-lactam benzylester [20].

After deprotection, poly(α-L-aspartic acids) or poly(β-L-aspartic acids) with molecular masses of 10 000–50 000 can be obtained:

	Naturally occurring poly(aspartic acids)	Homopoly(aspartic acid) produced by thermal polymerization [a]
Structure		
Subunits	α- moieties	α,β-moieties, polydisperse
n	< 50	depends on synthetic pathway

[a] Ideal structure.



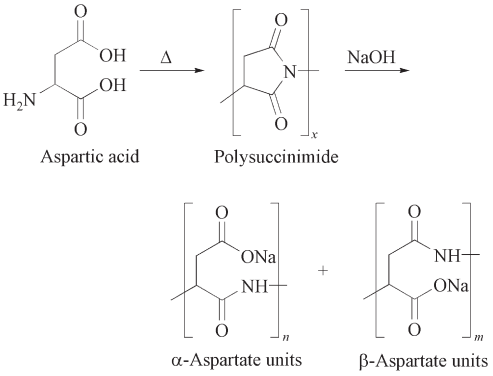
Poly(α-L-aspartic acid)



Poly(β-L-aspartic acid)

NMR studies (see Chapter 3) were done on the resulting compounds and it was found that the purity of the samples depends on the method of debenzylation [21–23]. During debenzylation of, e.g., poly(α-L-aspartic acid β-benzylester), a polysuccinimide-containing succinimide ring is formed which, after alkaline hydrolysis, yields mixtures of α- and β-linked aspartic acid units.

Solid-Phase Thermal Polycondensation. Commercial production would seem to be possible using the thermal polycondensation of aspartic acid in the solid phase, which has been known for a long time [14, 15, 17, 24–28]:



The reaction can be carried out in different types of drying reactors. The generation of dust from the dry starting material and the reaction product is a problem, making the installation of efficient filters necessary.

Because of its commercial availability, L-aspartic acid, which is produced by enzymatic methods, is used for the polycondensation. The reaction is carried out at temperatures of 160–240 °C. Polysuccinimide is formed as an intermediate which is hydrolyzed to a 30:70 mixture of α- and β-linked aspartic acid units. It could be shown that increasing the temperature improves the yield and molecular mass of the product, but also reduces its optical purity, and may end in complete racemization [29]. The thermally synthesized polyaspartate with an average molecular mass of 6000 is biodegradable and, in a low-biomass sludge experiment (SCAS, modified Sturm test), yielded approximately 70% mineralization in 28 days [30] (see Chapter 4).

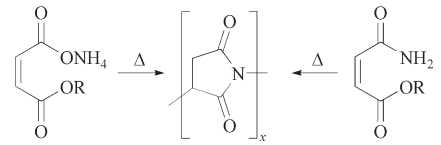
Thermal Polycondensation in the Presence of Catalysts. Another method for the synthesis of polyaspartates is the thermal polycondensation of L-aspartic acid in the presence of catalysts. Preferred catalysts are *ortho*-phosphoric acid and polyphosphoric acid [25]. The reaction yields a melt which is difficult to handle. In NMR and biodegradation studies, these polyaspartates showed less branching and improved biodegradability compared to those prepared without an acid catalyst [31–33] (see Chapter 4). In addition, these polyaspartates have a higher molecular mass of approximately 50 000.

Catalysts containing sulfur such as H_2SO_4, $NaHSO_4$, and NH_4HSO_4 were used to manufacture highly degradable, low-colored polyaspartates with molecular masses between 2000 and 20 000 [34] (see Chapter 4). Several acid catalysts were used in combination with organic solvents in which the polymer is dispersed to increase the molecular mass of polysuccinimide up to 64 000 [35]. To synthesize polyaspartates with special properties, biodegradable water-absorbent polymers were prepared by acid-catalyzed thermal polycondensation of L-aspartic acid in the presence of cyclic anhydrides [36]. In addition to organic and inorganic acids, transition metal salts, e.g., chlorides of Cu, Co, Ni, and Zn, were used as catalysts in the thermal polycondensation of L-aspartic acid and its ammonium salt. An increase in the molecular mass and preservation of the optical purity were achieved [37].

Thermal Polycondensation of Chemical Precursors of Aspartic Acid. All the aforementioned synthetic methods start with L-aspartic acid, global production of which is approx. 10 000 t/a. Worldwide demand for polycarboxylates (mostly non-biodegradable) is estimated at 100 000 t/a or more. Thus, a substitute should be available by a manufacture process which

can match that market. L-Aspartic acid is therefore not an adequate source for the production of all polyaspartates. Especially in the case of laundry detergents, dishwasher chemicals, and water treatment agents, the breakthrough of polyaspartates can only be achieved if large-scale production of tens of thousands of tons is possible. This can be achieved by using chemical precursors of aspartic acid.

The thermal polycondensation of maleic acid ammonium salt was described long ago [12] and repeated in several investigations [15, 24] In addition, maleamic acid, D,L-aspartic ammonium salt and a mixture of asparagine and maleic acid were used [16]. Because of their good availability, derivatives of maleic acid anhydride with ammonia, e.g., maleic acid ammonium salts and maleamic acid and its ammonium salts, were of special interest [38, 39]. Fumaric acid ammonium salt is also used [40]. Maleic acid anhydride is produced in volumes of approx. 300 000 t/a (estimated) and thus represents a source for the large-scale production of thermal polyaspartates:



Maleic acid ammonium salt R = H, NH_4 | Polysuccinimide | Maleamic acid or Maleamic acid ammonium salt

In general, the thermal polycondensation of aspartic acid precursors which are prepared in the form of concentrated aqueous solutions or in a dry form is carried out in a reaction melt. Special reactors are necessary in which the reaction melt can be transformed to a dry product [41]. At reaction temperatures of 160 to 240 °C, the starting material is rapidly converted to polysuccinimide. The water from the aqueous solution and from the condensation reaction is distilled off from the reaction mixture until dry polysuccinimide is obtained. The polysuccinimide can be hydrolyzed, e.g., in aqueous sodium hydroxide, to poly(α,β-D,L-aspartic acid sodium salt) containing an α:β ratio of 30:70. The molecular masses of the resulting products are about 1200 (number average) and 2400–2500 (weight average), and the biodegradability measured according to OECD 301 E reaches 60–70% [41–43].

3. Analytical Characterization and Detection

The molecular structure of poly(aspartic acid) (PASP) has been investigated mainly by using spectroscopic methods [36]. Especially NMR spectroscopy was an important tool to obtain information about the structural composition of PASP. Other methods such as infrared spectroscopy were also useful to analyze PASP or its copolymers.

3.1. ^{1}H NMR Spectroscopy

Polyaspartic acid (PASP) can be identified by NMR spectra. The signals measured in alkaline solution are shown in Figure 1.

Due to the polymer structure, there is no observation of sharp peaks, and the signals appear in the form of broader multiplets. In a mixture, of which the resonance signals of polyaspartic acid and of other compounds do not overlap, it is possible to quantitatively analyze PASP by using integrals. It is also possible to identify possible copolymer units in the molecule. Matsuyama et. al [44] determined the ratio of α- and β- amide units in the main chain by integrating the separated methine signals in the ^{1}H NMR spectrum.

3.2. ^{13}C NMR Spectroscopy

^{13}C NMR-Spectroscopy has also been used to answer questions about the molecular structure

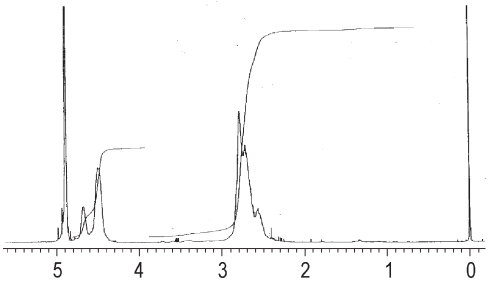


Figure 1. ^{1}H NMR spectrum of thermal PASP from aspartic acid in D_2O (pH 13, 400 MHz)

of PASP. Pivcova et al. [45] evaluated the ratio of α- and β- amide units using the methylene signals in the ^{13}C-NMR spectrum. They analyzed the amide bond sequence using the amide carbonyl signals and concluded that the distribution of the α- and β- bonds was random [47].

3.3. Gel Permeation Chromatography

The molecular mass was determined in aqueous solution by gel permeation chromatography (GPC). As a standard polymer, polyacrylates or polystyrene sulfonic acids can be used. There are also polyaspartic acids of a defined and unique chain length commercially available, which are suitable as standard materials. During the measurement it is important to keep the pH of the solution constant because the molecule extension is strongly dependent on the charge density which is influenced by the degree of dissociation. As a column filling, cross-linked polyhydroxyethyl methacrylate (poly-HEMA) can be used (see also →; Plastics, Analysis, Chap. 5.).

3.4. Isotachophoresis

Isotachophoresis (see → Electrophoresis, Chap. 9.) is a method which is low in cost because it can be carried out with a low amount of chemicals. Therefore, only a diluted aqueous buffer solution is necessary. It is very suitable for complex mixtures, also in extreme concentration properties. The method is based on the fact, that charged particles may be characterized by their migration behavior in the electric field. Different dissolved ions are sharply separated into defined fractions which are detected successively. Basic apparative device have been described by Everaerts [47] and Kaniansky et al. [48]. This method allows a quantitative analysis of polyaspartic acid even in presence of a range of other ions.

The sample is injected between two electrolytes, from which one has the highest, and the other the lowest mobility of all ions present in the system (leading and terminating electrolyte). By applying an electric field, anions and cations are separated according to their different mobility, if these are between the mobility of the two electrolytes. After reaching the stationary state, all distinguished zones move through the solution with the same speed (therefore the name "isotacho") being in direct contact to each other to maintain the electric circuit. For detection, ultraviolet radiation or conductivity can be used.

The detection of PASP is mainly important in commercial applications where the user needs information about the actual product concentration in his process. Especially in water conditioning the process control must include a permanent feedback of what amount of PASP must be dosed to compensate product decreases.

3.5. Fluorescence Spectroscopy

Thermally synthesized polyaspartic acid can incorporate traces of chromophoric structures into the polymer chain, thus allowing a photometrical analysis. PASP is excited in the absorption maximum at 336 nm and emits fluorescence light with a maximum at 411 nm [49]. The intensity of the emitted radiation is directly transformed into a concentration, as it is proportional to the fluorescence intensity. This way of analysis is suitable for most applications, in which a fast and reliable online control of the concentration of polyaspartic acid is required. The actually measured signal determines the amount of product to be added, by this way a minimum concentration can be kept up without uneconomic overdose. Portable instruments for a mobile measurement station are commercially available. They can be specially adapted to purposes with a frequent local move of the analysis set, and under outdoor conditions, for example to screen the concentration PASP in drainage systems at different distances from the dosing equipment.

3.6. Precipitation Titration

A method to be carried out with common laboratory equipment is a precipitation titration with ferric trichloride. The sample solution is mixed with hydrochloric acid to adjust the pH to 8. A 0.05 M $FeCl_3$ solution is dosed, and the turbidity is detected photometrically. The collected data are evaluated by using calibration curves which are measured with defined concentrations of polymers with a similar distribution of their molecular masses.

3.7. Polyelectrolyte Titration

The basis of the determination of polyanions is the formation of a polysalt by reaction of the polyanion with a counter-polycation against which it is titrated [50]. The polysalt reaction meets the conditions for a titrimetric determination: it proceeds essentially quantitatively and is very rapid. In many cases it is a reaction in the sense of a 1:1 reaction [51–57]. The endpoint of the 1:1 reaction between a polyanion and a polycation is indicated by the formation of an associate between the exceeding polycation and anionic metachromic dye, e.g., eriochrome black T.

4. Toxicological Properties and Environmental Fate

Chapter 2, already discussed the fact that thermal polyaspartates are accessible through both catalyzed and noncatalyzed reactions. Polyaspartates synthesized by the first method with sulfur-containing catalysts were tested according to OECD 301 B. Here, the biodegradability was measured by the quantity of carbon dioxide produced by microorganisms during metabolism of the test substance. After 16 days, more than 90% had been degraded already and complete degradation was achieved after 28 days [34].

However, noncatalyzed reactions also yield polyaspartates [poly(α,β-D,L-aspartate) with 70% β-isomer] which show quite high degradation rates of 70% mineralization after 28 days, measured by the modified Sturm test (OECD 301 B) [30]. The good degradability of thermal polyaspartate was demonstrated also by measuring the biological oxygen demand (BOD) in a diluted secondary effluent from a wastewater treatment plant as a source of flora. The trials conducted with solutions containing 3 mg/L of polyaspartate showed only 40% of the theoretical BOD after three weeks [26].

Recent tests have shown that thermal polyaspartates synthesized using phosphoric acid as catalyst had degradation rates of more than 90% in the Zahn-Wellens test (OECD 302 B) [42]. In the same test series, the catalytically manufactured polyaspartate was fully degraded after 7 d in the SCAS test (OECD 302 A) simulating a semicontinuously operated wastewater treatment plant with the addition of samples and blowdown once a day.

The excellent degradation behavior and, moreover, the very favorable toxicological properties of this kind of poly(aspartic acids) are quoted in [41] and [43]:

a)	Acute toxicity (rat, LD_{50} oral):	≥ 2000 mg/kg
b)	Fish toxicity (LC_0, 96h):	≥ 3200 mg/kg
c)	Toxicity to daphnia magna (EC_0):	≥ 2500 mg/L
d)	Bacteria (EC_0, OECD 209):	≥ 10 000 mg/L
e)	Algal growth (LOEC):	395 mg/L
	(NOEC):	125 mg/L
	(E_rC_{50}):	1070 mg/L
f)	Biodegradation tests:	
	Modified screening test (OECD 301 E), DOC removal, 28 days:	60 to 67%
	Carbon dioxide evolution test (OECD 301 B)	50 to 75%
	Zahn–Wellens test (OECD 302 B), DOC removal:	77%

5. Function and Applications

Chemically, polyaspartates are assigned to the class of polycarboxylates, which refers to the repeating carboxylate units along the polymer chain (each monomer aspartate unit features one carboxylate group). Consequently, polyaspartates showing some similar properties, effects, and eventually applications as the most prominent representative of the polycarboxylates, namely the polyacrylates (see → Polyacrylates). A main difference, however, is the biodegradability of the polyaspartates, which can be attributed to the potentially cleavable amid bonds in the molecule. Thus, a more environmental friendly alternative for the non-biodegradable polyacrylates for a lot of applications is available.

5.1. Functionality

The applications of polyaspartates (see Section 5.2) are based mainly on the following effects, which are explained in the following.

5.1.1. Dispersing Effect

The dispersing effect describes the phenomenon that agglomeration and subsequent settling of solid particles present in aqueous suspensions is

prevented. This is caused by the fact that polyaspartate, due to its polyanionic character, adsorbs onto the highly polar particle surfaces, resulting in equally (negatively) charged particles, which undergo an electrostatic repulsion.

Exemplarily, Figure 2 shows the dispersion effect of polyaspartate in comparison to polyacrylates of different molecular masses onto kaolin. High turbidity values mean high content of solids within the suspension after storage, i.e., reduced settling of kaolin.

The prevention of crystal agglomeration, due to electrostatic repulsion (and steric repulsion to a minor amount as well), is especially important within the process of mineral scale inhibition. Crystal agglomeration in oversaturated solutions is one cause for the formation of strongly adherent scale – a severe problem in water treatment and cleaning applications.

Besides the improvement of the suspension stability, the dispersing effect can cause a dramatic viscosity decrease of slurries (Fig. 3). Thus, a significant reduction of the water content for the production of, nevertheless easy-pumpable, high-solid-content slurries is achievable.

It seems to be that there is a dispersion effect of polyaspartate not only to inorganic solids but also to organic matter, because improved cleaning results in water/organic systems have been reported.

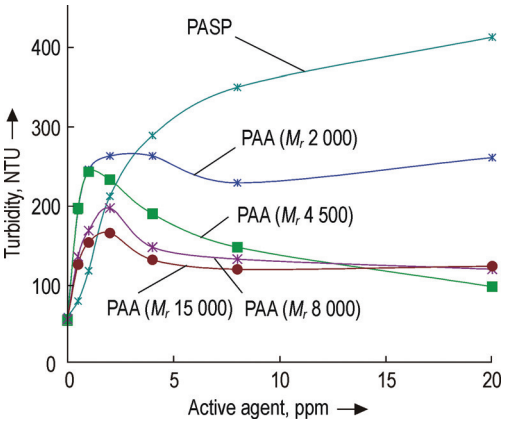


Figure 2. Comparison of polyacrylates (PAA) of different molecular masses and polyaspartate (PASP) on their dispersing activity to kaolin
NTU = national turpidity units

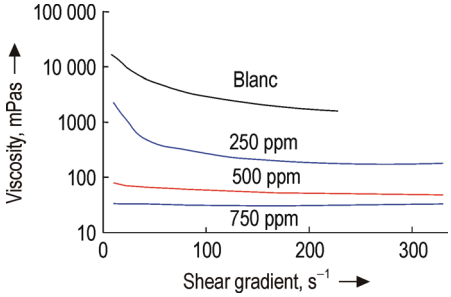


Figure 3. Viscosity of iron oxide slurries with polyaspartate as dispersing agent in various concentrations

5.1.2. Threshold Effect

The threshold effect describes the phenomenon that supersaturated solutions can be stabilized by inhibitors in far less than stoichiometric amounts related to the mineral ions causing supersaturation. Despite a considerable excess of the solubility product, the solutions remain clear in the presence of the inhibitor.

This threshold effect can be explained by an adsorption of the threshold inhibitor on the growth sites of the submicroscopic crystal nuclei which form in a supersaturated solution. This stops altogether, or at least delays, the growth of the crystal nuclei – such as added seed crystals and heterogeneous nuclei – for a long period of time. Thus, it can be concluded that the scale inhibition effect of threshold inhibitors is the result of kinetic rather than thermodynamic effects [58].

By stabilization of supersaturated solutions, threshold inhibitors are able to prevent the formation of mineral scale, a prevalent and severe problem in a lot of applications. The most important scale-forming minerals are carbonates and sulfates of the alkaline earth metals, in particular calcium and barium. Polyaspartate is a particular effective threshold inhibitor for alkaline earth metal sulfates (Fig. 4).

Polyaspartate is effective for calcium carbonate as well; however, it is to note that the phosphonates, which in contrast are not biodegradable, are more efficient with regard to this mineral.

It is obvious that scale inhibition is based on both, the threshold and the dispersing effect. However, it can be assumed that the threshold effect is the dominant effect in oversaturated

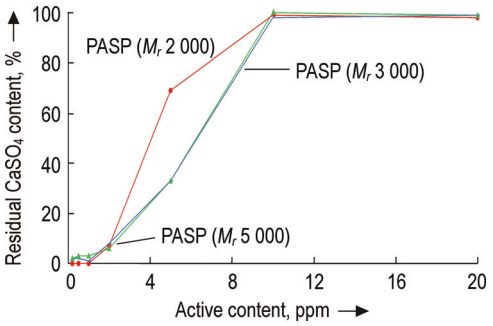


Figure 4. Calcium sulfate scale inhibition by polyaspartate Initial $CaSO_4$ content 10 000 ppm, pH 9, results after 24 h storage in a closed bottle at 60 °C (GPR 1391)

solutions in which no crystals (turbidity) have been formed (100% residual hardness or inhibition) because of the presence of an inhibitor.

5.1.3. Crystal Distortion

A contribution to scale inhibition is also crystal distortion. It means that the crystal shape is changed, which results in a loose, easy-removable precipitate. The mechanism of threshold inhibition through an adsorption of the inhibitor on the growth sites of the submicroscopic crystal nuclei also explains why the structure of the crystals which form when the inhibitor concentration is too low for complete inhibition is altered or distorted and incorporates a proportion of inhibitor.

5.1.4. Complexing Effect

In the case of the complexing effect, the active agent interacts with individual cations, i.e., in contrast to the dispersing and threshold effect mentioned above stoichiometric ratios are necessary. Polycarboxylates such as polyacrylates or polyaspartates have carboxylic groups or an amide nitrogen atom which may act as ligands towards metal ions. That means that these polycarboxylates may also show complexing activity. However, due to their polymeric structure the complexing activity is less prominent than the dispersant activity.

The higher carboxylate content per mass unit of polyacrylates compared to that of polyaspartates provokes a higher complexing activity especially towards calcium ions. On the other side, polyaspartates feature a more prominent dispersant character.

One exception may be the complexing activity of polyaspartates towards ferric irons. In the case of polyaspartate with a molecular mass of about 2000 (Baypure DS) a high complexing constant (log K) of 18.5 has been determined [60].

5.1.5. Corrosion Inhibition

The corrosion inhibiting effect of polyaspartate can be attributed to an adsorption of the polymer onto the metal surface, forming a protective film. It can be assumed that alkaline earth metals present in the aqueous solution are also incorporated into this film, as already known in the case of phosphonate corrosion inhibitors [60]. This could explain the better corrosion inhibition effectiveness at higher water hardness (Fig. 5). According to [65], polyaspartate is also effective in highly sour brine media.

5.2. Applications and Uses of Polyaspartates

5.2.1. Water Treatment

Industrial applications dealing with a large amount of water face the challenge of controlling corrosion and mineral scale formation onto functional equipment, e.g., piping and heat exchanger systems. Since some decades, mixtures mainly based of phosphonates and polycarboxylates have been used in the nowadays sophisticated

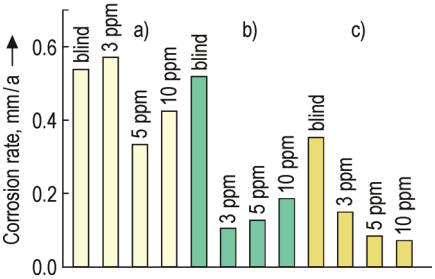


Figure 5. Corrosion inhibition effect of polyaspartate on carbon steel (Spinner test, St37) dGH = degrees of general hardness, dKH = deutsche Karbonathärte a) 17 dGH (300 ppm $CaCO_3$); 9 dKH (160 ppm $CaCO_3$), 3-d test period; b) 34 dGH (600 ppm $CaCO_3$); 18 dKH (320 ppm $CaCO_3$); 3-d test period; c) 54 dGH (900 ppm $CaCO_3$); 27 dKH (480 ppm $CaCO_3$); 7-d test period

cooling and process water treatment. Against the background of increasing interest in better biological degradable water treatment products, a lot of developments have been made in recent years. With regard to polyaspartate, they are based mainly on a substitution of the hitherto used non-biodegradable polycarboxylates (or in parts at least) by polyaspartates, which results in an improved overall biodegradability [62–66]. Due to the outstanding scale inhibition performance of phosphonates (e.g., PBTC) towards calcium carbonate, which in fact is the main scale forming species in cooling and process water applications, phosphonate substitution has taken place rather seldom. However, phosphorus-free products based on polyaspartate have been developed as well [67], which are of particular importance for applications/regions for which very strong legal constraints regarding environmental behavior exist. They are of interest also in the case that calcium sulfate is the predominant scale causer due to geological reasons.

Besides its good corrosion inhibiting effect, especially in combination with phosphonates or metal salts [68], an advantage of polyaspartate in water treatment is its outstanding calcium tolerance, i.e., no insoluble inhibitor salts are formed, which would reduce the active inhibitor content [62].

5.2.2. Detergents and Cleaners

Polycarboxylates – usually polyacrylate and poly (acrylate comaleinate) – have an outstanding function in the ternary builder system zeolith A–polycarboxylate–sodium carbonate in that they effectively prevent lime and soil depositions on laundry and washing machines (see → Laundry Detergents, → Zeolites, Chap. 7.). The mechanism of action is mainly based on the threshold effect [69, 70] (see Section 5.1.2). Environmentally friendly polyaspartates have been proposed as a substitute for non-biodegradable polyacrylates [71]. In addition, the detergency is improved [72]. This allows the formulation of a modern detergent with fully degradable structures. The efficiency of polyaspartate as a cobuilder in modern detergent formulations has been recently demonstrated [73]. Hydrophobic modified polyaspartates have been proposed for better detergency and improved whiteness of the fabric [74]. Sodium carbonate modified by polyaspartate can be used as carrier material in laundry detergents [75]. Low-temperature bleaching detergents containing (phthalimido)peroxyhexanoic acid are described with 3–12% polyaspartate as a cobuilder and stabilizer [76]. Polyaspartates are also suitable for the builder system of automatic dishwashing detergents with a good primary and secondary detergency [77], which may have also a good storage stability [78].

5.2.3. Mining and Oil Recovery

Due to its pronounced barium sulfate scale inhibition efficiency, polyaspartates find use in mining [79] and oil recovery applications. The biological degradability and the favorable ecotoxicological data are of a significant advantage because legal requirements are very high (especially within Europe) in this field of applications [80].

5.2.4. Other Uses

The following table gives a summary of other applications, the corresponding functions of polyaspartates and the resulting benefits.

Application	Function	Benefit
Paper	liquefaction of raw materials	clays and titanium dioxide are used as fillers for paper and must be liquefied before addition to the paper
Leather	dispersion of color pigments	improves the depth of color of the leather, thus reducing the amount of color pigments required
Textiles	dispersion of color pigments/ dyes	dispersion of colors in dyeing processes, especially in cellulosic fiber/reactive dye systems
Membrane cleaning	dispersion of dirt particles at the surface of the membrane	dispersion of dirt particles, cleaning and rinsing of scaled membrane surfaces, especially in the case of organic pigments
Agriculture	fertilizer/ nutrition enhancer	availability of components essential for nutrition to enhance the growth of the plants; no eutrophication because free from phosphorus; reduction of soil erosion
Pigments, colorants, coatings	dispersion of organic pigments	commonly available dispersants are not biologically degradable, e.g., lignine sulfonates; possible replacement by PASP as an environmentally friendly alternative

6. Polysuccinimide

6.1. Introduction

The synthesis and manufacture process was already described in Chapter 2. Usually, polysuccinimide is an intermediate in the production of polyaspartates, thus it may be easily isolated in a dry state.

6.2. Chemical Properties and Analytic Characterization

The chemical and physical properties of polysuccinimide are listed in the following:

Appearance:	slightly yellow- to brownish-colored powder, depending on the manufacturing process
Temperature of decomposition:	234–312 °C (exothermally)
Molar mass: [a]	4000 kg/mol
Solubility:	organic aprotic solvents such as dimethylformamide (DMF), dimethylacetamide (DMA), or dimethylsufoxide (DMSO); ethylene glycol (modest solubility) or di- or triethylenclycol.
Viscosity of a 30% solution in diethyleneglycol at 24 °C:	4800 mPas
Viscosity of a 30% solution in triethyleneglycol at 24 °C:	17 700 mPas
Heat of reaction of hydrolysis per monomer unit at 25 °C:	38.5 kJ/mol

[a] The PSI was obtained by a thermal, non-catalyzed process starting with maleic anhydride and ammonia.

Polysuccinimide may contain hydrolyzed succinimide rings which is equivalent to a content of polyaspartic acids or their salts. By means of IR spectroscopy the ratio of succinimide or amide carbonyl groups can be determined and thus the degree of hydrolysis in ratio to a given standard of polysuccinimide.

The hydrolysis of PSI to polyaspartate [81] depends on the following parameters:

pH
temperature
particle size/particle surface of the PSI

The hydrolysis can be monitored by the fluorescence technique (Fig. 6). To a water cycle

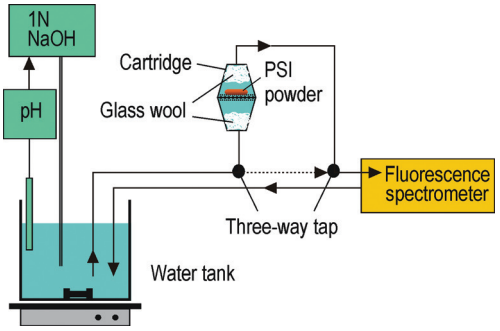


Figure 6. Hydrolysis of polysuccinimide in a closed water cycle Test parameters: $T = 22°C$; $V_{\text{deionized water}} = 2$ L, pH 8, mass of polysuccinimide (PSI) = 0.5 g, flow rate = 2 mL/min

with a 2-L water reservoir, fluorescence detector and pH control a bypass (containing polysuccinimide powder enclosed in a cartridge) is connected through a tree-way tap. The latter allows the separation of the bypass from the cycle. The polysuccinimide dissolution as a function of water flow rate and pH was investigated. The separation of the bypass containing polysuccinimide during the dissolution process at pH 8 gave the surprising result that the fluorescence activity did not rise further after the bypass separation but the overall sodium hydroxide consumption (Fig. 7).

This can be explained by a stepwise hydrolysis of polysuccinimide via succinimide-containing intermediates [82]:

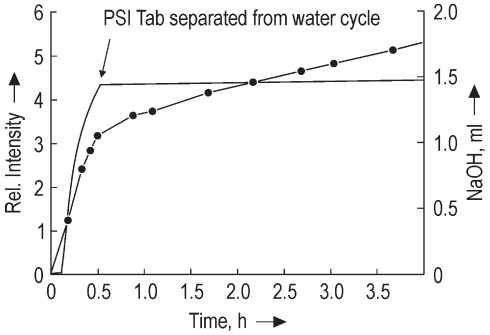
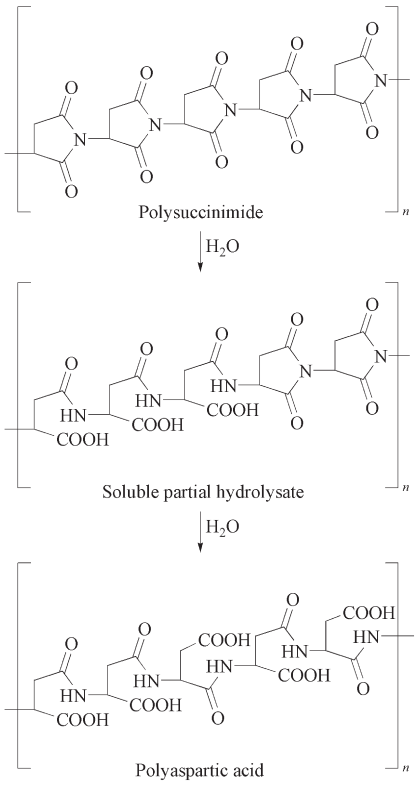


Figure 7. Monitoring the dissolution of polysuccinimide using the test and test conditions given in Figure 6



6.3. Applications and Uses of Polysuccinimide

Polysuccinimide (PSI) is an intermediate in the manufacture process of polyaspartates. Hydrolysis of PSI under alkaline conditions yields polyaspartates. The main application of PSI itself is to use it as a kind of depot for polyaspartate under more or less alkaline conditions. The slow hydrolysis at a neutral to slight alkaline pH allows the formulation of tablets with polysuccinimide as the main constituent which release traces of polyaspartate over a long period of time. These tablets can be used instead of a dosage system for polyaspartates in solution [83, 84]. The biodegradability and non-toxicity of the hydrolysis products as well as the long lifetime of the tablets in the range of several months make polysuccinimide the product of choice in the treatment of waters flowing through drainage systems in tunnels, disposal sites, dams, and power plants. The scaling is due to leaching of alkalinity and calcium ions from the cementous construction material [85].

The partial hydrolyzates occurring during hydrolysis of polysuccinimide are responsible for the erosion of calcite or other crystalline basic calcium salts. The deterioration of calcite can be demonstrated by a simple experiment: A tablet containing polysiccinimide is added on top of a column containing calcite (or marble) pieces. Tab water flows through the column from the top, so that the water washes around the tablet. After seven days of continuous flow, the calcite pieces have fragmented and are colored because of the adsorbed polyaspartate. The fragmentation can be explained by hydrolysis on the calcite surface [86]. Polyaspartate itself is capable of dissolving calcium carbonate at low pH; at high pH this is possible only at higher concentrations of 0.1 M [87]. The low pH may be obtained in the case of polysuccinimide application by hydrolysis of the adsorbed partial hydrolyzates.

If polysuccinimide is formulated with hydrolysis-accelerating substances (alkali metal hydroxide or carbonates, alkaline silicates or phosphates, solvents for polysuccinimide such as triethylene glycole), faster dissolving tabs can be made for cleaners or detergents. The advantage is a reduction of pH during the dissolution and the lower hygroscopicity of polysuccinimide compared to that of polyaspartate or other comparable polyanions such as polyacrylates [88].

The hydrolysis of polysuccinimide comes to an end at a pH of 3–4 [81]. A slurry is formed, which contains only small amounts of free polyaspartic acid together with most of the polysuccinimide intact is formed. This acidic dispersion can be used as a mild abrasive cleaner with a large depot for acidity in case of neutralization [88].

Polysuccinimide is a setting retarder for both cement [89] and gypsum [90]; in the latter case the redarding efficiency exceeds those of polyaspartate itself.

Polysuccinimide not only reacts with hydroxide but also with other nucleophiles as amines or sulfides. This can be used for odor-reducing formulations [91], also with zeolithes as a synergistic partner [92].

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Polybutenes

ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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1. Poly(1-Butene)

1.1. Production

Introduction. Poly(1-butene) is a thermoplastic polymer produced by solution polymerization of 1-butene with a Ziegler – Natta catalyst system. Hüls developed a process during the 1960s and produced the polymer in a 12 000 t/a plant in the Federal Republic of Germany. Mobil started to develop a process in 1968 and, together with Witco, built a plant in Taft, Louisiana with a capacity of 30 000 t/a. Shell (USA) bought the plant in 1977 and is at present the only commercial producer.

The feedstock of pure 1-butene is supplied from the Shell Higher Olefins Plant in Geismar, Louisiana.

The poly(1-butene) plant produces grades specifically developed for pipe and speciality film applications.

Process. The current commercial poly(1-butene) production process consists of seven primary unit operations: (1) polymerization, (2) deashing, (3) polymer/monomer separation, (4) monomer purification, (5) extrusion, (6) pellet blending, and (7) packaging (Fig. 1).

In the polymerization step the catalyst system is fed into the reactor with the purified 1-butene recycle stream. Hydrogen is added as a chain terminator to control the melt flow index of the polymer. Ethylene is fed to the reactor when producing random 1-butene – ethylene copolymers.

Polymerization catalyst residues must be removed from the product to preserve its long-term properties. In the deashing step, the poly (1-butene) is mixed with dilute caustic soda to dissolve and extract the catalyst components. The cleaned hydrocarbon – polymer phase and the catalyst- containing aqueous phase are then separated.

During the polymer/monomer separation step, unreacted 1-butene is separated from the poly(1-butene) for recycle to the reactor. Separation is carried out by heating the polymer solution under pressure then flashing off the monomer by rapidly reducing the pressure. The remaining molten polymer feeds the extrusion step, while the vaporized monomer flows to the monomer purification section of the process.

The monomer purification step accomplishes separation of impurities both heavier and lighter than 1-butene. Water is removed by azeotropic

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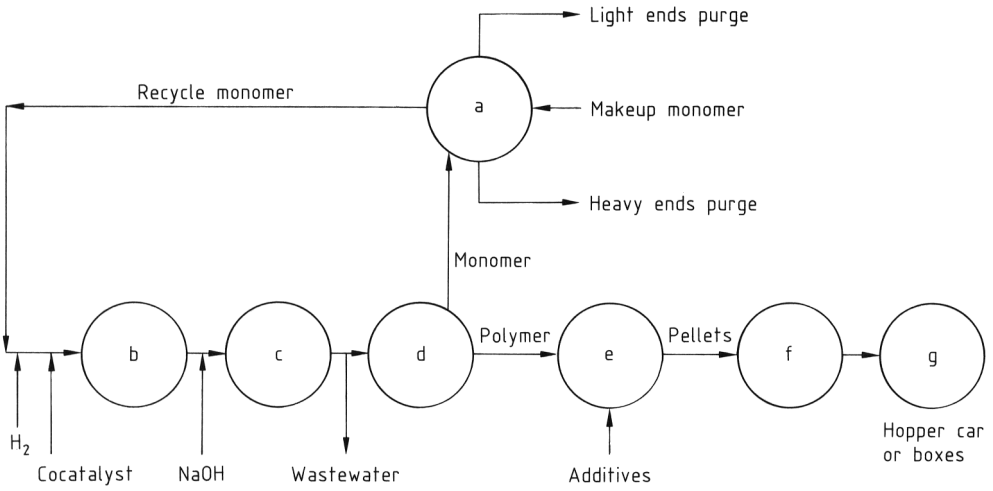


Figure 1. Flow sheet for the production of poly(1-butene)
a) Monomer purification; b) Polymerization; c) Deashing; d) Monomer/polymer separation; e) Extrusion and pelletizing; f) Blending and storage; g) Packaging

distillation. Fresh 1-butene is added to the process at this stage.

In the extrusion step further volatile hydrocarbons are removed, additives for color, product performance, processing, and stabilization are added, and the polymer is pelletized.

The pellets are pneumatically conveyed to the batch blending stage and then transferred to the packaging area. Pellets are typically sold in 450-kg boxes.

1.2. Properties

1.2.1. Structure and Physical Properties

The properties of a high-molecular material are essentially determined by the dimensions and structure of the molecular chain (fine structure) and by the thermomechanical history [1]. Since the fine structure of poly(1-butene) can be varied across a broad range by means of the polymerization process, a knowledge of this is essential for the spectrum of properties.

Molecular Structure. Polymerization with Ziegler – Natta catalysts produces both atactic and isotactic polymer. Atactic poly(1-butene) is virtually impossible to crystallize, while isotactic poly(1-butene) has a crystallinity of 40 – 55 % at normal cooling speeds.

The molecular chains in the crystal form helices. Depending on the crystallization conditions, poly(1-butene) forms 11_3, 3_1 or 10_3 helices, which differ in their helical dimensions [2–4] and give rise to different crystalline modifications (see below).

The isotactic content of poly(1-butene) is generally determined by the solubility in boiling diethyl ether ("ether extract"), whereby it is assumed that only the atactic components are soluble. However, infrared spectroscopy and X-ray crystallography have shown that the atactic extract contains crystallizable components, mostly of low molecular mass. A quicker and more reliable method of determining the atactic content is by evaluating the infrared band in the region of 920 cm^{-1} [5]. This leads to the following definition of the atactic content Y_a:

$$Y_a = \frac{\bar{\nu} - 918\,cm^{-1}}{30\,cm^{-1}}$$

where ν is the band position of the unknown sample in cm^{-1}.

The advantage of this method is that it is independent of the molecular mass and of the morphology of the sample.

Molecular Mass. The average molecular mass may be determined either by direct methods such as light scattering or osmometry, or by indirect methods such as determination of the intrinsic viscosity [6, 7]. The molecular mass is calculated from the viscosity number using the Mark – Houwink equation [7]. Mark – Houwink

Table 1. Characteristic data for crystal modifications of poly(1-butene)

	Modification II (tetragonal)	Modification I (hexagonal)	Modification III (orthorhombic)	Modification I′ (hexagonal)	Amorphous phase	Reference
Helix type	$11_3/40_{11}$	3_1	10_3	3_1		[3, 8, 10]
Helix length per monomer unit, nm	0.187	0.217		0.217		
Helix cross section, nm^2	0.055	0.044				
Specific volume at 25 °C, cm^3/g	1.1364	1.0453			1.1579	[11]
					1.16 for mod. II 1.14 for mod. I	[11]
Specific coefficient of volume expansion, $cm^3\ g^{-1}\ K^{-1}$	3.05×10^{-4}	3.13×10^{-4}			8.12×10^{-4}	[11]
Melting point, °C	ca. 125	ca. 140	93 – 98	100		[9, 12] [13] [14]
Heat of fusion, kJ/mol	ca. 3.1	ca. 6.7				[15] [16] [17]

equations for isotactic poly(1-butene), which give virtually identical molecular masses are as follows:

$$[\eta]_{n\text{-nonane}} = 5.9 \times 10^{-5} \times M^{0.80}$$
$$[\eta]_{\text{dekalin},135^\circ\text{C}} = 6.2 \times 10^{-5} \times M^{0.79}$$

These equations also apply to atactic poly(1-butene).

The molecular mass distribution can be determined easily by gel permeation chromatography in 1-chloronaphthalene as solvent. Industrial products have molecular nonuniformities $U = (M_w/M_n) - 1$ between 5 and 12 (M_w = weight-average value, M_n = number-average value).

Crystal Structure and Superstructure. Like most polymers isotactic poly(1-butene) can crystallize in various modifications. However, the polymorphism is more marked and of greater industrial significance in poly(1-butene) than in any other polymer. Four crystal forms of poly(1-butene) are known at present and are designated modification I, I′, II, and III [2, 8]. Characteristic physical data of these modifications are listed in Table 1.

Modifications I′ and III are formed on crystallization from solution. They are of no industrial importance. However, modifications II and I, which are obtained by crystallization from the melt, are industrially significant. All the crystal forms can be obtained from modification III in a single step [14], as shown in Figure 2. The transitions from one crystal form to another are monotropic. Modification I′ crystallizes preferentially from solution at lower temperatures [8], while at high temperature the orthorhombic modification III is produced [18, 19]. Modification III is also formed by precipitation, e.g., by addition of methanol to a benzene solution of poly(1-butene) [20]. Modifications I′ and III are also formed in solution or suspension polymerization [21].

The tetragonal modification II and the hexagonal form I are industrially important. As a melt cools, i.e., after most processing operations, form II crystallizes out first. This is thermodynamically unstable and in the absence of external mechanical stresses it changes monotropically into the stable hexagonal modification I after a period ranging from a few hours to several days, depending on the temperature and thermal history [2]. The transformation from II to I is associated with a change in various physical properties, e.g., an increase in melting point, density, [11] and modulus (Fig. 3).

These changes in properties are primarily due to the change in crystal modification. The

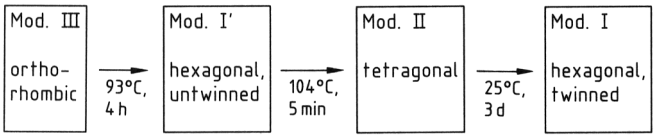


Figure 2. Monotropic interconversion of the four modifications of poly(1-butene)

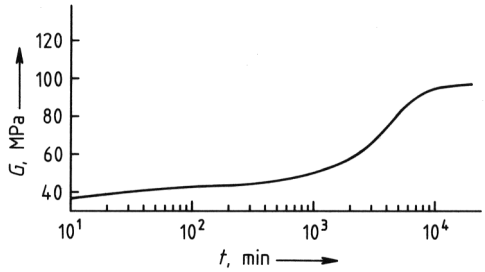


Figure 3. Time dependence of the shear modulus G of modification II of poly(1-butene)
Thermal history: 1 mm thick test bar cooled from the melt (160 °C) in air to the test temperature of 20 °C

degree of crystallization and the mean spherulite size remain virtually constant during the transition from II to I [11]. The crystallite size also remains unchanged [12]. This is a purely crystal – crystal transformation without experimentally detectable melting of modification II crystals.

The rate of conversion, as indicated for example by the half-value time $t_{1/2}$ depends on the thermal history (Fig. 4) and on the temperature (Fig. 4).

Mechanical stresses may significantly increase the conversion rate [22, 23]. Figure 6 shows the influence of constant tensile stress on the conversion rate, monitored by IR spectroscopy. Whereas these measurements show a stress-free sample to have a half-value time of 5500 min, the half value for a sample under a tensile load of 4.4 MPa is only ca. 10 min. Internal stresses and orientations have a similar effect to external stresses. The conversion of II

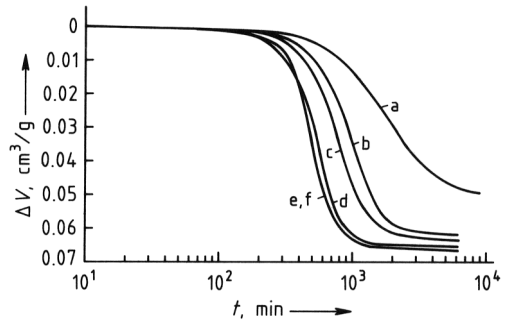


Figure 4. Time dependence of specific volume during transformation (II → I) of poly(1-butene) at 20 °C
a) Quenched; b) Crystallized for 200 min at 92 °C; c) Crystallized for 5700 min at 102 °C; d) Crystallized for 5600 min at 102 °C; e) Crystallized for 7500 min at 106 °C; f) Crystallized for 7200 min at 108 °C

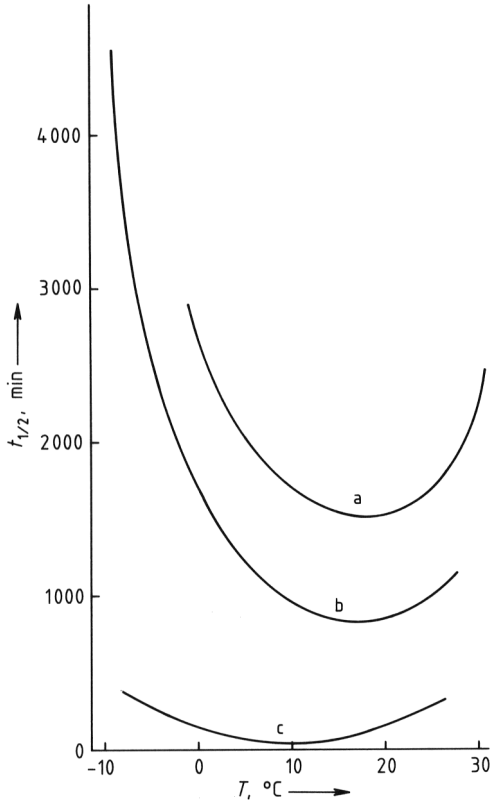


Figure 5. Temperature dependence of half-value time $t_{1/2}$ for the transition II → I
a) Pure poly(1-butene); b) Melt mixture of poly(1-butene) and polypropylene in the ratio of 1: 1; c) Poly(1-butene) with 30 % butyl stearate

to I is also accelerated by hydrostatic pressure [24]. The conversion rate can also be increased by certain additives, such as polypropylene or plasticizers (see Fig. 5) [8, 25, 26].

The molecular mass and the molecular mass distribution have virtually no effect on the conversion rate. However, the molecular mass does have significant influence on the rate of crystallization of modification II (Fig. 7). The crystallite and spherulite sizes of all crystal modifications can be varied over a broad range by modifying the cooling and crystallization conditions of the melt [16, 27, 28]. Surprisingly, the mean crystallite size and size distribution are not increased by subsequent tempering [27, 28]. This may be a reason for the low time dependence of certain mechanical properties (see Section 1.2.2).

The four modifications are distinguished analytically and characterized quantitatively

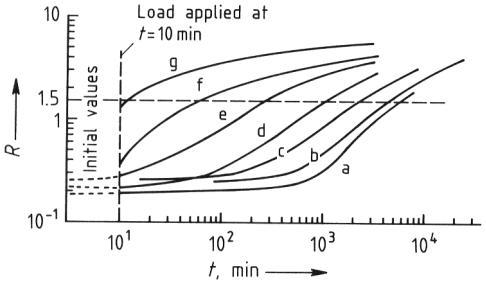


Figure 6. Poly(1-butene) conversion curves for modification II → I for various constant tensile stresses
R is the ratio of the IR extinction of modification I at 920 cm^{-1} to the extinction of modification II at 920 cm^{-1}. The half-value time $t_{1/2}$ (II → I) is reached when R has a value of ca. 1.5
a) 0 MPa; b) 0.12 MPa; c) 1.48 MPa; d) 1.91 MPa; e) 2.55 MPa; f) 2.95 MPa; g) 4.23 MPa

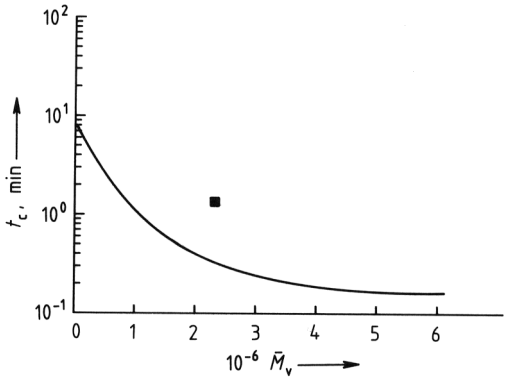


Figure 7. Crystallization time t_c of poly(1-butene) at 78 °C as a function of the viscosity-average molecular mass M_v
Curve: measurements on fractions, ■ unfractionated product

by a combination of X-ray, infrared, and differential thermal analysis [13–15, 29].

1.2.2. Application Properties

In normal processing operations, isotactic poly(1-butene) is heated to above its melting point. Therefore it is the unstable modification II which forms immediately after cooling, and is converted to the stable form I during storage or on application of mechanical stress. Since only the properties of form I are of interest from the point of view of applications, the statements below refer only to this modification.

In terms of density, melting point, and glass transition temperature, poly(1-butene) resembles polyethylene rather than polypropylene [30]. This similarity extends to cross-linked polyethylenes, although some of their properties naturally vary, depending on their cross-linking density [31]. Commercial material is around 40 % to 55 % crystalline. Since the crystallization rate is slow by comparison with polyethylene and polypropylene, superstructures which are of interest for applications can be obtained by the choice of cooling conditions [32]. Nucleators increase the rate of crystallization, leading in some conditions to a material that is somewhat more brittle at low temperature [32].

Mechanical Properties. Table 2 lists some mechanical properties of poly(1-butene), polyethylene, and polypropylene. According to the VDE hardness, poly(1-butene) is softer than polyethylene and polypropylene. However, the Shore hardness is virtually the same as for polyethylene. The surface gloss of components made from poly(1-butene) is similar to those made from polypropylene [33].

The rigidity of poly(1-butene) is relatively low. The flexural stress at conventional deflection and modulus of elasticity are lower than for polyethylene (Table 2).

Table 2. Hardness, rigidity and strength of low-pressure polyolefins [33]

Property	Test method	Polyethylene	Polypropylene	Poly(1-butene)
VDE hardness (60 s), MPa	VDE 0302	44 – 64	61 – 80	25 – 45
Shore D hardness	DIN 53 505	62 – 69	70 – 75	60 – 68
Flexural stress at conventional deflection, MPa	DIN 53 542	26 – 43	34 – 50	15 – 25
Modulus of elasticity, MPa	[a]	900 – 1200	1000 – 1500	500 – 900
Impact strength	DIN 53 453	no break	no break	no break
Notched impact strength, kJ/m^2	DIN 53 453	5 to no break	3 – 15	20 to no break
Brittle point, °C	ASTM D 746–57T	below − 70	+ 20 to − 5	− 10 to − 30

[a] Measured in Hooke range by bending tests.

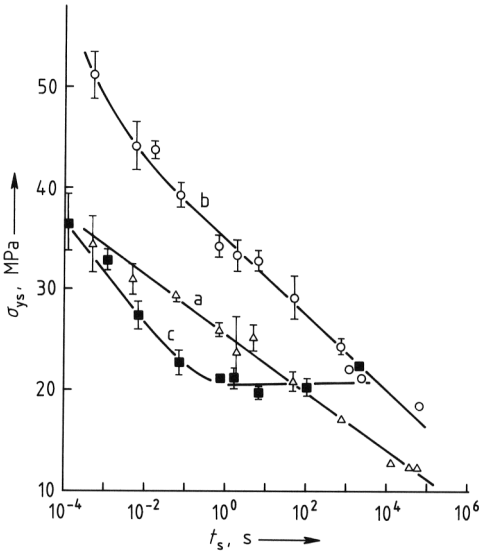


Figure 8. Yield strength σ_{ys}, measured in a tensile test at 22 °C, as a function of the stretching time t_s [34]
a) Polyethylene; b) Polypropylene; c) Poly(1-butene)

The impact strength and notched impact strength are significantly higher than those of polypropylene. Above 0 °C the values are similar to those for high molecular mass polyethylene, but at lower temperature they are inferior [33]. Nevertheless the low-temperature strength, as characterized by the brittle point, is relatively good [22, 33].

The stress – strain behavior of modification I differs noticeably from that of other polyolefins. The differences are not only in the shape of the stress – strain curve, which for industrial material has virtually no maximum [33, 34], but also in the dependence on time and temperature [35]. Figure 8 shows the yield strength σ_{ys}, measured in an uniaxial tensile test as a function of the stretching time t_s. Whereas the yield strength of polyethylene and polypropylene declines sharply with increasing stretching time, the values for poly(1-butene) remain virtually constant above 0.1 s. The good creep resistance and resistance to stress cracking of poly (1-butene) pipes subject to internal pressure [30] is due to the low time dependence of the mechanical properties.

Since this low time dependence of the mechanical characteristics is maintained at higher temperatures, poly(1-butene) is particularly suitable for hot-water pressure pipes [31, 36]. Figure 9 shows the burst hoop stress performance of poly(1-butene) pipe under

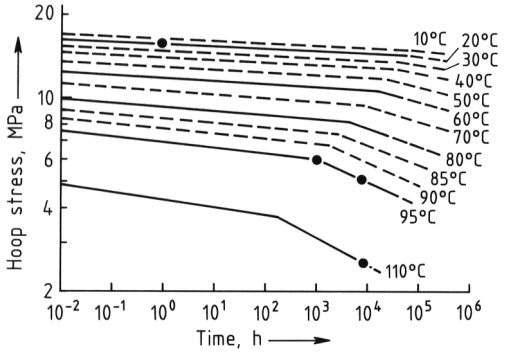


Figure 9. Burst hoop stress performance of poly(1-butene) pipes

internal pressure according to ISO-SEM (DIS 9080) [37].

As well as the outstanding resistance to stress cracking, the unusually good creep behavior is significant. The tendency to creep, i.e., to undergo plastic deformation below the yield point, is significantly lower than for other polyolefins, even at temperatures up to 100 °C [31, 33, 38]. This is also an essential requirement for the use of poly(1-butene) as a film material, particularly for the packaging sector [38].

Electrical Properties. The electrical behavior of poly(1-butene) does not differ significantly from that of polyethylene and polypropylene [33]. Apart from the usual quantities of stabilizers, it only contains residues of polymerization catalysts. Because of its good resistance to chemicals, outstanding resistance to stress cracking, and flexibility, poly(1-butene) is an important material for special applications in the cable and electrical industry.

Resistance to Chemicals and Gas Permeability. Because of its paraffinic structure, poly(1-butene) is resistant to most common chemicals such as acids, alkalies, salts, alcohols, and ketones. However, it swells or dissolves in hot aromatic and chlorinated hydrocarbons. It is less inert to aliphatic hydrocarbons than polyethylene and polypropylene and more prone to permeation [33, 39, 40]. A detailed table on the resistance of poly(1-butene) to chemicals is given in [38].

Permeability to gases and vapors, in particular water and oxygen, is comparable to that of polyethylene of similar crystallinity. Permeability to carbon dioxide, however, is higher [32].

1.3. Processing

Processing poly(1-butene) on conventional machines presents no problems. Because of its low crystallite melting point and particularly because of the rapid decrease in melt viscosity with increasing temperature, poly(1-butene) can be processed by extrusion (pipes, profiles, sheets), extrusion blow molding (hollow bodies), and injection molding (engineering products, sheathing for metals) [33]. Sheets made by extrusion or compression molding can be shaped hot or cold. A special feature is cold shaping of the relatively soft modification II. Articles shaped from this modification then become increasingly rigid as the conversion to modification I progresses.

1.4. Applications

Pipe. The major outlet for poly(1-butene) is currently in high-performance pipes, which exploit its creep resistance and long lifetime at elevated service temperatures, flexibility, light weight, corrosion resistance, and its ability to be heat welded [31]. It competes in plumbing and radiator heating applications with copper, where progress is mainly limited by resistance to replacing traditional working practises. In the underfloor heating pipe market it competes with other plastics such as cross-linked polyethylene and polypropylene.

The advantage of poly(1-butene) over other polymers in both these applications is its better ability to retain its mechanical and performance properties at elevated temperature. For instance a comparison of tangent modulus, yield stress, ultimate stress, and elongation at break within and transverse to the extrusion direction of the pipes shows a more balanced performance for pipes made of poly(1-butene) [41]. In the last decade the long-term properties of poly(1-butene) pipes and their lifetime at temperatures up to 120 °C have been studied [42] and the methodology for such long-term tests has been developed for various plastics [43–45].

Extrapolation methods give estimated lifetimes of 50 years at 70 °C [41]. A recent evaluation of pipes based on polymers as well as traditional materials, such as copper, favored poly(1-butene) [46].

The problem of oxygen diffusion in plastic piping systems, which was given as one explanation of corrosion in metal radiators, tanks, and boilers in the past, has been resolved by the use of multilayer pipes containing an oxygen-barrier layer and the addition of inhibitors to the circulating hot water [46].

Packaging. In the packaging sector, poly (1-butene) has become established in speciality film applications which require resistance to cooking temperatures, and in heat-seal layers for oriented polypropylene, which exploit the high compatibility of poly(1-butene) with polypropylene. The incompatibility of poly(1-butene) in blends with various polyethylenes and ethylene copolymers, such as low-density polyethylene, linear low-density polyethylene, high-density polyethylene and ethylene – vinyl acetate copolymers, forms the basis of peelable seals (see Fig. 10).

Peel-seal technology provides a robust pack, yet allows the consumer to open it easily without ripping or tearing. The key attributes of systems based on poly(1-butene) are the broad heat sealing range and the cohesive failure mechanism, which results in an aesthetically attractive package after opening. This is because cohesive failure propagates through the peel-seal layer itself due to the weaker intermolecular forces between the dissimilar materials, and results in clean uniform separation. Additional advantages are good clarity and a clean peel with no stringing [47, 48]. The more conventional system relies on delamination between layers as a result of adhesive failure and is also more difficult to control.

A correlation of peel-seal strength with blend composition and temperature is shown in Figure 11.

Manufacture of packaging film or sheet incorporating a poly(1-butene) peel-seal blend is possible by all the conventional processes such as film blowing or casting, sheet extrusion

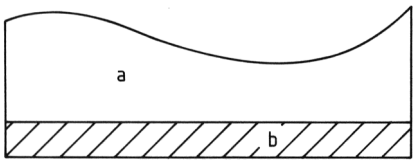


Figure 10. Cross section of a coextruded peel-seal layer on an LDPE substrate
a) LDPE substrate; b) Peel-seal blend LDPE in which incompatible poly(1-butene) particles are dispersed

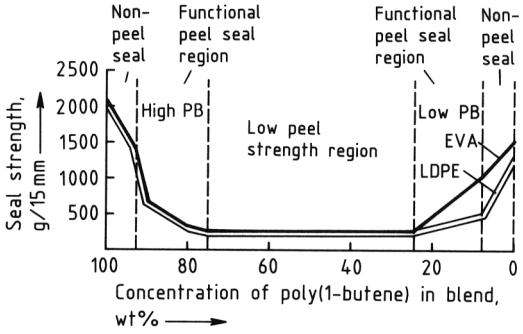


Figure 11. Dependence of peal-seal strength on blend composition

or coextrusion, extrusion or coextrusion coating, and lamination.

Poly(1-butene) peel seals are used in flexible packaging such as box liners for cereals, cake mixtures, and biscuits. In combination with more sophisticated barrier films, they are used for processed meat and vegetable packs. They are also used for packaging medical products.

An important growth area for peelable seals is in lids for rigid or semirigid containers. These range from the relatively simple yogurt, milk, and cream pots to individual-portion containers for microwave meals.

Two features of poly(1-butene) peel seals are considered to be of particular importance to the development of the next generation of high-performance packages. The first is their resistance to high-temperature cooking or sterilization. Often referred to as "retortability", this is an increasingly important feature both in the food and nonfood sectors. Poly(1-butene) peel seals can be made heat resistant by formulation with higher-temperature-resistant materials such as polypropylene or high-density polyethylene.

The second important feature is a distinct whitening effect when the seals are opened because of the characteristic cohesive failure mechanism. This gives a clear indication that the package has been opened or tampered with.

2. Polyisobutylene

2.1. Introduction

Industrially important polyisobutylenes can be divided into five groups:

1. Di-, tri-, and tetraisobutenes
2. Low molecular mass polyisobutylenes with $\bar{M}_n = 330 - 1600$
3. Medium molecular mass polyisobutylenes with $\bar{M}_n = 20\,000 - 45\,000$
4. High molecular mass polyisobutylenes with $\bar{M}_n = 75\,000 - 600\,000$
5. Ultra high molecular mass polyisobutylenes with $\bar{M}_n > 760\,000$

History. In 1925 LEBEDEW was the first to prepare polyisobutylene [49, 50]. He obtained products of varying chain length: liquids of oily to honey-like consistency; sticky, doughy materials; or solid, rubber-like materials.

Relatively uniform low molecular mass polyisobutylenes were first obtained by the company de Bataafse [51] by polymerizing isobutene at + 10 to − 10 °C in the presence of metal halides.

High molecular mass polyisobutylenes were first prepared by OTTO and MÜLLER-CUNRADI by polymerizing isobutene below − 10 °C in presence of volatile inorganic halides [52].

Polymerization Mechanism. Even in the early studies, two important aspects of the polymerization of isobutene were recognized: (1) catalysis with initiators of the Friedel – Crafts type, and (2) the inverse dependence of the molecular mass on the temperature. Subsequent studies led to the first formulations of a reaction mechanism [53].

According to these ideas, which essentially remain valid today, the reaction consists of the following steps:

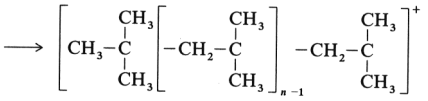
Initiation:

$$BF_3 + HX \longrightarrow H[BF_3X]$$

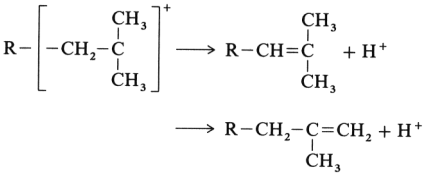
$$H[BF_3X] + \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}{=}CH_2 \longrightarrow \left[\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{CH_3-C}}}}\right]^+ [BF_3X]^-$$

Chain growth:

$$\left[\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{CH_3-C}}}}\right]^+ + n\,CH_2{=}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}$$



Chain termination:



The initiator is a Lewis acid (BF_3, $AlCl_3$) in combination with a proton source, which is usually present as a trace impurity, e.g., water, hydrogen, fluoride, or hydrogen chloride.

The competition between the growth reaction and chain termination determines the chain length (i.e., the molecular mass). Since the activation energy of chain termination is higher, increasing the polymerization temperature lowers the polymer chain length ($\ln M \sim 1/T$).

Meanwhile [54], a series of studies have appeared which have revealed a considerably refined view of the course of the reaction; yet a comprehensive mechanism which is consistent with all experimental findings is still lacking. Other studies deal with new initiators (aluminum alkyls; inorganic initiators such as acid clays and molecular sieves; Ziegler catalysts; high-energy radiation as an initiator). However, none of these new catalyst systems are used industrially. Industrial processes for polyisobutylene production still use the conventional Friedel – Crafts catalysts, boron trifluoride and aluminum chloride.

2.2. Production

2.2.1. Isobutene as Raw Material

The production of isobutene is described in → Butenes, Chap. 4, → Butenes, Chap. 5.

The purity requirements for the isobutene differ according to the type of polyisobutylene produced.

For the production of low molecular mass polyisobutylenes, butadiene-free C_4 fractions can be used, which apart from isobutene contain *n*-butane, isobutane, and *n*-butenes; stricter requirements are set for the isobutene for high molecular mass and solid polyisobutylenes.

During isolation of isobutene from C_4 fractions, an isobutene must be obtained which is as free from *n*-butene as possible. Primarily the content of *cis*- and *trans*-2-butene must be minimized. Both are powerful polymerization poisons and chain terminators. On the other hand, 1-butene can be used as a regulator in the production of high molecular mass and solid polyisobutylenes.

2.2.2. Low Molecular Mass Polyisobutylenes

Figure 12 shows the layout of the Cosden Petroleum continuous process, which can be regarded as a kind of fluidized-bed process.

A liquefied refinery-gas mixture with $C_1 - C_5$ hydrocarbons and an isobutene content of 3 – 50 % is freed from pentenes in a preliminary distillation, enriched in isobutene in an absorption column, washed in a wash tower with ca. 20 % caustic soda solution to remove sulfur, cooled in a heat exchanger, dewatered in a water separator, dried in silica gel towers and, after further low-temperature cooling in a second heat exchanger, introduced into the lower part of the reaction vessel. The polymerization takes place here at temperatures between − 43 and +16 °C and pressures of 0.1 – 0.35 MPa, so that the liquid phase is maintained. The catalyst used is a mushy suspension of finely divided (50 – 100 mesh) aluminum chloride in dry, liquid polyisobutylene, which is prepared in a mixing tank and supplied to the reaction vessel by a gear pump.

The quantity of aluminum chloride is about 10 – 20 % of the total hydrocarbons in the reaction mixture. The activity of the aluminum chloride is increased by adding 0.08 – 0.12 % hydrogen chloride (relative to aluminum chloride) as activator and accelerator. Water or chloroform have the same effect. The diameter of the reaction zone (A) and the feed rate of the catalyst slurry are so matched to each other that the aluminum chloride particles do not settle. Zone (B) of the reaction vessel, with a diameter two to six times that of zone (A), reduces the flow rate by a factor of about three to four, and functions as a calming zone. It merges into the settling zone (C), in which the aluminum chloride particles settle and are pumped off as a suspension through the offtake pipe which extends into zone (B). This catalyst slurry

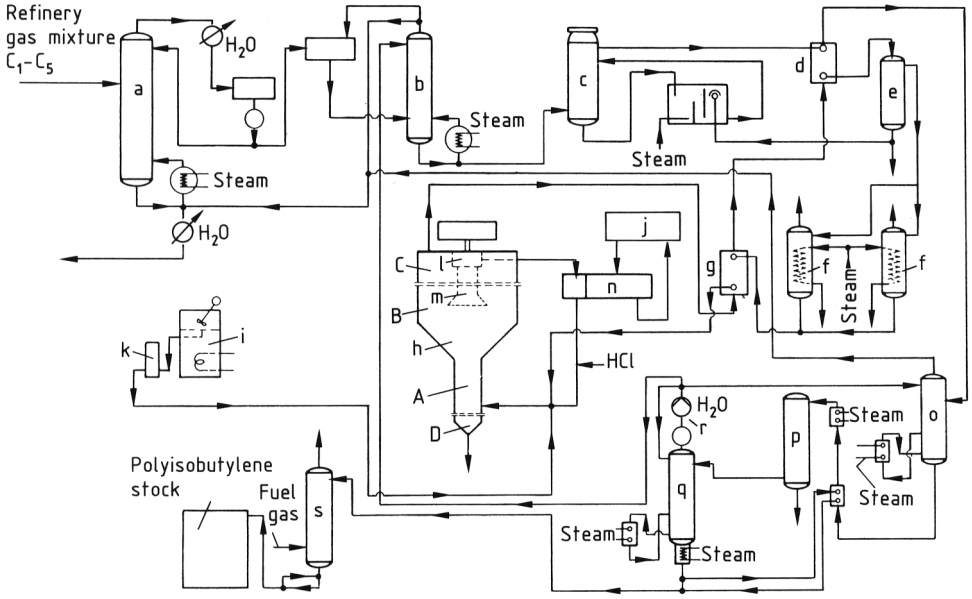


Figure 12. Cosden Petroleum process for producing low molecular mass polyisobutylene
a) Preliminary distillation; b) Absorption column; c) Caustic soda solution wash tower; d) Heat exchanger; e) Water separator; f) Silica gel towers; g) Heat exchanger; h) Reaction vessel; i) Mixing tank; j) Refrigeration unit; k) Gear pump; l) Pump; m) Offtake pipe; n) Cooler; o) Stripping column; p) Clay-filled tower; q) Distillation column; r) Water cooler; s) Pressure column; (For A to D, see text)

returns via a cooler into the reaction zone (A). Spent, aggregated catalyst is discharged at the bottom of the reaction zone.

A variant of the process uses separate vessels for polymerization and for catalyst settling.

From the settling zone flows a clear, light solution of liquid polyisobutylene in unreacted starting material. To improve the yield, the reaction mixture is pumped at least four times, but usually more than eight times, through the reaction zone (A). The clear polymer solution flows through the heat exchangers (g) and (d) to cool the isobutene and, after a water wash to remove acidic constituents, into a stripping column in which about one to two thirds of the inert, unreacted starting material is distilled off. After post-treatment of the concentrated polymer solution in a clay-filled tower, which may precede the stripping column, all volatile constituents of the starting material, especially unpolymerized isobutene, are vaporized in a distillation column and returned via a water cooler into the absorption column. In a further column, the last traces of volatile constituents are distilled from the liquid polyisobutylene at atmospheric pressure.

Aside from this process of the Cosden Petroleum Corp., others have been developed. For a description of the BASF and Exxon processes, see [55, pp. 94 – 97], [56].

2.2.3. Medium Molecular Mass Polyisobutylenes

The basic principle of the Exxon process for producing medium molecular mass polyisobutylenes (Fig. 13) [57] resembles the process for low molecular mass polyisobutylenes. However, a purer isobutene is used as starting material and pentane or hexane is added as solvent. The polymerization temperature must be lower to obtain a higher molecular mass. A mixture prepared from fresh isobutene, recycled isobutene, and hexane with 30 % isobutene and 70 % hexane is brought via a heat exchanger and a cooler to the polymerization temperature of – 40 °C and fed into the reaction vessel. Simultaneously, a slurry of 5 % finely divided aluminum chloride in hexane at a temperature of below – 23 °C flows into the reaction vessel.

The polymerization takes place with powerful stirring so that the aluminum chloride does

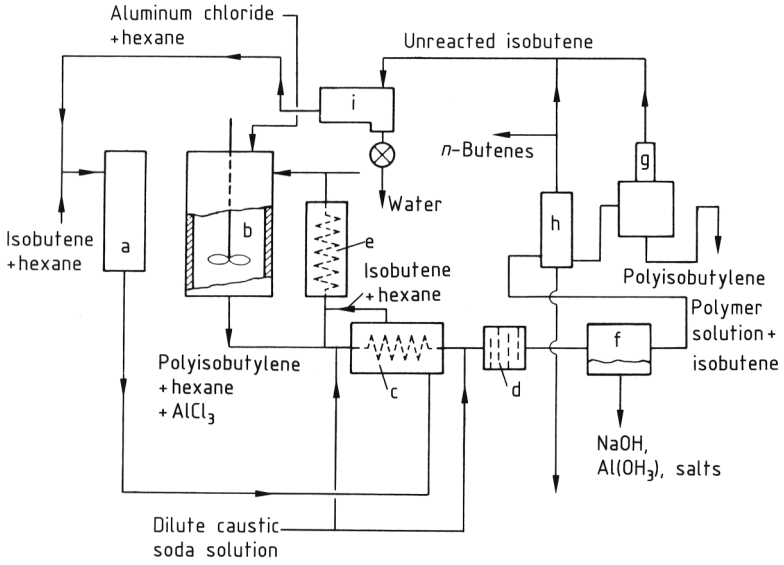


Figure 13. Exxon process for producing medium molecular mass polyisobutylenes
a) Mixing vessel; b) Reaction vessel; c) Heat exchanger; d) Nozzle mixer; e) Cooler; f) Settling tank; g) Degasser; h) Degassing vessel; i) Water separator

not settle, and external cooling. The throughput is 378.5 L/h isobutene – hexane mixture and 0.454 kg/h $AlCl_3$. The resulting solution of polyisobutylene in hexane with suspended aluminum chloride is drawn off, and after it has passed through a heat exchanger an excess of dilute caustic soda solution is added to destroy the catalyst. After thorough mixing in a nozzle mixer, the mixture of polymer solution and dilute caustic soda solution runs into a settling tank, where it forms two layers. The lower layer, consisting of dilute caustic soda solution, aluminum hydroxide, and salts, is discarded. The upper layer, consisting of a solution of polymer in hexane and unreacted starting material, is fed into a degassing vessel, in which the lower boiling components, principally unreacted isobutene, are stripped off at 99 °C and 0.35 bar. *n*-Butenes if present are removed from the system to avoid poisoning the reaction. In a second degasser, the last traces of volatile constituents are removed. The unreacted isobutene is condensed, dewatered in a water separator, and added as recycle isobutene to the starting mixture.

In its batch process for producing medium molecular mass polyisobutylenes, BASF makes use of the chain-terminating effect of diisobutene [55, pp. 88 – 91], [58].

In a conical reaction vessel with good thermal insulation, pure, dry liquid isobutene and pure, dry liquid ethylene as internal coolant are mixed in the ratio 1 : 2. The quantity of diisobutene added to the isobutene depends on the desired molecular mass of the polyisobutylene. A sufficient quantity of gaseous boron trifluoride for the polymerization is then carefully introduced into the mixture. The mixture starts to boil, and the evaporating ethylene removes the heat of polymerization. The polyisobutylene remains behind in the reaction vessel in the form of a white foam. It is removed from the vessel and freed from all volatile constituents in a degassing machine.

2.2.4. High Molecular Mass Polyisbutylenes

BASF and Exxon have developed continuous processes for producing high molecular mass solid polyisobutylenes [55, pp. 97 – 104].

BASF Belt Process. In the belt process, the conical polymerization vessel of the BASF batch process described above is replaced by a continuous polymerization belt (Fig. 14) [59].

A gently inclined trough-shaped continuous steel belt, 16 – 18 m long and 50 cm wide, runs

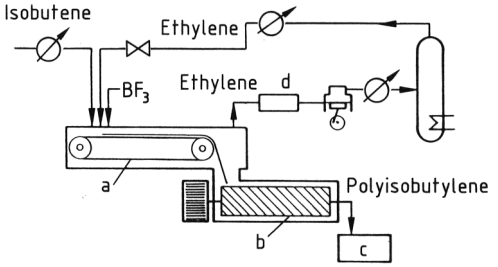


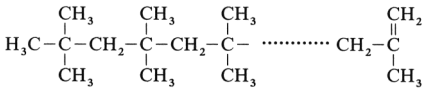
Figure 14. BASF belt process for high molecular mass polyisobutylenes
a) Steel belt; b) Twin-screw machine; c) Cooling and compounding; d) Purification

in a gastight housing over a drive roller and a tension roller. A mixture of pure, dry liquid ethylene and isobutene in the ratio 1 : 1 flows through a pipe onto one end of the steel belt. From a second pipe a solution of boron trifluoride in the same quantity of ethylene as is mixed with the isobutene is added. The quantities of cocatalyst and chain-length regulator [55, pp. 82 – 91]depend on the desired molecular mass. The polymerization starts instantly. It continues at the boiling point of the liquid ethylene (−103.7 °C) and in a short time is ended. The heat of polymerization is absorbed by the evaporation of ethylene. The vaporized ethylene is recycled via a purification and liquefaction system. The polyisobutylene is stripped from the steel belt with a scraper and degassed and homogenized in a twin-screw machine.

Exxon Process. Polyisobutylene is also produced by the process used for butyl rubber (see → Rubber, 4. Emulsion Rubbers) [60].

2.3. Structure

The polymer obtained by cationic polymerization has the following structure:



In the stretched state polyisobutylene gives a well-developed X-ray diffraction pattern which shows that 8 monomers with their 16 methyl groups are arranged in an almost regular helix around the principal axis, forming one translation period of the chain after 3 rotations [61].

It has been shown by IR spectroscopy that the principal end group is the methylene group [62].

2.4. Properties

The rubber-like polyisobutylenes, like all other polyisobutylenes, owe their physical and chemical properties to their paraffinic character. This results in a low glass transition temperature, low specific thermal conductivity, very low water vapor permeability, high dielectric strength, high resistivity, low dielectric constant, low dielectric loss factor, high ageing resistance, and rot resistance as well as an unusually wide-ranging chemical resistance. The good solubility in hydrocarbons and chlorohydrocarbons and the insolubility in alcohols, esters, and ketones also result from the paraffinic nature of the polyisobutylenes.

At room temperature, polyisobutylenes are resistant to dilute and concentrated hydrochloric acid, sulfuric acid, phosphoric acid, chlorosulfonic acid, phenolsulfonic acid, naphthalenesulfonic acid, formic acid, acetic acid, ammonia, potassium hydroxide solution, caustic soda solution, as well as aqueous calcium hydroxide, aqueous hydrogensulfite, copper sulfate solution, potassium permanganate solution, hydrogen peroxide, chromic acid, and dichromate solution. Above 80 °C, concentrated sulfuric acid causes carbonization and concentrated nitric acid causes decomposition.

Some properties of polyisobutylene that are independent of the degree of polymerization are as follows:

Density, g/cm^3	0.92
Volume coefficient of thermal expansion at 20 °C, K^{-1}	6.3×10^{-4}
Specific heat, kJ kg^{-1} K^{-1}	2.0
Glass transition temperature (DSC), °C	− 60
Thermal conductivity, W K^{-1} m^{-1}	0.19
Refractive index n_{20}^{D}	1.51
Dielectric constant ϵ_r (50 Hz, 20 °C) DIN 53 483	2.2
Dielectric loss factor tan δ (50 Hz, 20 °C) DIN 53 483	$\leq 5\times10^{-4}$
Water vapor permeability, g m^{-1} h^{-1} mbar^{-1}	2.5×10^{-7}

Further properties are listed in Tables 3 and 4.

Table 3. Properties of polyisobutylenes dependent on degree of polymerization, exemplified by Oppanol B (BASF)

Oppanol	Viscosity, Pa · s		Intrinsic viscosity $[\eta]$, cm^3/g	Number-average molecular mass $\bar{M}_n$ *
	at 20 °C	at 100 °C		
Low molecular mass				
B 3	25	0.2 ± 0.02		820
Medium molecular mass				
B 10	5.0×10^4	2.2×10^2	27.5 – 31.2	24 000
B 12			34.0 – 39.1	30 000
B 15	5.0×10^5	3.0×10^3	45.9 – 51.6	40 000
High molecular mass				
B 50	1.5×10^8	8.0×10^5	113 – 143	120 000
B 80			178 – 236	180 000
B 100	3.6×10^8	6.7×10^7	241 – 294	250 000
B 120			295 – 361	300 000
B 150			416 – 479	425 000
B 200	1.5×10^{11}	1.0×10^9	551 – 661	600 000
Ultra high molecular mass				
B 246			> 770	> 760 000

* $\bar{M}_n = {}^{0.94}\sqrt{\frac{[\eta]10^3}{2.27}}$

Table 4. Behavior of Oppanol B100 and B200 towards solvents (weight increase by swelling in wt % at room temperature)

Storage time	3 1/2 days		30 days	
Oppanol type	100	200	100	200
Acetone	1.7	1.5	3.9	3.6
Alcohol	0.1	< 0.1	0.35	0.2
Benzene	400	400	500	500
Butyl acetate	34	24	34	37
Carbon tetrachloride			soluble	
Chlorobenzene			soluble	
Chloroform			soluble	
Cyclohexane			soluble	
Cyclohexanone	9	7.4	24	18
Dimethylformamide	0.6	0.6	2.1	1.7
Ether	200	100		
Ethyl acetate	18	12	21	20
Ethylene glycol	0.6	1.4	0.9	2.0
Gasoline			soluble	
Glycerol	0.6	0.6	1.0	1.6
Hydrogen sulfide			soluble	
Isobutanol	1	0.3	2.4	0.7
Isooctane			soluble	
Methanol	< 0.1	< 0.1	0.1	0.1
Methyl acetate	8	5	7.8	10
Methylene chloride	200	200	200	200
Mineral oil			soluble	
Nitrobenzene	3	2	5.4	4.5
Olive oil	4	1.5	4.2	3.1
Paraffin			soluble	
Paraffin oil			soluble	
Tetrahydrofuran			soluble	
Toluene			soluble	
Water	< 0.1	< 0.1	0.1	0.1
Xylene			soluble	

2.5. Uses and Processing

The low molecular mass polyisobutylenes are used as plasticizing components for modifying sealants. In addition, they are used for producing insulating oils.

After further functionalization with polar groups, the low molecular mass polyisobutylenes are used as dispersants in fuel and lubricant additives.

The medium molecular mass polyisobutylenes are chiefly used as raw materials for adhesives and sealants. Due to their very low water-vapor permeability, permanently flexible sealants based on polyisobutylene – carbon black are important in the production of sealed double glazing units. Combinations of polyisobutylene with paraffin or wax are used for impregnating paper and board.

The breaking point of bitumen is lowered and its flexibility improved by addition of medium molecular mass polyisobutylene.

High molecular mass polyisobutylenes are used as blends with medium molecular mass grades for producing self-adhesive compounds, e.g., for adhesive plasters.

Because of their good tolerance by the skin, filled polyisobutylenes are used to produce sealing rings for colostomy bags.

Unstabilized polyisobutylenes are used in chewing gum bases.

Blending polyisobutylenes with paraffin oil and inorganic fillers gives permanently elastic sealants, which are usually marketed in extruded form as strip or round-profile string.

High molecular mass polyisobutylenes with high filler contents are used to produce sheets that are used for sealing buildings against groundwater and seeping water as well as for protection against corrosion and radiation. Conductive and magnetic polyisobutylene sheetings are also available.

The cold impact resistance of polypropylene is improved by blending with polyisobutylene. The sensitivity of polyethylene to environmental stress cracking is reduced by adding polyisobutylene.

Polyisobutylenes are compatible with natural and synthetic rubber and with reclaimed rubber.

Solutions of ultra high molecular mass polyisobutylenes ($\bar{M}_n > 760\,000$) in organic solvents even in low concentrations ($<< 1\,\%$), have pronounced viscoelastic properties and distinctly increased extensional viscosity.

Polyisobutylene can be compounded on a roll mill or in an internal mixer. Compounding is carried out at 140 – 170 °C to minimize thermal degradation of the polyisobutylene.

2.6. Commercial Products

BASF, Germany:	Oppanol B 3 (liquid); Oppanol B 10, B 12, B 15 (flexible resin-like, tacky); Oppanol B 50, B 80, B 100, B 120, B 150, B 200, B 246 (solid, rubber-like)
Exxon, United States:	Vistanex LM-MS, LM-MH (flexible resin-like, tacky); Vistanex MM L-80, MM L-100, MM L-120, MM L-140 (solid, rubber-like)

In addition, a range of low molecular mass polyisobutylenes are marketed.

2.7. Copolymers [63]

Isobutene – isoprene – divinylbenzene terpolymers are produced under conditions similar to those used for butyl rubber, with the addition of divinylbenzene. Unlike butyl rubber, they exhibit no cold flow.

Isobutene – styrene copolymers behave similarly to polyisobutylenes or butyl rubber.

The copolymers have no economic significance.

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Polycarbonates

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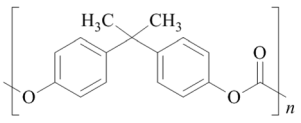
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1. Introduction

The first aromatic polycarbonates were prepared by Einhorn in 1898, based on resorcinol or hydroquinone, by reaction with phosgene in a pyridine solution. The resorcinol-based polycarbonate decomposed at 190°C, while the hydroquinone-based resin had a melting temperature above 280°C. In 1902, Bischoff and von Hedenström obtained the same products, using diphenyl carbonate instead of phosgene.

Aliphatic polycarbonates were prepared by Carothers already in 1930. The crystalline products had a melting temperature below 100°C and resulted from the reaction of diethyl carbonates and glycols. In 1941, the Pittsburgh Plate Glass Company (PPG Industries, Inc.) introduced a product based on the allyl ester of diethylene glycol carbonate cross-linked with peroxides to give a colorless, transparent material (Section 2.4).

Meanwhile, Schnell at Farbenfabriken Bayer (now Bayer MaterialScience AG) and independently Fox at General Electric Company were trying to create a polymer with superior properties to poly(ethylene terephthalate) (PET), which had been developed in 1946. Schnell turned his attention to polycondensation reactions using 2,2-bis(4-hydroxyphenyl)propane, known as bisphenol A (BPA), which was already being used for the production of epoxy resins. Consequently, in 1953 he discovered 2,2-bis(4-hydroxyphenyl)propane polycarbonate (**1**), also termed bisphenol A polycarbonate [24936-68-3] (BPA-PC), which still is the economically most important polycarbonate. The first trial products had melting temperatures of 225–230°C. Simultaneously, Fox had concentrated his activities on polyester resins. By chance he discovered a transparent material, which was identified as BPA-PC as well [1–4].



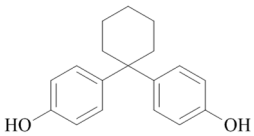
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The polymer was first produced industrially and introduced to the market in Europe in 1958 by Farbenfabriken Bayer and in the USA in 1960 by Mobay Chemical Corporation (a former joint venture of Monsanto Company and Bayer AG) and General Electric.

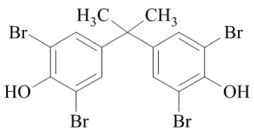
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The great commercial success of BPA-PC is due to its unique combination of key properties: extreme toughness, outstanding transparency and high heat distortion resistance. In addition, polycarbonate has a broad potential as blend partner with other polymers such as polyesters (PET, PBT) and rubber-modified polymers (e.g., ABS, ASA).

In addition to bisphenol A, many other bisphenols have been converted to (co)polycarbonates [5–11]. However, very few of them have been used as (co)monomers in industrial polycarbonate production. Examples include 1,1-bis(4-hydroxyphenyl)cyclohexane [843-55-0] (bisphenol Z, BPZ) (**2**) and 2,2-bis(3,5-dibromo-4-hydroxyphenyl) propane [79-94-7] (tetrabromobisphenol A, TBBPA) (**3**):



2

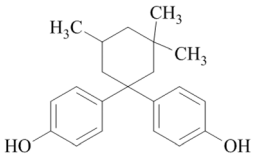


3

Formerly, BPZ was used as a comonomer for bisphenol A in special polycarbonates for cast film production. It improved the solubility and reduced the crystallization tendency of the polycarbonate during the casting procedure.

TBBPA has been cocondensed with bisphenol A in order to increase the flame resistance of the polycarbonate. Also, its pure oligocarbonate has been used as flame retardant in special polycarbonate compositions (Section 2.3).

In the late 1980s, 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane [129188-99-4] (BP-TMC) (**4**) has become important for the development of highly heat resistant polycarbonates [12], which have been on the market since 1990.



4

BPA-PC can be modified not only by cocondensation of bisphenol A with other bisphenol monomers, but also by cocondensation with blocks of other polymers.

Polysiloxane blocks [10–15] have become industrially important in this respect (Section 2.2).

2. Properties

2.1. Bisphenol A Polycarbonate

Industrial BPA-PCs for injection molding and extrusion have weight-average molar masses M_w of 18 000–35 000. Compared to other thermoplastics, the degree of polymerization of BPA-PC is relatively low. The number of repeating units in commercial products is only approximately 70–140. Therefore, it is astonishing, that this low degree of polymerization leads to the extraordinary toughness and heat resistance which are typical of polycarbonate. The toughness and impact strength of BPA-PC are considerably higher than those of other amorphous single-phase thermoplastics [e.g., polystyrene, poly(methyl methacrylate)].

The tough fracture of BPA-PC depends on its molecular mass. With increasing molar mass, the tough-to-brittle transition is shifted to lower temperatures. For general purpose grades, brittle fracture is observed below −10°C [16]. Special grades, such as impact-modified polycarbonates and siloxane-modified copolycarbonates, keep their toughness down to temperatures of approximately −40°C or even lower.

The high transparency of BPA-PC and its high heat resistance ($T_g \approx 150$°C, which is 50°C above that of polystyrene) are very important for its uses and applications. Long-term stability of BPA-PC against heat aging in air can be achieved up to 120°C or more, depending on the test method.

Table 1. Typical properties of BPA-PC (Makrolon 2805, Bayer MaterialScience)

Property	Test standard	Value
Tensile modulus, MPa	ISO 527-1, -2	2400
Yield stress, MPa	ISO 527-1, -2	66
Yield strain, %	ISO 527-1, -2	6.2
Stress at break, MPa	ISO 527-1, -2	70
Nominal strain at break, %	ISO 527-1, -2	> 50
Impact strength at 23°C, kJ/m^2	ISO 179-1eU	unbroken
Impact strength at −30°C, kJ/m^2	ISO 179-1eU	unbroken
Notched impact strength at 23°C, kJ/m^2	based on ISO 179-1eA	75
Notched impact strength at 23°C, kJ/m^2	based on ISO 179-1eA	16
Ball indentation hardness, N/mm^2	ISO 2039-1	115
Vicat softening temperature (50 N; 120°C/h), °C	ISO 306	146
Temperature of deflection under load (1.8 MPa), °C	ISO 75-1,-2	125
Coefficient of linear thermal expansion, K^{-1}	ISO 11359-1,-2	6.5×10^{-5}
Thermal conductivity (23°C; 50 % R.H.), W m^{-1} K^{-1}	ISO 8302	0.2
Burning behavior at 0.75 mm	UL 94	Class V-2
Glow-wire flammability test (GWFI) at 0.75 mm, °C	IEC 60695-2-12	850
Oxygen index (method A) in %	ISO 4589-2	28
Relative permittivity (100 Hz/1 MHz)	IEC 60250	3.1/3.0
Dissipation factor (100 Hz/1 MHz)	IEC 60250	$5 \times 10^{-4}/90 \times 10^{-4}$
Volume resistivity, Ω m	IEC 60093	10^{14}
Surface resistivity, Ω	IEC 60093	10^{16}
Electrical strength at 1 mm, kV/mm	IEC 60243-1	34
Moisture absorption (23°C, 50% R.H.), %	analogous to DIN 53 495-1 L	0.15
Refractive index (Procedure A)	ISO 489	1.586
Luminous transmittance (clear transparent materials) at 1 mm, %	ISO 13468-2	89
Density, kg/m^3	ISO 1183-1	1200

BPA-PCs are soluble in chlorinated hydrocarbons (e.g., chloroform, dichloromethane, chlorobenzene) and nonhalogenated solvents (e.g., pyridine, *m*-cresol). They are insoluble in water, alcohols, and (cyclo)aliphatic hydrocarbons.

BPA-PCs are generally amorphous and thus transparent when processed by injection molding or melt extrusion.

By special means, however, crystallinity can be induced to a certain extent, which can be observed by X-ray diffraction. For this purpose, heating at temperatures between the softening point and the crystalline melting point (ca. 260°C), treatment with solvents (e.g., acetone, toluene), and stretching of fibers or films is applied [6].

Decomposition of polycarbonate depends on temperature, processing conditions and formulation. As a rule of thumb, processing temperatures far beyond 320°C should be avoided for general-purpose grades.

BPA-PC has a low flammability (oxygen index 26). Its flame resistance can be improved considerably by adding small amounts of flame retardants (Section 2.3).

Although the mechanical properties continue to increase above $M_w = 35\,000$, BPA-PC with molar mass greater than 40 000 cannot be processed due to its extremely high melt viscosity. In the past, such high molecular mass polycarbonates, however, have been cast from solution into films with desirable properties. See also → Films.

At molecular masses below 18 000, mechanical and thermal properties (e.g., toughness, elongation at break, heat resistance) deteriorate sharply.

Amongst others, mechanical and thermal properties of BPA-PC are influenced by its end groups. Introducing alkyl phenols instead of phenol as chain terminator leads to improved properties [12, 17].

Some typical properties of a standard BPA-PC are given in Table 1.

2.2. Modified Bisphenol A Polycarbonate (Copolymers)

BPA-PC exhibits tough fracture and outstanding notched impact strength above −10°C.

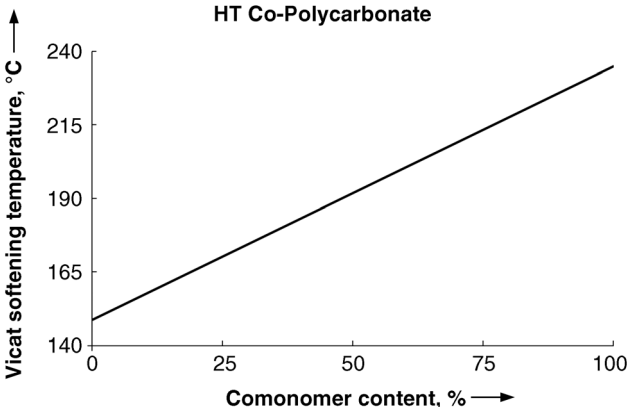
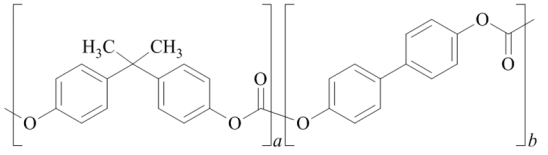


Figure 1. Vicat temperature as a function of comonomer content

Below −10°C however, the tough fracture changes to a brittle fracture and the notched impact strength is considerably reduced.

The notched impact strength at low temperatures can be improved by different means. For example, the copolycarbonate of BPA and 4,4′-dihydroxydiphenyl (DOD) **5** exhibits outstanding toughness at low temperatures, partially improved environmental stress cracking behavior (ESC), and, due to the larger amount of aromatic segments, extended flame retardant properties.



5

Of commercial importance is the incorporation of polysiloxane blocks into the polymer backbone [10, 13]; this shifts the tough–brittle transition to below −40°C. A siloxane content of 2–10 wt% produces a satisfactory effect. Polydimethylsiloxane blocks are coupled to the polycarbonate via the hydroxyphenyl end groups (**6**).

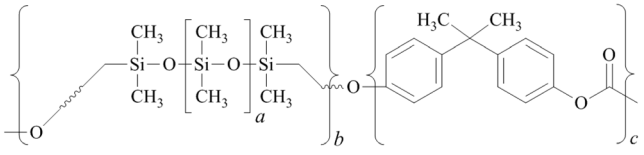
Corresponding products are commercially available, for example Lexan EXL grades from Sabic Innovative Plastics.

Partial replacement of the carbonate groups in BPA-PC by terephthalate or isophthalate groups leads to aromatic polyester carbonates with higher heat distortion resistance[14, 15].

Nowadays, this class of polyester carbonates has been almost completely replaced by high-heat copolycarbonates (PC-HT), e.g., Apec grades from Bayer MaterialScience and Lexan XHT grades from Sabic Innovative Plastics. In these polymers, a second bisphenol is used as comonomer in the polycondensation reaction with BPA. Glass temperatures up to 240°C can be achieved. For example, by using 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane (BP-TMC) [12], the heat resistance can be adjusted.

Insofar, commercially available products reflect technical requirements, usually expressed by the Vicat temperature, which is directly linked to the amount of comonomer (Fig. 1).

These copolycarbonates are transparent, tough, and colorless, even at high glass transition temperatures [12]. They exhibit better heat and weatherability properties (less yellowing



6

than the polyestercarbonates). Their melt viscosities are comparable with those of polysulfones, polyethersulfones, and polyetherimides having comparable glass transition temperatures.

Several other copolycarbonates have been developed in the past to meet specific requirements such as improved scratch resistance or reduced birefringence. However, none of these products has reached large-volume production so far. Some were already withdrawn from the market.

Besides linear polycarbonates, branched grades have been developed for certain applications. They can be obtained, for example, by cocondensation of multifunctional phenols such as 1,1,1-tris(4-hydroxyphenyl)ethane (THPE) with BPA. The resulting polymers show structural viscosity and provide higher melt stiffness [10, 12, 18–21]. They are particularly suitable for melt extrusion. They have a reduced viscosity under the shear stress in the extruder, and after leaving the extruder nozzle the melt is highly viscous and thus sufficiently stable. Complicated extrudates, such as multiwall sheets, can be produced with high accuracy. The structural viscosity of melts of these polycarbonates is also important for the production of large hollow articles by extrusion blow molding (e.g., 5-gallon water bottles).

2.3. Bisphenol A Polycarbonate with Additives

Most of the additives discussed in this section are described in detail elsewhere (→ Plastics, Additives).

Mold-Release Agents. The addition of small amounts (< 1 wt%) of mold-release agents to the polycarbonate improves the mold release of complicated parts [10]. Most commonly used are fatty acid esters of higher alcohols, especially pentaerythritol tetrastearate (PETS) or glycerol monostearate (GMS).

See also → Release Agents.

Flame Retardants. In the past, flame resistance of BPA-PC has been increased by incorporating small amounts of tetrabromobisphenol A [10]. In rare cases, tetrabromo-BPA oligocarbonates themselves are still used as additives to improve flame retardancy. For ecological reasons, the use of brominated flame retardants is rapidly decreasing.

Today, specific additives are commonly used. For example, flame resistance is significantly improved by the addition of small amounts (< 1 wt%) of special salts, such as potassium perfluoro-*n*-butane-1-sulfonate or potassium diphenylsulfone-3-sulfonate [22–25]. The tendency to form flaming drips after ignition can be reduced by adding small amounts (< 1 wt%) of polytetrafluoroethylene (PTFE) [26]. To achieve higher surface quality (gloss), PTFE–SAN batches are used. However, these additives lead to nontransparent and opaque compounds.

For transparent applications, only small amounts of the above-mentioned salts can be used. Recently, highly branched, transparent polycarbonates with improved flame-retardant properties have been introduced into the market.

Light Stabilizers. Ultraviolet light, especially in combination with atmospheric oxygen and moisture, causes decomposition of BPA-PC. Decomposition starts with a photo-Fries rearrangement, which leads to the formation of salicylates, followed by benzophenones [10, 11]. These structures absorb visible light in the short-wavelength region and are thus responsible for the yellowing of polycarbonates. Stabilization against degradation by UV light (i.e., against yellowing) is important for exterior uses and applications and can be achieved by adding small amounts (< 1 wt %) of derivatives of benzotriazole, hydroxyphenyltriazine, or benzylidene-bis-manonate [11].

Reinforcement. Glass fibers are generally used to improve rigidity, stiffness, and dimensional stability. In addition, the coefficient of thermal expansion is reduced.

For polycarbonate compounds different kinds of glass fibers are available, such as chopped strands, long fibers, milled fibers, and glass bubbles. Typical ranges cover 10–35 wt%. [10, 11, 27]. As expected, however, glass fibers reduce impact and notched impact strength significantly.

For extreme stiffness, carbon fibers are used.

Recently, polycarbonate composites, e.g., with glass or carbon fiber fabric, are gaining more interest.

Heat and process stabilizers (e.g., organic phosphites or phosphonites) can be added to the polycarbonate to prevent thermal oxidation during manufacturing and processing at high temperature [10]. They react with hydroperoxides formed by autooxidation of the polymer backbone, act as oxygen scavengers, and prevent degradation as they get oxidized. These stabilizers are called secondary antioxidants. They are often used in combination with primary antioxidants like sterically hindered phenols to further improve the performance of the polycarbonate composition.

Colorants and Pigments. A wide range of colored transparent or opaque polycarbonates is obtained by using appropriate amounts of soluble organic dyes or inorganic pigments. For transparent applications, only small amounts (less than 1%) of soluble organic dyes can be used. Special colorants are also approved for medical applications and food contact.

When using inorganic pigments, such as TiO_2, $BaSO_4$ or talc, resulting compositions are translucent or opaque. Concentrations may be up to 15%, for example for highly reflecting white compounds. Dependent on their concentration, these insoluble substances lead to a reduction of mechanical properties, especially impact and notched impact strength as well as elongation at break.

Miscellaneous Additives. Special additives are used for dedicated applications. For example, organic and inorganic infrared absorbers are applied to improve heat management in cars with transparent PC sunroofs. They also fulfill strict absorption requirements of polycarbonate grades for welding goggles or laser marking of injection molded parts. Antistatic agents prevent parts from dust attraction and thermal conductive compounds are gaining importance with respect to heat dissipation of LED lighting assemblies.

Blowing agents (e.g., 5-phenyltetrazole and phenyldihydroxo-oxadiazonone) can be added during thermoplastic processing into moldings to obtain low-weight foamed structures (→ Foamed Plastics, Section 4.15 Polycarbonate Foams) [10].

2.4. Aliphatic Polycarbonates

Besides the thermoplastic aromatic polycarbonates, a group of various aliphatic systems is gaining more and more economical importance. Different molecular architectures are used in various technical applications.

The polymerization of diethylene glycol bisallylcarbonate (ADC) in presence of a peroxy initiator leads to a highly cross-linked system (CR-39, PPG Industries, Inc.). Due to its outstanding optical properties, it has been used for ophthalmic lenses and sunglasses for decades.

Telechelic aliphatic polycarbonates with a molar mass of approximately 2000 g/mol, obtained in a melt polycondensation process of hexanediol with diphenyl carbonate, are used as raw materials for coatings and thermoplastic polyurethanes (TPU). The carbonate groups provide better stability against hydrolysis than the ester group in polyester diols. The coatings exhibit excellent outdoor weatherability properties. They can be applied from solution or in the form of aqueous dispersions.

A special group of new raw materials are polyether carbonate diols in which carbon dioxide is used as carbonate source (sustainability) [1].

Furthermore, high molecular mass aliphatic PCs for injection molding have been developed. In these materials, isosorbide is employed as biobased comonomer. The resulting products, e. g., Durabio from Mitsubishi Chemical Corporation, combine enhanced optical properties with good mechanical and thermal characteristics. The property profile is intermediate between poly(methyl methacrylate) (PMMA) and BPA-PC.

3. Blends

3.1. General

Initial approaches to using BPA-PC as a blend partner date back to the late 1960s. At that time acrylonitrile–butadiene–styrene (ABS) was the preferred candidate, and the resulting blends

saw increasing growth rates in the following decades. Nowadays the most important and commercially established blends are those with ABS graft polymers [28–30] and those with poly(butylene terephthalate) (PBT) or poly(ethylene terephthalate) (PET) in combination with impact-resistance modifiers such as ABS [28, 29, 31]. Of the produced polycarbonate, an estimated more than 20% is used in polycarbonate blends. Both classes of blends add technical benefits to the key properties of BPA-PC. Compared to ABS, BPA-PC–ABS blends have improved heat resistance. They also exhibit good light stability and surface quality. Compared to BPA-PC, processability and high toughness, especially at low temperature (tough fracture in the notched impact strength test) are typical benefits. Blends of BPA-PC with poly(alkylene terephthalates) and impact-strength modifiers have high heat distortion resistance and high toughness, even at low temperature. Their resistance to gasoline and other solvents is better than that of BPA-PC. Both classes of PC blends offer high flexibility in designing properties in wide ranges and thus allow tailor-made products according to customer requests.

3.2. PC–ABS Blends and PC–ASA Blends

BPA-PC is a linear polymer with a low rate of crystallization. Thus, it is regarded as an amorphous polymer with a glass transition temperature T_g of approximately 145°C. Its maximum use temperature is approximately 130°C and, because of its excellent thermal oxidative stability, this almost coincides with its continuous use temperature (125°C). BPA-PC is noted for its excellent impact resistance due to the high segmental mobility of the polymer chain (gamma transition at–100°C [32]).

ABS, on the other hand, is a highly ductile material with a Vicat softening temperature of about 100°C. Typical ABS materials consist of mixtures of a rubber-free SAN copolymer and a SAN-grafted polybutadiene rubber. The low T_g of polybutadiene rubber (below–70°C) is the reason for excellent notched impact strength of this class of polymers, especially at low temperatures (below −20°C). In acrylic–styrene–acrylonitrile polymers (ASA), the SAN-grafted polybutadiene rubber is replaced by SAN-grafted poly(butyl acrylate) rubber with a T_g of ca. −40°C. The benefit of ASA compared to ABS is better UV stability due to the absence of double bonds in the polymer backbone that are sensitive to oxidation.

Polycarbonate blends with ABS have been successful because they combine typical PC properties, e.g., heat distortion, ductility and flame retardancy with those of ABS, e.g., ductility at low temperature, processability, and improved chemical resistance. The mixture of PC and ABS is physically stable because the carbonate group of the PC and the nitrile group of the SAN matrix interact [33] and provide just enough compatibility for a useful blend. Figure 2 shows the typical morphology of a PC–ABS blend with PC as matrix component and SAN copolymer and ABS graft polymers as disperse phase.

Optimum interaction between the polymers is obtained for SAN copolymers containing 25–30 wt% acrylonitrile [33]. Intrinsic compatibility can be enhanced through addition of a third component containing ester groups, e.g., PMMA or poly(butylene terephthalate) (PBT) [34], an effect that can be explained in terms of mutual miscibility.

These PC–ABS blends offer higher heat distortion temperature than ABS, combined with good processing characteristics [35–37]. Depending on PC–ABS ratios, the Vicat softening temperature of the blend can be varied between 100°C (ABS level) and 140°C (PC level). Typical technical data of these blends are summarized in Table 2. All products show ductile impact behavior at–30°C. Polycarbonate blends with ABS resins have been successfully used in automotive interior and exterior applications [35, 38].

PC–ASA blends offer a better resistance towards UV light and weathering compared to PC–ABS. Applications include instrument panels, electrical distribution boxes, and kitchen exhaust hoods [39]. Because this advantage is achieved at the expense of poorer mechanical properties, their share of the total market of PC–styrenics blends is relatively small.

Typical unfilled PC–ABS blends have a tensile modulus in the range of 2000–2300 MPa.

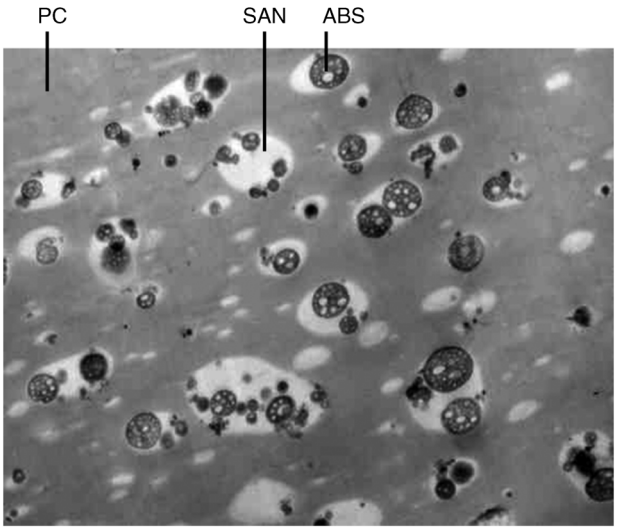


Figure 2. Electron micrograph showing the morphology of a flame-retardant PC–ABS blend (Bayblend, Bayer MaterialScience)

Higher values can be reached by adding mineral fillers (e.g., talc) or glass fibers. With 20% talc a tensile modulus of nearly 5000 MPa and with 20% glass fiber more than 7000 MPa can be obtained.

In general BPA–PC suffers from stress-crack sensitivity coupled with poor chemical resistance. The latter prevents PC from being used in automotive applications where frequent contact with gasoline and oils would ruin its mechanical and thermal properties. Therefore it is one of the most important targets of blending technology to improve this drawback. Chemical resistance of BPA-PC can be improved by blending with ABS or ASA or with semicrystalline polyester resins. PC–ABS blends are less sensitive against aromatics, ketones, esters, and hydrocarbons compared to BPA-PC itself.

PC–ABS blends provide good paintability and better UV stability if PC is the continuous phase [40–43]. The addition of UV absorbers to PC–ABS blends improves the protection of ABS against the damaging effects of UV light. PC–ASA blends provide superior weather resistance, which makes them suitable for outdoor applications.

Table 2. Typical technical properties of PC–ABS blends with different ratios (Bayblend, Bayer MaterialScience)

	Test	Units	PC:ABS 45:55	PC:ABS 60:40	PC:ABS 70:30
Melt viscosity (MVR* 260°C/5 kg)	ISO 1133	cm^3/10 min	12	12	12
Injection molding					
melt temperature	ISO 294	°C	260	260	260
molding shrinkage (parallel and transverse)	ISO 294-4	%	0.55–0.75	0.55–0.75	0.55–0.75
Tensile test	ISO 527-1, -2				
modulus		MPa	2100	2200	2300
stress at break		MPa	49	52	55
strain at break		%	>50	>50	>50
Izod notched impact strength	ISO 180/A				
23°C		kJ/m^2	40	45	48
−30°C		kJ/m^2	36	41	38
Heat distortion					
HDT A	ISO 75-1, -2	°C	95	100	109
Vicat B/120	ISO 306	°C	112	120	131

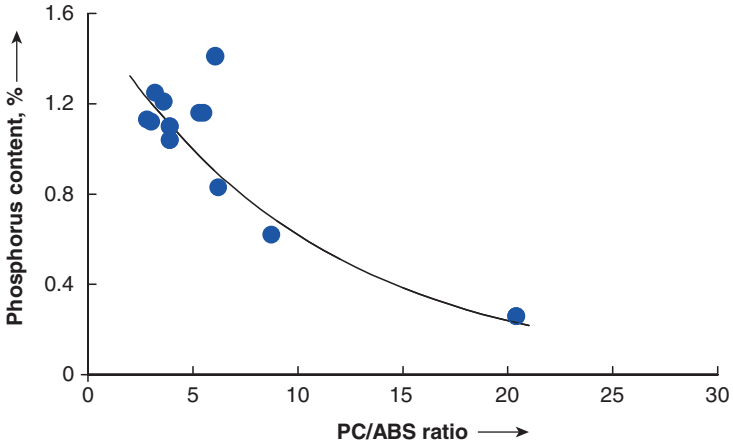


Figure 3. Phosphorus content as function of PC–ABS ratio to achieve a rating of UL 94 V-0 at 1.6 mm (Bayblend, Bayer AG)

Flame-retardant PC–ABS blends were introduced in the 1980s. Due to their balanced properties, they have found widespread applications as housing materials in the electrical and electronics industry, where UL 94 V and UL 94 5V are the most important fire safety specifications. These materials exhibit good electrical insulating capability. Major applications are instrument panels [44] and business equipment housings [45]. Today, flame-retardant PC–ABS blends are firmly established in the market as an independent product category and have reached at least an equal share compared to non-flame-retardant PC–ABS blends.

Until the late 1980s, bromine compounds and antimony oxide as a synergist were the state of the art as flame retardants for PC–ABS. As a result of the ecological discussions in Europe, especially in Germany and the Nordic countries, many global producers of computers and related equipment are seeking to obtain so-called eco-Labels such as the Swedish TCO 99 and German Blue Angel Marks, which require bromine- and chlorine free material for the housings [46]. Aryl phosphates such as triphenyl phosphate (TPP) as well as oligophosphates such as resorcinol bis(diphenyl phosphate) (RDP) and bisphenol A–bis(diphenyl phosphate) (BDP) are utilized as effective flame retardants [47]. Additionally, small amounts of PTFE (< 0.5%) are incorporated as antidripping agents.

The amounts of aryl phosphate necessary to reach a rating of V-0 according to UL 94 at 1.6 mm thickness depends on the PC–ABS ratio. Due to the different inherent flame retardancies of polycarbonate and ABS, the PC–ABS ratio determines the amount of phosphate flame retardant. The higher the PC–ABS ratio, the lower the phosphorus concentration required for a rating of V-0 (Fig. 3).

In the early 1980s, TPP was the most commonly used flame retardant in PC–ABS blends. Due to its high phosphorus content of 9.5% and its volatility, it is highly effective. However, under certain processing conditions TPP tends to migrate to the surface (plate out). To overcome this disadvantage, TPP was replaced by the much less volatile BDP [47]. Mixtures of TPP and oligophosphates such as BDP are also effective and advantageous for certain applications [48].

In order to meet UL 94 V-0 rating at a thickness less than 1.5 mm and to follow the trend to thinner molded articles, certain inorganic materials (i.e., talc, aluminum oxides) are added to improve the effectiveness of the phosphates [49].

Depending on PC/ABS ratios in these flame-retardant blends, the technical properties can be modified over a wide range. Vicat softening temperatures between 90 and 135°C can be achieved. Mechanical properties can be designed between ductile materials with high

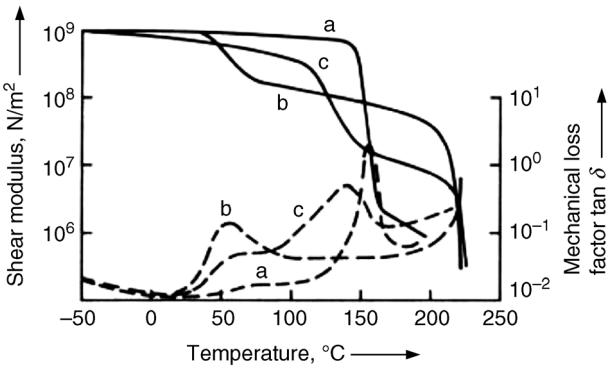


Figure 4. Dynamic mechanical properties of PC (a), PBT (b), and PC-PBT blends (55:45) (c): shear modulus (---) and mechanical loss factor (—) as function of temperature

notched impact strength and materials with tensile modulus up to 7000 MPa (by reinforcement with mineral fillers or glass fibers).

3.3. PC–Polyester Blends

The most important polyesters which are commercially used as blend partners for PC are poly (ethylene terephthalate) [25038-59-9] (PET) and poly(butylene terephthalate) [24968-12-5] (PBT). PBT crystallizes within 1–3 s, whereas PET crystallizes within 15–20 s. PBT's higher melt flow and faster crystallization lead to a shorter cycle time. The advantage of PET over PBT is its higher melt temperature (256 vs. 226°C).

PC–polyester blends combine the benefits of polyesters (chemical resistance due to crystallinity) with those of BPA-PC (impact resistance, also at low temperatures). In the resulting blends the stress-crack sensitivity of PC can be improved significantly. In order to achieve balanced mechanical properties, PC–polyester blends can also contain ABS or methyl methacrylate–butadiene–styrene (MBS) grafted impact modifiers. The most attractive market for PC–polyester blends is automotive applications such as high-class front-end modules and other exterior car body parts. Front-end modules made of PC–polyester blends can withstand an impact with a speed of 5 km/h at high and low temperature.

Blends of PC with polyesters are based on a partial miscibility of the two components in the amorphous phase [50–52]. Thermal and dynamic mechanical analysis shows a sharp T_g transition for PC at about 150°C [10], and a sharp melting point at about 225°C with a broad glass transition for PBT due to the presence of crystalline and amorphous portions of the polyester. The partial miscibility of PC and PBT is indicated by a shift of the PC's T_g to about 140°C in a PC/PBT blend.

Blending the two resins results in a complex co-continuous morphology. Resistance towards chemicals (e.g., oils and lubricants) is significantly enhanced compared to PC. However, the impact properties of these blends are still insufficient for automotive applications. Modification with a rubber compound (frequently core–shell impact modifiers such as MBS or ABS) solves this problem [53 → Polymer Blends].

The key to morphology control and thus mechanical properties is control of transesterification. Care should be taken to prevent reactions (Fig. 5) catalyzed by residual polycondensation catalysts present in the PBT [54–56]. Addition of proprietary stabilizer packages is commonly practiced. In addition, processing temperatures of 270–290°C should not be exceeded.

PC–PET blends have similar properties to their PBT analogs [44, 57, 58]. The lower crystallization rate of PET allows the development of transparent materials for use as housing materials in medical applications by virtue of

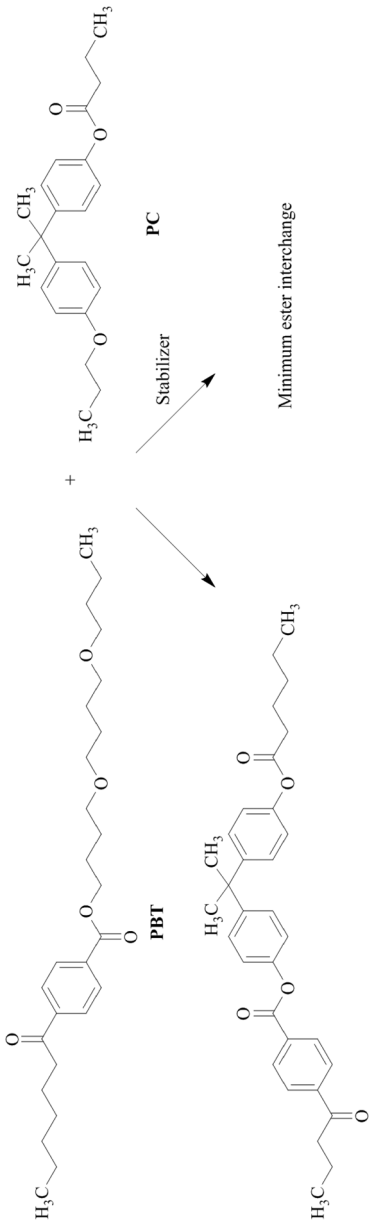


Figure 5. Ester interchange reaction between PC and PBT

their good dimensional stability, clarity, and low water absorption. The products have better chemical resistance than PC and are impact-modified to give acceptable low-temperature impact performance.

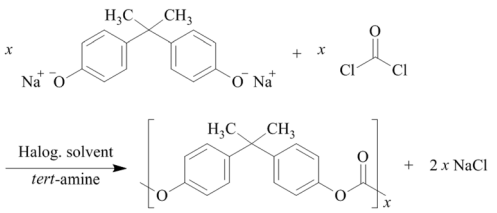
Over the last decade, the portfolio of PC–polyester blends has been extended to mineral- and glass fiber reinforced versions with a tensile modulus of more than 3000 MPa, and to flame-retardant products with V-0 rating according UL 94 V standard (halogen- or phosphorus-based flame retardants).

Highly transparent blends of BPA-PC with amorphous polyesters (e.g., Xylex resins from Sabic Innovative Plastics) exhibit good flowability for thin-wall applications and their impact strength is similar to polycarbonate. In comparison to PC, these products provide better resistance against certain chemicals and solvents.

4. Production

4.1. Interfacial Polycondensation

Interfacial polycondensation is currently used for the industrial production of polycarbonates [6, 9, 10]. Bisphenol A is treated with phosgene at 20–40°C in a two-phase mixture consisting of an aqueous, alkaline phase and an immiscible organic phase:



BPA is first dissolved in the aqueous phase as sodium bisphenolate and phosgene is dissolved in the organic phase, which generally consists of chlorinated hydrocarbons (e.g., dichloromethane). The reaction occurs at the organic–inorganic interface to produce carbonate oligomers, which then enter the organic phase. A 10–20 mol% excess of phosgene (relative to the amount of bisphenol A) is

generally used because a small proportion of the phosgene is hydrolyzed. The hydrolysis products (NaCl and Na_2CO_3) are dissolved in the aqueous phase. The polycondensation is catalyzed with tertiary aliphatic amines (e.g., triethylamine). During the polycondensation reaction the aqueous phase is kept at alkaline pH values (9–14).

Monofunctional phenols, e.g., phenol and 4-*tert*-butylphenol, are added as chain terminators to control the molecular mass. These compounds then form the terminal groups of the polycarbonate bound via carbonate groups.

Polycarbonate production can be carried out batchwise in stirred tanks or continuously in cascades of stirred tanks or in tubular reactors in which the organic and aqueous phases are finely distributed by shear forces. After completion of the polycondensation, the aqueous alkaline phase, which contains sodium chloride and sodium carbonate, is separated from the organic phase (e.g., by centrifugation). The organic phase is washed with dilute acid (e.g., hydrochloric or phosphoric acid) to neutralize the alkali. The organic phase is finally washed free of electrolytes with demineralized water. All wash stages are generally performed in separators.

Industrially, various processes are used to isolate the polycarbonate from solution. The most important are:

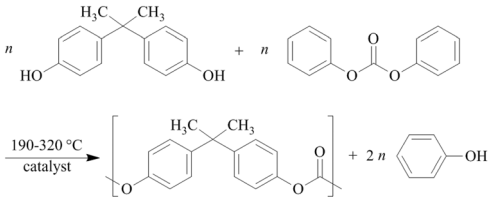
1. Precipitation with nonsolvents for polycarbonate (e.g., heptane)
2. Precipitation by introduction of the solution into hot water and subsequent evaporation of the polycarbonate solvent
3. Evaporation of the solvent in extruders or strand evaporators

Both precipitation processes lead to powders, from which granules are obtained by pelletizing extruded strands. If the polycarbonate is isolated by evaporation of the solvent (chlorinated hydrocarbon) in an extruder, the granulate is obtained directly.

Stabilizing or modifying additives are generally fed into the polycarbonate during extrusion at the end of the production process or in a subsequent compounding step.

4.2. Melt Transesterification

Diphenyl carbonate is transesterified in a solvent-free melt with bisphenol A to form polycarbonate [6, 10]:



During this process phenol is split off and removed by distillation. Stirred tanks, helical reactors, or screw reactors (extruders) can be used. The reaction is usually catalyzed with very small amounts of, e.g., alkaline or phosphonium salts at high temperatures and reduced pressure. The temperature is initially low and the pressure is slightly reduced (e.g., 200°C at 20 kPa). During the course of reaction the temperature is raised to ca. 290–310°C and the pressure is further reduced to 0.1 kPa. Towards the end of the reaction the temperature must be high enough to maintain a sufficiently high melt flow and the pressure must be as low as possible to remove all of the eliminated phenol from the viscous melt. The polycarbonate is finally spun in the form of strands and granulated.

The melt transesterification process was the first industrial process for the production of polycarbonate. It is recently again gaining more and more importance due to the development of phosgene-free production processes [12]. Reaction of carbon monoxide with alcohols in the presence of catalysts gives dialkyl carbonates that can, in turn, be treated with phenol to form diphenyl carbonate [12]. The latter can then be treated with bisphenol A, as described above, to produce polycarbonate by melt transesterification. Catalyst systems and the purity of raw materials have been further improved. In contrast to interfacial polycondensation, defect structures are formed during the melt condensation (Fries rearrangements). Nevertheless, the obtained

product quality of general purpose grades is comparable.

By applying a dedicated catalyst, even branched grades are accessible without adding a separate branching agent as comonomer, which is not possible in the interfacial process.

5. Processing

Prior to processing, BPA-PC must be dried to a residual moisture content of less than 0.02 wt%. For extrusion and high-quality applications such as transparent goods or optical discs, the residual moisture content should not exceed 0.01 wt %. The use of a dry-air dryer with a dew point below −30°C and a drying time of 3–4 h at 120°C are recommended. For optical applications or glazing products, the drying time may be nearly twice as long. The dried granules should be conveyed with dried air from the dryer to the injection molding machine in order to avoid the absorption of moisture.

For extruded goods with high output volume such as sheets, foregoing drying is not practical. In these cases, moisture is removed during plasticization by a degassing unit in the extruder.

All modern plastics injection molding machines are suitable for polycarbonate processing. Machines with three-section screws with a length/diameter ratio of 20:1 to 23:1 and a screw/channel depth ratio of 2:1 to 2.5:1 are recommended. The heating systems and regulating instruments must be designed for operation up to at least 350°C or up to 400°C (for high-heat copolycarbonates).

Melt temperatures vary from 280 to 320°C, depending on the grade. The mold temperature is usually 80°C.

Due to their different heat resistance, processing temperatures for high-heat copolycarbonates or polycarbonate blends need to be adapted correspondingly (Table 3).

For extrusion, high-viscous or structurally viscous branched polycarbonates are particularly suitable (Section 2.2). Hollow articles, films, sheets, profiled sections, pipes, and strands are examples of extruded products.

Extruder screws should have a length/diameter ratio of 25:1 (three-section screws) or 33:1 (extruders with degassing unit).

Table 3. Typical melt and mold temperatures for the injection molding of polycarbonates

	Melt temperature, °C	Mold temperature, °C
BPA-PC	280–320	80–120
PC-HT	330	100–140
PC–ABS blends	240–280	60–80
PC–polyester blends	240–280	60–80

In general, very high temperatures or long residence times of the polymer melt in the molds should be avoided as this may lead to deterioration due to a decrease in molecular mass.

Semifinished products such as sheets, films, and profiles can also be made from BPA-PC. Slow cooling in air or water is required to obtain low-stress products. Depending on size and output, the cooling temperature can vary from 40°C for thin profiles up to 130°C for massive sheets.

The temperature at the nozzle outlet is ca. 230–300°C, depending on melt viscosity and output volume.

Films and sheets of BPA-PC can be subjected to thermoforming. BPA-PC can also be polished to a high gloss, coated, printed, embossed, or vacuum-metallized and bonded with solvents. Two-pack adhesives (mainly polyurethane adhesives) are suitable for bonding BPA-PC parts to one another and to other materials. Parts made of BPA-PC may also be joined to each other by vibration, ultrasonic, friction-heated tool, and hot-gas welding. The polymer can also be machined, sawed, and drilled.

6. Applications

Electrical/Electronics Sector. The electrical/electronics sector is the classical and a major user of BPA-PC [4, 12, 59] because of the special combination of properties: outstanding electrical insulation, good flame retardance, high heat resistance, excellent toughness, dimensional stability, and transparency. Moreover, these properties are largely independent of temperature and atmospheric humidity.

The trend to minimize the size of electrical devices requires parts with higher heat resistance, because at the same time wall thickness must be reduced. This leads to an ongoing substitution of ABS or acrylate styrene acrylonitrile (ASA) materials by polycarbonate.

Due to higher demands regarding flame resistance, PC–ABS blends are used to a large extent, as the utilized flame retardants meet current directives such as the European Waste Electrical and Electronic Equipment (WEEE), the Restriction of the Use of certain Hazardous Substances (RoHS), and the IEC 60335-1 standard for domestic appliances.

Typical applications include housings for mobile devices such as cell phones, notebooks, and tablets, but also for flat-panel displays, TV sets, and other appliances. Other applications include smart meters, lighting, power supplies, and distributor equipment such as lamp sockets, multiple contact strips, relay parts, power plugs, safety switches, components for electronic calculators, fluorescent tube sockets, current meters, and winding supports.

A relatively new application for BPA-PC is injection-molded complex-shaped lenses and optics for light-emitting diodes (LEDs), which are energy-saving and long-lasting illuminants. Besides the requirement for high transparency, BPA-PC is used due its better thermal and dimensional stability compared to PMMA, as well as its lower water absorption. Special light-management solutions can also be implemented with PC films, such as light decoupling films for organic LEDs (OLEDs) and light-guiding lenticular films having a fine network of lenses that combine the light points of individual LEDs into a lighting band.

Automotive Sector. In automobiles, BPA-PC reduces weight, increases the efficiency and durability of assemblies, and improves the looks of a vehicle due to greater freedom of design compared to glass or metal. Important properties are the high impact strength, heat resistance, and transparency. BPA-PC is used, for example, in headlight covers and reflectors, as well as radiator grills (PC–PET).

In the last years, replacement of metal parts by metallized plastic is gaining more and more attention. This leads to a significantly higher quality ranking of plastics, providing them with a premium surface appearance. The different metallization processes being applied result mainly from the adhesion of the metal to the layer.

Of special importance in this field are PC–ABS blends, which enable electroplating processes through oxidation of the rubber component and subsequent activation of the surface.

BPA-PC and PC-HT can also be metallized by vacuum metallizing and sputter coating. These methods use evaporated metal, which is condensed on the cold surface of the plastic in a vacuum chamber, resulting in a dense film having a high reflectivity (see also → Plastics Processing, 3. Machining, Bonding, Surface Treatment).

Metallized surfaces require high-quality raw materials as well as sophisticated injection molding processes, since surface defects are easily detectable.

While decorative metallic coatings enable thermoplastic parts to function as economical, lightweight alternatives to metals, functional metallic coatings provide EMI shielding, circuit paths, or high reflective surfaces. Major applications are reflectors in automotive lighting systems, e.g., head lamp lenses, radiator grills, and others.

PC–ABS blends have become very important in dashboards, where good heat resistance, high toughness and tough fracture (splinter-free fracture) are required at low temperatures [10, 12, 60]. Blends of polycarbonate and PET or PBT and impact strength modifiers are used in premium front-end modules, where low-temperature impact strength (down to −40°C) and resistance to gasoline are necessary. The latter property is affected favorably by partially crystalline polyesters.

In particular the need to reduce fuel consumption and the corresponding vehicle emissions as well as the trend towards electromobility have given new impetus to lightweight construction with BPA-PC. Hereby, automobile glazing with transparent polycarbonate is particularly attractive, because it permits solutions that are up to 50% lighter than glass–an important fact when considering the size of panorama roofs or complete tailgate modules. Similarly, part of the high battery weight in electric vehicles can be

compensated. In addition, the good thermal insulation of PC compared to glass panes reduces the energy required to heat the vehicle interior, as shown by recent developments. This conserves the battery, and extends the range of the electric vehicle. Concepts like electromobility also lead to new application possibilities for PC that are remote from the vehicle. One example is the housing of charging stations, for which a PC-ABS blend is already in series production. For automobile interiors, formable PC hardcoat films are gaining ground for the production of decorated high-gloss components.

Building and Construction. Wide application areas for solid and multiwall sheets of PC continue to be architecture, traffic, safety, and transport. The transparency, extreme toughness, and moderate price of polycarbonates make them suitable for window panes and roofing. Multiple-wall sheets of polycarbonate combine optimum impact strength, good light transmission, light weight, and thermal insulation with minimal material consumption (low wall thickness) [61]. Therefore, polycarbonate is a suitable material that meets the increasing demands for higher energy efficiency in buildings. Sheets made of BPA-PC have become firmly established in industrial buildings such as railway stations and sports stadiums, but are as well used as roofs for greenhouses, safety glazing in ice hockey arenas and as windows for telephone booths and gymnasiums.

Optical Information Storage Systems. Although continuously declining, a very large amount of PC is used for the production of optical data storage devices such as CD, DVD, and Blu-ray discs. These storage devices are also used as supplements for advertising and special offers in magazines with high print runs. Moreover, thanks to their robustness and reliability, they are still popular as media for safe storage of personal data [4, 59].

The use of BPA-PC for optical information storage systems is described in [10–12].

The main requirements fulfilled by polycarbonate are high transparency, low birefringence, good mechanical and dynamic stability, good heat distortion resistance, and excellent flow properties.

Miscellaneous Uses. Further important areas of use of polycarbonates include office equipment (casings, covers, keyboards) and extruded, coextruded or laminated films and sheets (credit cards, cover sheets, capacitor sheets), foams (electrical distributor boxes, housings), medical applications (blood oxygenators, hemodialysis separating membranes in dialyzers, sterilizable equipment), packaging (water tanks, food containers), domestic applications (electric razors, sink units), and photographic or optical applications (camera cases, lenses, optical fibers).

Another application area for PC that is growing in importance is the use in furniture. The transparency lends it an appealing optical weightlessness. Special grades have been developed in order to meet the requirements for flame resistance for use in public buildings, such as fire standards UNI 8456, 8457, 9174, and 9175 [59].

Economic Aspects In 2013, global PC consumption amounted to some 3.62×10^6 t. Global PC consumption for blends grew more than sevenfold between 1990 and 2013, from about 85 000 to 615 000 t/a, corresponding to an annual increase of almost 10%. This exceptional growth was due to automotive applications and the boom in the IT sector.

Estimates predict a worldwide mid-term growth of the PC market in the medium one-digit percentage range. Hereby, the main contribution will come from countries in the Asia-Pacific region (primarily China) and South and East Europe, but also from new applications. The amount of PC used in various sectors is shown in Table 4 [59].

Table 4. Polycarbonate application split in 2013 (source: Bayer MaterialScience estimation, various press announcements)

Application	Market share, %
Electrical, information technology & communications	33
Mobility (mainly automotive)	16
Optical discs	15
Construction (primarily panels)	15
Consumer products	15
Appliances	4
Medical	2

Table 5. Main polycarbonate producers and trade names (source: Bayer MaterialScience estimation, various press announcements)

Producers	Main trade names
Bayer MaterialScience	Makrolon®, Apec®, Bayblend®, Makroblend®
Sabic Innovative Plastics	Lexan®, Cycoloy®
Styron (formerly Dow)	Calibre®, Pulse®
LG Chem (formerly LG-Dow)	Lupoy®
Teijin	Panlite®, Multilon®
Mitsubishi*–Sam Yang	Iupilon®, Novarex®, Trirex®, Triloy®
Idemitsu	Tarflon®, Tariloy®
Chi Mei	Wonderlite®, Wonderloy®
Samsung Cheil	Infino®, (Staren)®, Hopelex®
Kazanorgsintez	Green Tower®
Unigel Plasticos (formerly Pdb)	Durolon®

* Mitsubishi Gas, Mitsubishi Chemical, Mitsubishi Engineering Plastics.

The largest PC consumer in 2013 was the Asia-Pacific region with about 60%. Some 23% were accounted for by countries in the EMEA region (Europe, Middle East, and Africa). The NAFTA area contributed 15% to overall consumption, and Latin America 2%.

The world's largest single PC market is China, which accounted for 36% of global consumption in 2013. Apart from Japan, responsible for 6% of worldwide PC sales, also the other Asian countries have significant PC markets (about 18% of sales).

The number of PC producers is not large, but is growing steadily. Bayer MaterialScience and Sabic are still the two largest producers with each about 27% of global capacities. Other major producers include Mitsubishi (12%), Teijin (10%), and Styron (6%).

The expansion of PC capacities in Asia is proceeding steadily; first Asian producers are starting to export PC to Europe and the USA. Table 5 lists main producers and trade names.

7. Recycling

Even at the end of life phase of a whole product life cycle (including production and use phase), the polycarbonate (PC) in a product is still a valuable resource which can be recovered. Recovery options for PC include mechanical recycling (regaining PC as secondary raw material), feedstock recycling (regaining building blocks for chemical synthesis), and recovery of the embedded energy as a substitute for virgin fossil fuels.

In the past, several recycling technologies have been developed for PC itself as well as for special applications in which PC is used. The majority of published information in this field concentrates on three main areas.

The first area deals with the recovery of PC from optical data storage applications like CDs. Processes and machines for the removal of coatings and metallization are mainly the subject of patents. Examples range from sand blasting [62], crushing and milling [63], to chemical (acidic, basic, oxidative) washing procedures [64]. Material produced in that way can be directly re-used, e.g., for blending with other polymers [65], or further processed to improve its quality, e.g., by an increase in molecular weight [66].

The second area focuses on chemical methods to recover monomers such as BPA or aromatic carbonates as feedstock. A number of methods for the degradation of PC exist, e.g., by hydrolysis, alcoholysis (including glycolysis), or aminolysis [67]. In this field, current research focuses on optimizing the efficiency in recovering valuable building blocks. Especially ways of degrading PC without the need for solvents are subject to current research. For example, degradation with supercritical/critical media or "mild" catalysis has been reported in this field [68–70].

The third area of research is thermal decomposition, i.e., pyrolysis, of PC. Heating waste PC under defined conditions can yield

synthesis gas and liquid hydrocarbons for synthesis or fuel applications. Here, increasing the pyrolysis efficiency and limiting the number of byproducts are future challenges which could be solved by newly developed catalysts [67].

However, all recycling operations rely on a certain input amount and quality of waste material which typically depends on the waste management system that is established locally for different waste streams. The quality of PC parts can range from clean and separate (e.g., production waste, so-called post industrial waste) to polluted and comingled collections (e.g., post-consumer mixed-waste bins). The recycling of PC in post-consumer waste remains a challenge due to the partially low PC content and the high demands on sorting technology.

8. Toxicology and Environmental Aspects

Harmful effects of polycarbonates are not known if properly handled [71]. Polycarbonates have not proved toxic when included in rat feed at a concentration of 6% [72].

The toxicity of the gases produced by combustion of flame-resistant polycarbonates (according to DIN E 5346/37) is similar to or lower than that of wood, wool, or cotton [73]. For safety precautions, exhaust gas and wastewater control, and toxicology of phosgene, see → Phosgene.

Several states have regulated the use of polycarbonate for the manufacture of articles which are intended to come into contact with foodstuffs. In the USA, the FDA has published the requirements for polycarbonate resins in its 21 Code of Federal Regulations (CFR), § 177.1580. In the European Union (EU), the Commission Regulation (EU) No. 10/2011 of 14 January 2011 (and its amendments) specifies the requirements for "plastic materials and articles intended to come into contact with food".

The (German) Federal Institute for Risk Assessment (BfR) issues recommendations for the use of certain materials in food-contact applications, e.g., Recommendation XI for "polycarbonates and mixtures of polycarbonates with other polymers or copolymers".

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Polyester Resins, Unsaturated

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ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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1. Introduction

Unsaturated polyester resins (abbreviated as UP resins according to DIN 7728, part 1) undergo cross-linkage to form thermosetting plastics (DIN 16 945). Most UP resins are medium- to low-viscosity, liquid solutions of unsaturated polyesters in copolymerizable monomers (usually styrene) as cross-linking agents.

Unsaturated polyesters are formed by polycondensation of unsaturated and saturated dicarboxylic acids with diols. UP resins are hardened (cured) or cross-linked by free-radical polymerization with initiators (e.g., peroxides) and accelerators at normal temperature (10 –40 °C), or with peroxides alone above 80 °C. The unsaturated groups of the polyester chains react with the double bonds of the copolymerizable solvent monomer. Solid products are formed that are used as molding materials or in paints. They are also reinforced with fibers or filled, and used as putties or mortars.

Vinyl ester resins, which are also termed phenacrylate resins (DIN 16 946, part 2), are polyadducts of liquid epoxy resins and acrylic acid in styrene. Strictly speaking, they are not unsaturated polyester resins, but since they are processed, cured, and used similarly, they are also discussed.

2. Raw Materials

The properties of unsaturated polyesters depend on the nature and quantitative ratios of the raw materials (α-, β-unsaturated dicarboxylic acids, saturated dicarboxylic acids, and diols), as well as on the condensation conditions. Many different materials are quoted in the patent literature and in reference manuals [1–5]. However, only those described here are of practical importance. This limited number of raw materials has hardly changed since the early 1970s and permits wide variation as regards the processing and properties of UP resins.

A larger number of double bonds in the polyester chain increases the reactivity, the heat of reaction released during curing, and the thermal stability of the end product. The incorporation of long-chain dicarboxylic acids or diols increases the flexibility of the cured substance.

Unsaturated Dicarboxylic Acids. Maleic anhydride and fumaric acid are used almost exclusively as unsaturated acid components. They are described in detail elsewhere, see → Maleic and Fumaric Acids.

Maleic anhydride [108-31-6] is not as expensive as fumaric acid and contains one mole of

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water less than the free dicarboxylic acid, which is favorable for condensation. During condensation maleic acid largely rearranges into the isomeric form, fumaric acid. This rearrangement can also be promoted by catalysts.

Fumaric acid [110-17-8] is only used when the degree of rearrangement of maleic acid to fumaric acid is insufficient for the required properties of the UP resins. Use of fumaric acid instead of maleic anhydride in the condensation improves the thermal stability and mechanical properties of the product. The disadvantages of fumaric acid compared with maleic anhydride are its higher cost and higher water content.

Saturated Dicarboxylic Acids. *Phthalic acid* [88-99-3] is used exclusively in the form of phthalic anhydride [85-44-9] (→ Phthalic Acid and Derivatives). On account of its favorable price and diverse potential uses, it is employed in all standard resins.

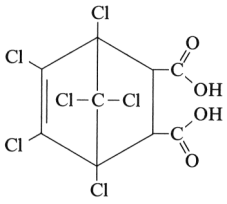
Isophthalic Acid [121-91-5] (→ Terephthalic Acid, Dimethyl Terephthalate, and Isophthalic Acid) has a better thermal stability, mechanical strength, and resistance to chemicals than phthalic acid.

Terephthalic Acid [100-21-0] (→ Terephthalic Acid, Dimethyl Terephthalate, and Isophthalic Acid) is used in resins where high impact strength, thermal stability, and weather resistance are required.

Tetrahydrophthalic Anhydride [935-79-5] yields resins having a high impact strength but limited weather resistance. It is used primarily for resins employed in paints and automotive body fillers.

Adipic Acid [124-04-9] (→ Adipic Acid) is used on account of its flexible carbon chain to produce soft resins and mixed resins that are employed to plasticize harder resins.

Hexachloroendomethylenetetrahydrophthalic (HET) acid [115-28-6] yields resins with low flammability and good chemical resistance.



Tetrabromophthalic acid [13810-83-8] also lowers flammability, but tends to produce strong discoloration in sunlight due to the release of bromine.

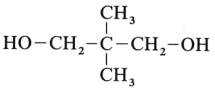
Diols. *Ethylene glycol* [107-21-1] (→ Ethylene Glycol) is inexpensive, but it sharply reduces the styrene compatibility of UP resins. It is generally used in combination with other diols such as diethylene glycol, dipropylene glycol, or butylene glycol.

1,2-Propanediol [57-55-6] , propylene glycol, is by far the most widely used diol for standard resins (→ Propanediols). It has good styrene compatibility, only slight tackiness after curing in air, and good mechanical properties.

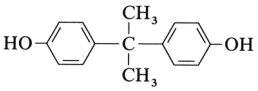
Diethylene Glycol [111-46-6] and *dipropylene glycol* [110-98-5] result in plasticization of the resins and increased water absorption. They are used mainly in combination with 1,2-propanediol to adjust the mechanical properties or refractive index of the cured resin.

1,3-Butanediol [107-88-0], butylene glycol, (→ Butanediols, Butenediol, and Butynediol) improves weather resistance, but is not used as often as the aforementioned diols on account of its high price and limited availability.

Neopentyl Glycol [126-30-7], 2,2-dimethyl-1,3-propanediol (→ Alcohols, Polyhydric, Section 2.3.1.) increases the thermal stability, chemical resistance, and weather resistance of UP resins. Particularly when combined with isophthalic acid, it yields high-quality products for use in chemical plant construction.



Ethoxylated or Propoxylated Bisphenol A [80-05-7] is very often used for resins with a high thermal stability and extremely good resistance to chemicals. With resins formulated from these diols it should be borne in mind that traces of phenolic groups can interfere with curing.



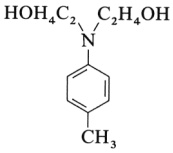
Bisphenol A

Although *bis(hydroxymethyl)tricyclodecane* [26896-48-0] is expensive, it imparts high thermal stability and chemical resistance, with tack-free hardening of uncovered surfaces.



Dibromoneopentyl Glycol [3296-90-0] is used to reduce combustibility. A disadvantage is that hydrogen bromide readily splits off during polycondensation and attacks the walls of the reaction vessel. Dibromoneopentyl glycol is therefore seldom used.

N,N-*Bis(2-hydroxyethyl)*-p-*toluidine [3077-12-1]* is sometimes incorporated into the polyester chain by condensation to obtain resins that cure at normal temperatures with benzoyl peroxide but without an accelerator.



Monomers for Cross-Linking UP Resins. Vinyl, allyl, and acrylic compounds are suitable monomers for the cross-linking of UP resins. They are readily miscible with the resins and their homopolymerization rate does not exceed the copolymerization rate with the unsaturated polyester chain. In most cases low- to medium-viscosity UP resins are required. *Styrene* [100-42-5] is by far the most suitable monomer for these products (→ Styrene). The styrene content is normally between 25 and 45 wt%.

The following vinyl compounds are often recommended as alternatives, but are of little practical importance:

α-Methylstyrene [98-83-9] is insufficiently reactive. *4-Methylstyrene* [622-97-9] would be the most suitable alternative to styrene for technical reasons [6], but has an unpleasant odor and is not produced on an industrial scale.

Vinyltoluene, an isomeric mixture mainly of 4- and 3-methylstyrenes, is not very suitable on account of its low reactivity and unpleasant odor.

Divinylbenzene [1321-74-0] is not available in large amounts.

Methyl Methacrylate [80-62-6] copolymerizes with difficulty with unsaturated polyesters. It is used in combination with styrene, however, to improve weather resistance and to lower the refractive index. The ratio of the refractive index of the resin to that of the glass fiber reinforcement determines the transparency of finished parts such as domelights and light panels.

Diallyl Phthalate [131-17-9] is used as a cross-linking agent in the production of pourable, solid UP resin molding compositions. The viscosity of diallyl phthalate is too high for liquid UP resins and copolymerization is too slow for curing at room temperature.

Triallyl Cyanurate [101-37-1] is also a conventional cross-linking agent for solid molding compositions.

3. Production

UP resins are usually produced by batchwise condensation of dicarboxylic acids or anhydrides with diols. Continuous esterification of acid anhydrides and epoxides may, however, also be employed.

Batchwise Condensation. Dicarboxylic acids are esterified with diols at 180 – 230 °C in a nitrogen atmosphere in heatable, coolable reactors while stirring. Esterification is generally performed with a slight excess (up to 10%) of diols. The water formed in the reaction is distilled off. Passage of nitrogen through the reaction mixture promotes removal of water and increases the esterification rate considerably. The end point of the condensation is determined by measuring the acid number and, possibly, also the hydroxyl number and the viscosity. Commercial UP resins have a mean molecular mass of 2000 – 4000.

The still liquid melt is cooled and then dissolved, while stirring, in styrene in coolable mixers. The styrene contains inhibitors such as hydroquinone or *tert*-butylcatechol (see Chap. 4).

Even if the same raw materials are used, the resin products may differ as regards their processing properties and end properties depending

on the amount of excess glycol, the temperature, and reaction conditions.

In the case of raw materials with widely differing esterification rates, two-stage condensation must be used to obtain uniform buildup of the polyester chain and thus favorable end properties. For example, if isophthalic acid and maleic acid are added simultaneously to the reaction vessel, maleic acid is incorporated more quickly into the polyester chain. In the case of isophthalic acid resins, isophthalic acid should therefore first be condensed with glycol in a molar ratio of 1 : 2 to form a bishydroxy ester. Esterification should be continued after adding maleic anhydride.

Azeotropic esterification is important only for certain paint resins. An entraining agent (e.g., toluene or xylene) is added and during condensation the water is distilled off together with the toluene. The toluene is then separated from the water with a dephlegmator and returned to the reactor. At the end of the reaction the toluene must be removed from the resin (e.g., with a thin-film evaporator).

Continuous Esterification of acid anhydrides and epoxides is a very elegant, economic method. However, it is limited to the small number of raw materials that are available as anhydrides or epoxides. It cannot, therefore, meet the demands of the polyester processors for different resin types. Thus, for example, the extremely important isophthalic and terephthalic acid resins cannot be produced by this method because the dicarboxylic acids do not form anhydrides. The method is recommended only for producers with very large sales of standard resins.

The raw materials (e.g., maleic anhydride, phthalic anhydride, and propylene oxide) are converted into polyesters by reacting them for ca. 20 min and 200 °C, generally in the presence of catalysts. In contrast to batchwise condensation, no water of reaction is formed.

4. Additives

See also → Plastics, Additives

Inhibitors are used to prevent premature polymerization and to modify the reaction times. The most important are hydroquinone, 1,4-benzoquinone, *tert*-butylpyrocatechol (*tert*-butylcatechol), toluhydroquinone (methylhydroquinone), and 3,4-di-*tert*-butyl-*p*-cresol (3,4-di-*tert*-butyl-4-hydroxytoluene). All these inhibitors have specific effects and are used for different resin types. In some cases they are added prior to condensation, in other cases they are dissolved in styrene and added after condensation.

Optical Brighteners are added to slightly yellowish resins for certain uses (e.g., transparent products or white buttons). Blue dyes, which become decolorized during curing, are commonly used as curing indicators.

Commercially available *light stabilizers* (e.g., substituted benzophenones and hydroxyphenyltriazoles) prevent premature yellowing of the hardened resins in sunlight.

Thixotropic Agents have to be added to prevent sagging or dripping of the resins when applied to vertical surfaces. Finely dispersed silica is mainly used for this.

Most UP resins have a tacky surface when cured in air. Tackiness can be prevented by adding *skin-forming agents*, generally paraffins. The formation of a paraffin film also reduces styrene emission in pressureless processing. Resins containing such additives are termed “environmentally friendly” or “milieu polyesters”.

The additives listed above are generally added to the resin by the resin manufacturer. The following substances are added to the resin by the processor.

Hardened UP resins have a surface resistance of $>10^{13}$ Ω. In order to prevent buildup of electrostatic charge, graphite and metal powders can be added as *antistatic agents* to reduce the surface resistance to ca. 10^4 Ω.

Flame retardants include chlorinated paraffins and antimony trioxide. Aluminum hydroxide (hydrated alumina) is employed on a large scale for parts used in the electrical industry that have to be halogen-free (halogens can attack copper contacts and hydrogen chloride may be released during fires).

Both soluble *dyes* and insoluble *pigments* can be used for coloring. Pigments have to be made into a paste in resins or plasticizers before being added.

Fillers include chalk, quartz flour, and quartz sand. The type and amount of filler depend on the final use and desired properties of the resin. Filled resins serve as putties, compression molding compounds, casting compounds, mortars, and concrete. The fillers must be dry so that they do not to affect curing.

Blowing Agents are used to produce polyester foams, various additives and systems are used for this (e.g., azodicarbonamide, *tert*-butylhydrazinium chloride and iron(III) chloride).

Thickening Agents are required for the production of sheet molding compounds (SMC), and bulk molding compounds (BMC). Magnesium oxide and, in some cases, magnesium and calcium hydroxides are normally used. These agents are mixed with fillers and used to impregnate glass fibers, thereby converting the molding compound into a highly viscous state.

Low-Shrink and Low-Profile Additives are solutions of thermoplastics in styrene and are added to reduce volume shrinkage occurring during curing. Polystyrene, poly(vinyl acetate), poly(methyl methacrylate), saturated polyesters, cellulose acetobutyrate, and polycaprolactams are usually used. Polyethylene with a particularly low melting point is used to improve the properties of sheet molding compounds. On account of its insolubility it has to be added to the resin batch as a powder immediately before processing.

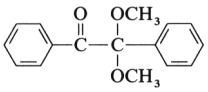
5. Curing

At normal temperatures UP resins can be cured with peroxides and accelerators. The most important systems include hydroperoxides (e.g., methyl ethyl ketone peroxide, cyclohexanone peroxide, and acetylacetone peroxide) with cobalt octanoate or, in exceptional cases, also vanadium octanoates or naphthenates, as well as benzoyl peroxide (dibenzoyl peroxide) with aromatic amines (e.g., *N,N*-dimethylaniline, *N,N*-diethylaniline, and *N,N*-dimethyl-*p*-toluidine).

Moisture slows down or prevents curing with hydroperoxides and cobalt salts, but does not affect reactions with benzoyl peroxide and amines. Complete curing generally requires heating above the glass transition temperature of the cross-linked polyester. Only completely cured products exhibit optimum mechanical properties and resistance to weathering and chemicals.

At elevated temperatures only peroxides are required for curing, accelerators are unnecessary. Examples include dibenzoyl peroxide above ca. 80 °C, *tert*-butyl 2-ethylperhexanoate above ca. 100 °C, and *tert*-butyl perbenzoate above ca. 120 °C.

UP resins can also be completely cured in a few minutes by exposing them to UV light from high-pressure mercury vapor lamps in the presence of photosensitizers, e.g., benzoin ether [24650-42-8] (*ω*,*ω*-dimethoxy-*ω*-phenylacetophenone).



Some acyl phosphine oxide compounds [7] can be used in combination with the aforementioned UV sensitizers to allow curing in normal daylight.

Detailed information about optimum curing systems and reaction conditions for specific uses are given in the data sheets published by resin and reactant manufacturers.

During the transition from the liquid to the solid state, UP resins shrink by 5 – 8 % depending on their double bond content. Compensation of shrinkage by thermoplastics additives is discussed in Chapter 4.

6. Types of UP Resins

Many types of UP resins are available. Selection depends on processing properties and end properties. Processing properties include reactivity, viscosity, and thickening behavior with magnesium oxide. End properties include mechanical behavior, thermal stability, flammability, resistance to chemicals, and color.

Resins may be liquid (low-, medium- or high-viscosity) or solid. Their reactivity may be low, average, or high. A wide range of UP resins can be produced by appropriate choice of the following factors: type and quantity of raw materials, degree of condensation, acid and hydroxyl numbers (and thus the nature of the terminal groups), and the content of cross-linking monomers and other additives. Consequently, comparison or

exchange of related resin types from different producers may be difficult.

Standard Resins are formulated from inexpensive raw materials and have a wide variety of uses. They can be supplied with or without additives (light stabilizers, thixotropic agents, accelerators, or UV sensitizers).

Elastic Grades have a high flexibility and elongation at break due to the incorporation of long-chain monomers, and are generally used in admixture with more brittle types. Some highly elastic grades are used for jointless roof coverings on account of their weather resistance and high elongation at break of up to 200 % in tensile tests.

Flame-Resistant Resins generally contain chlorine or bromine in the polyester chain or in added compounds. Flammability can be adjusted to satisfy widely differing regulations and standards by using other additives such as phosphorus compounds, antimony compounds, and aluminum hydroxide.

Resins with a high chemical resistance are mainly synthesized from special raw materials such as isophthalic acid, terephthalic acid, neopentyl glycol, ethoxylated or propoxylated bisphenol A or bis(hydroxymethyl)tricyclodecane. They are used particularly in chemical apparatus (pipes and vessels).

Resins for *sheet molding compounds (SMC) and bulk molding compounds (BMC)* have specially adjusted ratios of acid and hydroxyl numbers and a constant water content. This ensures controlled thickening with magnesium oxide (MgO). Low-shrink and low-profile additives may also be added to the individual types, compatibility depends on the degree of unsaturation [8].

Resins for *fillers and putties* are preaccelerated with aromatic amines. This ensures accurate adjustment of curing with benzoyl peroxide and allows sanding within a short period of time. Rigid and plasticized resins are available for repair putties and light-colored products for marble putties.

Resins for free-flowing *compression molding compounds* are generally supplied monomer-free in powder form to the molding compound producers, who formulate the compounds with cross-linking agents (e.g., diallyl phthalate or triallyl cyanurate) and fillers.

Trade Names. Important trade names of UP resins in Europe and the United States include:

Alpolit	Hoechst
Altek	Alpha Corp.
Aropol	Ashland Chemical Corp.
Beetle	BIP
Civic	Neste Oy
Crystic	Scott Bader
Hetron	Ashland Chemical Corp.
Lamellon	DSM
Leguval	Bayer and DSM
Marco	US-Steel Corp.
Norpol	AS Jotun-Group
Norsodyne	Cray Valley
Palatal	BASF
Polylite	Reichhold Chemicals
Roskydal	Bayer
Selectron	PPG Industries
Sniatron	Alusuisse
Sirester	SIR
Torolithe	Routtand S. A.
Trusurf	OCF Fiberglas Corp.
Uralam	Synthetic Resins
Vestopal	Hüls
Viapal	Vianova Kunstharz

Due to company takeovers or mergers and sales of know-how and trade names, assignment of trade names to manufacturers may change.

7. Testing and Properties

A distinction should be made between the properties of UP resins in the as-supplied state (Table 1) and properties after curing (Table 2).

In order to determine the properties in the as-supplied state, simple, rapid tests are desired by producers and customers for quality assurance. Testing is generally carried out by agreement

Table 1. Properties of styrene-containing UP resins in the as-supplied state

Property	Test method	Test value
Acid number	DIN 53 402	10 – 30 mg KOH/g
Styrene content	DIN 16 945	25 – 45 %
Viscosity at 25 °C	DIN 53 015	0.2 – 4.5 Pa · s
Density at 20 °C	DIN 51 757	1.07 – 1.3 g/cm^3
Flash point	DIN 51 755	35 °C
Refractive index at 25 °C	DIN 53 491	1.524 – 1.559

Table 2. Properties of cured UP resins without fillers or reinforcement fibers (without soft resins)

Property	Test method	Test value
Density at 23 °C	ISO/R 1183	1.20 – 1.40 g/cm^3
Flexural strength	ISO 178	80 – 160 N/mm^2
Outer fiber strain	ISO 178	2 – 7 %
Impact strength	ISO 179 small test bar	6 – 15 kJ/m^2
Tensile strength	ISO/R 527 test specimen 1	40 – 90 N/mm^2
Elongation at break	ISO/R 527 test specimen 1	1.5 – 5 %
Compressive strength	ISO 664	150 – 180 N/mm^2
Ball indentation hardness 10”	ISO 2039	200 – 245 N/mm^2
Barcol hardness (934–1)		35 – 48
Modulus of elasticity (bending)	DIN 53 457 Section 2.3.	3400 – 4300 N/mm^2
Mean specific heat		1.10 – 1.45 kJ kg^{-1} K^{-1}
Thermal stability (heat distortion)	ISO 75 method A	60 – 145 °C
Thermal conductivity	DIN 52 612	0.16 – 0.18 W m^{-1} K^{-1}
Coefficient of linear expansion	VDE 0304 Part 1 § 4	60 – 115 10^{-6} K^{-1}
Volume resistivity	IEC Publ. 93	>10^{15} Ω · cm
Surface resistivity	IEC Publ. 167	>10^{13} Ω
Dielectric dissipation factor		
at 800 Hz	IEC Publ. 250	0.003 – 0.005
at 1 MHz		0.015 – 0.035
Relative permittivity at 800 Hz	IEC Publ. 250	3.0 – 3.5
Comparative tracking indices	IEC Publ. 112	CTI>600 CTI>600M
Dielectric strength	IEC Publ. 245	35 – 45 kV/mm

between suppliers and customers according to national standards, but also according to in-house procedures. The resins are often dispatched with test certificates describing the contents of the delivered batch.

Important properties used to characterize the liquid resins in the as-supplied state include the acid number, solids content, viscosity, refractive index, and reactivity. The acid number, solids content, and viscosity can be used to evaluate the degree of condensation and mean molecular mass. Further important properties of liquid resins are color, flash point, and density.

The acid number is measured by titration with potassium hydroxide solution. The solids content can be determined with automatic thermobalances by evaporating the volatile constituents (basically styrene). Viscosity is checked with rotating-cylinder viscometers, but also by measuring efflux times from temperature-controlled flow cups. The viscosity can be lowered by dilution with styrene or other monomers. The refractive index is measured in refractometers, and is used to monitor the correct composition of the resin.

The reactivity of UP resins is generally determined by measuring the rise in temperature that occurs during curing. This method is more sensitive than differential scanning calorimetry. The initial temperatures chosen often depend on the subsequent processing temperatures (e.g., room temperature or the temperature of hot compression molds). Measurements differ widely as regards heating bath, vessels, thermocouples, amount of resin, and nature and amount of the reactants. Accurate comparisons of product data sheets published by various manufacturers cannot therefore be made. Examples of measurement setups are given in DIN 16 945.

The thickening of resins for SMC and BMC with magnesium oxide is an important property but is difficult to measure quickly. An ISO standard is currently being prepared which involves accelerated thickening at elevated temperature, and allows conclusions to be made about thickening behavior at room temperature. This test is satisfactory for resin processors, but resins with the same results may behave differently when tested under normal thickening conditions at 25 °C.

In most cases cured UP resins are relatively brittle, addition of fillers and reinforcing materials (e.g., glass fibers) is required to obtain technically useful properties. Nevertheless,

cured UP resins must be tested in the pure state. Production of test specimens requires care and experience because factors such as internal stress arising during curing can falsify the results. Mechanical, thermal, and electrical properties are measured (Table 2). The tensile strength, elongation at break, and thermal stability are particularly important for comparing the performance of different resins.

8. Uses and Economic Aspects

UP resins are only used without fillers or reinforcing agents in small amounts for embedding decorative objects, in furniture lacquers, adhesives, paints (→ Paints and Coatings, 1. Introduction) and casting resins (impregnating resins) for insulating electrical equipment (→ Insulation, Electric).

The majority of UP resins are reinforced with glass fibers which impart high strength and rigidity to molded parts. Natural fibers (e.g., jute) and synthetic fibers are also used in elastic molded parts.

Casting compounds, putties (→ Paints and Coatings, 1. Introduction), and UP resin concrete are produced using fillers with different particle sizes and compositions.

The most important uses of UP resins follow:

Automobile Construction. Parts for special-order vehicles, caravans, and agricultural vehicles are produced by hand from glass-fiber-reinforced UP resins. Flat sheets and panels for truck superstructures and containers are produced industrially in continuous laminating processes. Body parts for automobiles and commercial vehicles are produced from preimpregnated SMC.

On account of their outstanding resistance and impact strength behavior, pressed parts made from UP resins reinforced with natural or synthetic fibers are employed in car interior fittings, engine compartments, and vehicle underbodies; they have gained a considerable market share. Filled UP resins are used as automobile repair putties.

Building Industry. The use of light panels made of glass-fiber-reinforced UP resins has greatly declined. UP resins with glass fiber reinforcement are used for domelight crowns, facade elements, cellar window frames, and light shafts made from SMC. Beacons, chimneys, and large aerials are wound from UP resins and glass fibers. Highly elastic casting compounds are used for flat roof coverings. Drainage systems with channels, catch basins, and gasoline separators are produced industrially from polyester concrete. Imitation marble and onyx can be produced from UP resins, colorants, and chalk (marble) or aluminum oxyhydrate (onyx); they are used to produce inexpensive, high-quality sanitary ware.

Electrical Industry. The electrical industry is still a main customer for molded parts made from SMC and BMC. Examples include cable distribution cupboards and switching cupboards, skirting boards for lamps, multiway connectors, switch covers, and clamping sleeves. Coils and windings are impregnated with UP resins.

Pipes, Vessels, and Apparatus. Cylindrical molded components reinforced with glass fibers for the chemical industry and oil transportation are fabricated in winding and centrifugal processes from chemically resistant resins whose chemical resistance is appropriate for the intended use. Glass-fiber-reinforced UP resins are also used for fertilizer and fodder silos and cooling towers.

Boat and Shipbuilding. Glass-fiber-reinforced UP resins have long been used for building sports, life-saving, and fishing boats. Larger vessels (e.g., 50-m long minesweepers with 30-mm thick sides) are now also being built from this material.

Miscellaneous Uses. Other molded parts made from glass-fiber-reinforced UP resins include machinery covers and casings, sports equipment, toys, garden furniture, and traffic signs. Important areas of use of nonreinforced UP resins include buttons, buckles, fashion accessories, and furniture finishings.

Economic Aspects. In 1988 ca. 1.3×10^6 t of UP resins were consumed worldwide.

Following a fall in consumption as a result of the oil crises at the end of the 1970s and subsequent stagnation, polyester resins have recently experienced an increase in consumption. This is

Table 3. International distribution of the areas of use for UP resins (10^3 t)

	United States	Western Europe	Japan
Building and construction	241	125	74
Automobile construction	50	78	9
Pipes and vessels	62	61	67
Boats and shipbuilding	155	55	23
Electrical industry	13	28	9
Paints and other nonreinforced products	68	30	30
Miscellaneous uses	31	73	18
Total consumption	620	450	230
of which			
BMC/SMC *	64	58	58
Polymer concrete (in building and construction)	62	36	16
Production capacity	800	540	300

* BMC=bulk molding compounds; SMC=sheet molding compounds.

primarily due to increased use in the automobile industry, especially in compression molding and resin transfer molding.

Consumption according to areas of use is listed in Table 3. The apparent excess capacities in this table are somewhat misleading because they include alkyd resin capacities for the paint sector. The capacity of the UP resin manufacturers is fully utilized and an expansion in capacity can be expected in the next few years.

9. Occupational Health and Environmental Aspects [9]

Toxicological and environmental aspects of unsaturated polyester resins are principally determined by the properties of styrene (→ Styrene). Styrene is a liquid with a relatively high vapor pressure which means that there may be considerable emissions, particularly when polyesters are processed in open molds.

Irritation of the eyes and mucous membranes of the upper respiratory tract is observed and depends on the exposure period and concentration of styrene in the inspired air. Tiredness, loss of concentration, and similar symptoms have been reported at styrene exposure levels above 100 ppm at the workplace.

Styrene and styrene-containing UP resins were classified in 1988 by the EC as "slightly hazardous" with the danger symbol x_n, R-phrase 10 inflammatory, R-phrase 20 health hazard if inhaled, and R-phrase 36/38 eye and skin irritant. A grading with the R-phrase 45 "Can cause cancer" was specifically excluded.

In 1989 in the United States, styrene was classed by OSHA as not carcinogenic, and was included in the category "Avoidance of narcosis". The TLV-TWA value was reduced from 100 ppm to 50 ppm.

In Germany the MAK value was reduced from 100 ppm to 20 ppm in 1987 on account of reported neurotoxic effects. It was announced that the carcinogenic effects of styrene would be reexamined.

Maximum workplace concentrations for various countries follow (ppm):

Austria	200
Belgium	50
Commonwealth of Independent States	1.2
Czechoslovakia	47
Denmark	25
Finland	20
France	50
Germany	20
Italy	50
Japan	50
Netherlands	100
Norway	50
Poland	12
Sweden	20
Switzerland	50
United Kingdom	100
United States	50

In many countries these concentrations will probably be lowered in the near future.

The observance of low maximum workplace concentrations does not present any particular problem in the production of styrene, polystyrene, and styrene copolymers nor in the processing of polystyrene and styrene copolymers. In UP resin processing, however,

it is often almost impossible to satisfy this requirement.

Styrene emissions can be considerably reduced by ventilation devices at the workplace, by using "environmentally friendly resins" that contain a skin-forming agent such as paraffins (Chap. 4), or by completely enclosing automatically operating plants. Statutory regulations (e.g., TA-Luft in Germany) impose limits on the discharge of evaporated styrene and waste-gas treatment plants are necessary if fairly high levels of emissions are reached (e.g., >100 mg/m^3 in TA-Luft).

Prolonged exposure of the skin to liquid UP resins often leads to irritation, and particular care must be taken when working with the peroxides used as curing agents on account of their corrosive effect. Goggles should always be worn to protect the eyes when handling peroxides.

UP resins are flammable and hazard classifications differ in individual countries. The content of volatile monomers (styrene), the flash point, and the viscosity of the resins are usually decisive factors. Details are given in the manufacturers' safety data sheets.

Liquid UP resins containing styrene as cross-linking agent and must not pass into the ground water. Relevant statutory regulations governing the storage and transportation of UP resins must be strictly observed. Storage tanks for UP resins should be installed in catchment basins to trap any leakages or escaping product.

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Polyesters

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1. Introduction

Classification. Polyesters are defined as all polymers which contain repeating units of the ester group



in the polymer chain. Polyesters are generally produced by condensation of polyfunctional carboxylic acids (or their derivatives) with polyfunctional alcohols. Other methods of production include polycondensation of hydroxycarboxylic acids and polymerization of cyclic esters (e.g., lactones).

Polyesters with widely varying properties can be produced depending on the starting materials:

1. High molecular mass linear polyesters (M_r >10 000) are produced from difunctional alcohols and dicarboxylic acids (or their derivatives, e.g., diesters or dichlorides) or from polymerizable lactones. They can be processed thermoplastically to molding materials (*thermoplastic polyesters*, Chap. 3). The term thermoplastic polyesters also includes polycarbonates, see → Polycarbonates.
2. Low molecular mass polyesters ($M_r \leq$10 000) from saturated aliphatic or aromatic dicarboxylic acids and difunctional or mixtures of di- and trifunctional alcohols are linear or slightly branched *intermediates for polyurethanes* (see Chap. 2).
3. Low molecular mass polyesters ($M_r \leq$10 000) from di-, tri-, and polyfunctional alcohols and polyfunctional, usually aromatic carboxylic acids or saturated or unsaturated fatty acids are classified as *alkyd resins*, see → Alkyd Resins.
4. *Unsaturated polyesters* are polyesters which can copolymerize with unsaturated

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compounds and are formed from polyfunctional alcohols and polyfunctional unsaturated carboxylic acids. After copolymerization with monomers such as styrene they can also be classified as thermosets, see→ Polyester Resins, Unsaturated.

2. Polyesters as Intermediates for Polyurethanes

In 1937 O. BAYER developed an addition polymerization method for the synthesis of polyurethanes that was based on the reaction of diisocyanates with polyols [1]. Hydroxy-functional polyesters were soon introduced as reactants. The only highly branched polyesters known at that time were based on aromatic dicarboxylic acids, and they resulted in hard, highly cross-linked products that were processed in coatings and molding compounds [2]. In 1942 H. PINTEN treated moderately branched aliphatic hydroxypolyesters with a diisocyanate and obtained a rubbery-elastic material ("I-Gummi") [3]. Systematic study of the reactions of linear and moderately branched hydroxypolyesters with excess diisocyanates, and subsequent treatment of these intermediates with water, diols, diamines, and other compounds containing reactive hydrogens, resulted in a wide range of polymers displaying advantageous properties (e.g., thermosets, thermoplastics, cast elastomers, hard and soft foams, molding compounds, hard and flexible coatings). Polyurethanes came to be known as "tailor-made polymers" [4], [5]. This diversity was partly a result of great flexibility with respect to starting materials, mean molecular mass, and mean functionality.

Today, a broad spectrum of hydroxypolyesters with mean molecular masses between 400 and 6000, hydroxyl numbers of 28 – 300 mg KOH/g, and acid values generally under 1 mg KOH/g are employed as intermediates in the manufacture of polyurethanes. Highly branched polyesters, made largely from aromatic or hydroaromatic dicarboxylic acids, find use as binders for polyurethane coatings (DD coatings, Bayer), → Paints and Coatings, 1. Introduction, [6].

The present review is limited to a discussion of linear and moderately branched hydroxypolyesters derived from aliphatic starting materials.

2.1. Raw Materials

Adipic acid is most commonly employed as the acidic component. Other dicarboxylic acids such as oxalic, succinic, and glutaric acid are of lesser importance because the resulting polyesters exhibit lower stability toward hydrolysis. Higher molecular mass aliphatic carboxylic acids (azelaic acid, sebacic acid) are economically unattractive. "Dimeric acids" [7], produced by the dimerization of unsaturated plant fatty acids and hydroxy-functional monocarboxylic acids, find application in special situations. The hydroxy-functional acid dimers afford the corresponding polyesters [8] by self-condensation onto a starter diol. Aromatic dicarboxylic acids such as phthalic acid (in the form of the anhydride), isophthalic acid, and terephthalic acid are sometimes added as modifiers. Typical diol components are ethylene glycol, diethylene glycol, 1,2-propanediol, 1,3-butanediol, 1,4-butanediol, neopentyl glycol, and 1,6-hexanediol. Glycerol, trimethylolethane, trimethylolpropane, and hexanetriol are employed to obtain branched polymers. Developments in the synthesis of hydroxypolyesters include the use of raw materials such as ϵ-caprolactone, which affords polycaprolactone [9] via ring-opening polymerization on a starter polyol. Oligo- or polyethers can also be incorporated into the polymer chain, leading to the corresponding etheresters [10].

2.2. Production

2.2.1. General Information

The only currently economic method for the production of polyesters is direct esterification of dicarboxylic acids with diols [11]. Since esterification is a reversible equilibrium reaction, the process can only be driven to completion if the resulting water of condensation is continuously removed. Polyesterification represents an example of *condensation polymerization*. Not only are monomeric units added to the growing chains, but individual chains also react with one other because they may have both carboxyl and hydroxyl terminal groups. The esterification conditions also permit constant transesterification within the chain itself. Consequently, polyesters exhibit relatively broad molar mass distributions,

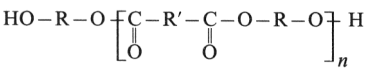
which can be calculated using the Schulz–Flory method [12], [13]. Transesterification also accounts for the fact that, if more than two starting materials are employed, these become incorporated into the polyesters in a statistical way regardless of their time of introduction.

The esterification of a dicarboxylic acid with a diol represents a higher-order reaction. In the absence of an added catalyst, and if the reverse reaction is prevented by removal of the resulting water, the kinetics of the reaction can be described as third order [14], [15] because the acidic groups themselves exert a catalytic effect on the reaction:

$$\text{Reaction rate} = k \cdot [\text{OH}] \cdot [\text{COOH}]^2$$

When an esterification catalyst is utilized, its influence becomes dominant and esterification exhibits second-order kinetics. Esterification is catalyzed by acids, bases, and transition-metal compounds. However, the commercial use of catalysts is limited because all catalysts tend to have undesirable effects on subsequent polyurethane reactions. In the case of polyesters that are used in reactions where traces of catalyst do not interfere, synthesis is catalyzed with low concentrations (ppm) of compounds of titanium, tin, or antimony. The appropriate starting ratios for the synthesis of a given hydroxypolyester can, in theory, be calculated from the desired number-average molecular mass (M_n), which can in turn be determined from the hydroxyl number.

Given the simplified formula



a linear polymer would result from n mol of dicarboxylic acid (HOOC−R′−COOH) and n+1 mol of diol (HO−R−OH). The degree of polycondensation, n, is calculated as follows:

$$n = \frac{M(\text{polyester}) - M(\text{diol})}{M(\text{dicarboxylic acid}) + M(\text{diol}) - 2M(\text{water})}$$

Losses of diol accompanying the removal of water of condensation and as a consequence of side reactions (formation of ethers and aldehydes) usually require the addition of an empirically determined excess of diol which depends upon the type of diol and the reaction conditions.

The first phase of the esterification is conducted under an inert atmosphere (nitrogen, car-bon dioxide) and the water of condensation is removed rapidly by distillation through a column at >130 °C. Once an acid value of about 30 has been reached, the reaction must be accelerated in a second phase by facilitating the removal of water from the esterification equilibrium. This is done by application of a vacuum (vacuum-melt method), introduction of a carrier gas (usually carbon dioxide), or recirculation of an entrainer such as toluene or xylene (azeotropic distillation). The last approach is not applicable when the diol component is ethylene glycol or 1,2-propanediol, which themselves form azeotropic mixtures with the entrainers.

A low acid value (<1 mg KOH/g) is desired. This means that the reaction mixture tends to become highly depleted in one reactant toward the end of the reaction, greatly reducing the rate. This second phase of polyester synthesis therefore requires a large fraction of the overall reaction time (e.g., 20 of 30 h).

2.2.2. Industrial Production

Polyesters are produced industrially either batchwise or continuously according to a variety of methods. The vacuum-melt and the purge-gas-melt methods are preferred, the azeotropic method finds only limited application.

Batchwise Vacuum-Melt Method [16]. The apparatus constitutes a closed system, comprising a stirred-tank reactor equipped with an anchor agitator, a distillation column, a condensor, a receiver, and a vacuum pump. The starting materials are heated in the reactor, with stirring but in the absence of air. Heat is provided by electrical energy, high-pressure steam, or a heat-transfer medium. In the first phase of the reaction the temperature is held between 125 and 220 °C under ambient pressure and ca. 90 % of the resulting water is removed by distillation. A mixture of oligoesters is produced which is immediately condensed to polyester in the second reaction phase at 170 – 230 °C and with stepwise reduction of the pressure to 0.005 bar. Residual water of reaction is distilled from the mixture, together with excess diol and minor byproducts such as low molecular mass

aldehydes and ketones (present in ppm amounts relative to the polyester). The process is monitored constantly by measuring the acid value, the hydroxyl number, and the viscosity.

Example of the preparation of a polyester with an average molecular mass of 2000 from ethylene glycol and adipic acid. A mixture of 86.8 kmol of adipic acid and 95.6 kmol of ethylene glycol, including an empirically determined excess of 1.1 kmol ethylene glycol, is heated with stirring under nitrogen to 130 °C. Once distillation begins the temperature of the reaction mixture is raised to 200 °C over the course of 10 h. During this period 156 kmol of water of reaction is distilled into the receiver. When distillation is complete, the acid value of the reaction mixture is ca. 55 mg KOH/g. The pressure in the apparatus is subsequently reduced in stages to 0.01 bar at constant temperature over a period of 15 h. During this period the remainder of the water of reaction is distilled off, along with excess ethylene glycol and byproducts. The reaction mixture has the following properties: hydroxyl number, 55.5; acid value, 0.7; viscosity, 0.515 Pa · s at 75 °C; water content, 0.02 wt %. After pressure equilization with nitrogen and cooling to 110 °C, the polyester product (7.7 kmol) is transferred to a storage tank.

Purge-Gas – Melt Method [17]. This process differs from the vacuum-melt method in that during the second phase of reaction the distillable products are removed by passage of an inert gas (N_2, CO_2) through the mixture rather than by lowering of the pressure. This method increases the loss of diol, a fact that must be taken into account in the raw material calculations. The apparatus must also be suitably adapted: the reactor is equipped with a gas inlet and the distillation column is replaced by a simple distillation tube. A vacuum pump is not required.

Azeotropic Method [18]. This process is conducted at atmospheric pressure in the presence of an inert solvent (e.g., toluene or xylene) which entrains and removes the water of reaction. A vacuum-melt apparatus can be adapted to the azeotropic method by including facilities for removal and continuous recycling of the entrainer solvent. Lower reaction temperatures (125 – 190 °C) are used and permit polyester to be produced under milder conditions. Solvent residues in the final product are removed under vacuum.

Wastewater and Exhaust Air. Both the water of reaction and the process exhaust air contain excess diols and reaction byproducts which are biodegradable in dilute aqueous solution. The processes do not therefore present environmental problems if an exhaust air purifier and a biological water treatment system are employed.

Construction Materials. The materials used for constructing the equipment must satisfy a variety of demands. High resistance to corrosion is essential with respect to the acidic reaction medium and the distillates to prevent contamination of the polyester with traces of metal. Moreover, stress may also arise in the reactor materials due to the high reaction temperatures. These requirements are best met by highly alloyed austenitic chromium – nickel – molybdenum steels, for example V 4 A steel (DIN 1.4571).

The material requirements posed by the raw materials and hydroxypolyester products are less severe. Stainless steel (V 4 A, V 2 A), pure aluminum, $AlMg_3$ alloy, and in special cases even unalloyed steel can therefore be used for pipes and containers for storage and transport.

2.3. Quality Specifications and Testing

Since hydroxypolyesters are subjected to further processing to polyurethanes, they must satisfy stringent quality criteria that can only be obtained through a high degree of product standardization. The most important input data for the polyurethane reaction include the hydroxyl number (DIN 53 240), acid value (DIN 53 402), water content (DIN 53 979), color number (iodine number, DIN 6162; Hazen/APHA, DIN 53 404), and viscosity (DIN 53 015), and are fixed within narrow tolerances for each type of polyester. Individual products often have additional quality criteria that depend on further processing.

The acid value is a measure of the content of terminal carboxyl groups in the polymer and is especially important. A minimum acid value is preferred because terminal carboxyl groups react with isocyanates much more slowly than hydroxyl groups, and can therefore lead to chain termination during polyaddition. Furthermore, the reaction of carboxyl groups with isocyanates produces amide functions and carbon dioxide,

which can result in undesirable bubble formation in the polyurethane. Finally, residual acid in a polyester has negative effects on catalysis of the polyurethane reaction and the stability of the polyurethane product toward hydrolysis. Consequently, an acid value limit is mandatory for polyesters (generally <1 mg KOH/g, but often <0.5 mg KOH/g).

The presence of even trace amounts (ppm levels) of metals, acids or bases, fats, silicone oils, and other surface-active agents in polyesters must be avoided. Such impurities can originate from the starting materials or the processing equipment; their removal is extremely difficult, if not impossible. Consequently, both starting materials and apparatus must be subjected to rigid standards. The analytical data cited in Section 3.1 for the thermoplastic polyester raw materials must be regarded as minimum standards.

Manufacturers utilize the test methods already described, and other specially developed tests for product and process quality control. An applications test is often conducted for final quality assessment.

2.4. Properties

Physical Properties . The diverse applications of polyester-polyurethanes require a wide variety of starting materials. Pure polyadipates of ethylene glycol, 1,4-butanediol, and 1,6-hexanediol are waxy crystalline substances with softening points around 40 – 50 °C. Their crystallinity helps to provide the polyurethane products with outstanding physical characteristics, especially with regard to elasticity, tensile strength, and notch resistance. In some application areas, however, a tendency to harden at low temperatures or as a result of stress (crystallization of elongation) is problematic.

Polyesters made from mixtures of the aforementioned diols, alone or in combination with other diols, can be advantageous in such cases, and are either liquid or greasy at room temperature. 1,2-Propanediol, 1,3-butanediol, diethylene glycol, and neopentyl glycol afford liquid polyadipates.

Due to their broad molecular mass distributions (Schulz–Flory distribution) [12], [13], the polyesters have a relatively high viscosity (e.g., ca. 600 mPa · s at 75 °C and a mean molecular mass of 2000). Densities range between 1.1 and 1.5 g/cm^3. The flash points (DIN 51 758) lie above 200 °C, and the ignition points (DIN 51 794) above 400 °C. Polyesters are relatively soluble in common organic solvents, including acetone, ethyl acetate, and toluene.

Chemical Properties. Terminal hydroxyl groups are largely responsible for the chemical properties of the polyesters, which undergo reactions typical of alcohols. The most important reaction from an applications standpoint is the facile, quantitative addition of hydroxyl groups to the isocyanate groups of di- and polyisocyanates, which affords segmented, high molecular mass polyester-polyurethanes (→ Polyurethanes).

The polyesters exhibit a certain degree of sensitivity toward hydrolysis, and newly formed acidic groups have an autocatalytic effect. The rate of hydrolysis is also increased by the same compounds that catalyze esterification. Resistance to hydrolysis is a function of polyester structure and increases with increasing hydrophobic character and with decreasing ester-group content [16]. Polyesters derived from long-chain diols and dicarboxylic acids are more stable than those based on short-chain starting materials. Diethylene glycol polyesters exhibit only marginal resistance to hydrolysis because of the hydrophilic effect of their ether groups. During further processing acid acceptors (e.g., carbodiimide, epoxides) are often added as hydrolysis stabilizers.

2.5. Storage and Transportation

During storage and transportation of polyesters, exposure to moisture and temperatures above 120 °C must be prevented to avoid undesirable effects during polyurethane production. The products are either stored in sealed, air-tight drums at ambient temperature or in heated, insulated containers under nitrogen at 70 – 110 °C. As liquids they are transported in barrels or in heatable, insulated bulk containers; as solids they are transported in drums.

The construction materials mentioned in Section 2.2.2 are generally utilized for storage and transport vessels; barrels are usually constructed from tin-free steel. Turbidity is sometimes observed in polyesters that are liquid at ambient temperature but have been stored for long periods of time at low temperature; this can be alleviated without affecting the quality of the product by heating the polyester briefly to 80 °C.

Recommendations regarding storage and transport conditions for polyesters are provided by manufacturers. Handling of polyesters presents no significant hazards—a consequence of their chemical characteristics. Spilled material is best treated by mixing it with sand and then sending it to an approved waste disposal site, or by burning it in an appropriate incinerator.

2.6. Uses and Economic Aspects

Hydroxypolyesters are sometimes reacted either alone or in combination with diols or diamines to give segmented polyurethanes, which are marketed as aqueous dispersions, solutions, or as powders that are thermoplastically processable or soluble in special solvents (→ Fibers, 6. Polyurethane Fibers; → Polyurethanes). In other cases they are combined on site with polyisocyanates and various additives to form soft to hard foams, elastomers, adhesives, flexible coatings, and joint fillers.

The polyesters described above are marketed by a number of firms; individual product types are further characterized by appended letters and/or numerical indices. Examples of trade names include:

Baycoll, Bayflex, Baygal, Baytec, Baytherm	Bayer
Crestapol	Bayer
Daltogel, Daltolac, Daltorez	Scott Bader
Desmophen	ICI
Diorez	Bayer
Estolan	Briggs and Townsend
Fomrez	Lancro Chemicals
Lumitol/Elastophen	Witco Chem. Corp.
Multron/Multrathane	BASF
Nippolan	Miles Inc. (formerly Mobay Chem. Corp.)
Polyesteralkohol/Systol	Nippoly
Vulkollan	BASF Schwarzheide GmbH
	Bayer

Estimated production capacities in 1983 were (in 10^3 t/a):

Federal Republic of Germany	89
German Democratic Republic and Poland	15
EC	188
United States	44
Japan	21
World	277

Worldwide consumption in 1983 was estimated at ca. 200 000 t.

3. Thermoplastic Polyesters [19–25]

The history of thermoplastic polyesters (see also → Fibers, 5. Polyester Fibers) goes back to 1929 with the pioneering work of CAROTHERS. The first thermoplastically processible polyesters synthesized from adipic acid and ethylene glycol were described by him in 1932. Polyesters only became of industrial interest in 1941, with the synthesis of high melting point products based on terephthalic acid.

The rapid industrial development of polyesters after World War II was initially restricted to polyester fibers based on poly(ethylene terephthalate) [25038-59-9] (PETP), poly(oxy-1,2-ethanediyloxycarbonyl-1,4-phenylenecarbonyl). A polyester based on poly(1,4-dimethylenecyclohexane terephthalate) [25135-20-0], PDCT, occupies a special position (see also → Fibers, 5. Polyester Fibers).

Poly(ethylene terephthalate) was subsequently also used in the production of films (see also → Films, Section 6.8.).

Thermoplastic polyesters were first employed as construction materials in 1966 [26], and were initially based on poly(ethylene terephthalate). In 1970 the more readily processible poly(butylene terephthalate) [24968-12-5] (PBT), poly-(tetramethylene terephthalate), poly(oxy-1,4-butanediyloxycarbonyl-1,4-phenylenecarbonyl) was introduced onto the market.

A short time later these homopolyesters were supplemented by a series of thermoplastic copolyesters which are suitable for specific areas of application due to their special properties [27]. These copolyesters include polyetherester block copolymers as thermoplastic elastomers; copolyesters based on 1,4-cyclohexanedimethanol for hard, glass-clear injection molded articles; and other thermoplastic copolyesters of varying composition for powder coatings, paint binders (→ Paints and Coatings, 1. Introduction), and hotmelt adhesives.

Recently a new class of fully aromatic thermoplastic polyesters has been developed – liquid crystalline polyesters [28], [29]. These polymers have aroused great interest on account of their outstanding mechanical and thermal

properties. Two such products are commercially available, one being synthesized from 4-hydroxybenzoic acid and 6-hydroxy-2-naphthoic acid, and the other from 4-hydroxybenzoic acid, terephthalic acid, and 4,4′-dihydroxybiphenyl.

3.1. Raw Materials

Thermoplastic polyesters are generally produced from dicarboxylic acids and dihydric alcohols. The most common raw materials follow:

Dicarboxylic acids (and derivatives)
Dimethyl terephthalate [120-61-6]
Terephthalic acid [100-21-0]
Dimethyl isophthalate [1459-93-4]
Isophthalic acid [121-91-5]
Dimethyl adipate [627-93-0]
Adipic acid [124-04-9]
Azelaic acid [123-99-9]
Sebacic acid [111-20-6]
Dodecanoic diacid [693-23-2]
1,4-Cyclohexane dicarboxylic acid [1076-97-7]
Dimethyl-1,4-cyclohexane dicarboxylate ester [94-60-0]

Hydroxycarboxylic acids and lactones
4-Hydroxybenzoic acid [99-96-7]
6-Hydroxy-2-naphthoic acid [16712-64-4]
Pivalolactone [1955-45-9]
ϵ-Caprolactone [502-44-3]

Dihydric alcohols and bisphenols
Ethylene glycol [107-21-1]
1,2-Propanediol [57-55-6]
1,3-Propanediol [504-63-2]
1,4-Butanediol [110-63-4]
1,4-Cyclohexanedimethanol [105-08-8]
2,2-Dimethyl-1,3-propanediol [126-30-7]
1,6-Hexanediol [629-11-8]
Poly(tetrahydrofurandiol) [9040-43-1]
4,4′-Dihydroxy-1,1′-biphenyl [92-88-6]
1,4-Hydroquinone [123-31-9]

Terephthalic acid is by far the most important dicarboxylic acid. This compound was previously difficult to obtain in sufficiently pure form, dimethyl esters of dicarboxylic acids were therefore mainly used as raw materials. Lactones, hydroxycarboxylic acids, and bisphenols are of lesser importance.

Particularly stringent requirements are placed on the purity of the raw materials because impurities can either interfere with polycondensation via chain termination or branching (e.g., mono- or polyfunctional compounds) or can lead to undesirable secondary reactions and discoloration under the high reaction temperatures. These requirements apply to polyesters used as starting material for fibers, but particularly to the plastics sector where polyesters with substantially higher molecular masses are needed.

Analytical requirements for the four most important raw materials are as follows:

Dimethyl Terephthalate (DMT). For production and properties see → Terephthalic Acid, Dimethyl Terephthalate, and Isophthalic Acid.

Purity (GC analysis)	>99.9 %
Solidification point (min.)	140.63 °C
Saponification value	577.8 mg KOH/g
Acid value (max.)	0.03 mg KOH/g
Acid value after 4 h at 175 °C (max.)	0.06 mg KOH/g
Color of the melt after 24 h at 170 °C (max.)	10 (Hazen number)
Color in H_2SO_4 (max.)	10 APHA
Fe content (X-ray fluorescence) (max.)	1 ppm
Nitro groups and nitroso groups should also be absent	

Terephthalic Acid (TA). For production and properties, see → Terephthalic Acid, Dimethyl Terephthalate, and Isophthalic Acid. The purity of "polymer grade" terephthalic acid must satisfy appropriate requirements for the production of fibers, films, and molding compounds. As a rule terephthalic acid is available with the following specifications:

Acid value	675 ± 2 mg KOH/g
Ash content (max.)	15 ppm
Metals (atomic absorption) (max.)	10 ppm
of which Fe (max.)	2 ppm
Co, Mo, Ni, Ti, Mg (max.)	1 ppm
Ca, Al, Na, K (max.)	2 ppm
4-Carboxybenzaldehyde (polarography) (max.)	25 ppm
Water content (Karl Fischer) (max.)	0.5 %
Color in 5 % dimethylformamide (max.)	10 APHA

Under certain conditions (absence of fluorenone structures, maintenance of a defined color

index) the 4-carboxybenzaldehyde content can reach 200 ppm without impairing the polyester quality [30].

Ethylene Glycol. For production and properties, see → Ethylene Glycol.

Relative density d_{20}^{20}	1.1151 – 1.1156
Boiling point range	196 – 200 °C
Solidification point	−11 to −13 °C
Acid content as acetic acid (max.)	0.005 %
Fe content (max.)	0.07 ppm
Chlorine compounds	none
Diethylene glycol content (max.)	0.08 %
Water content (max.)	0.08 %
Ash content (max.)	0.005 g/100 mL
Acetaldehyde content (max.)	30 ppm
Color index after 24 h at 170 °C	<10 (Hazen number)
UV transparency at m	
220 µ	70 %
275 µm	90 %
350 µm	95 %

1,4-Butanediol. For production and properties, see → Butanediols, Butenediol, and Butynediol, Section 1.3.

Purity (GC analysis) (min.)	99.3 %
Water content (max.)	0.05 %
Solidification point (min.)	19.5 °C
Color index (max.)	10 APHA
Ash content	0

3.2. Production

3.2.1. General Principles

Two-Stage Process. Generally, thermoplastic polyesters are produced in two stages. In the first stage a polyester precondensate (M_n 100 – 2000, depending on the molar ratio of the starting compounds) with the formula

$$HO{-}Y{-}O(OC{-}X{-}COO{-}Y{-}O)_x\,H, x \approx 1 - 10$$

is produced by transesterification of dicarboxylic diesters or by esterification of the dicarboxylic acid HOOC−X−COOH with excess dihydric alcohol HO−Y−OH. The precondensate then reacts in a second step (i.e., polycondensation) with the elimination of dihydric alcohol to form high molecular mass polyesters (M_n>10 000) of the formula:

$$HO{-}Y{-}O(OC{-}X{-}COO{-}Y{-}O)_y\,H, y \geq 100$$

Transesterification and esterification are equilibrium reactions that are accelerated by catalysts. The reactions are continuously displaced towards the polyester precondensate by removing the more volatile alcohol or water.

Polycondensation is also an equilibrium reaction, which is shifted towards the high molecular mass polyester by constant removal of the eliminated diol or water (application of a vacuum or purging with an inert gas), and is accelerated by catalysts. The higher the desired molecular mass of the polyester, the more severe are the conditions required to remove the diol and water. Polycondensation is a step-growth reaction (of the type A – A+B – B=diol + dicarboxylic acid or A – B=hydroxycarboxylic acid), which leads to nonuniform end products. The molecular mass distribution can be calculated from the molar ratio of diol to dicarboxylic acid and/or from the conversion p [31]. With a stoichiometric ratio of the A and B groups, the mass fraction W_x of the degree of polycondensation x can be specified as a function of the conversion p [32]:

$$W_x = \frac{(M_L + M_U x)}{[M_U + M_L(1-p)]}\, p^{x-1}\,(1-p)^2$$

M_L and M_U denote the molecular masses of the leaving molecules L and basic units U, respectively. For negligibly small molecular masses of the leaving molecules ($M_L/M_U \rightarrow 0$) or as an approximation for high conversion rates ($p \rightarrow 1$), the equation transforms to the Schulz –Flory distribution function

$$W_x = x p^{x-1}(1-p)^2$$

Introduction of the mean degree of polycondensation $P_n = 1/(1-p)$ gives

$$W_x = \frac{x}{P_n^2}\left(1 - \frac{1}{P_n}\right)^{x-1}$$

The relationship $P_n = 1/(1-p)$ clearly shows that a minimum degree of polymerization of 100 can only be achieved with conversions of > 99 % (p=0.99).

The kinetics of esterification, transesterification, and polycondensation [33–40] have been

investigated in great detail. See also → Polymerization Processes, 1. Fundamentals, Chap. 1., → Polymerization Processes, 1. Fundamentals, Chap. 2.. In general, polycondensation is regarded as a second-order reaction [41], [42], with an activation energy that depends strongly on the catalyst system (PETP: uncatalyzed 96.6 kJ/mol [41], catalysis with manganese acetate 40.8 kJ/mol [42]).

Other Processes. In addition to the conventional two-stage process for producing linear thermoplastic polyesters, many other processes are used with other starting compounds. Addition of ethylene oxide to dicarboxylic acids gives bis(2-hydroxyethyl) esters. In analogy with the previously described esterification and transesterification products, these esters undergo polycondensation with the elimination of ethylene glycol [43].

Fully aromatic polyesters with a high melting point are produced by interfacial polycondensation of dicarboxylic dichlorides with bisphenols in the presence of bases and with elimination of hydrogen chloride [44]. Dicarboxylic acids also react with diesters (preferably acetates) of dihydric alcohols with the elimination of acid [45].

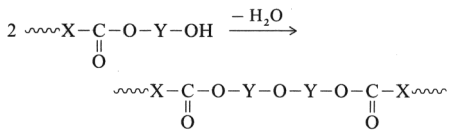
The esterification of an anhydride with a dihydric alcohol or the transesterification of anhydrides with epoxides yields linear polyesters [46], [47].

A special process for producing high molecular mass thermoplastic polyesters involves the polymerization of lactones in the presence of organometallic compounds [48].

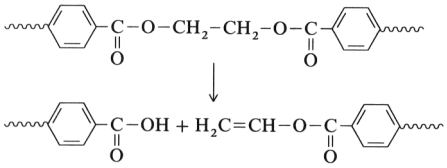
Secondary Reactions [49–51]. In all methods for producing linear thermoplastic polyesters, secondary reactions that occur during polycondensation can alter the stoichiometric ratio and thus terminate polycondensation or confer undesirable properties on the end product.

The most important secondary reactions include:

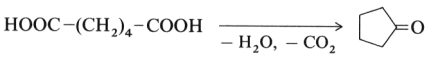
1. Ether formation to produce diethylene glycol units (Y=C_2H_4)



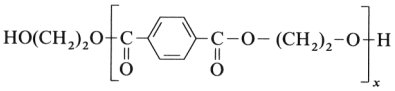
2. Dehydration of ethylene glycol to form acetaldehyde, or of 1,4-butanediol to form tetrahydrofuran
3. Ester pyrolysis which in the case of PETP, for example, produces carboxyl groups (poorer resistance to hydrolysis) and olefins (discoloration):



4. Ring formation between two adjacent carboxyl groups (particularly pronounced in adipic acid):



3.2.2. Production of Poly(Ethylene Terephthalate) from Dimethyl Terephthalate



Poly(ethylene terephthalate) (PETP) is produced industrially both batchwise and continuously. The apparatus used for these processes is also suitable for the production of other thermoplastic polyesters. For the sake of simplicity, however, the batchwise production of PETP is discussed here. Separate vessels are often used to melt the starting compounds and for the transesterification and polycondensation reactions.

Melting. Dimethyl terephthalate (DMT) is melted at 150 – 160 °C in a stirred tank heated with steam, carrier oil, or electricity in an inert atmosphere (nitrogen).

Transesterification. The molten DMT and ethylene glycol are reacted in heated, stirred transesterification reactors at 150 – 200 °C. At the start of the reaction (at normal pressure in a nitrogen atmosphere) the lower temperature range is preferred to minimize sublimation of

DMT. The methanol released during the transesterification is continuously distilled off from the reaction mixture. The excess of ethylene glycol is normally ca. 0.5 – 1 mol/mol DMT.

The use of catalysts is essential to achieve a reasonable transesterification rate at moderate temperatures. Although the catalysts listed in the patent literature cover practically the whole periodic system, weakly basic compounds such as amines, metal oxides, alkoxides, and acetates are used as transesterification catalysts in practice at a concentration of 0.01 – 0.1 wt % referred to DMT. Systematic investigations showed that the rate constant for the transesterification of DMT with ethylene glycol correlates with the electronegativity of the catalyst metal ion [52]. Metal compounds in which the electronegativity of the metal ion is in the range 1 – 1.7 are most effective (e.g., acetates of Ca, Mg, Zn, Cd, Pb, and Co). An almost identical order is found when the stability constants of the metal dibenzoylmethane complexes are related to the rate constants of the transesterification reaction [53].

The choice of a suitable catalyst is an important factor in the production of PETP as regards the economy of the production process and quality of the end product. Transesterification should proceed as quantitatively as possible because residual methyl ester groups can interfere with subsequent polycondensation [54]. This is particularly true if the activity of the transesterification catalysts is lowered by additives introduced at the polycondensation stage. The course of transesterification is therefore controlled by the amount of methanol released, whereby entrained ethylene glycol has to be taken into account (density measurement or ultrasonic monitoring).

Polycondensation. The transesterification product is added as a melt to the polycondensation reactor, which can be heated to over 300 °C and must be equipped with a very efficient stirrer. Some of the excess ethylene glycol is often first distilled off at normal pressure (protective gas, nitrogen) by gradually increasing the temperature to ca. 250 °C. Polycondensation then follows, with a reduction in pressure and a further increase in temperature. In order to obtain sufficiently high molecular masses, temperatures of ca. 270 – 280 °C at a final vacuum of <1 mbar are required.

Like the transesterification reaction, the polycondensation reaction has to be accelerated by catalysts. All the catalysts used for transesterification are, in principle, also suitable for polycondensation because the two reactions are extremely similar. The catalyst remaining in the reaction mixture after the transesterification can therefore be used further for polycondensation. This approach does not always provide satisfactory products, however, because active transesterification catalysts decrease the thermal stability of PETP [55]. In many cases the transesterification catalyst is therefore masked with suitable additives (mainly phosphorus compounds) and replaced by special polycondensation catalysts, usually antimony, germanium, titanium, or lead compounds at a concentration of 0.005 – 0.05 wt % referred to DMT.

Rapid polycondensation is achieved by quickly removing the eleminated ethylene glycol by means of intensive mixing and a maximum polymer melt surface area. In conventional polycondensation plants this is achieved by intensive stirring. Distribution of the polymer melt in thin-film procedures as in thin-layer evaporators or in annular disk reactors is, however, more effective for obtaining very high molecular masses.

Polycondensation is stopped when a defined melt viscosity (measure of the molecular mass), is reached. The power consumption of the stirrer motor is often an adequate indicator of melt viscosity. In order to terminate polycondensation, the vacuum in the reaction vessel is removed with oxygen-free nitrogen and the melt is expelled from the reactor either under nitrogen pressure or, preferably, with spinning pumps. The melt is directly quenched with water and comminuted into chips or pellets to prevent oxidation by atmospheric oxygen.

Conventional batchwise and continuous polycondensation produces PETP that is processed into threads and fibers (solution viscosity ca. 50 – 80 cm^3/g measured in phenol/tetrachloroethane 60/40 wt % at a concentration of 0.0023 g/cm^3, see Section 3.3).

Before further processing the PETP must be carefully dried at 80 – 130 °C to reduce the water content to below 0.01 wt %. Drying is performed with the same apparatus used for solid-phase postcondensation. Heating during drying causes crystallization of PETP which

is necessary to avoid agglomeration of the particles during prolonged storage.

A PETP with a fairly high intrinsic viscosity, such as can be produced with the thin-layer evaporator or annular disk reactor, is required for the plastics sector. Alternatively, however, the comminuted PETP (chips, pellets, etc.) is often subjected to solid-phase postcondensation for a fairly long time (~20 h) at temperatures of up to 250 °C in an inert gas stream or in vacuo, resulting in an increase in molecular mass. The rate-determining step in this reaction is diffusion of the eliminated ethylene glycol from the polymer particles, which depends on the particle size [56]. Postcondensation in the solid phase can be performed either batchwise (in vacuum dryers or in a fluidized bed) or continuously (in countercurrent with hot nitrogen).

Production Example for PETP [57]. 12.8 kg of DMT and 8.1 kg of ethylene glycol are transesterified in the presence of 3.32 g of manganese acetate and 0.83 g of cobalt acetate for 3 h at 195 °C under nitrogen in a 30-L steel reactor equipped with an anchor-type stirrer and a distillation column. The liberated methanol is distilled off. 10.76 g of triphenyl phosphate is then added and stirred in for 30 min at 195 °C; 2.75 g of germanium oxide and 0.5 g of tetraisopropyl titanate are added and stirring is continued for a further 30 min.

The temperature of the reaction mixture is then raised to 280 °C within 6 h and the pressure subsequently reduced to 0.3 mbar in 2 h. After a further 2 h under these conditions the vacuum is removed with nitrogen. The polyester melt is extruded in the form of strands, which are cooled in water and then pelletized. The solution viscosity of the polyester is 62 cm^3/g (in phenol/tetrachloroethane 60/40, concentration 0.0023 g/cm^3).

3.2.3. Production of Poly(Ethylene Terephthalate) from Terephthalic Acid

The direct esterification of terephthalic acid (TA) with ethylene glycol became important when economic processes were developed for producing fiber-grade TA [58]. An important advance was made when the reaction times were reduced by performing esterification under pressure (2.7 – 5.5 bar) at temperatures above the boiling point of ethylene glycol (198 °C) [59], [60].

Table 1. Quality specifications for additive-free PETP used for film production [61]

Specification	Raw material	
	DMT	TA
Intrinsic viscosity, cm^3/g	65 ± 0.015	65 ± 0.015
Carboxyl terminal groups, mmol/kg	20 – 30	20 – 30
Ash content, wt %	<0.04	<0.02
Diethylene glycol content, wt %	0.5 – 1.2	0.7 – 1.2
Filter value (15 μm filter braid), bar cm^2/kg	<30	<30

The TA process now yields products that are qualitatively competitive with the polyesters produced in the DMT process (see Table 1) [61].

In new plants direct esterification is the preferred method of PETP production. The advantages of direct esterification with TA compared with transesterification with DMT are

1. The higher reaction rate
2. The lower weight of TA compared with DMT (storage costs)
3. The use of water instead of methanol as condensation agent
4. No transesterification catalyst is required
5. Higher molecular masses are obtained

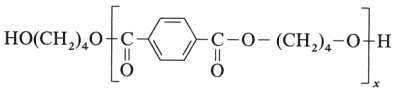
Temperatures of around 220 – 260 °C are generally maintained to overcome the sparing solubility of TA. The water formed is continuously removed by distillation. The molar ratio of ethylene glycol to TA should be < 2 (in most patents < 1.5 is specified) to suppress formation of diethylene glycol (see). Direct esterification is possible without catalysts, but can be accelerated by basic catalysts (amines) or transesterification catalysts (usually Sb_2O_3).

Esterification is followed by gradual pressure release, the temperature is simultaneously increased and excess ethylene glycol is distilled off. The formation of PETP takes place in the polycondensation stage, which proceeds analogously to the DMT – ethylene glycol process as regards temperature, pressure, and catalysts (see Section 3.2.2, a detailed process description is given in [62], [63]).

Direct esterification at normal pressure can be achieved in a PETP precondensate as reaction medium, in which TA is readily soluble [64]. This process is particularly suitable for continuous direct esterification.

The secondary reactions occurring during polycondensation are of decisive importance in determining the quality of the PETP (see). Ether formation results in diethylene glycol units which have adverse effects on dyeing behavior but also lower thermal and UV stability (for the mechanism of diethylene glycol formation, see [65]). Free carboxylic groups formed by ester pyrolysis have a negative influence on the postcondensation and hydrolysis stability of PETP. Ester pyrolysis also produces olefinic decomposition products that lead to discoloration of PETP.

3.2.4. Production of Poly(Butylene Terephthalate)



Poly(butylene terephthalate) (PBT) is produced analogously to PETP. The currently preferred process is still the transesterification of DMT with 1,4-butanediol followed by polycondensation. The main byproduct is tetrahydrofuran, formed from 1,4-butanediol by dehydration (see). Although some alkyl tin compounds lower tetrahydrofuran formation, the resulting polymers have a lower thermal stability [66]. Although tetrahydrofuran formation is catalyzed by acids, TA is increasingly used as a raw material instead of DMT [67], [68]. For the advantages of the TA method, see Section 3.2.3.

Transesterification of DMT is performed with a slight excess of 1,4-butanediol (molar ratio 1,4-butanediol: DMT < 2, preferably 1.3 –1.7) at 160 – 220 °C and normal or excess pressure. Soluble titanium compounds are generally used as transesterification catalysts.

Polycondensation at ≤ 260 °C and < 1 mbar is usually also catalyzed by soluble titanium compounds (generally tetraalkyl titanates).

PBT can generally be subjected to polycondensation in the melt to give products with higher molecular masses than PETP (solution viscosity up to ca. 120 cm^3/g, measured in phenol – tetrachloroethane, weight ratio 3 : 2 at 25 °C, concentration 0.0023 g/cm^3). The product is dried in the same way as PETP, see Section 3.2.2. For some uses in the plastics sector (optical waveguide coverings, coatings for bowden wire, headlight dimmers) a higher molecular mass PBT is required, which can also be obtained by solid-phase condensation.

Production Example for PBT [69]. 8.0 kg of DMT and 5.9 kg of 1,4-butanediol (molar ratio with respect to DMT 1.6) are added to a 30-L reactor equipped with an anchor-type stirrer. After heating the mixture to 150 °C, 160 g of a 7 % solution of titanium tetrabutylate in 1,4-butanediol is added over 100 min while stirring to initiate transesterification. After gradual heating to 200 °C over 1.5 h, transesterification is continued for a further 3.5 h at 200 °C, and the methanol formed is distilled off.

The pressure is reduced from 1 bar to 1.3 mbar over 2 h, and the temperature is subsequently increased from 200 to 245 °C in 1 h. Continued heating at 245 °C and 1.3 mbar for ca. 5 h gives a polymer with an intrinsic viscosity of 124 cm^3/g.

3.2.5. Production of Other Partially Aromatic Polyesters

Other high molecular mass thermoplastic polyesters, such as poly(1,4-cyclohexylenedimethylene terephthalate) [25135-20-0], PDCT, copolyesters or copolyetheresters (see → Fibers, 5. Polyester Fibers) are produced in a similar way to PETP and PBT. The different melting points of the end products and different reactivities of the monomers must, however, be taken into account. Depending on their chemical constitution (diol, diester, and diacid), the cocomponents (see Section 3.4) are added before, during, or after the transesterification phase, or before or during the esterification phase.

Production examples for polyesters based on 1,4-cyclohexanedimethanol [1,4-bis(hydroxymethyl)cyclohexane] and for polyetheresters are given in [70–72].

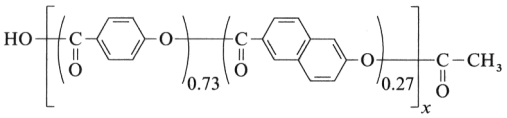
3.2.6. Production of Fully Aromatic, Liquid Crystalline Polyesters

Fully aromatic, liquid crystalline polyesters can be produced in the melt by three main processes. Direct esterification of phenols with aromatic carboxylic acids in the presence of catalysts

such as titanium tetrabutyrate or dibutyl tin diacetate is described in [73]. On account of the high reaction temperatures (>300 °C) there is however the danger of decarboxylation of the carboxylic acids, and the method is therefore restricted to monomers that are stable at the melting point.

A second process involves reacting phenyl esters of aromatic carboxylic acids with relevant phenols. The phenyl esters can be produced by direct esterification or by reaction of diphenyl carbonate with dicarboxylic acids, with the formation of carbon dioxide and phenol.

The commercially available liquid crystalline polyesters Vectra [81843-52-9] and Xydar [31072-56-7] are produced by a third method: acidolysis of phenolic acetates with aromatic carboxylic acids [74], [75].

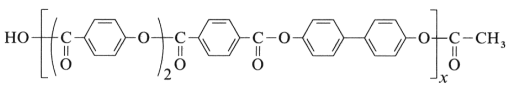


Vectra

Vectra is synthesized from 4-hydroxybenzoic acid and 6-hydroxy-2-naphthoic acid. Xydar is prepared from 4-hydroxybenzoic acid, 4,4′-dihydroxy-1,1′-biphenyl, and terephthalic acid. The basic structural formulae shown below can be modified by using other monomers such as isophthalic acid or 4-aminobenzoic acid, or by using a different monomer ratio [75–78]. In order to acetylate the phenolic hydroxyl groups, the monomers are added to a stainless steel stirred tank, followed by an excess of acetic anhydride under an inert gas atmosphere (nitrogen). Too large an excess of acetic anhydride affects the color of the polymer and leads to the formation of mixed anhydride structures. Most patents specify a molar ratio of acetic anhydride to phenolic OH groups of 1.02 – 1.18.

The acetylation reaction is performed at 120 – 150 °C under reflux and is complete after 1 to 5 h. The acetic acid that is formed and any acetic anhydride still present are distilled off. The temperature is then raised in stages to ca. 320 °C and a low molecular mass prepolymer is formed. Polycondensation is then usually carried out by gradual reduction of the pressure (<15 mbar) and distilling off further acetic acid until the desired molecular mass (10 000 – 30 000) is obtained. In contrast to Vectra, the maximum molecular mass of Xydar (*mp* 421 °C) in the melt is limited by the higher melting point and higher melt viscosity. Consequently, the Xydar prepolymer, which is still liquid at 320 °C, is discharged from the reactor under an inert gas, granulated, and postcondensed in the solid phase (inert gas or vacuum) at a maximum temperature of 365 °C.

Vectra is synthesized exclusively from high-purity hyroxycarboxylic acids and can, in theory, undergo polycondensation to yield products of infinitely high molecular mass. The molecular mass can be limited by adding small amounts of 4,4′-diacetoxybiphenyl [79]. Catalysts may, however, be added to accelerate acetylation and polycondensation (ca. 25 – 500 ppm referred to the polymer). Catalysts include alkali-metal acetates (e.g., sodium or potassium acetate) and acids (e.g., *p*-toluenesulfonic acid or 2-naphthalenesulfonic acid). Iron ions have a high catalytic activity in the production of Vectra [74]. The iron content of the polymer should not, however, exceed 50 ppm because this has an adverse effect on its thermal properties.



Xydar

Xydar is often synthesized in the presence of potassium sulfate (25 – 50 ppm referred to the polymer) to improve processibility and appearance of the polymer [75].

Production Example for Vectra [74]. 24.05 kg of 6-hydroxy-2-naphthoic acid and 47.85 kg of 4-hydroxybenzoic acid are added to a 151.4-L steel reactor (stainless steel 316) equipped with a helical stirrer, a solids and liquid trap, and a distillation column. The reactor is alternately evacuated (ca. 9 mbar) and flushed with nitrogen three times. 49.90 kg of acetic anhydride (technical quality) is then added. The reaction mixture is heated to 120 – 140 °C and kept at this temperature for 1 h. The temperature is then raised to 200 °C in 1.5 h. Polycondensation takes place at 200 –327 °C over a period of 3 h under nitrogen (2.8 m^3/h), followed by 1.25 h (at 327 °C) in vacuo (ca. 13 mbar). The hot polymer melt is then extruded and comminuted. The intrinsic viscosity of the polymer in

pentafluorophenol at 60 °C (concentration 0.1 wt %) is 540 cm^3/g.

3.3. Analysis

Thermoplastic polyesters have to be analyzed before they are processed. The most important parameter to be determined is the molecular mass because this influences the processability of the molding compounds and the mechanical properties of the article produced from the polyester.

In most cases the molecular mass is determined indirectly via the reduced or specific viscosity (in cm^3/g) in a capillary viscometer (→ Plastics, Analysis). The intrinsic viscosity [η] is thus obtained by extrapolation of the reduced viscosity to zero concentration and from this the molecular mass M [80] according to

$$[\eta] = KM^a$$

For polymers with a range of molecular masses, M becomes M_n (number average), M_w (weight average), or M_v (viscosity average) depending on the method of determination. See also, → Plastics, General Survey, Section 2.2.2..

The reduced viscosity depends on the solvent, concentration, and temperature. For quality control it is normally sufficient to specify the solution viscosity under defined conditions.

The constants K and a have been determined for PETP and PBT under various conditions (see Table 2). For PBT a correlation between the reduced viscosity and M_w is also described [86].

The melt viscosity η_m is just as important a quantity as the solution viscosity as regards the processing of thermoplastic polyesters. Measurement under defined conditions (temperature, viscometer, shear rate, etc.) is sufficient for monitoring quality. Like the solution viscosity, the melt viscosity is related to the molecular mass [87]:

$$\eta_{m,0} = KM_w^{3.5}$$

where $\eta_{m,0}$ is the melt viscosity in Pa · s at a shear rate of 0. Values for K in Pa · s are

PETP[88] : $1.13 \times 10^{-14} \exp(-11.9755 + 6082.1/T)$
PBT[85] : 1.02×10^{-14} at 250 °C

Investigations on the melt viscosity of polyetheresters and fully aromatic, liquid crystalline polyesters are described in [89].

The molecular mass distribution of thermoplastic polyesters is determined only in special cases (for methods see [90]), for example to establish the influence of process or reactor technology on the polyesters. Most linear polyesters exhibit a Schulz – Flory distribution (see Two Stage Process). Further information on the quality of thermoplastic polyesters is obtained by measuring the melting point, glass transition temperature (both preferably by differential thermal analysis), the hydroxyl terminal groups [91], acid terminal groups [92], and the diglycol content [93].

The water content [94] is also of great importance for the processing of thermoplastic polyesters because water often causes hydrolytic decomposition at high processing temperatures. The equilibrium water content, for a given degree of polymerization P_n must not be exceeded on account of the danger of hydrolytic decomposition. This content can be calculated for high conversions from the approximate formula

$$P_n = \sqrt{\frac{K}{n_{H_2O}}}$$

where K is the equilibrium constant and n_{H_2O} denotes the number of moles of water per mole of monomer. For example, the maximum water content for PETP ($K \approx 4$) with a molecular mass $M_n \approx 10\,000$ ($P_n = 100$) is 0.01 wt %.

Table 2. Constants K and α for PETP and PBT

Polyester	Solvent	K	α	Method of determination	Reference
PETP	phenol – tetrachloroethane 1 : 1, 20 °C	0.0755	0.685	terminal group determination (M_n)	[81]
PETP	2-chlorophenol, 25 °C	0.030	0.74	terminal group determination (M_n)	[82]
PETP	2-chlorophenol, 25 °C	0.0425	0.69	sedimentation, diffusion (M_w)	[82]
PETP	phenol-1,2-dichlorobenzene 1 : 1, 25 °C	0.0469	0.68	light scattering (M_w)	[83]
PETP	phenol – tetrachloroethane 3 : 2, 25 °C	0.0468	0.68	light scattering (M_w)	[84]
PBT	phenol – tetrachloroethane 3 : 2, 30 °C	0.0116	0.87	terminal group determination (M_n)	[85]
PBT	phenol-1,2-dichlorobenzene 1 : 1, 25 °C	0.0437	0.72	light scattering (M_w)	[83]

A further criterion for the use of thermoplastic polyesters in the fiber or plastics sector is the intrinsic color. This is usually specified as a blue – yellow value (measured with an electric remission photometer) [95].

3.4. Co-Components and Additives [96]

Thermoplastic Copolyesters. The dyeability, elasticity, pilling behavior, shrinkage, hydrophilicity, and flame resistance of polyester fibers can be improved by condensation with appropriate comonomers [97].

The crystallinity, melting point, glass transition temperature, elasticity, flammability, solubility, and other properties of thermoplastic polyesters used in the plastics sector can be modified by selective co-condensation.

Examples of such copolyesters are glass-clear (amorphous) copolyesters based on 1,4-cyclohexanedimethanol, terephthalic acid, and isophthalic acid (i.e., poly(1,4-cyclohexylenedimethylene terephthalate-co-isophthalate) [26124-27-6] [98]); elastic copolyesters based on 1,4-butanediol, poly(tetrahydrofurandiol), and terephthalic acid (i.e., poly(butylene terephthalate-co[multibutylenoxy] terephthalate) [71], [72]; neopentyl-glycol-containing copolyesters with good solution properties in paint solvents [99]; and copolyesters based on 1,4-butanediol, terephthalic acid, and isophthalic acid with relatively low melting points for hotmelt adhesives [100]. Thermoplastic copolyesters with elevated glass transition temperatures (and thus improved heat resistance) can be obtained by incorporating heterocyclic diols during condensation [101]. For the production of copolyesters, see 3.2.5.

Additives. Raw polymers are seldom processed as such into semifinished or finished articles. Additives are usually added to the polymers in a process known as compounding or formulation. Compounding processes (e.g., mixing, kneading, extrusion, pelletization) are of great importance because the properties, processing, and use of thermoplastic polymers are substantially determined by the additives (e.g., nucleating agents, fillers, flame retardants, stabilizers, pigments).

Nucleating Agents [102], [103]. See also → Plastics, Additives, Section 9.1. The processibility of PETP in injection molding is mainly determined by its slow crystallization rate and by the associated danger of cold crystallization (tendency to distortion). High molding temperatures (ca. 140 °C) and addition of nucleating agents are therefore necessary to accelerate the nucleation rate. Inorganic substances such as talc, magnesium oxide, or clay are added as nucleating agents in concentrations of 0.001 – 1 % with a maximum particle size of 2 – 3 μm. Organic compounds include salts of aromatic carboxylic acids, fatty acid salts, Montan waxes, and polymers such as polyethylene. The nucleating agents can be added at any stage during PETP production or as a powder to the granulate.

PBT and PBT copolyesters with polytetrahydrofuran generally crystallize so rapidly that nucleation is not necessary.

Glass Fibers [104]. See also → Plastics, Additives, Chap. 7. The heat resistance, rigidity, and hardness of thermoplastic polyesters can be considerably increased by adding glass fibers or beads. For example, the heat distortion temperature (according to Martens, DIN 53 458) of PBT reinforced with glass fiber varies as follows:

Heat distortion temperature, °C	50	75	120	160	190
Glass fiber content, wt %	0	10	20	30	50

The glass reinforcement may be added as beads, ground glass fiber, staple glass fiber, or long glass fiber. Maximum heat resistance, rigidity, and hardness are achieved by adding long glass fibers. These additives are mixed with the thermoplastic polyesters in special extruders in a separate compounding stage; amounts of up to 50 % are commonly employed.

Flame Retardants. See also → Flame Retardants, and → Plastics, Additives, Chap. 6. Thermoplastic polyesters (PETP and PBT) have a relatively low flammability because they escape the action of the flame due to melting and droplet formation (oxygen index of PBT, 23 %; UL 94 rating, HB); see also → Flame Retardants, Chap. 3.). Fillers and, in particular, glass fiber reinforcement prevent droplet formation, resulting in a sharp increase in flammability (oxygen index of PBT reinforced with 10 % glass fiber, 19 %). Legislation is increasingly

promoting the use of self-extinguishing, nondrip plastics formulations.

Self-extinguishing thermoplastic polyesters are obtained by incorporating ca. 30 % of flame retardants, which are usually aromatic halogenated compounds combinedwith antimony oxide [105] or with phosphorus compounds [106] (see also → Flame Retardants). Examples are brominated polycarbonates [107] and polystyrenes [108], or ethylene(tetrabromophthalimide) in combination with antimony oxide. A combination of red phosphorus and antimony oxide is also used, particularly with PETP [109].

The flame retardants are not normally added during the production of thermoplastic polyesters, but in a subsequent compounding stage.

The polybrominated diphenyl ethers are suspected of producing polybrominated dibenzodioxins and dibenzofurans in the event of fire [110]; they are therefore no longer used in Germany, and interest in halogen-free flame retardants has greatly increased. Up to now, however, only developments and improvements of conventional systems, such as microencapsulated red phosphorus, ammonium polyphosphates, magnesium hydroxide, and magnesium carbonate have been described [111], [112]. The magnesium compounds have the disadvantage that they have to be added in substantially higher amounts and may therefore seriously affect the polymer properties.

Fully aromatic liquid crystalline polyesters have a low flammability and do not require flame retardants.

Stabilizers. See also → Plastics, Additives, Chap. 2., → Plastics, Additives, Chap. 3.. In contrast to PETP and PBT, thermoplastic polyetheresters are extremely sensitive to photooxidative decomposition [113] and must be stabilized. Stabilizers include sterically hindered phenols or amines, which are added to the starting substances in an amount of 0.1 –0.5 wt % or are incorporated in the polymer melt [114].

The antioxidant 4,4′-bis(α,α′-dimethylbenzyl) diphenylamine has been approved by the FDA for use in phthalate, isophthalate, and terephthalate polyesters with 1,4-butanediol and polytetrahydrofuran.

Pigments [115], [116]. Pigments with an adequate heat resistance (e.g., titanium dioxide, carbon black, phthalocyanines, quinacridones, cadmium yellow) are suitable for coloring thermoplastic polyesters.

Admixture of Other Polymers. The properties of partially aromatic thermoplastic polyesters can be selectively improved by blending with other polymers. See also, → Polymer Blends, Section 4.7.. PBTs whose impact properties have been improved with polybutadiene graft rubbers are used in car bumper systems [117]. Impact strength can also be increased by adding polyethylene [118]. Higher flexibility is obtained by blending with polyether elastomers [119].

New alloying components such as styrene –maleic anhydride copolymers or acrylonitrile – styrene – acrylate copolymers also expand the application range, particularly of PBT [120]. Polymer blends of bisphenol-A-polycarbonate with PBT or PETP have good low-temperature strength and low shrinkage values, they have been commercially successful for several years [121].

Blends with polyurethanes and polyamides [122] or poly-ϵ-caprolactone [123] are also described.

3.5. Properties

The properties of thermoplastic polyesters depend primarily on the starting compounds (dicarboxylic acids, diols), their molecular mass, and added fillers. The properties of PETP, PBT, and PDCT as fiber raw materials are described in → Fibers, 5. Polyester Fibers, Chap. 2..

PETP and PBT. The two most important thermoplastic polyesters for the plastics sector, namely PETP and PBT, can be described as partially crystalline polymers. They have a high hardness and rigidity, good creep strength, high dimensional stability, and very good slip and wear behavior [124], [125]. Whereas PBT occurs almost exclusively in the partially crystalline form, PETP can also be processed into amorphous molded bodies with high transparency; on heating to 70 – 100 °C this transparency is lost due to postcrystallization. Transparency can, however, be retained if the polyester chains are forcibly oriented, for example by biaxial stretching and heat setting (transparent films of PETP, → Films, Section 6.8.).

A special property of PETP is its slow crystallization, which necessitates molding temperatures of ca. 140 °C and the use of a nucleating agent and crystallization accelerator (see).

PBT and PETP are resistant to water, weak acids and bases, alcohols, ketones, ethers, aliphatic hydrocarbons, and chlorinated aliphatic hydrocarbons at room temperature.

Solvents for PBT and PETP include hexafluoro-2-propanol, hexafluoroacetone, and 2-chlorophenol (mixed solvents, see Table 2).

Hydrolysis proceeds rapidly in the melt in the presence of moisture. The dependence of the hydrolysis rate on temperature and moisture content has been investigated [126], [127].

The most important mechanical, thermal, and electrical properties of PETP and PBT are summarized in Table 3.

Polyetheresters [128–130]. Thermoplastic polyetheresters are block copolymers synthesized from mutually incompatible rigid crystalline and soft amorphous segments. The rigid segments generally consist of an aromatic polyester (e.g., PBT), whereas the soft segments consist of an aliphatic polyether [e.g., poly(butylene glycol) or

Table 3. Properties of PETP and PBT [125]

Property	Test method	PETP			PBT		
		Partially crystalline	30 % glass fiber reinforced	Partially crystalline (standard grade)	Partially crystalline (tough grade)	30 % glass fiber reinforced	30 % glass fiber reinforced with flame retardant
Mechanical (23°C)							
Tensile strength and yield stress, N/mm^2	DIN 53 455	73	150 – 170	52	38	130 – 140	110 – 120
Elongation at break, %	DIN 53 455	300	2	>250	>250	2	2
Modulus of elasticity tensile test), N/mm^2	DIN 53 457	2850	10 000 – 12 000	2700	1100	8500 – 10 000	9000 – 11 000
Bending strength, N/mm^2	ASTM D 790	118	230 – 250	85	43	200 – 210	190 – 200
Impact strength, kJ/m^2	DIN 53 453		25 – 40			30 – 40	20 – 25
Notched bar impact strength, kJ/m^2	DIN 53 453	4	6 – 14	5	23	8 – 19 *	6 – 14 *
Ball indentation hardness, N/mm^2	DIN 53 456	170	200 – 230	139	86	200 – 230	210 – 240
Physical and thermal							
Density, g/cm^3	DIN 53 479	1.37	1.58	1.31	1.29	1.53	1.66
Moisture absorption (saturation 23 °C, 50 % relative humidity), %	ASTM D 570	0.35	0.25	0.20	0.20	0.13	0.10
Deflection temperature under load, °C	ISO/R 75, method A	82	225	50	50	205 – 225 *	205 – 225 *
Linear coefficient of expansion, $10^{-5}\ K^{-1}$	ASTM D 696	7	3	8	13	3	3
Flammability	UL 94						V-0
Crystallite melting point, °C	differential thermal analysis	255 – 260	255 – 260	220 – 225	200 – 205	220 – 225	220 – 225
Electrical							
Volume resistivity, Ω · cm	VDE 0303, part 3	$>10^{14}$	$>10^{15}$	$>10^{15}$	$>10^{15}$	$>10^{15}$	$>10^{15}$
Surface resistance, Ω	VDE 0303, part 3	$>10^{13}$	$>10^{13}$	$>10^{13}$	$>10^{14}$	$>10^{13}$	$>10^{13}$
Dielectric loss factor tan δ, 50 Hz	VDE 0303, part 4	0.0015	0.002	0.002	0.007	0.0024	0.0025
10^6 Hz		0.019	0.016	0.020	0.021	0.018	0.016
Dielectricity constant ϵ_r, 50 Hz	VDE 0303, part 4	4.3	4.3	3.8	3.7	4.4	4.5
10^4 Hz		3.5	4.4	3.2	3.7	3.8	3.8
Dielectric strength, kV/cm	IEC Pub 234, (2 mm plate)	200	170	150	180	170	170

* Upper values refer to grades reinforced with long fibers.

poly(ethylene glycol)]. On account of the physical cross-linking of the rigid and soft domains, polyetheresters behave like elastomers at the service temperature ($>T_g$, $<mp$). The cross-linking sites are, however, thermally labile and the polymers can therefore be thermoplastically processed above the melting point.

Important thermal, mechanical, and electrical properties of polyetheresters are summarized in Table 4.

The very low glass transition temperature of the polyether (ca. −50 °C) and the high melting point of the polyester (ca. 200 °C) result in polymers with a very broad service temperature range. Polyetheresters with Shore-D hardnesses of 35 – 72 can be formulated by varying the block length and the ratio of the rigid and soft components.

The special properties depend on the nature of the rigid and soft segments. Copolyesters based on butylene glycol terephthalate crystallize very rapidly from the melt, in contrast to polymers synthesized from ethylene glycol terephthalate blocks. Copolymers with poly-(propylene oxide glycol) and poly(tetramethylene ether glycol) exhibit similar swelling behaviors in water and oil. On the other hand, polymers

Table 4. Properties of polyetheresters [131], [132]; Xydar [133], [134]; and Vectra [134]

Property	Test method	Polyetherester	Vectra		Xydar	
			A 950 (base type)	A 130 (30 % glass fiber reinforced)	SRT 300 (base type, high-melting)	G 330 (30 % glass fiber reinforced)
Mechanical (23 °C)						
Tensile strength, N/mm^2	DIN 53 455	9 – 46	156	188	138	117
Elongation at break, %	DIN 53 455	170 – 700	2.6	2.1	4.9	2.6
Tensile modulus of elasticity, N/mm^2	ASTM D 638		9700	16 600	16 600	12 000
Bending modulus of elasticity,						
−40 °C, N/mm^2	ASTM D 790	160 – 2400				
23 °C N/mm^2	ASTM D 790	50 – 600	9000	15 000	13 800	11 600
100 °C N/mm^2	ASTM D 790	30 – 210				
Bending strengh, N/mm^2	ASTM D 790				131	150
Notched bar impact strength according to Izod, J/m	ASTM D 256	without break				
−40 °C						
23 °C	ASTM D 256	without break	520	150	130	176
Hardness, Durometer *D*, points	DIN 53 505	35 – 72				
Physical and thermal						
Density, g/cm^3	ASTM 0792	1.1 – 1.3	1.4	1.6	1.4	1.6
Moisture absorption, %	ASTM D 570	0.2 – 0.6	0.02	0.02	<0.1	<0.1
Heat distortion temperature (HDT/A, 1.82 N/mm^2), °C	ASTM D 648	<50	180	230	355	252
Linear coefficient of expansion, 10^{-6} K^{-1}						
Longitudinal	ASTM D 696	ca. 90 – 200	−5	5		5
Transverse		ca. 90 – 200	75	65		
Flammability	UL 94	HB	V-0	V-0	V-0	V-0
Melting point, °C	differential scanning calorimetry	148 – 219	280	280	421	
Vicat softening point, °C	DIN 53 460	80 – 207	145	177		
	ASTM D 1525				369	
Electrical						
Volume resistivity, Ω · cm	DIN 53 482	10^{10}–10^{14}	10^{16}	10^{16}		
Surface resistance, Ω	DIN 53 482	$>10^{11}$	4×10^{13}	8×10^{13}		
Dielectric loss factor tan δ, 10^6 Hz	ASTM D 150	0.036 – 0.06	0.02	0.017	0.041	0.033
Dielectric constant ϵ_r, 10^6 Hz	ASTM D 150		3.3 (kHz)	3.7	3.1	3.6
Dielectric strength, kV/mm	ASTM D 149		39	43	23	35

based on hydrophilic poly(ethylene oxide glycol) swell markedly in hot water, but less in oil. The incorporation of poly(propylene oxide glycol) decreases the thermal stability.

Polyetheresters have a good notched bar impact value at low temperature, high strength, flexibility, and abrasion resistance. On account of their partially crystalline nature they are insoluble in most solvents, exceptions include *m*-cresol and tetrachloroethane which are used as solvents for viscosity measurements. The swelling resistance in oils, aliphatic and aromatic hydrocarbons, alcohols, ketones, and esters improves with increasing hardness. Polyetheresters are extremely impermeable to fuels. Their good hydrolysis resistance can be improved by adding polycarbodiimides [135].

The resistance of polyetheresters to light, heat, and oxidation is lower than that of PBT or PETP (for stabilization, see).

Liquid Crystalline Polyesters [136–138]. The two partially crystalline polyesters Xydar and Vectra have only been on the market since the mid 1980s. These liquid crystalline polymers (LCPs) represent one of the most interesting developments in the technical plastics sector. See also → Liquid Crystals, Chap. 4.; → Plastics, General Survey, Section 5.3..

On account of their rod-shaped molecular structure, the polymer chains are partially ordered in the melt. The macromolecules adopt a parallel orientation in microscopically small regions, with the result that the melt exhibits properties of both a solid (order) and a liquid (mobility). This intermediate state is termed liquid crystalline. Xydar and Vectra have nematic phases, i.e., the longitudinal axes of the molecules are parallel, but the molecular centers of gravity are irregularly distributed (→ Liquid Crystals, Section 3.1.). Under the influence of a shear force, such as occurs in normal thermoplastic distribution, the microscopically ordered regions can be macroscopically oriented. This orientation is retained in the solid state and is responsible for the outstanding properties of liquid crystalline polyesters. These properties are, however, strongly orientation-dependent due to the anisotropy of the polymers. LCPs cannot therefore be compared with conventional thermoplastic polymers solely on the basis of values measured on uniaxial test bodies. Nevertheless, LCPs differ from "conventional" thermoplastics as regards the following properties (see also Table 4):

1. Their coefficient of thermal expansion is unusually low for polymers and can reach the values of steel; it can be adapted to other materials by varying the processing conditions2) Good processibility: on account of their very low melt viscosity, even filigree structural parts can easily be filled
2. Low melt enthalpy (short cycle times)
3. Low flammability: V-0 rating according to UL 94 with wall thickness <0.8 mm
4. High heat resistance
5. Resistance over a wide temperature range to solvents, fuels, and most chemicals, except oxidizing acid and strong alkali
6. Resistant to radiation and transparent to short-wavelength light
7. Low water absorption
8. Very good mechanical properties (strength, impact resistance, modulus of elasticity)

The anisotropy of the mechanical properties and the thermal coefficient of expansion can be reduced by adding fillers (glass fibers, minerals), which simultaneously improve surface quality. LCPs have a poor weld strength, in unfilled LCPs it is about half the strength transverse to the flow direction. To overcome this, special molded parts are constructed in which the weld is located in such a way that it is not subsequently exposed to high stress.

The most important mechanical, thermal, and electrical properties of LCPs are summarized in Table 4.

3.6. Uses

Poly(Ethylene Terephthalate). More than 85 % of PETP is processed into fibers (→ Fibers, 5. Polyester Fibers, Section 3.4.). Poly-(1,4-dimethylenecyclohexane terephthalate) is used for special fibers (see → Fibers, 5. Polyester Fibers, Section 4.2.). The production of high-grade, heat-resistant PETP films is described in → Films, Section 6.8.. A large proportion of PETP is used to produce gastight bottles for carbonated beverages (see Section 3.8). Highly stressed technical molded parts such as bearings, gearteeth, cam wheels, connectors, bolts,

screws, and washers are produced from PETP by injection molding [139].

On account of the processing difficulties (see Section 3.4) fewer molded parts are made from PETP than from PBT. If new developments aimed at reducing the high molding temperatures prove to be successful, this proportion may rapidly increase [140]. Injection molding machines are mainly used for processing.

Trade names include Arnite, Akzo; Crastin, CibaGeigy; Grilpet, EMS-Chemie; Impet, Hoechst Celanese; Melinite, ICI; Rynite, Du Pont; Techster, Rhône-Poulenc; Valox, GE Plastics.

Poly(Butylene Terephthalate). PBT too can be spun into fibers (see → Fibers, 5. Polyester Fibers, Chap. 4.), which can be colored, without carriers, with disperse dyes and used in the carpets sector [141]. Trade names are sometimes the same as for PETP fibers. Examples include Trevira, Hoechst; Tergal, Rhône-Poulenc; Fortrell, Celanese.

Most PBT is processed by injection molding and extrusion, a relatively low-viscosity formulation is used for injection molding, and a medium- to high-viscosity formulation for extrusion.

Examples of injection-molded PBT products (unreinforced and reinforced) include housings for heated domestic appliances (e.g., coffee-making machines, egg boilers, toasters, hair-dryers); bearing bushes, trip cams, gear wheels, fan wheels, ropesheaves, and pump impellers for the mechanical engineering sector; coil formers, capacitor covers, plug boards, and lamp sockets (often with flame retardants) for the electrical sector.

Protective covering for optical waveguides, films, sheets, monofilaments, and hydraulic lines are produced by extrusion. Paper and board can also be extrusion coated.

Trade names include B. Arnite, Akzo; Celanex, Hoechst Celanese; Crastin, Ciba-Geigy; Grilpet, EMS-Chemie; Orgater, Atochem; PBT, Toray; Pibiter, Montedison; Pocan, Bayer; Rynite, Du Pont; Techster, Rhône-Poulenc; Tenite, Eastman Kodak; Ultradur, BASF; Valox, GE Plastics; Vestodur, Hüls.

Copolyesters. Reference has already been made to possible uses of *thermoplastic copolyesters* (Section 3.4). Copolyetheresters [synthesized from dimethyl terephthalate, 1,4-butanediol, and poly(tetrahydrofuran)diol] are used on account of their high flexibility in the cold (without plasticizers), particularly for winter sports articles (e.g., ski brakes, soles for cross-country ski shoes, disks for ski poles). A novel field of application is crawlers for snowmobiles, where high abrasion resistance is also required. Copolyetherester elastomers can be processed by rotational casting into tires for vehicles not intended for use on roads (lawnmowers, garden tractors, golf trolleys), and into hydraulic oil tanks. Highly flexible pipes (e.g., for hydraulics lines) can be produced by extrusion.

Trade names include Hytrel, Du Pont; Arnitel, Akzo; Lomod, General Electric Plastics.

Amorphous copolyesters [99] produced from dimethyl terephthalate, terephthalic acid, isophthalic acid, neopentyl glycol, ethylene glycol, and other monomers are soluble in conventional solvents and can be processed into highly elastic, sterilization-resistant coatings (coil coatings). See also → Paints and Coatings, 1. Introduction.

Trade names include Dynapol L, Hüls; Vitel, Goodyear.

Partly crystalline copolymers based on poly (butylene terephthalate-*co*-isophthalate) are valuable hotmelt adhesives [100] for the shoe industry (shoe soles) or furniture industry.

Trade names include Dynapol S, Hüls; Vestamelt, Hüls.

Copolyesters based on similar starting components are used for powder coatings that produce highly flexible, weather-resistant coatings [142].

Trade names include Dynapol P, Hüls.

Liquid Crystalline Polyesters. Xydar and Vectra types cannot be used without reinforcement or fillers on account of their marked anisotropic properties and tendency to fibrillation. They are usually reinforced or filled with glass fibers, carbon fibers, or minerals and are processed by injection molding.

Areas of application exploit the properties described in Section 3.5. Examples include the

automotive and aviation industries, where good thermal and mechanical properties, inherent flame resistance, and low fume formation are important for interior fixtures and fittings.

On account of the low thermal expansion, high heat resistance, and favorable electrical properties, LCPs are employed in the microelectronics and optoelectronics sectors, mainly for integrated circuits, connectors, coil formers, lighting fixtures, and sheathing for glass fiber cables.

On account of their good resistance to chemicals and solvents, LCPs are used as packings in distillation columns and for fuel lines. Vectra (Hoechst-Celanese) and Xydar (Amoco) are transparent to microwave radiation, and are therefore used for microwave cookware and structural parts in microwave ovens.

3.7. Toxicology

High molecular mass polycondensates are usually considered to be biologically inert. However, the biological effect of polymers can be influenced by soluble or volatile components of monomers, oligomers, additives, and degradation products.

The toxicology of PETP has been investigated, especially for its use as a packaging film and textile fiber. No toxic effects were observed [143]. Tests on bacteria showed that neither PETP polyester nor other substances contained in PETP bottles extracted with dichloromethane were mutagenic [144].

PETP, BPT, and various copolyesters with 1,4-cyclohexanedimethanol and/or poly(tetrahydrofurandiol) are permitted by the FDA. They can therefore be used in contact with foods under particular conditions (viscosity, extract content, temperature, etc.) in accordance with CFR from 1988: CFR 170.1240; CFR 177.1315; CFR 177.1590; CFR 177.1630; CFR 177.1660.

Polyterephthalate diol esters are approved by the German health authority (Bundesgesundheitsamt) for use according to the food and commodity law (Aug. 15, 1974). The starting materials which can be used are 1,4-butanediol, ethylene glycol, 1,4-cyclohexanedimethanol, poly(ethylene glycol), terephthalic acid, dimethyl terephthalate, isophthalic acid, adipic acid, azelaic acid, dimethyl azelate, sebacic acid, dimethyl sebacate, *n*-dodecanedioic acid.

3.8. Economic Aspects [140], [145–151]

PETP and PBT. The above-average growth in thermoplastic polyesters that occurred at the start of the 1980s has continued. Double-figure growth rates (ca. 15 %) in the PBT and PETP molding materials sector have been achieved worldwide. Table 5 shows the development of demand for PETP and PBT between 1984 and 1989.

Most thermoplastic molding materials are processed in glass-fiber-reinforced form. PETP molding compounds are difficult to process and are therefore used in substantially smaller amounts than PBT molding compounds. The main areas of use are electrical engineering and electronics (25 – 30 % of overall production) and automobile construction (20 – 25 % without blends).

PBT – PETP blends, which have a good surface quality, as well as PBT – polycarbonate blends with high impact strength have become important. The amount of PBT used for blends in 1988 was ca. 10 000 t/a in Western Europe and ca. 20 000 t/a in the United States. The amount of PETP used for blends in 1988 was ca. 2000 t/a in Western Europe and 10 000 t/a in the United States.

PBT is largely used for construction materials, whereas PETP is mainly processed into fibers, sheets, films, and beverage containers. In 1989 15.6×10^6 t of synthetic fibers were produced worldwide; polyester fibers, primarily PETP, accounted for 8.4×10^6 t (54 %). The development of consumption for PETP sheets, films, and bottles is given in Table 6.

Films and sheets of PETP are chiefly used in the photographic sector, magnetic tapes, and packaging materials.

Table 5. Development of demand for PETP and PBT molding materials (without blends) in 10^3 t

	1984	1986	1988	1989
PETP				
United States	9	13	18	20
Japan	6.5	8	10	12
Western Europe	3.8	5	6	8
PBT				
United States	36	51	60	66
Japan	29	39	49	55
Western Europe	19	23	29	31

Table 6. Development of consumption for PETP sheets/films and bottles in 10^3 t

Region	1984	1986	1988	1989
United States				
Sheets/films	209	200	232	237
Bottles	243	291	334	360
Western Europe				
Sheets/films	130	170	190	195
Bottles	70	110	175	195
Japan				
Sheets/films	93		180	
Bottles	27		65	

Polyetheresters. The worldwide demand for polyetheresters based on dimethyl terephthalate, 1,4-butanediol, and polytetrahydrofuran was estimated to be 38 000 t in 1991. Of this figure, the United States accounts for 22 000 t and Western Europe and Japan 8000 t each. The annual growth rates are 10 – 15 %. The most important areas of use are hoses, cables, and automobile parts.

Liquid Crystalline Polyesters. The plant capacities for LCPs are ca. 9000 t/a, of which Vectra (Hoechst-Celanese) accounts for ca. 2300 –3600 t/a [152] and Xydar (Amoco) for ca. 4500 t/a [153]. The demand in the United States (ca. 90 % of overall demand), Western Europe, and Japan is currently considerably lower, at ca. 2500 t/a. However, high average growth rates, particularly in the electrical engineering and electronics sector, of at least 15 % to more than 20 % per annum are anticipated [154].

The major proportion (ca. 60 %) of LCPs is used for electrical and electronics components as well as for microwave-transparent cook ware. The remainder is used in the industrial, telecommunications, automotive, and aviation sectors.

3.9. Recycling

Polyesters (PETP, PBT) play an important role in the production of beverage bottles, foils, films, and fibers. The local authorities, in particular, protest against the increase in the volume of waste caused by the use of nonreturnable polyester bottles. In countries in which these bottles have already been introduced (e.g., USA, Japan,France,Italy,and the UK)laws have been passed to enforce the return and reutilization of the bottles. Because of this, the recycling rate for PETP bottles in the United States, for example, is 90 % [155]. In Europe the proportion of collected PETP is ca. 4 %. Two methods are used for recycling polyester: (1) direct reuse after comminution and washing, and (2) alcoholysis.

It is more difficult to directly reuse PETP foils and films of which the majority consist of composite materials. Such waste can only be processed by combustion or chemical recycling via pyrolysis.

Reuse. Prerequisites for good recycling of PETP materials are [156]:

1. There must be a sufficient amount of homogeneous recyclable material
2. An economical recycling process must be available for cleaning and separating the materials
3. The recovered plastic must have a sufficiently large market and a sufficiently high price to warrant economical recycling

This means that in designing and manufacturing a product, allowances have to be made for its subsequent recycling product. As a result of its high density (1.32 – 1.40 g/cm^3), PETP can be efficiently separated from most other plastics. Separation from poly(vinyl chloride) (PVC) is possible with the help of flotation. High standards are required during sorting for reuse as material for bottles. Due to the incompatability of PETP with the majority of other plastics the proportion of the latter should not exceed 100 ppm, i.e., only one polyethylene or PVC bottle should be among 10 000 PETP bottles.

In addition to collection, the following costs are estimated:

Sorting	0.3 DM/kg
Grinding	0.2 DM/kg
Washing, dryin	0.4 DM/kg

In the United States a new plant has been built by Du Pont and Waste Management of North America (WMNA) in Chicago (capacity 20 000 t/a); it separates the PETP chips and converts them to clean polymer. Du Pont then uses or sells the final product [155].

In every recycling step some cyclic and linear oligomers are formed. Especially the linear oligomers cause some problems during processing.

Hydrolysis and Alcoholysis. Another way to break down polyester is hydrolysis or alcoholysis which sometimes requires drastic reaction conditions and long reaction times. The hydrolysis of polyesters results in the formation of carboxylic acids and alcohols, from which new polyester can only be produced after separation and purification.

The breakdown of polyesters is more readily achieved by alcoholysis. The diols and dicarboxylates are formed according to the following reaction scheme:

$$\sim\!\sim R'-CO-O-R-O-CO-R'-CO-O-R\sim\!\sim \xrightarrow{R'OH}$$

$$\sim\!\sim R'COOR' + HOROH + R'OOC-R'-COOR' + HOR\sim\!\sim$$

If methanol is used for the alcoholysis of PETP, the monomers used for its polymerization are reformed. If multifunctional alcohols are employed, polyols can be produced, which can be modified and used for various purposes (e.g., for the production of polyurethane foam). Both processes are carried out on a commercial scale in the United States [157].

Glycolysis to monomer (dihydroxyethyl terephthalate)and low molecular mass oligomers represents a compromise between the regeneration of the starting materials by methanolysis or hydrolysis and direct remelt extrusion. Glycolysis signifies degradation with glycols [158]; it is less expensive than methanolysis or hydrolysis and more versatile than remelt extrusion. The resultant low-viscosity monomer can easily be filtered and is repolymerized to a useful molecular mass; it is used as a comonomer and ingredient for controlling luster, color, etc.

Glycolytic recycling can be a batch or continuous process, the rate depending on temperature, catalyst, state of subdivision of the feedstock and the glycolytic PETP ratio. In addition, the final monomer composition is controlled by the reaction time and holdup time after depolymerization. Low ratios of glycol to ester permit higher temperatures and faster reactions but result in higher molecular mass oligomers. Side reactions occurring during depolymerization are minimized by the addition of a buffer such as sodium acetate and by limiting the storage time at high temperature. PETP scrap suitable for glycolytic recycling includes production waste, fibers, films, flakes, and bottles; however, ingredients leading to side reactions, copolymers, end caps, or color must be minimized for critical products and satisfactory repolymerization rates.

Pyrolysis. If the polyester waste is highly soiled or combined with other materials, then in most cases it can only be chemically recycled by pyrolysis [159]. Pyrolysis denotes thermal decomposition under the exclusion of air. Mixtures of hydrocarbons are obtained, whose value is smaller than that of the glycolysis products but higher than that of the pure calorific value.

In the process developed by the University of Hamburg, polyester and other plastics are broken down in a fluidized bed that is indirectly heated by radial thermal pipes [160]. The fluidized bed consists of fine-grained sand (0.3 – 0.5 mm) and is heated to 650 – 850 °C. The pulverized polyester waste is transferred into the fluidized bed with a screw. After leaving the reactor the pyrolysis products are freed of entrained sand and fillers in a cyclone and cooled, whereby oils are condensed and expelled. The residual gas serves for the fluidization of the bed and as heating gas for the burner and other purposes. The plant has a capacity of 20 – 50 kg/h.

120.5 kg of chips consisting of PETP or exposed photographic films were fed with a screw (capacity 18.9 kg/h) into the fluidized bed and heated to 768 or 700 °C, respectively [161]. Table 7 summarizes the product groups obtained from PETP. The fraction of water, which is low (2.1 wt %), is the result of adhering moisture and formation during the decomposition of PETP. There are more water and solid residues in the pyrolysis products of film materials (Table 8). The

Table 7. Products obtained after pyrolysis of 120.5 kg polyester at 768 °C in a fluidized bed

Products	Content	
	kg	wt %
Gas	61.2	50.8
Benzene- and toluene-boiling fractions	26.7	22.2
High-boiling fraction	12.8	10.6
Tar ($bp > 340$ °C)	8.7	7.2
Soot (organic solids)	8.6	7.1
Water	2.5	2.1

Table 8. Components (wt %) obtained after pyrolysis of PETP at 768 °C and film material (PETP, polyethylene, and gelatin) at 700 °C

Component	Pure PETP	Used film
Hydrogen	0.30	0.37
Methane	3.80	5.28
Ethane	0.24	1.70
Ethylene	1.50	3.44
Propene	0.08	1.73
Butene	0.01	0.41
Butadiene	0.04	0.27
Carbon dioxide	17.20	17.30
Carbon monoxide	24.70	16.39
Benzene	18.30	7.79
Toluene	2.50	1.48
Styrene, ethylbenzene	2.55	6.26
Indene	0.41	0.23
Naphthalene	1.40	2.04
Biphenyl	1.47	0.97
Fluorene	0.18	0.10
Ketones, acetates	0.15	0.12
Acetophenone	1.40	1.81
Other compounds	11.87	11.15
Carbon black, fillers	7.10	13.40
Water	2.10	8.76

main gaseous components are carbon monoxide and dioxide. Of the hydrocarbons, on-ly methane and ethylene have notable percentages. The net calorific value (13.4 MJ/m^3) is ca. 40 % of the value for natural gas. As a result of its hydrogen content of 8.7 vol % the gas burns with a less vigorous flame.

The largest oil fraction is the benzene- and toluene-boiling fraction, in which the benzene, toluene, and xylene (BTX) aromatics account for over 97 %. This means that pyrolysis of 1 t of polyester waste yields 215 kg of the petrochemically valuable BTX aromatics. The concentrations of the aliphatic and heteroatom-containing hydrocarbons are both < 0.2 wt %. These low concentrations make the processing of this pyrolysis oil fraction to BTX aromatics very much easier.

In contrast, the high-boiling components, constitute a multicomponent system. This fraction, including tars, accounts for 17.8 wt %. The main components are naphthalene, biphenyl, indene, and acetophenone. The high content of acetophenone (10 wt %) is characteristic of the pyrolysis of polyester (PETP). This compound is not formed during the pyrolysis of polyolefins. After pyrolysis the remainder of the oxygen bound to the polyester is distributed as follows: 62 % in carbon dioxide, 31.6 % in carbon monoxide, 5.5 % in water, 0.75 % in acetophenone, and 0.15 % in other keto-compounds and carboxylic acids.

The pyrolysis of polyester and composite materials such as films (PETP, polyethylene, gelatin) in the fluidized bed showed that oxygen-containing plastics can be largely defunctionalized and high proportions of mononuclear aromatics can be obtained.

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Polyethylene

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1. Introduction

Worldwide polyethylene manufacturing and consumption volume represents approximately 40% of the total demand of all thermoplastic materials and approximately one third of the demand of the overall plastic material (Fig. 1).

With its simple and inexpensive structure, chemical resistance, relatively good physical properties, a density that is lower than that of most other polymers, and relatively low environmental impact, polyethylene is the material of choice for many applications that span from medical implants (ultrahigh-molecular-mass polyethylene, UHMWPE), devices, and packaging, via energy and infrastructure materials (pipe and electrical), to flexible food packaging and many others. The overall capacity (2010) globally installed for manufacturing one of the forms of polyethylene is in the order of 100×10^6 t/a, and its growth rate still approximately equals that of the gross domestic product [1].

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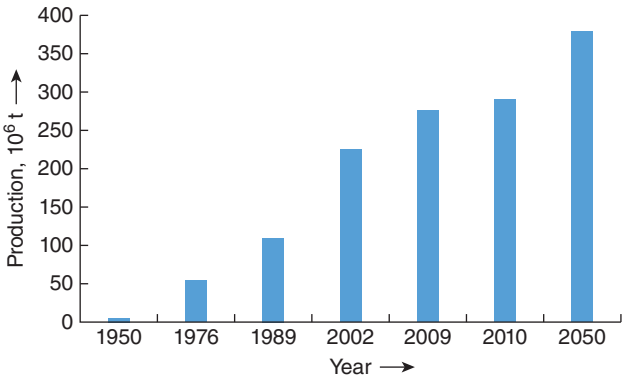


Figure 1. Global manufacturing of polymer materials in 10^6 t/a

Based on their original manufacturing process, polyethylenes can be divided into two large groups of materials: high-pressure and low-pressure `polyethylene. More often, they are devided into classes based on the density of the polymer, typically into three groups: low-density polyethylene (LDPE), which is material made in the high-pressure process, high-density polyethylene (HDPE); and linear low-density polyethylene (LLDPE) The density of polyethylene is in direct correlation with its crystallinity, which further depends on the branching of the polymer chain and the content and nature of the comonomers, which usually are α-olefins or short-chain polar alkyl compounds. Theoretical density of the fully amorphous polyethylene is 880 kg/m^3, and fully crystalline material would have a density of 1000 kg/m^3 [2].

Since the introduction of the single-site catalysts, LLDPE has often been further divided into two other groups: Ziegler–Natta LLDPE (znLLDPE) and single-site LLDPE (mLLDPE, with m standing for metallocene).

Historically, LDPE was the first ethylene polymer invented and manufactured industrially. The invention was made by chance and careful observation by the ICI scientists Gibson and Fawcett in the early 1930s [3]. Mixing ethylene and benzaldehyde at 170°C under a pressure of approximately 200 MPa led to the formation of polymeric-like materials that have been identified as polyethylene. The density of the material made at the high temperature and under high pressure was measured to be 915–920 kg/m^3 indicating a relatively low degree of crystallinity owing to a high level of branching. Polymerization of ethylene under these conditions is initiated by free radicals and, as such, the polymerization consists of a few main and side reactions generating radical centers at random molecules and locations in the growing polymer chains. Coupling any two of the radical centers leads to establishing chemical bonds between them that possibly and often result in forming branches or cross-linking of polymer chains.

First initiators or catalysts that enabled polymerization of ethylene at lower pressures and temperatures were discovered in the early 1950s by three research groups working independently at Standard Oil (Indiana, USA), Phillips Petroleum [4], and in the group of Karl Ziegler at the Max Planck Institute for Coal Research in Mülheim an der Ruhr, Germany [5]. Phillips and Ziegler catalysts have been commercialized extensively and are still used for manufacturing of almost 90 vol% of all polyolefins. Phillips and Ziegler catalysts are transition-metal-based coordination catalysts that initiate a "one-unit-at-the-time" chain-growing reaction for olefin polymerization that produces essentially linear polyethylene with a density of approximately 960 kg/m^3, HDPE. These catalysts are also called coordination catalysts.

Innovation of another group of coordination catalysts was made possible by the invention of methyl aluminoxane (MAO) by the group of Walter Kaminsky in the early 1980s [6]. MAO is a product of partial hydrolysis of trimethylaluminum, a highly reactive compound that explodes in contact with water. Organometallic complexes of transition metals containing one or two cyclopentadienyl rings as ligands, which are described earlier than MAO and found to be largely inactive as catalysts in combination with the "traditional" activators, aluminum alkyls, become very potent polymerization catalysts

when mixed with MAO. These are known as single-site catalysts.

LLDPE is the product of a coordinative polymerization initiated by Ziegler or single-site catalysts, by which ethylene is copolymerized with an α-olefin. The product is highly branched containing the alkyl rests of comonomer that are attached to the polymer backbone chain. As a result of the branching, crystallization of the polymer is disturbed resulting in low density of the material. More importantly, many other physical characteristics of the polymer such as toughness are also affected by the incorporation of the comonomer. LLDPE was first introduced in 1960 by DuPont Canada [7] on the small scale, and its commercial exploitation became significant only after Union Carbide introduced their Unipol technology for gas-phase polymerization, a much more economically viable and flexible polymerization process [8]. Gas-phase polymerization was yet another breakthrough in polyethylene polymerization and it was adopted by many other companies. LLDPE is now manufactured worldwide almost exclusively by the low-pressure polymerization processes.

Coordination catalysts are deactivated by most oxygen-containing and/or polar compounds. Therefore, copolymerization of ethylene with polar comonomers is not achievable at low pressure by using coordination catalysts. The free-radical process is used to produce copolymers of vinyl acetate, acrylates, methacrylates, and the corresponding acids, but chain transfer prevents the use of higher olefins because of the drastic reduction in molecular mass of the polymer.

Although some processes and/catalyst types are more suited for manufacturing certain types of polyethylene described above, many manufacturing plants can produce more than one class of materials. Sometimes, even the same catalyst can be used for manufacturing a wider scope of polyethylene densities as well.

2. Properties

2.1. Molecular Structure and Morphology

For definitions and means of measurements of polymer properties, see → Plastics, General Survey and → Plastics, Analysis.

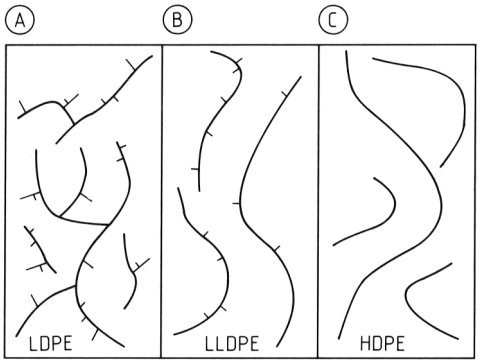


Figure 2. Schematic molecular structure of three types of polyethylene
A) Low-density polyethylene; B) Linear low-density polyethylene; C) High-density polyethylene

Molecular Structure. The molecular structures of the three types of polyethylene classified by their density, LDPE, HDPE, and LLDPE can mainly be distinguished by the branching of the polymer chain that determines the crystallinity of the material. In Figure 2, the structure of three grades is illustrated.

As a product of radical polymerization, the high-pressure product, LDPE, is highly branched and partially cross-linked. The molecular mass distribution (MMD) of polymer chains of different degrees of polymerization and molar masses present in the material is typically broad.

LLDPE is predominantly linear containing short-chain branches equally distributed throughout the chain. The length of the branches depends solely on the comonomer used, which influences the physical properties of the polymer. The homogeneity of the comonomer incorporated is defined as both distribution of the comonomer across the polymer chains of different sizes and uniformity of branching distribution in one chain, which is a significant factor that influences quality and performance of the final material. The higher quality materials, which are tougher, exhibit, for example, more puncture resistance, better processability, and contain branches that are more uniformly distributed across chains of all sizes, whereby the distance between them tends to be equal.

The comonomer distribution depends largely on the catalyst used for manufacturing, but it can be influenced and partially tailored by some advanced multimodal polymerization processes such as the Borstar process invented by Borealis.

Improving comonomer homogeneity is one of the main goals of catalyst research performed by numerous industrial research organizations. One of the main benefits of using single-site catalysts for manufacturing LLDPE is that these catalysts enable improved comonomer utility and incorporation homogeneity. Some single-site catalysts feature even so-called reverse comonomer distribution producing polymers for which the branching frequency and amount increases with the molecular mass of the polymer chains. Those materials are often also superior in their physical performance [9]. The MMD of LLDPE depends on the factors common for all other materials manufactured by coordination polymerization.

HDPE, which is higher in density, contains less comonomer incorporated and fewer branches. Still, for most applications that require higher physical performance such as pipes, distribution of the few branches also plays an important role. Typically, HDPE materials have a much broader MMD than LLDPE. This is needed for keeping these higher density and often higher molecular mass materials processable.

Crystal Structure. Crystallization of polyethylene is a much faster process than of other similar polymers, for example, polypropylene. Crystallization occurs in the form of platelets and lamellae, similar to the crystallite structures of low-molecular-mass paraffin waxes (→ Waxes, 4. Petroleum Waxes). Their thickness is typically in the range of 8–20 nm and the melting point of the polymer depends in part on the thickness of lamellae [10].

Polymer chains typically fold and, thus, tend to be oriented perpendicular to the length of lamella, and not parallel to it as one could expect (Fig. 3).

As the degree of branching influences the folding and crystallization, the thickness of the lamellae also depends on it. Conditions of crystallization are also an important factor that influences their thickness; therefore, slow cooling, also called annealing, leads to thicker lamellae.

Tie molecules are typically long-chain, high-molecular-mass molecules that partially crystallize in more than one lamella tying the two or more units. They are important components for those materials that need to be tough and exhibit higher crystallinity, density, and, at the same time, little brittleness.

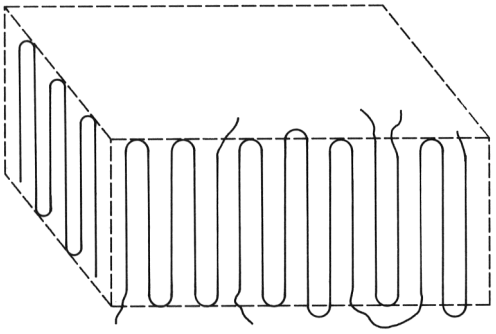


Figure 3. Folded-chain lamellar crystal of polyethylene

Short-chain branches and their specific geometry disturb the crystallization process and are thermodynamically excluded from the crystalline lamellae. As mentioned above, branches cause chain folding leading to thinner lamellae that contain alkyl rests of the branches on the surface of the lamellae. The rate of crystallization influenced by the cooling intensity may be high enough to cause kinetic inclusion of the branches also in the mostly crystalline region creating less than fully defined regions that cannot be simply categorized into amorphous and/or crystalline areas. The significant fraction of such a polymer resides then in the interfacial fraction [11, 12].

Branches can also play a role in "forcing" a part of the long polymer chain to crystallize in more than one lamellae thus creating a tie molecule. Therefore, creating homogeneous comonomer distribution also for HDPE is one of the key features of a polymerization catalyst.

Slower cooling causes a lower number of nucleation sites with crystallization growing from these sites centers outwards until the surfaces meet. The resulting spherulites have then banded-bent structures as seen under a polarizing microscope, which scatter light and produce the effect seen as "milkiness" of polyethylene. The crystallites themselves are much smaller than the wavelength of the light, and, therefore, cannot be the cause for this optical effect [13]. Hence, ethylene copolymers can be at the same time transparent and at least partially crystalline.

With the development of the single-site catalysts based on organometallic Ti complexes containing only one cyclopentadienyl ligand instead of two, which have their active sites

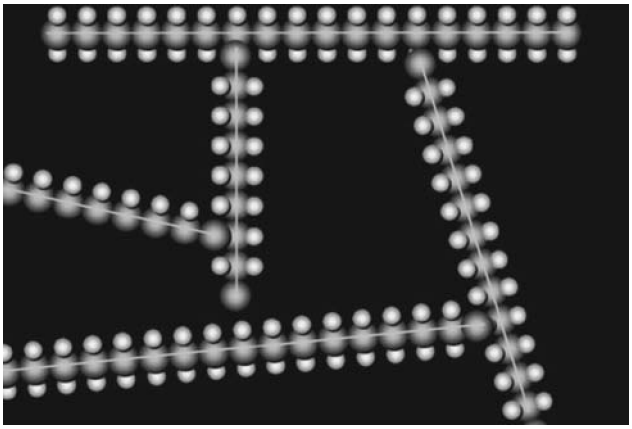


Figure 4. Schematic representation of LCB polyethylene

rather exposed and approachable by the monomer and/or comonomer and are also called constrained geometry catalysts, it was now possible to manufacture polyethylene with so-called long-chain branches, LCBs [14] (Fig. 4).

In the course of polymerization, chain propagation and β-hydrogen rearrangement occurs by leaving a polymer chain with the vinyl terminal group that can become a macromonomer. Incorporation of the vinyl group into another growing polymer chain produces branches with the long polymer chain attached to the backbone structure, similar to what happens in the radical polymerization during manufacturing of LDPE. The presence of long-chain branches has a significant effect on the rheological behavior of the polymers that show pronounced shear thinning (nonlinear decrease of viscosity at higher shear). Consequently, the processability of the material is significantly improved over that of similar materials that contain no LCB.

Block Copolymers. It has been recognized very early that it is difficult to improve all properties of the material at the same time by changing the amount of comonomer, i.e., the branching in the polymeric chain. Therefore, block copolymers have been developed by Dow Chemicals that consist of polyethylene chains containing segments with many short-chain branches attached to the segments of a homopolymer in alteration. Block copolymers result from polymerizations with two single-site catalysts, one very efficient in incorporating the comonomer, and the other not capable of copolymerizing any other olefin than ethylene. These so-called chain shuttling agents are main-group metal–alkyl compounds that function as "transfer vehicles" for growing polymer chains from one transition-metal active site to the other without stopping the growth of the chain. Parts of the chain that grew on one active site then contain more comonomer incorporated than the parts that grew on the other active site, and the result is a block copolymer. The possible advantages of the new materials are higher elasticity, temperature resistance, higher temperature of crystallization, etc. [15] → Plastics, General Survey, Section 5.3.6 Block Copolymers.

2.2. General Properties

Polyethylene in its natural form, free of additives and pigments, is a white material that melts at 120–140°C, does not dissolve in any solvent at room temperature, and typically has no smell or taste. Lower density polyethylenes, LDPE and LLDPE, are softer solids, transparent in bulk. Films made out of the lower density polyethylene are also transparent and have a yielding feel. Higher density material is opaque and more rigid. HDPE film is stiff and crisp in appearance.

Different grades of polyethylene are typically characterized by their density and melt flow rate (MFR) that is also sometimes known as melt flow index (MFI) [16]. Density is most

often measured gravimetrically by weighing a polyethylene specimen submerged in water under controlled conditions. Specimens for the density measurement are usually annealed, conditioned at an elevated temperature for a certain time, and then slowly cooled down to room temperature. MFR is described by the amount of polymer heated to 190°C and melted that passes through a die of defined size under the defined load of weights. Polyethylene powder or pellets are placed in heated and tempered cylinders under a piston. After a certain period of time needed to melt the material, the piston is loaded with the prescribed weight and the flow of polyethylene through the die is measured. The amount of material in grams that flows during exactly ten minutes is the MFR of that material at the applied load (Fig. 5).

The ratio between MFR values obtained under different loads of weight is known as the melt flow ratio, usually labeled as flow rate ratio (FRR), and typically the results obtained at a load of 21 kg are divided by the result of the 2.1 kg measurement. This ratio is significant because the dependence of viscosity of the molten polyethylene on the applied shear is not linear but highly depends on the broadness molecular-mass distribution of the material as well as on other characteristics such as content of LCBs. Therefore, LDPE with the high content of LCBs has much higher FRR than typical LLDPE. The FRR is a good indication of the processability of the polymer and the amount of energy needed to extrude the material. MFR and FRR are quick methods to characterize polyethylene and differentiate its grades. They are, however, too crude for making any further conclusions on the viscosity or other rheological properties of the material.

The behavior of polyethylene under shear is shown in Figure 6, in which the dependences of the viscosity on the shear rate of an LDPE and an LLDPE are compared. At sufficiently low shear rates the viscosity of all polyethylenes becomes Newtonian, that is, it is independent of the shear rate. Owing to the narrow MMD, the viscosity of LLDPE is less shear dependent than that of LDPE, and LLDPE has a higher viscosity under the higher shear conditions used in processing equipment. In Table 1 the physical

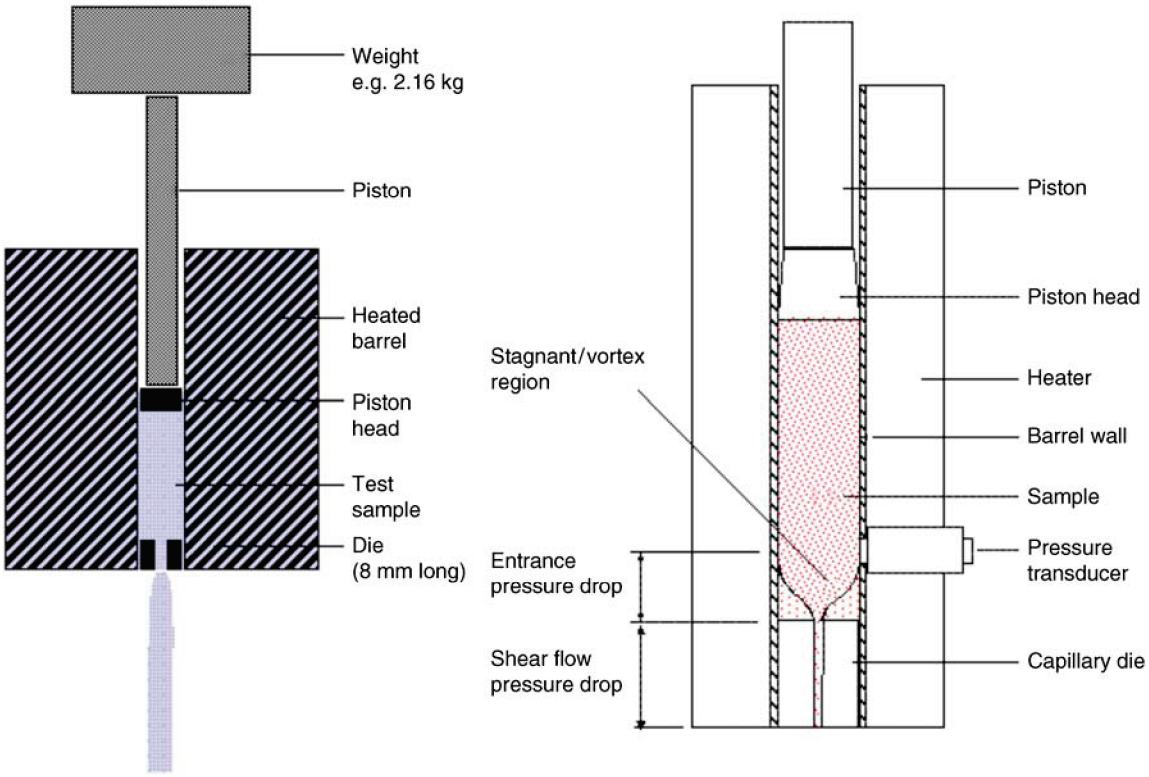


Figure 5. Melt flow indexer and capillary rheometer, which can alternatively be used

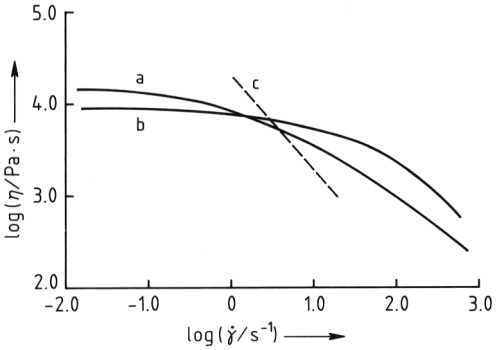


Figure 6. Dependence of viscosity η on shear rate $\dot{\gamma}$ for two polyethylenes
a) Low-density polyethylene; b) Linear low-density polyethylene; c) Apparent shear rate in melt flow index test

properties of the different grades of polyethylene are listed.

By observing the melt behavior during an MFR test, one can obtain an indication on the die swell and die swell ratio under different loads. The observation indicates elastic memory of the material, another important parameter for processing of polyethylene.

While polyethylene is considered as chemically resistant and inert material, it requires stabilization to sustain environmental influences at extended exposure. Free radicals from oxygen can cause uncontrolled cross-linking of polymer chains changing physical characteristic of the material. Also exposure to various other substances can alter the material: surface-active compounds can cause cracks at the stressed parts over time, and certain solvents such as toluene, for example, cause material swelling. Therefore, immediately after polymerization, the polymer is usually compounded with additives that improve long- and short-term stability, and/or modify the properties of the polyethylene. These additives are UV stabilizers, antioxidants, slip agents, antiblock additives, and others.

One of the ways to characterize stability and chemical inertia of polyethylene is by testing its so-called environmental stress crack resistance. The test is performed by placing a polyethylene specimen under a certain stress and immersing it in a solution of a reagent that can cause an impact on its resistance to stress, i.e., detergent,

Table 1. Properties of some typical polyethylenes (data from Repsol Quimica)

Property	LDPE	HDPE	LLDPE	Method	Standard
Polymer grade	Repsol polyethylene 077/A	LyondellBasell Hostalen GD-4755	BP LL 0209		
Melt flow index (MFI), g/600 s	1.1	1.1	0.85	190°C/2.16 kg	ASTM D1238
High load MFI, g/600 s	57.9	50.3	24.8	190°C/21.6 kg	ASTM D1238
Die swell ratio (SR)	1.43	1.46	1.11		
Density, kg/m^3	924.3	961.0	922.0	slow annealed	ASTM D1505
Crystallinity, %	40	67	40	DSC	
Temperature of fusion (max.), °C	110	131	122	DSC	
Vicat softening point, °C	93	127	101	5°C/h	ASTM D1525
Short branches**	23	1.2	26	IR	ASTM D2238
Comonomer		butene	butene	NMR	
Molecular mass*					
M_w	200 000	136 300	158 100	SEC	
M_n	44 200	18 400	35 800	SEC	
Tensile yield strength, MPa	12.4	26.5	10.3	50 mm/min	ASTM D638
Tensile rupture strength, MPa	12.0	21.1	25.3		
Elongation at rupture, %	653	906	811		
Modulus of elasticity, MPa	240	885	199	flexure	ASTM D790
Impact energy,					
unnotched, kJ/m^2	74	187	72		ASTM D256
notched, kJ/m^2	61	5	63		ASTM D256
Permittivity at 1 MHz	2.28				ASTM D1531
Loss tangent at 1 MHz	100×10^{-6}				ASTM D1531
Volume resistivity, Ω · m	10^{16}				
Dielectric strength, kV/mm	20				

* Corrected for effects of long branching by on-line viscometry.
** Number of methyl groups per 1000 carbon atoms.

at a controlled, possibly elevated temperature [17]. The time that passes before the specimen yields to stress is measured and it indicates stability of the material.

As mentioned above, density correlates to crystallinity of polyethylene and is a good indicator of it. Furthermore, crystallinity is also measured by differential scanning calorimetry (DSC) that provides the melting and softening point of the polymer as well as enthalpy of fusion.

FTIR and NMR spectroscopy are the two methods that can accurately measure branching in polyethylene. NMR spectroscopy is also used to measure the amount of long-chain branches [18].

Comonomer distribution is measured by the methods that are based on crystallization and elution, such as temperature-raising elution fractionation (TREF) Polyethylene is completely dissolved at high temperatures and the solution is then introduced to the column packed with an inert support such as glass beads. The polymer solution is then cooled down slowly at a controlled rate, allowing crystallization in an onion-like structure with the branching gradient. The potential for crystal formation is dependent on the branching content and, therefore, the highly branched fractions will form the crystals at lower temperature and will be last to deposit on the inert support. With passing the solvent through the column and by increasing the temperature at controlled rate, fractions are eluted with the increasing crystalline content as a function of time and temperature (Fig. 7) [19].

Typical LLDPE materials prepared by using a Ziegler catalyst will always contain some homopolymer that is eluted at temperatures above 90°C. Branched fractions elute first, and the shape of the peaks depend on their homogeneity.

Finally, so-called hyphenated techniques (such as GPC–FTIR) and cross-fractionation techniques (such as TREF–GPC) have become extremely useful in characterizing and investigating the microstructure of polyethylene. These techniques represent combined methods in which the polymer is fractionated first on the basis of one attribute, i.e., its molecular mass, and then the fractions are further fractionated or tested on the basis of another attribute, i.e. branching. GPC–FTIR technique is extensively used for determining the distribution of SCB across the molecular mass in polyethylene.

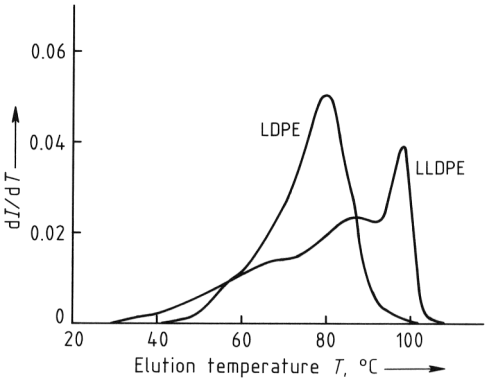


Figure 7. Temperature rise elution fractionation curves (I is the cumulative weight fraction)

An important feature of polyethylene is its relative toughness, i.e., resistance to stress. A standard method to measure toughness of film materials is determination of its dart drop index (DDI). A dart is let to drop from a defined height at a framed film. The weight of the dart needed to puncture the film is measured. DDI gives the weight at which the dart punctures the film in at least 50% of experiments. The DDI depends very much on the density of the material, but also on the comonomer distribution in it. It is known that polyethylene made with single-site catalysts, in which comonomer is more evenly distributed across the molecular mass, has a much higher DDI than materials made with Ziegler catalysts.

Other measurements of polyethylene's toughness are elongation at break and puncture resistance.

The length of the short-chain branches in the polymer chain, and thus the choice of the comonomer, affects the toughness of LLDPE. While the performance of 1-butene copolymers is sufficient for simpler packaging applications, increased DDI values, puncture resistance, and elongation at brake can be achieved with higher α-olefins such as 1-hexene and 1-octene.

Film materials are characterized by their optical performance, gloss, and haze, whereby more gloss and less haze indicate more transparent and better appearing films. Furthermore, sealing temperature (the minimum temperature needed to weld two layers of polyethylene together) and strength are important features of polyethylene films.

Other parameters such as barrier properties of polyethylene films and permeability of oxygen and/or moisture vapors are not at the level of those of other polymers such as ethylene–vinyl acetate copolymer (EVA). However, polyethylene is still an important packaging material used for many applications in the food and other industries.

As a viscoelastic material, polyethylene exhibits creep behavior, which means that strain produced by applying stress on the polyethylene specimen is time dependent and can be multiplied if measured after several days of exposure to stress compared to strain measured after only a few seconds. In Figure 8, the strain-versus-time curve is shown for an HDPE specimen at a constant tensile stress of 6.5 MPa [20].

The creep is a consequence of a relative mobility of amorphous regions of polyethylene at room temperature. If polyethylene is used for long-term applications, creep as well as possible crack formation and failure need to be taken into account. Prolonged high stress may lead to failure under conventionally measured yield stress.

LDPE or high-pressure polyethylene produced with peroxides as polymerization initiators is a very-high-purity polymer that contains low amounts or no traces of metal residuals. Therefore, LDPE is very suitable as insulator for high-frequency cables: With no polar groups in the polymer chain and its high purity, LDPE has a very low loss tangent that is appropriate for the wire and cable applications. Other polyethylenes, LLDPE and HDPE, do contain catalyst residuals, Phillips, Ziegler, or single-site, and are, therefore, less pure and/or suitable for these uses.

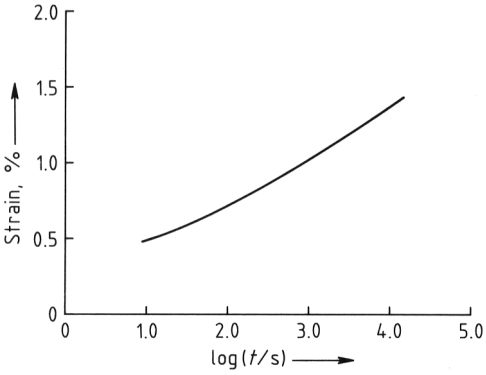


Figure 8. Tensile creep of HDPE (Rigidex 006–60) [20]

Because of its purity and inertia to chemical agents, polyethylene, specifically the ultrahigh-molecular-mass polyethylene, UHMWPE, with polymer chains that have molar masses in excess of $1–2 \times 10^6$, is often used as the material of choice for manufacturing medical prosthesis, artificial joints, knees, and hips. The process of qualifying materials for medical and/or food applications is strictly regulated by regulatory bodies such as Food and Drugs Administration in the USA and other country regulatory bodies.

2.3. Unimodal and Multimodal Polyethylene

As a product of coordination polymerization that is usually terminated by chain transfer or cleavage of the metal–carbon bond, polyethylene is always a mixture of polymer chains of different lengths with different molar masses. Distribution of the polymer chains of different lengths, with different molar masses, is an important descriptor of polyethylene materials.

The most significant parameter is the broadness of the MMD, which originates in the polymerization process or the catalyst used or both. To produce polymers with narrow MMD, the polymerization needs to occur under constant and uniform conditions in one reactor, and the catalyst needs to contain few types of active sites. In contrast, catalysts containing more types of active sites will produce polymer chains of various lengths, depending on the active site nature, and the distribution will be broader.

Typically, different catalyst classes contain more or less types of active sites, and, therefore, produce polymers with broader or narrower MMD. Single-site catalysts are well defined compounds, sometimes also very well characterized, and the polymer that they deliver typically has a very narrow MMD, indicating one only type of active site (a “single-site”). Ziegler catalysts, however, are less well defined chemicals, and tend to contain several types of active sites resulting in broader MMDs in

the polyethylene for which they are used. Finally, the polyethylene with the broadest MMD is made with Phillips chromium-based catalysts.

Polymer chains of different lengths containing a more or less uniformly distributed comonomer contribute to the performance of the material. For example, higher molecular mass chains are needed to provide toughness and bubble stability in film materials. Lower molecular mass chains improve processing of the material. The broadness of the MMD also determines processing performances of the polymer and, for example, the optical performance.

Polyethylene materials that have a rather narrow MMD are usually called unimodal materials. If the distribution is divided into more than one group of polymer chain lengths (one molecular mass group), it is called multimodal, and if there are two groups, it is called bimodal.

PE manufacturers prefer to use only few catalyst types at one plant with transitions of two different formulations as rarely as possible. Therefore, the MMD, which is defined by the choice of the catalyst, is given and cannot easily be changed by modifying the number of types of active sites. Thus, to increase the number of freedom degrees and improve the ability to design polymer materials as needed, bimodal or multimodal polymerization plants have been developed and implemented. These plants operate with two or more polymerization reactors in series and polymerization occurs in these reactors under different conditions, which are controlled separately. The catalysts used at the beginning of the reaction and growing polymer particles of later stages "travel" through the cascades of reactors and are exposed to different polymerization conditions. By choosing and controlling the conditions, the length of polymer chains and branching content in each polymerization stage can be influenced, and, therefore, molecular mass and comonomer distribution can be actively designed.

The bimodal polymerization process enable manufacturing of advanced polyethylene materials typically used for manufacturing pressure pipes for transportation of gases and/or liquids. These pipes need to sustain pressure, sometimes at elevated temperatures, over an extended period of time. Usual life expectance needed for the pipes is more than 50 years and the pressure is approximately 10 MPa. The material providing the required performance is high-molecular-mass, high-density polyethylene. High mechanical resistance, i.e., resistance to pressure, stems from the highly crystalline part of the polymer that crystallizes as folded-chain lamellae. Given their high crystallinity, these chains do not need to, and should not be very long. To maintain the pressure for long time and avoid rapid crack propagation, by which the crystalline lamellae split from each other and the pipe becomes brittle, the high-density parts need to be connected by tie molecules, long polymer chains that partially cocrystallize in more than one lamellae creating a network between the units. Tie molecules need to be long, have high molecular mass, and are branched to a certain extend to avoid more than partial crystallization [21].

Manufacturing of the described materials with the appropriate combination and design of components to achieve the required performance is performed by polymerization processes with two or more reactors. Lower molecular mass homopolymer is typically produced in the first reactor. The material is then transferred into the second reactor in which the conditions are different and new polymer chains produced there are longer and contain some comonomer. In addition, to achieve the right design and MMD broadness that enables easier processing of the overall high-molecular-mass polymer, two potentially different types of polymer chains are manufactured in a subsequent manner so that every polymer particle eventually contains both types, securing good dispersion in the final material after compounding.

2.4. Ultra-High-Molecular-Mass Polyethylene (UHMWPE)

Ultra-high-molecular-mass polyethylene is a polyethylene with a molecular mass higher than 1×10^6, typically between 3 and 6×10^6. UHMWPE is a product of coordination polymerization at usually lower temperatures with high ethylene concentration in the reactor. Both Ziegler and single-site catalysts can be used for manufacturing UHMWPE.

This type of materials cannot be characterized by the usual size-exclusion technique

(GPC), because it is not completely soluble in the commonly used solvents even at very high temperatures. Its viscosity is extremely high, and thus, it is not possible to measure the MFR of the material either. Viscosity molecular mass can be determined for a certain UHMWPE by a modified method for measuring the relative viscosity of very diluted polymer solutions in decaline at 135°C, provided that the polymer is dissolved completely.

UHMWPE normally contains no comonomer so there is no branching in the linear polymeric chain. Still, the density of the material is only 940 kg/m^3 because the length of the chains and the extremely high viscosity hinder the crystallization process.

The UHMWPE cannot be processed conventionally by melting the polymer in an extruder and shaping it in the molten form. Instead, there are few other methods to convert UHMWPE:

- Sintering into large blocks under pressure and at elevated temperature to obtain a material that can be used for machining objects or cutting tapes out of the solid material
- Ram extrusion into rods and objects that are also used for machining into final products
- Gel spinning for manufacturing fiberlike materials

As sintering is one of the primary ways to process UHMWPE, the size and regularity of the polymer particles that are generated in the polymerization process is of particular importance. Smaller spherical particles with uniform particle size distribution provide for more successful sintering. Therefore, it is advantageous to use a batch polymerization process for manufacturing UHMWPE. Unlike in the continuous process, the residence time in the batch process is identical for all polymer particles and it can be assumed that they grow following the same kinetics, thus taking the same shape and dimensions at the end of the polymerization.

UHMWPE is used for applications for which hardness and durability is needed. Gel-spinning-produced fibers are extensively used for manufacturing bullet proof vests and other impact protection equipment. Films cut from the UHMWPE blocks are used as the lower layer of modern skis, and UHMWPE-made wheels are used for conveyer belts that transport high loads. Because of high purity, hardness, and durability, UHMWPE is used for manufacturing medical prosthesis and artificial joints.

Blending of UHMWPE with other materials, lower molecular mass polyethylene for example, is a rather difficult process. The difference in viscosities of the materials disables good dispersion of the materials. This is particularly due to the fact that the long chains are entangled with each other, which further increasing viscosity of the material. By using diluted catalysts, either in solution or supported on very low loadings, it is possible to obtain so-called disentangled UHMWPE, which contains polymer chains that are separate from each other. Viscosity of such a material is considerably lower than that of the entangled one and, thus, it can be, to a certain extent, blended with other materials [22].

2.5. Ethylene Copolymers

Branching effects crystallinity and further performance of polyethylene. One of the principle reasons for copolymerizing ethylene with α-olefins is to reduce and/or control their crystallinity to gain toughness, softness of the material, and other physical characteristics needed for certain applications. Propene is the only comonomer that, if incorporated, can partake in crystallization.

LLDPE is one of the higher volumes thermoplastic materials used worldwide, mostly for packaging applications. VLDPE or polyethylene-based plastomers and elastomers with densities in the range of 860–900 kg/m^3 are also very important in standalone applications, i.e., films, but also as materials to be blended to other thermoplastic materials as impact modifiers.

Coordination copolymerization of ethylene with polar comonomers is not possible because of the reactivity of the catalysts with the polar groups. The only process that enables incorporation of monomers such as vinyl acetate and other esters and acids is through a high-pressure radical polymerization process. In Table 2 the principal types of ethylene polar copolymers are

Table 2. Principal types of ethylene copolymers

Comonomer	Abbreviation	Feature	Catalysis*
Vinyl acetate	EVA	flexibility	FR
Methyl acrylate	EMA	flexibility, thermal stability	FR
Ethyl acrylate	EEA	flexibility at low temperature, thermal stability	FR
Butyl acrylate	EBA	as for EEA	FR
Methyl methacrylate	EMMA	flexibility, thermal stability	FR
Butene	VLDPE	flexibility at low temperature, thermal stability	Z, SS
Hexene	VLDPE	as for butene copolymer	Z, SS
Octene	VLDPE	as for butene copolymer	Z, SS
Acrylic acid	EAA	adhesion	FR
Methacrylic acid	EMAA	adhesion	FR
Methacrylic acid + Na^+ or Zn^{2+} (ionomer)		adhesion, toughness, stiffness	FR
Acrylic acid + Zn^{2+} (ionomer)		adhesion, toughness, stiffness	FR
Carbon monoxide	PK	polyketone, stiffness, high melting	**
Norbornene	COC	cycloolefin copolymer, transparency	SS

* FR = free radical, Z = Ziegler catalysis, SS = single-site catalyst.
** Novel group VIII catalyst.

listed that are in commercial production. Of these, the vinyl acetate copolymers are produced in the largest quantities.

At room temperature, the amorphous regions of the copolymer (where the comonomer groups are concentrated) are mobile and the effect of introducing a comonomer is to reduce the stiffness progressively (Fig. 9).

In addition to the branches that result from comonomer incorporation, the branches that are formed under the high-pressure synthesis conditions also contribute to the reduction in crystallinity. Below room temperature, there are differences in crystallinity between ester copolymers having different glass transition temperatures T_g of the amorphous material. The T_g of the copolymers follow the T_g of the ester homopolymers and results in EEA and

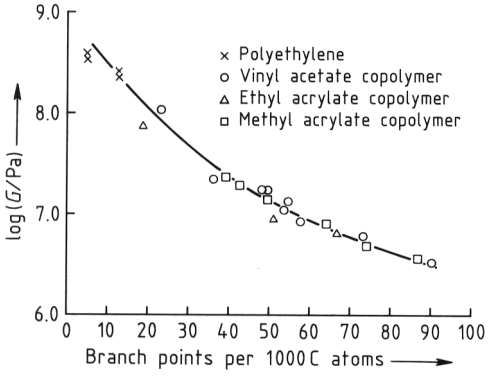


Figure 9. Dynamic modulus G (ca. 2 Hz) at 23°C as a function of total branch points

EBA copolymers (see Table 2) that are flexible down to lower temperatures than EVA copolymer, with EMMA copolymer having the highest T_g. The VLDPEs produced by the LLDPE processes should have the best low-temperature properties, particularly in the case of narrow composition distribution polymers. Properties of three typical EVAs and a VLDPE [23] are listed in Table 3.

The methacrylic and acrylic acid copolymers are produced to provide enhanced adhesion, particularly in coextruded films or laminates. Not included in Table 3 are terpolymers, in which acid monomers are used together with ester comonomers to improve adhesive properties.

The ionomers are produced by the partial neutralization of acidic copolymers containing 10 wt % of (meth)acrylic acid by sodium or zinc ions. The ionic salts and the unneutralized acid groups form strong interchain interactions, producing a form of thermally labile cross-linking in both the solid and the molten states. The T_g of the amorphous material in ionomers is slightly above room temperature, resulting in a stiffness similar to that of LDPE at room temperature. However, the stiffness of most ionomers decreases rapidly with increasing temperature above 40°C. The polyketone (PK) and cycloolefin (COC) copolymers are both developments in which ethylene is present as a 50 mol % alternating copolymer [24]. The PK materials are believed to be made with a novel group VIII catalyst [25]. They are targeted for

Table 3. Properties of ethylene copolymers

Property	EVA (Repsol PA-501)	EVA (Repsol PA-538)	EVA (Repsol PA-440)	VLDPE (DSM TMX 1000)[a]	Condition	Standard
Vinyl acetate content, wt %	7.5	18	28			
Melt flow index, g/600 s	2	2	6	3	190°C/2.16 kg	ASTM D1238
Density, kg/m^3	926	937	950	902	rapid annealed	ASTM D1505
Vicat softening point, °C	83	64		66		
Tensile strength, MPa	16	16	11	11.5	50 mm/min	ASTM D638
Elongation at rupture, %	700	700	800		TMX 1000: 0.4 m/s	
Modulus of elasticity, MPa	156[b]	47[b]	24[b]	95[c]		
Permittivity at 1 MHz	2.46	2.70				ASTM D1531
Loss tangent at 1 MHz	0.014	0.035				ASTM D1531
Volume resistivity, $\Omega \cdot$ m	2.0×10^{15}	2.5×10^{14}				
Dielectric strength, kV/mm	19	20				

[a] Octene copolymer.
[b] 0.2% strain, 100 s.
[c] ASTM D790.

medium-stiffness applications and also have good barrier properties for hydrocarbons. The carbonyl group, however, makes the polymers susceptible to degradation by sunlight. The COC materials from Topas Advanced Polymers (former Hoechst) make use of the remarkable catalyst activity and copolymerization ability of the single-site catalysts [26] and the high transparency and low birefringence allow its use in compact disks and transparent packaging.

3. Polymerization Chemistry

3.1. Polymerization

(→ Polymerization Processes, 1. Fundamentals). Ethylene polymerization is an exothermic reaction that generates 93.6 kJ/mol (3.34 kJ/g) of energy. Given the specific heat of ethylene of 2.08 $JK^{-1}\ g^{-1}$, the temperature in the gas phase rises for approximately 16°C for each 1% conversion to polymer.

Heat management, in particular, removal of heat and controlling the polymerization temperature are among the key challenges in a commercial polymerization process. Depending on the process, there are different strategies to remove heat from polymerization effectively and enable high-throughput polymerization reactions without compromising the operability of the process.

Besides applying cooling agents and removing heat through the walls of the reactor, circulation of gas in the gas-phase process carries the heat away from the polymerization reaction to the heat exchanger, where it is cooled down before it is injected again into the reactor. In addition, higher boiling inert materials are used in the gas-phase process as so-called condensing liquids. Liquids are injected into the reactor in which they evaporate taking considerable amount of heat away. They become a part of the recycle gas that is then passed through the heat exchanger where the liquids are condensed, separated, and then injected into the reactor again.

Solution polymerization process is an adiabatic process in which heat of the reaction is used to maintain the high temperature needed to dissolve polyethylene in the solvent. Eventually, the heat is removed from the polymer by evaporation of the solvent after the polymerization.

3.2. Free-Radical Catalysis

Polymerization Elements. High-pressure polymerization process is initiated by free radicals that are a product of homolytic cleavage of the O–O bonds in added peroxides. Very high pressure of ethylene in the range of 150 and 350 MPa is needed to achieve a reasonable concentration of the monomer. Temperature in excess of 160°C enables the polyethylene product to be dissolved in the unreacted ethylene. In addition, the conditions are optimized for high production and conversion rates to maintain the economical viability of the needed sizeable investment in the polymerization plants. Conversion of 20% of the monomer is typically achieved in approximately 40 s, making the

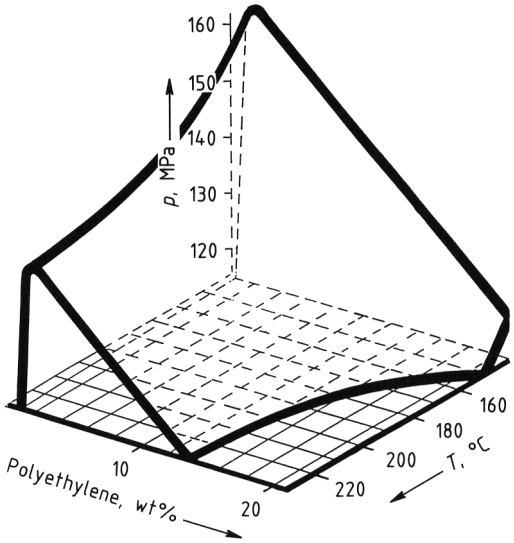


Figure 10. Schematic cloud point surface for ethylene – polyethylene

residence time in the reactor extremely short in comparison with residence times of other processes. A polyethylene schematic phase diagram for an ethylene–polyethylene system is shown in Figure 10.

For a more detailed account of the effect of molecular mass and MMD on the phase equilibrium, see [27].

The single-phase ethylene–polyethylene mixture allows the reaction to take place as a classical free-radical-initiated solution polymerization (→ Polymerization Processes, 2. Modeling of Processes and Reactors). Some aspects, which are particularly important for ethylene systems, are the following:

1. The very high monomer pressure, as stated before, sometimes reaches 350 MPa contributing to the very high reaction rate. In addition to concentrating the monomer that remains in the gaseous phase, it influences the rate constant [28] by enabling the reactant to reach the transition state. Changing the pressure from 0 to 200 MPa is calculated to increase the polymerization rate by a factor of approximately 12 [29].
2. The activation energy for ethylene polymerization is 32 kJ/mol, and the elevated polymerization temperature of ca. 250°C, which, owing to the temperature gradient in the reactor, can in some spots reach over 300°C, certainly contributes to high polymerization rates. As the polymerization is initiated by the radicals that are a product of bond cleavage, there is no risk of deactivating the initiator at the high temperature as it would be in the case of typical Ziegler or single-site catalysts.
3. Chain transfer process (Fig. 11) is the reaction by which a free radical center of an alkyl, for example, a growing polymer

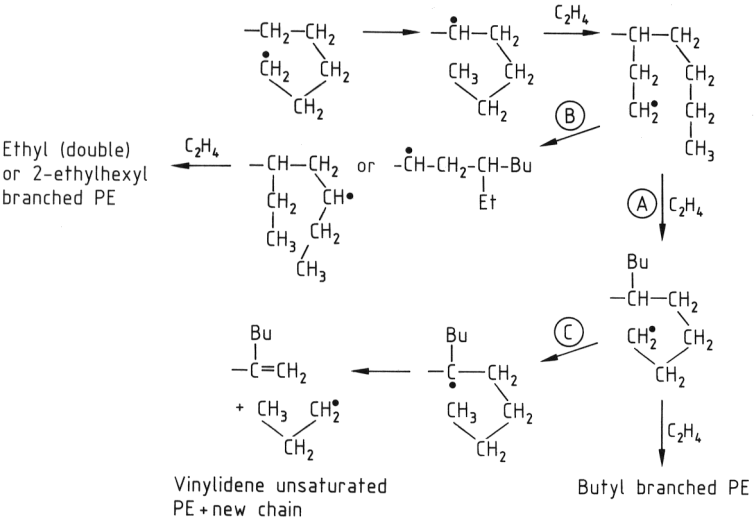


Figure 11. Principal intramolecular chain-transfer reactions

chain, attacks another alkyl group, abstracts a hydrogen atom creating a saturated alkyl chain, and frees another radical. This process has higher activation energy than the polymerization reaction, and it is favored by the increased temperature of the radical polymerization reaction. Consequently, the molecular masses of the polymer chains depend on the reaction temperature and can be limited if the temperature is higher. In addition, purity of the feedstock material, absence of all chemicals that might favor the chain-transfer process is essential for radical polymerization. On the other hand, targeted use of the same agents is an option to control the molecular mass of the polymer. Chain-transfer agents used commercially are hydrogen, propane, propene, acetone, and methyl ethyl ketone. Chain transfer to some compounds with very active hydrogen atoms such as propene and particularly the higher alkenes can lead to radicals that are insufficiently reactive towards ethylene to re-initiate new chains rapidly, and result in reduced reaction rates. The alkyl radical of a growing polymer chain can attack the rest of the chain by forming a ring and abstracting a hydrogen atom from the fourth methylene group down the chain. This is called intramolecular chain transfer. In this so-called back-bite mechanism described by M.J. Roedel of DuPont [30], the chain continues growing from that fourth carbon atom in the chain, and a butyl rest remains as a branch in the backbone polymer chain. If, after the addition of one ethylene molecule to the newly formed secondary radical, a further back-bite occurs (Fig. 11B), a pair of ethyl branches or a 2-ethylhexyl group is formed. A further possibility, shown in Figure 11C, is that back-bite occurs to a branch point, and the tertiary radical then decomposes into a new short radical, leaving a vinylidene group at the end of the polyethylene chain. This process is the principal chain-termination mechanism in LDPE, and concentrations of vinylidene groups approach one per number average molecule for LDPEs produced at high temperature.

4. If the chain transfer takes place between two chains as an intermolecular chain transfer branches are formed that are considerably longer, LCBs. The same process also causes broadening of the MMD of LDPE. Typically, LDPE chains contain more branches if they are longer, which is a consequence of the increased number of potential sites for radical attacks in the longer chains, assuming that every free radical will grow a polymer chain until the polymerization is terminated by the chain-transfer or radical combination reaction. Statistically, the probability for termination is the same irrespective of whether the polymerization and growth of the particular chain has been started by an initiator or by a radical that itself is a product of a chain-transfer reaction. Therefore, statistically all chains, irrespective of whether they are in the polymer backbone or branches, have the same statistical length, but branches are sometimes slightly longer in the absolute length than the backbone chains themselves. In addition to temperature and pressure that accelerate the chain-transfer mechanism, also the concentration of dissolved polymer plays an important role. Polymer that is dissolved in the polymerization media is more accessible to alkyl radicals for attacks, and, therefore, the amount of branching is directly proportional to the concentration. This again is the reason for the significant difference in products between tubular and autoclave high-pressure reactors. Tubular reactors made out of relatively narrow and very long steel pipes behave similarly to plug-flow reactors, and stirred autoclave reactors can be seen as typical continuously stirred tank reactors (CSTRs). Thus, the concentration of dissolved polymer at the site of polymerization is different in the two types of reactors and the LCBs of the products as well. Theoretical analyses for autoclave [31–33], and tubular [34] reactors have been presented.
5. High-pressure polymerization was discovered in 1933 by Gibson and Fawcett of ICI by a mistake that caused ingress of oxygen traces in highly pressurized pipes [3], heated to a high temperature, containing ethylene. Oxygen, or the free radicals resulting from the cleavage of the O−O bond at the high temperature, was the first radical initiators for the radical ethylene polymerization reaction. For some time, oxygen was

used in the early commercial processes. However, the mechanism by which oxygen forms free radicals is rather complicated, and at lower temperatures oxygen can act as an inhibitor [35]. To achieve much better control of the polymerization kinetics, in the modern plants specifically designed organic peroxide molecules or, more often, a mixture of them are used. They have defined temperature of radical formation and lifetime suited for the specific needs of the process. Typical initiators are listed in Table 4. Oxygen is still used in combination with other initiators in the tubular reactors only.

6. Initiators are often called "catalysts" even though they are not catalysts according to the definition of catalysis and catalysts, because the radicals are consumed and destroyed in the process. Still, one molecule that generates radicals initiates polymerization of many ethylene molecules, and the polymerization, although exothermic, is not a spontaneous process. In that sense the role of initiators can be seen as "catalyst-like".

Table 4. List of commercially used initiators for radical polymerization

Chemical description	*T*s max.*, °C	*T*s min.*, °C	1 h half-life temperature**, °C
2,5-Dimethyl-2,5-di(*tert*-butylperoxy)hexane	40	10	134
tert-Butylperoxy-2-ethylhexyl carbonate	20		117
tert-Amylperoxy-2-ethylhexanoate	5	−20	91
tert-Amyl peroxypivalate	−10		72
tert-Amylperoxy-2-ethylhexyl carbonate	20		113
2,5-Dimethyl-2,5-di(2-ethylhexanoylperoxy)hexane	15	−20	86
2,5-Dimethyl-2,5-di(*tert*-butylperoxy)hexyne-3	30	0	141
tert-Butyl peroxy-2-ethylhexanoate	10	−30	91
1,1-Di(*tert*-butylperoxy)cyclohexane	25		113
tert-Butyl peroxyneodecanoate	−10	−30	64
tert-Butyl peroxyneodecanoate, 75% solution in odorless mineral spirits	−10	−20	64
tert-Butyl peroxypivalate, 25% solution in odorless mineral spirits	−5	−20	75
tert-Butyl peroxypivalate, 40% solution in odorless mineral spirits	−5	−15	75
tert-Butyl peroxypivalate, 75% solution in odorless mineral spirits	−5	−15	75
tert-Butyl peroxyneoheptanoate, 75% solution in odorless mineral spirits	−10		67
tert-Butyl peroxydiethylacetate	15	−30	93
1,1-Di(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane	25		105
1,1-Di(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane, 50% solution in odorless mineral spirits	25		105
1,1-Di(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane, 75% solution in odorless mineral spirits	25		105
1,1-Di(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane	25		105
3,6,9-Triethyl-3,6,9-trimethyl-1,4,7-triperoxonane, solution in isoparaffinic hydrocarbons	40	10	146
3,6,9-Triethyl-3,6,9-trimethyl-1,4,7-triperoxonane, solution in isoparaffinic hydrocarbons	40	10	
Di(3,5,5-trimethylhexanoyl) peroxide, 37.5% solution in odorless mineral spirits	0	−15	77
Di(3,5,5-trimethylhexanoyl) peroxide, 50% solution in odorless mineral spirits	0	−10	77
Di(3,5,5-trimethylhexanoyl) peroxide, 75% solution in odorless mineral spirits	0	−10	77
tert-Butyl peroxyisobutyrate, 50% solution in odorless mineral spirits	10		98
tert-Butyl peroxy-3,5,5-trimethylhexanoate, 30% solution in odorless mineral spirits	25	−20	114
tert-Butyl peroxy-3,5,5-trimethylhexanoate, 60% solution in odorless mineral spirits	25	−20	114
1,1,3,3-Tetramethylbutyl peroxy-2-ethylhexanoate	5	−20	88
1,1,3,3-Tetramethylbutyl peroxyneodecanoate, 70% solution in odorless mineral spirits	−15		57
1,1,3,3-Tetramethylbutyl peroxypivalate, 75% solution in odorless mineral spirits	−15	−25	66
tert-Butyl peroxy-3,5,5-trimethylhexanoate	25	−20	114
Di-*tert*-butyl peroxide	40	−30	141
tert-Butylperoxy isopropyl carbonate	25	−20	117
tert-Butyl peroxybenzoate	25	10	122
2,2-Di(*tert*-butylperoxy)butane	30		116
Di(2-ethylhexyl) peroxydicarbonate,	−20		64
tert-Butyl peroxyacetate	10	−15	119
tert-Butyl cumyl peroxide	40		136
tert-Amyl hydroperoxide, 85% solution in water	30		190
1,1,3,3-Tetramethylbutyl hydroperoxide	25	−5	159

* T_s = storage temperature.

** 1 h half-life temperature = temperature at which concentration of the radical source is reduced by 50% after 1 h of being exposed to it.

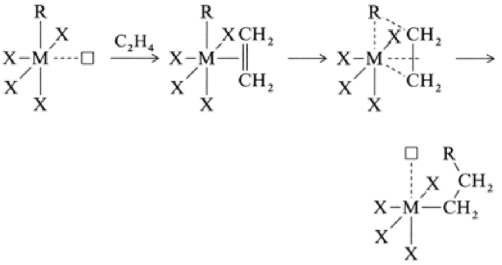
7. The mechanism of kinetic chain termination is by combination of radicals. This further widens the MMD in LCB systems if the rate of initiation–combination is high [33].
8. Characteristics of the high-pressure ethylene polymerization manufacturing are also occasional runaway or decomposition reactions, also called "decomps". In these reactions ethylene decomposes into carbon and a mixture of methane and hydrogen. These too are highly exothermic reactions, which, according to the theoretical calculations, could cause increase of the final temperature and pressure in the reactor to 1400°C and 620 MPa (reactors are normally operating at 250°C and 200 MPa). As the decomposition is not otherwise avoidable, the high-pressure plants are designed for this sudden and abrupt increase in temperature and pressure. They are equipped with rapture disks and/or fast pressure release mechanisms. Still, decomps appear as controlled explosion of the plants that are usually followed by discharging the inventory of the reactor into free space emitting a black cloud of carbon. Modern control strategies based on thorough monitoring of conditions in the reactor contribute to less frequent decomps occurrences in high-pressure plants.

$$C_2H_4 \rightarrow C + CH_4 \Delta H = 127\ kJ/mol$$
$$C_2H_4 \rightarrow 2C + 2H_2 \Delta H = 53\ kJ/mol$$

3.3. Coordination Polymerization

3.3.1. Mechanism

Coordination polymerization is a typical chain polymerization reaction in which the polymer chain grows one monomer unit at the time. The name coordination stems from the principle mechanism that is based on the coordinative bonding of the double-bond containing monomer with the transition metal complex that features a free electron orbital capable of accepting π-electrons of the double bond. After the rearrangements, a σ-bond between the metal and carbon atom is formed and the coordinative site is freed for a new monomer to be bonded with the active site.



The second and all further monomer units are inserted between the first and/or preceding carbon atom, and the chain becomes longer by that one unit. Consequently, polymer chains grow from the side connected to the transition metal [36].

All three types of catalysts that are used for low-pressure polymerization of ethylene, Phillips, Ziegler, and single-site, are based on the same mechanism and they all contain a transition metal as a principle component.

Several reasons exist for termination of the coordination polymerization, for example, β-hydrogen rearrangement, in which the hydrogen atom in the β-position to the active site is abstracted and transferred to the incoming olefin. The chain growth continues with the new monomer unit and a vinyl double bond at the end of the polymer chain on the leaving chain is formed. Alternatively, in the presence of hydrogen in the reactor, hydrogen molecules can coordinate instead of the monomer, which leads to hydrogenolysis of the metal–carbon bond of the growing chain. The products are a saturated polymer chain, an alkane, and metal hydride species [37]. The metal hydride is further active in polymerization, and a new polymer chain can be formed on the active center. This process can occur many times until the active site is deactivated by poisons and/or side reactions.

On the basis of the described chain termination mechanism, hydrogen is often used as the molecular-mass controlling agent in coordination polymerization.

Coordination polymerization mostly produces linear polymer chains and the only way to introduce branching is incorporation of comonomers, typically 1-butene, 1-hexene, or 1-octene. Olefins with internal double bonds, such as 2-octene, cannot be incorporated into the polymer backbone and are catalyst poisons.

They coordinate with the transition metal, but the next step, formation of the σ-bond, is sterically hindered and does not take place. Therefore, the active site becomes blocked for further polymerization.

As the products of the β-hydrogen transfer are polymer chains with a vinyl group at the end of the chain, they could theoretically become reengaged in the polymerization as so-called macromonomers. However, this is sterically hindered, given the length of the alkyl rest attached to the vinyl group. Single-site catalysts that are based on organometallic complexes containing one cyclopentadienyl ligand only, in which the coordination sphere of the active site is designed to be sterically open and accessible by large molecules, can indeed copolymerize also these macromonomers, and the result of this process are LCBs also in the low-pressure polymerization products.

3.3.2. Catalysts

In the case of coordination polymerization, the use of the term catalyst for the initiators is both somewhat inappropriate and very common. Ziegler catalysts and most Phillips catalysts require activation that occurs in the polymerization reactor. Ziegler catalysts are activated by aluminum alkyls and Phillips catalyst by the monomer. Therefore, more appropriate term would be catalyst precursors, at least for the two classes of catalysts. Single-site catalysts are typically formulated so that they contain the complex precursor and activator, and are ready to polymerize from the beginning. In addition, all coordination polymerization catalysts are destroyed in the process and cannot be recovered. Still, they enable and accelerate polymerization with very large turnover numbers, and, therefore, the term catalysts is commonly accepted and used.

Catalysts for all particle-forming polymerization processes, which include all polymerization processes except solution polymerization, are used in their supported form, impregnated on an inert carrier. This is to achieve good dispersion of the catalyst in the polymerization reactor, improve local heat transfer from the active site, secure active site separation and avoid mutual deactivation by two or more active sites, improve resistance to catalyst poisons and a few other reasons.

Carriers are typically highly porous materials that have a spongelike structure under the optical microscope. Due to the high porosity, carriers have large specific surface areas in the order of 250 m^2/g of material. Metal oxides such as SiO_2 and metal halides such as $MgCl_2$ are often used as typical carriers for olefin polymerization catalysts. Depending on the polymerization process, the carrier particles can have sizes from approximately 5 to approximately 50 μm in diameter. It is always advantageous if the particle size distribution is as narrow as possible.

Polymer particles are formed in the particle forming process following so-called replica mechanism and their basic shape is identical to the shape of the catalyst particle that caused their formation, just several times larger (Fig. 12).

Polymerization occurs on the active sites that are distributed across the carrier particle inside the pores on the surface of the carrier material. After the initial stage of polymerization, the polymer is formed in the pore cavities creating

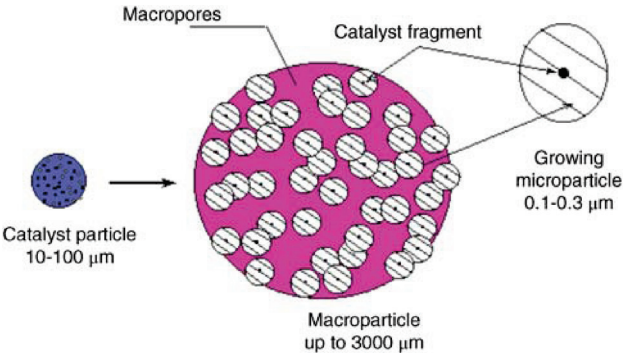


Figure 12. Catalyst particle growth by replication

certain hydrodynamic pressure at the pore walls. Under the pressure, particle structure and pore walls break but the polymer that is bound to all parts of the particle still keeps them together maintaining the form of the primary particle [38].

In the described mechanism, diffusion of monomer, access to the active site is not hindered by the growing polymer mass and the polymerization continues.

3.3.2.1. Phillips Catalysts

Phillips catalysts are extensively used for manufacturing polyethylene worldwide and over one third of the overall polyethylene volume is produced by using one of these catalysts.

They are typically supported catalysts that are manufactured by impregnation of the above-described carriers with an aqueous solution of chromium salts. Owing to its high solubility in water, CrO_3 originally was the main source of Cr for manufacturing Phillips catalysts. Given the high toxicity of Cr^{VI+} compounds, CrO_3 has been exchanged by less poisonous trivalent chromium salts. Loading of chromium in the supported catalyst can vary between 0.2 and 1.0% based on the total catalyst weight. Carrier impregnated with the salt is calcined in an air-driven fluidized bed at the temperature between 500 and 900°C to remove absorbed water and surface hydroxyl groups. By this process, chromium is converted into surface chromate (Fig. 13) by oxidation from the lower oxidation

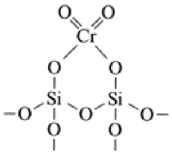


Figure 13. Chromate attached to the silica surface

state found in the trivalent salt used as the chromium source.

If it contacts ethylene or some other reducing agent, the catalyst is reduced and activated. The reduction by ethylene is the reason for prolonged initiation time of Phillips catalysts that have not been pretreated with activators such as carbon monoxide. After activation, Phillips catalysts do not need further alkylation or any other co-catalyst to polymerize ethylene. Owing to the large variety of active sites obtained in the process of activation, Phillips catalysts usually produce polyethylene with broad MMD.

Importantly, chromate is only active if attached to the support, which seems to be a part of the active site as well (Fig. 14).

As the characteristics of the support are very important for all coordination polymerization catalysts, choice or treatment of carriers can be the differentiating factor causing diversity in catalyst performance, enabling production of a variety of compounds.

The carriers are commonly supplied already impregnated with chromium, and only the

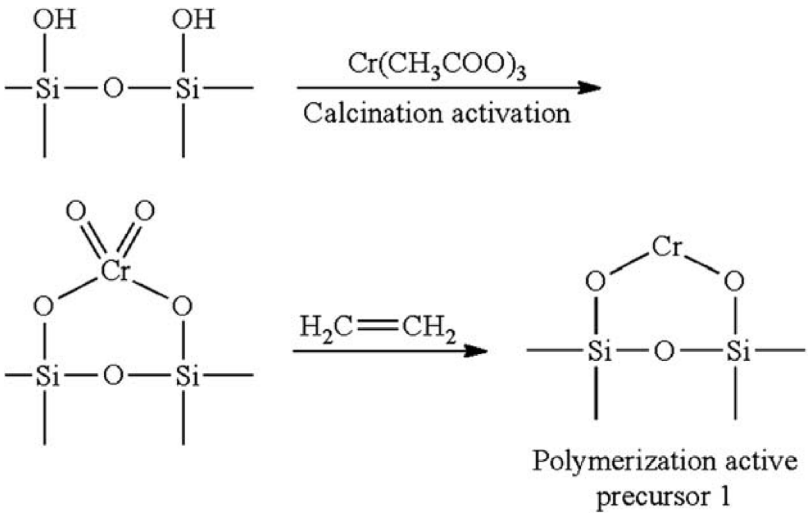


Figure 14. Active sites of a chromium based catalyst

activation step is performed by the polyethylene manufacturer at the plant.

Hydrogen, the common chain-transfer agent used for controlling the molecular mass of the polymer produced with almost all other coordination catalysts, cannot be used with Phillips catalysts because it is oxidized to water by the chromate groups. Very often, supports used for preparing chromium catalysts are titanated, treated with Ti containing compounds to bond chromium atoms to the support through titanate bonds [39]. This treatment enables manufacturing of polymers with a lower molecular mass, higher MFR, and even broader MMD.

Chain termination is the most common end of the polymerization. If chromium catalysts are the initiators, the β-hydrogen transfer process leaves chromium hydride, an active species that can start a new polymer chain, and the polymer chain with the vinyl group at its end (Fig. 15).

β-Hydrogen transfer is favored by high temperatures, and adjusting the polymerization temperature can be used to some extent as the means of molecular mass control.

Productivity of chromium catalysts is in excess of 5 kg/g leaving only traces (ppm) of Cr metal in the polymer.

Chromium catalysts are still very important and widely used in the commercial manufacturing of polyethylene. This, however, is no longer reflected in the intensity of research in the area of catalysis. Most companies and academic organizations are focused on other catalyst classes, mostly single-site, postmetallocene and/or Ziegler catalysts.

3.3.2.2. Ziegler Catalysts

Ziegler catalysts are coordination polymerization catalysts that are based on the transition metals from the fourth group of the periodic system: titanium, zirconium, and hafnium. They were discovered in 1953 at the Max Planck Institute for Coal Research in Mülheim an der Ruhr, Germany, in the research group of KARL ZIEGLER [40]. ZIEGLER was initially interested in polymerization of butadiene with main group metal alkyls as initiators. Attempting the polymerization with aluminum alkyls, he found so-called "Aufbau" reactions, insertion of ethylene molecules into the metal–carbon bond of aluminum alkyls. The reaction occurs at an ethylene pressure higher than 8 MPa and temperature higher than 80°C. Products of the aufbau reaction are oligomers of ethylene that contain up to 100 ethylene molecules. Research of the oligomerisation lead to the discovery of the so-called nickel effect: dimerization of ethylene catalyzed by Ni^0 complexes in the presence of aluminum alkyls. Presence of elemental Ni in the reactor, caused by aggressive cleaning of high-quality steel, turned the aufbau reaction into dimerization resulting in isobutene as the main product. Having discovered and explained the Ni effect, ZIEGLER expanded his interest to other transition metals and their interactions with aluminum alkyls and ethylene, looking for other unexpected effects. When $ZrCl_4$ was exposed to ethylene in the presence of aluminum alkyls, white linear polyethylene was formed, and Ziegler catalysts have been discovered.

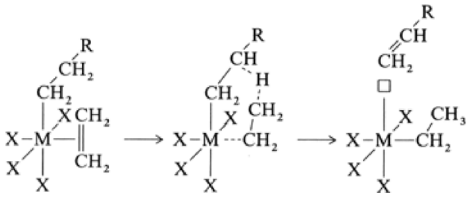


Figure 15. β-Hydrogen-transfer-to-olefin mechanism

Later on, the catalysts have been used for polymerization of propylene by GIULIO NATTA in Ferrara, Italy. NATTA contributed significantly to the development of polypropylene, as well as to the theoretical explanations of the polymerization mechanism. Therefore, a Nobel Prize for chemistry was awarded to these two researchers in 1963 and the polymerization is known as Ziegler–Natta polymerization.

Early development of Ziegler catalysts was driven by the need to increase catalyst activity and eliminate the need for extraction of catalyst residuals from the polymer. First catalysts used in the commercial ethylene polymerization were based on reduction of $TiCl_4$ with aluminum alkyls resulting in crystalline β-$TiCl_3$. This was a self-supported catalyst in which only a very small part of all transition-metal atoms were participating in the polymerization.

Catalyst productivity was improved first by choosing different, longer alkyl aluminum compounds and alkoxytitanium chlorides [41, 42], so that the extraction was not needed any longer. While the activity of titanium was improved, it

was still demonstrated that only less than 1% of the transition-metal atoms are active in the catalysis. The explanation for the low-active-site count in the catalysts was in the low accessibility of the titanium atoms due to the low number of them exposed at the surface of the crystallite largely containing titanium chloride.

To increase the accessibility by diluting Ti atoms and making them more effective in polymerization, inert metal oxides like silica and alumina were tried as supports for early supported Ziegler catalysts. Deposition of $TiCl_4$ directly on the surface of the oxides did not produce expected effects regarding activity increase [42], and the first significantly more active catalysts were manufactured by using Mg(OH)Cl as the carrier [43]. Since then, Mg compounds, mostly $MgCl_2$, have been among the important constituents of all Ziegler catalysts. Silica-supported catalysts include Mg-containing complexes of Ti atoms deposited on the carrier. Pure $MgCl_2$, generated either by precipitation or spray drying of Mg alkoxides, is often used as the support for Ziegler catalysts.

Increase in catalyst activity obtained by supporting is believed to be a result of the improved accessibility and larger participation of Ti atoms, which means a larger number of active sites per engaged Ti, and not a result of increased activity of single active sites. Furthermore, the support also affects the number of types of active sites, typically reducing them, which leads to somewhat narrower MMD (Fig. 16).

To further modify MMD, Lewis bases such as THF are often added to Ziegler catalysts. It is believed that the electron donors selectively deactivate some types of active sites effectively narrowing MMD.

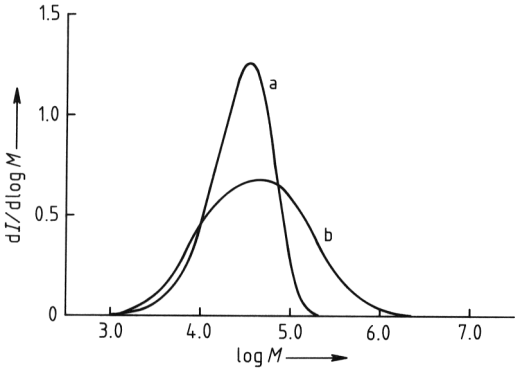


Figure 16. MMD curve of a Ziegler HDPE compared with simple statistical theory
a) Most probable distribution; b) Hostalen GD-4755

Shape and size of supported Ziegler catalysts are, for most processes, very relevant features that determine their usability and range of products that can be manufactured using them. As surface area increases and tortuosity decreases in smaller particles, all resulting in improved accessibility of active sites, catalyst productivity increases by reducing the diameter of the support. At the same time, heat removal from smaller particles is more efficient. On the other hand, a definite size of particles is needed for processes in which entrainment, that is, carry over out of the polymerization reactor, is possible.

Narrow particle size distribution is always advantageous enabling accurate sizing of catalyst particles appropriate to the process needs.

Spherical shape and smoothing of the particle's outer surface play an important role in generating static electricity caused by triboelectric motion in the reactor. Rougher surfaces cause more friction leading to higher charge in the reactor, and static electricity is often the root cause of undesired reactor fouling, that is, deposition of polymer in the reactor that disturbs normal operation of it.

Ziegler catalysts are efficient in incorporating comonomers in the ethylene backbone of the polyethylene chain. They are used for manufacturing the whole line-up of low-pressure polyethylenes from linear, very high density materials to plastomers and elastomers. Distribution of the incorporated comonomer, however, is not ideally homogeneous in polymers made with Ziegler catalysts: shorter chains with lower molecular mass often contain more branches than longer chains. As homogeneity of branching is a key feature providing for improved physical performance of the polymer, the current development of Ziegler catalysts is focused on improving their copolymerization performance.

Ziegler catalysts can usually produce polymers of very high molecular mass that sometimes reaches the UHMWPE range. Molecular mass of the polymer is controlled by use of a chain-transfer agent, typically hydrogen, in the reactor. Relative molar ratio between hydrogen and ethylene determines the reactivity ratio between propagation and chain transfer, and

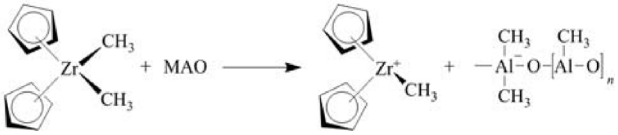


Figure 17. Metallocene activation with MAO

the molecular mass can be fine-tuned by modifying the ratio of concentrations.

Chain termination by β-hydrogen transfer that results in unsaturation occurs also if polymerization is initiated by Ziegler catalysts, but not as often as with other catalysts. Polyethylene prepared with Ziegler catalysts does not usually contain any long-chain branches.

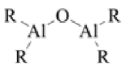
Ziegler catalysts are used in both, supported and unsupported forms. All particle-forming processes need the catalysts to be supported. In the solution process, Ziegler catalysts are formulated in-line by mixing dissolved components of the catalyst formulation immediately before or in the reactor.

3.3.2.3. Single-Site Catalysts (Metallocenes)

For a characterization of metallocenes, see also → Metallocenes. Metallocenes are organometallic compounds, complexes of metals with two cyclopentadienyl ligands creating a sandwichlike structure. Their structure has been accurately described for the first time in the early 1950s by WILKINSON [44] and FISCHER [45] independently. The first characterized metallocene was ferrocene, bis(cyclopentadienyl) iron.

As soluble and well defined compounds, metallocenes of the fourth group of transition metals have been tested early as potential precursors for Ziegler catalysts for ethylene polymerization. With aluminum alkyls as activators, titanocene, zirconocene, or hafnocene exhibit very low if any activity in polymerization.

Invention of aluminoxanes, in particular, methyl aluminoxane (MAO) by KAMINSKY [46, 47], was the key for use of metallocenes in olefin polymerization (for details on MAO, see → Aluminum Compounds, Organic):



When activated with MAO, metallocenes are highly active polymerization catalysts that produce polymers with features that are advantageous over those of polyethylenes produced by other catalysts (Fig. 17).

The structure of MAO was not well described and understood for a very long time, and it was recognized from the beginning that a rather large excess of MAO is needed to activate metallocene complexes. Still, it was clear that the catalysts originated from the metallocenes containing few, most likely only one, type of active sites: the resulting polyethylene had the theoretically narrowest MMD. This is the reason why this catalyst class is also called single-site catalysts. Furthermore, after the initial invention, many monocyclopentadienyl metallorganic compounds and some other compounds not containing the cyclopentadienyl (Cp) ring at all, none of them formally fitting the name metallocene any longer, were found to be very active in polymerization of ethylene. For that reason the name single-site catalysts is broader and more applicable to the class of these advanced catalysts.

Single-site catalysts have been developed further, and besides MAO activation, activation with Lewis acidic compounds capable of abstracting an alkyl group, typically methyl, of the transition metal and creating an ion pair, became well understood and are now commercially used [48]. Boron compounds such as tris (pentafluorophenyl)borane or trityl tetrakis(pentafluorophenyl) borate are known to react with methyl derivatives of organometallic compounds to create a loosely separated ion pair active in the polymerization of olefins (Fig. 18).

Various other strategies for activation of single-site catalysts have been developed, which include use of mixed activators and or active supports.

There are several features that distinguish single-site catalysts from other coordination polymerization catalysts. The active sites of the single-site catalysts are tetrahedrally coordinated and, therefore, more accessible than the active sites of Ziegler catalysts that are in an

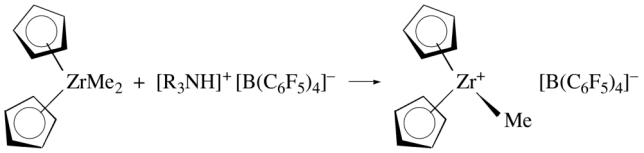


Figure 18. Borate activation of a dimethyl derivative of a metallocene complex (by product aniline not shown)

octahedral coordination. As highly reactive and relatively sterically open compounds, single-site catalysts are very sensitive to impurities. They react with the oxygen-containing compounds, and, of course, moisture, even if they are present in traces, becoming deactivated for polymerization. Unlike Ziegler catalysts, however, containing only one or few types of active sites, poisoning of single-site catalysts does not change the product quality, but only reduces catalyst activity and productivity. MMD and comonomer distribution do not change as a result of poisoning.

Furthermore, so-called hydrogen and comonomer responses of single-site catalysts differ by an order of magnitude from those typical for other catalysts such as Ziegler catalysts. The molar ratio between the chain-transfer agent, hydrogen, and ethylene needed to obtain certain lower molecular mass polyethylenes is in the range of 10^{-7} if a single-site catalyst is used, whereas a Ziegler catalyst would need several percent of chain-transfer agent in the polymerization gas composition. Similar observations are made for the comonomer-to-ethylene molar ratio needed to achieve branching.

Single-site catalysts are very efficient in incorporating comonomers, which means that the reactivity ratios for ethylene and longer α-olefins incorporation into the polymer chain are not only more similar than with other catalysts, but also the incorporation is much more homogeneous and the branches in the resulting polymer chain are spaced evenly across the chains of all lengths.

Some single-site catalysts incorporate comonomers in a reverse mode, that is, the longer chains contain more comonomer than the shorter chains, rendering their physical performance extraordinary well [49].

Single-site catalysts have an excellent comonomer utility, the ratio between the comonomer used in the polymerization reaction and comonomer needed to achieve certain density and/or branching. This advantageous comonomer utility is a consequence of their many advantageous features mentioned above. Firstly, because of the low comonomer concentration needed, losses of comonomer are much smaller than for those catalysts that need an order of magnitude higher concentration of the longer chain comonomers, the residuals of which remain adsorbed in the polymer particles and are often lost. Secondly, because of the improved homogeneity of the single-site-catalysts reaction products, same density is achieved with lower number of branches because the branches, every one of which is functional in disturbing crystallization, are evenly spaced, improving physical performance of the polymeric product. Finally, because of the even distribution of comonomer across the polymer chains of different lengths, the smaller number of branches improves the physical performance more efficiently than if they are concentrated in the shorter chains.

The polymerization reaction mechanism for single-site-catalyzed polymerization is very similar to the mechanism described for coordinative polymerization with Ziegler catalysts, which means that chain propagation and termination reactions follow the same steps. Some single-site catalysts are more prone to the β-hydrogen transfer termination, that is, they are more sensitive to higher temperatures, leading to polymers that contain more vinyl unsaturated end groups. This, in combination with the improved active-site accessibility, enables re-engagement of the macrocomonomers (polymer chains containing a vinyl group) in the polymerization resulting in branches that are as long as the polymer chain previously created (LCBs). As described above, LCBs, even at very low concentration, bring specific rheological and physical properties. The LCB-containing polymers are easier to process and have improved properties.

Since the initial discovery of single-site catalysts, many organometallic compound classes have been developed as precursors for

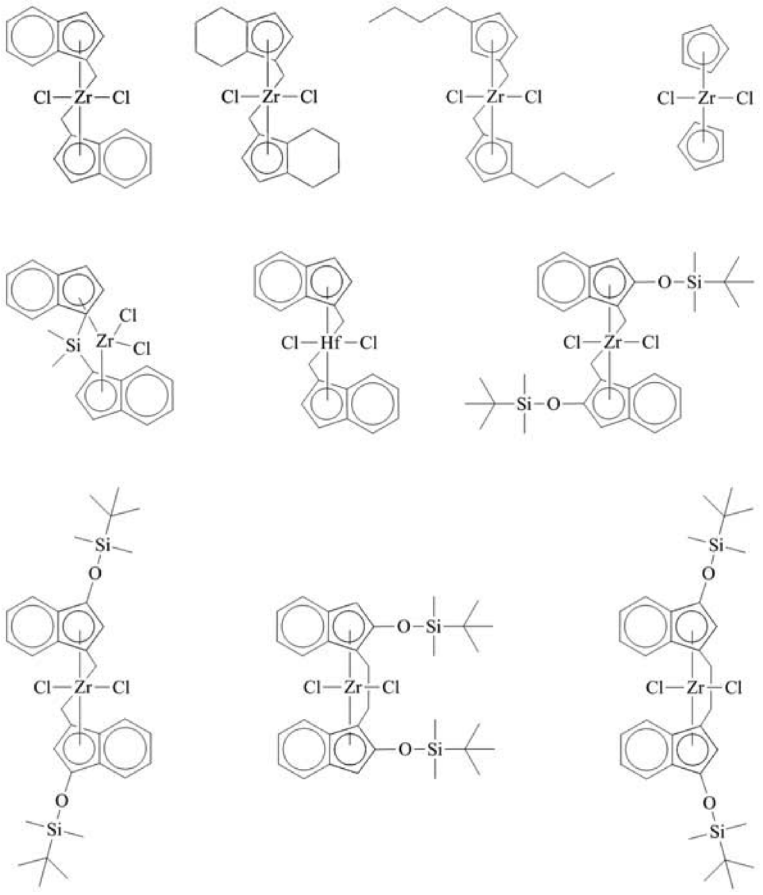


Figure 19. Typical metallocene complexes structures that are used commercially in polyethylene production

polymerization catalysts. As the active sites of the single-site catalysts are chemically well characterized and defined, they can be designed by using advanced molecular modeling techniques to perform in the desired way. Besides, the classic metallocenes and their derivatives are still used commercially. Examples are shown in Figure 19.

Mono-Cp compounds became commercially important with the innovation of the constrained geometry catalysts and phosphinimine ligands (Fig. 20).

Single-site catalysts can also be used in both their supported and unsupported form. If supported, they are usually combined with the activator, and the solid catalyst is formulated so that it is ready to polymerize immediately, and does not require activation and/or precontact as other coordination catalysts. Combining the precursor with the activator and injecting them together can create a challenge, making fast dispersion of the catalyst powder more important after injection into a continuous reactor to avoid agglomerations of polymer particles formed in the first moments of the catalyst's injection in the polymerization media. Supporting single-site catalysts and

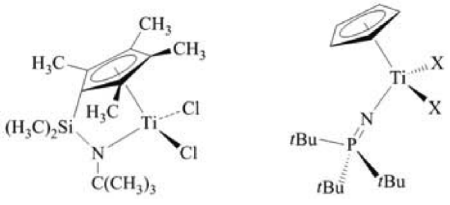


Figure 20. Constrained geometry catalyst and phosphinimine ligand based complex

occasional prepolymerization of the supported material usually stabilizes the catalyst and increases its robustness to impurities. Prepolymerization includes limited growth of the catalyst particles by polymerizing a small amount of monomer, comonomer, or any other olefin, which can be performed on- or offline. The kinetics of the catalyst is also influenced to some extent by its interaction with the support. In some formulations, the support can take an active role in contributing to the catalyst activity increase.

Single-site catalysts are often used in their unsupported form in the solution polymerization process, in which they are dissolved and combined with an alkylating reagent and an activator immediately before adding them to or inside the continuous-polymerization reactor.

4. Raw Materials

All polymerization processes for manufacturing polyethylene are sensitive to impurities. Some initiators already react with oxygen that is present in trace (ppm) amounts or moisture, and many other compounds can decrease or completely stall polymerization. Using high-quality material and purification of the raw material is often the key factor for obtaining good-quality material in an economically viable way. Purity specifications for polymerization-grade ethylene are listed in Table 5.

Most processes for polymerization of ethylene used commercially are continuous with the constant flow of raw materials through the polymerization reactors. Conversion of ethylene, depending on the process, is usually rather low, which is similar for other ingredients. Therefore, the raw materials leaving the reactor are purified, sometimes separated, and the polymerization composition is rebuilt before it is injected back into the reactor.

Table 5. Specifications for polymerization-grade ethylene*

Ingredient	Concentration
C_2H_4	>99.9 vol %
CH_4, C_2H_6, N_2	<1000 vol ppm
Olefins + diolefins	<10 vol ppm
Acetylene	<2 vol ppm
H_2	<5 vol ppm
CO	<1 vol ppm
CO_2	<1 vol ppm
O_2	<5 vol ppm
Alcohols (as MeOH)	<1 vol ppm
H_2O	<2.5 vol ppm
Sulfur	<1 vol ppm
Carbonyl sulfide	<1 vol ppm

* Data obtained from Repsol.

4.1. Ethylene

For further information on ethylene and ethylene production see → Ethylene.

Worldwide yearly production of ethylene was 109×10^6 t in 2006. Most of ethylene used for manufacturing polyethylene is produced by steam cracking. In the last decade, shale-gas exploitation and use for ethylene production became a significant factor in the polyethylene industry. The abundance and relatively inexpensive exploitation of it is influencing the polymer price and availability fostering new developments, particularly in North America [27].

In an effort to reduce environmental impact of manufacturing polyethylene, some polyethylene producers have developed so-called "green polyethylene" manufactured by using ethylene produced from renewable sources. Sugarcane is used as the base raw material for producing ethanol that is further dehydrated into ethylene. Ethylene is then polymerized to polyethylene in the conventional way.

Purity of ethylene is an important factor for manufacturing polyethylene. For most processes and catalysts the maximum amount of oxygen and/or moisture in ethylene cannot exceed several ppm, which is similar for all other oxygen-containing impurities. Most industrial crackers deliver ethylene that is rather pure enough, but methods to purify the feed stream online are often used. These are purification columns in which the gas is passed through a material that selectively binds impurities. Zeolites with defined pore size are used to physically remove moisture from ethylene, and various de-oxo beds that are based on metal ions in their lower oxidation state that oxidize in contact with oxygen are used to remove traces of oxygen [2].

4.2. Comonomers

The most important comonomers used for manufacturing various grades of polyethylene are

linear α-olefins, butene, hexene, and octene. There are several methods used for industrial manufacturing of the linear α-olefins: oligomerization of ethylene, Fischer–Tropsch synthesis, and dehydratation of higher alcohols. Most of the processes are not selective, producing a mixture of olefins, and require careful separation and purification. Methods for purification are similar to those used for purification of ethylene with the added care needed to avoid isomerization of the α-olefins. Internal olefins effectively deactivate coordination catalysts by their ability to establish a coordinative bond between the double bond and the metal active site, blocking sterically and electronically further rearrangements that should generate a σ-bond between the metal and carbon atom. De-oxo beds can, in a longer contact with a-olefins, accelerate isomerization and, therefore, it is important to use them in a dynamic mode.

Polar comonomers can be polymerized in radical polymerization only. The vinyl acetate and acrylate esters used as comonomers in the free-radical process are normally commercial-quality materials typically already stabilized to prevent homopolymerization while kept in storage or during pumping, but still active for the copolymerization reaction. In addition, they must be freed of dissolved oxygen by nitrogen sparging.

4.3. Other Materials

Initiators, coordinative catalysts and radical sources, are manufactured mostly by very specialized producers, very often also as custom synthesis.

Catalysts for solution process polymerization are formulated online by mixing solutions of the catalyst ingredients immediately before adding to or in the polymerization reactor.

Hydrogen is commonly used as the chain-transfer agent needed for molecular-mass control.

Besides the raw materials described above, there are other materials that are used either as polymerization process aids, post-reactor additives needed for product stabilization, pigmenting, or providing other final product properties.

Important components of all commercial polymerization processes are the inert materials used as diluents in slurry and solution processes, and as heat removing agents in the gas-phase process. These are typically hydrocarbons that are volatile and easily removable from the final product, having as high as possible heat capacity, and are not interacting with the polymerization process and/or the polymer.

Antifouling agents are often needed to avoid polymer deposition on the walls of polymerization reactors. These often are as antistatic agents that prevent static electricity charge of polymer.

Stabilizers are antioxidants needed to quench possible radical reactions in the formulated product leading to cross linking of the polymer chains.

One of the most commonly used pigments is carbon black that also serves as the UV-light stabilizer of polyethylene.

5. Production Processes

Commercial polyethylene manufacturing plants are among the largest industrial manufacturing processes. Current world's scale plants are capable of manufacturing 650 000 t of polyethylene per year, corresponding to the hourly production rate of more than 75 t.

Most processes are operated in the continuous mode, 24 hours per day and without any unnecessary interruptions. They are automated to the extent that they can be operated in the normal production mode with very few operators, with shifts seldom exceeding ten people.

Many manufacturing plants are integrated with the production of raw materials, located in the immediate vicinity of ethylene crackers that supply the monomer directly to the polymerization unit. This is advantageous for reasons such as transportation savings but also quality assurance coming from the direct supply.

Given the manufacturing volume, it is obviously beneficial that the plants are located close to the customers and markets where the material is sold and consumed.

The modern plants are rather versatile and can produce a variety of grades, sometimes also different types of polyethylene. Use of more than one type of catalysts is as well possible, further increasing the flexibility. Transitions between the products and/or catalysts is, however, very costly and a risky operation that

requires high operational skills and careful planning to avoid further costs and operability issues with the manufacturing.

With the ever-increasing demand for product quality and improved physical performance, the need for additional degrees of freedom needed for tailoring the product, that is, designing its molecular characteristics that provide for the improvements, is growing as well. The plants are, therefore, becoming increasingly complex in terms of the number of reactors and possibilities to control the polymerization conditions.

Polyethylene plants are divided into two principal groups: high-pressure and low-pressure polymerization processes.

5.1. High-Pressure Process

High-pressure processes are used mostly for free-radical-initiated polymerization that requires high monomer concentration and temperature, but can also be used for polymerization initiated with coordination catalysts.

A typical high-pressure process is shown schematically in Figure 21.

There are two types of high-pressure processes that are distinguished on the basis of the form of the polymerization reactor: autoclave and tubular. An autoclave reactor is a typical CSTR reactor, and a tubular reactor behaves at least partially as a plug–flow reactor. To achieve the desired conversion and reaction rate, both types of reactors need to operate under a very high pressure that is in the range 150–200 MPa for autoclave reactors and 200–350 MPa for tubular ones. This high pressure presents a particular challenge for the technology that needs to operate continuously in a safe and reliable way.

Besides the size of the reactor walls, special construction expertise is needed to provide for increased fatigue resistance of the materials. Joints and connections in a high-pressure plant are designed in a way that uses the pressure to increase sealing forces [50].

The intellectual property obtained from the development of the high-pressure polymerization technology is very often kept by the owners as trade secret, deliberately choosing to not seek for a patent protection that would mean eventual exposure of the knowledge to the competition.

After the invention and commercial implementation of LLDPE in the early 1960s, the overall assumption in the industry was that the time of the high-pressure process has passed

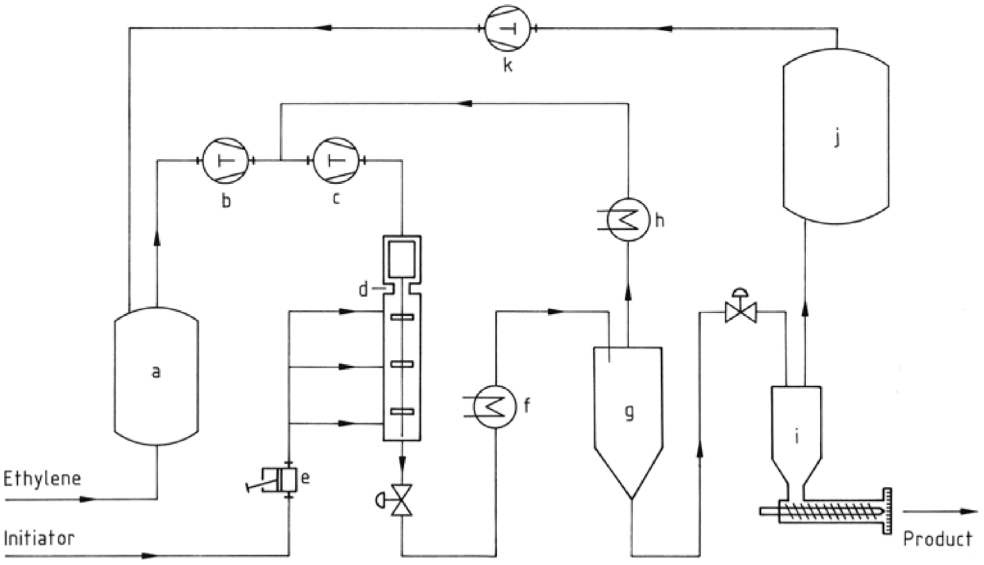


Figure 21. High-pressure process
a) Ethylene stock tank (5 MPa); b) Primary compressor; c) Secondary compressor (200 MPa); d) Autoclave reactor; e) Initiator pumps; f) Product cooler; g) Separator (25 MPa); h) Recycle cooler; i) Low-pressure separator and melt extruder; j) Low-pressure stock tank (0.2 MPa); k) Booster compressor

with LLDPE expected to fully take over the market and applications served by the LDPE material. On the contrary, owing to the specific characteristics of LDPE, that is, physical performance coming particularly from the long-chain branches and highly branched structure of the polymer, LDPE remained irreplaceable. It is still routinely blended to almost all LLDPE film materials to improve and ease processability of a final product or in multilayer application. Opposite to the 1960s' expectations, a few world-scale high-pressure plants have been built since then and a few other companies are considering expanding the capacities even further.

5.1.1. Autoclave Reactor

An autoclave high-pressure reactor as shown in Figure 22 is a typical adiabatic CSTR reactor, stirred mechanically with the feed stream inlet and product outlet to secure continuous operations of the reactor.

Heat of the reaction is not actually removed but rather adsorbed by the fresh monomer entering the reactor. Therefore, temperature control is achieved by maintaining the balance between the feed of the fresh monomer and conversion that again is achieved by dosing the initiator or mixture of them to different zones of the reactor. For a range of commercial initiators used in both, autoclave and tubular processes, see Table 4.

Most autoclave reactors are multizone reactors with two or more segments operating at different, increasing temperatures from 180°C to 290°C. Residence time in an autoclave reactor is typically between 30 and 60 s, and the volume of it is up to 1 m^3. Per-pass conversion of ethylene in an autoclave reactor is at the level of 20%.

Autoclave reactors are particularly prone to the above described runaway decomp events and, therefore, have to be equipped with rupture disks and possibilities for fast discharge of the content.

5.1.2. Tubular Reactor

Tubular reactors are typical plug-flow reactors, sometimes also called piston-flow reactors. The key assumption for the plug-flow reactors is that the fluid in them is perfectly mixed in the radial direction and not mixed in the axial direction.

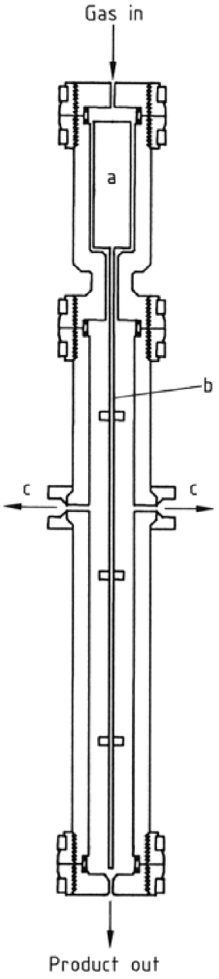


Figure 22. High-pressure autoclave reactor
a) Stirrer motor; b) Stirrer shaft; c) Bursting disk ports

Consequently, the composition of the fluid can be better described by the position of it in the reactor than by the time that the fluid has spent in it.

To assure mixing in radial but not in axial direction, tubular reactors need to have a very high *l* over *d* ratio, so most tubular reactors used for high-pressure polymerization are very long with narrow tubes coiled by combining straight segments that are connected by 180° bends. The inner diameter of the tubes is approximately 60 mm and they are as long as up to 1000 m, with thick tube walls needed to sustain high pressure of the reaction.

To achieve the required temperature control, the tubes are jacketed and equipped with

numerous thermocouples and inlets for initiator, gas, or other ingredients that are located mostly in the junctions.

Automatic temperature control is even more critical for the tubular reactors than for the autoclave ones. Due to the length of the reactor and the plug-flow nature of the polymerization, it is not always and everywhere possible to achieve absolutely efficient heat removal through the reactor wall, and temperature spikes can occur at almost any position of the tube when the reaction temperature is reached.

An important element of this rather sophisticated temperature control is the combination of different initiators, liquid peroxides, and oxygen, and their dosing to the reactor at the chosen spots.

Tubular reactors have two significant advantages over the autoclave ones: due to the advanced temperature control it is possible to recognize temperature increases early enough to react timely and reduce the reaction rate so that the decomp occurs less frequently, leading to overall higher conversion of ethylene. Most of the newly built high-pressure polymerization plants are based on the tubular technology.

5.1.3. High-Pressure Copolymers

Ethylene copolymers and terpolymers with polar comonomers are becoming increasingly important owing to their very specific performance that cannot be achieved by any other materials not even by blending of grafting different polymers in the post-reactor process.

These copolymers show particularly interesting performance when combined with cross-linking agents in the post-reactor treatment. Due to the improved heat deformation resistance and thermal oxidative stability, combined with the very low impurities level in the polymer, these materials are very well suited for manufacturing the insulation for medium- and high-voltage cables.

Polar monomers, often oxygen containing, deactivate all coordinative catalysts and can be copolymerized with ethylene in the radical polymerization high-pressure process only.

Some obvious modifications to the polymerization plant are needed to enable copolymerization: supply of the comonomer in its purified form, precise dosing in terms of amounts and reactor position, separation and recycling of the unreacted comonomer, removal and recycling of the unreacted comonomer from the product, etc.

5.1.4. Linear Low-Density Polyethylene

A typical high-pressure plant can be converted and/or used for coordination polymerization, manufacturing high- or linear low-density polyethylene. Several companies have at least explored the possibility, particularly as a means to extend the lifetime of a mature high pressure plant or as a response to the anticipated diminishing demand for LDPE.

There are no obvious advantages in terms of catalyst performance or product quality of utilizing a high-pressure technology for coordination polymerization.

5.2. Coordination Polymerization—Low-Pressure process

Polymerization of ethylene at low pressure became possible in the 1950s, after the coordinative catalysts have been invented. Besides the substantially lower complexity of the hardware needed for the polymerization, the fundamentally different polymerization mechanism also delivers fundamentally different products, linear polyethylenes, unlike highly branched and cross-linked LDPE.

Introduction of the crystalline polyethylene and further developments of copolymers that have a controllable and tunable degree of crystallinity significantly widened the use of polyethylenes for those applications that could not be serviced by LDPE.

5.2.1. Suspension (Slurry) Process

Polymerization of ethylene in a slurry, in which supported or solid catalyst and growing polymer particles are suspended in an inert hydrocarbon, has some important advantages from the process point of view: mixing is relatively readily achievable; heat removal from the polymer particles is very efficient; in case a low-boiling solvent is used, removal of the hydrocarbon at the end of the polymerization is relatively simple; it is inexpensive; etc. Therefore, the first process developed for commercial polymerization with Ziegler catalysts was a slurry process.

At the beginning of its commercial exploitation, the polymerization with chromium-based (Phillips) catalysts required removal of the catalyst residuals from the final polymer. After development of higher activity and well dispersed catalysts that could be left in the product in the 1960s, the use of the slurry polymerization technology also for Phillips catalysts became economically viable (Fig. 23).

The slurry process used today can be operated with coordinative catalysts from all classes. Owing to the partial solubility of polyethylene comonomers with low crystallinity, the slurry process is somewhat limited and not totally suited for manufacturing LLDPE.

Batch Slurry Polymerization Process. Polymerization in the slurry can be performed in the batch or in the continuous mode. Batch mode polymerization occurs in a stirred autoclave reactor in which temperature and pressure are maintained constant throughout the polymerization run. The main reason for operating a commercial manufacturing plant in the batch mode is the need for uniform product particles of UHMWPE products. UHMWPE is often processed by compression molding by which the material is not melted but sintered. Shape and size of the polymer particles play a key role in this kind of product processing, justifying the less economically attractive batch polymerization process.

Continuous Slurry Polymerization Process. The most common form of continuous polymerization processes that are operated in the uninterrupted mode is based on the loop reactors. Loop reactors are made out of the relatively large diameter jacketed pipes that, connected together, form a loop. The polymer suspension is pumped continuously through the loop with the fluid velocity between 5 and 10 m/s.

The diameter of the typical slurry polymerization reactor is 50 cm and they could be up to 300 m long. Concentration of the solids in the slurry is up to 60%. Depending on the polymer manufactured and the diluents used, the operating temperature and pressure can be between 70 and 105°C and 5 and 10 MPa, respectively. Residence time in a slurry loop reactor is between 40 min and 3 h, depending on the process.

There are several ways how the catalyst can be supplied to a continuous or any other slurry reactor. The simplest way is by suspending of supported or solid catalyst in a mineral oil and then pumping this suspension into the circulating fluid in the polymerization reactor. Alternatively, catalyst powder can be mixed with the liquid diluents to create viscous suspension, mud. The catalyst mud is then transferred through a rotary valve into the diluents stream that is pumped into the reactor.

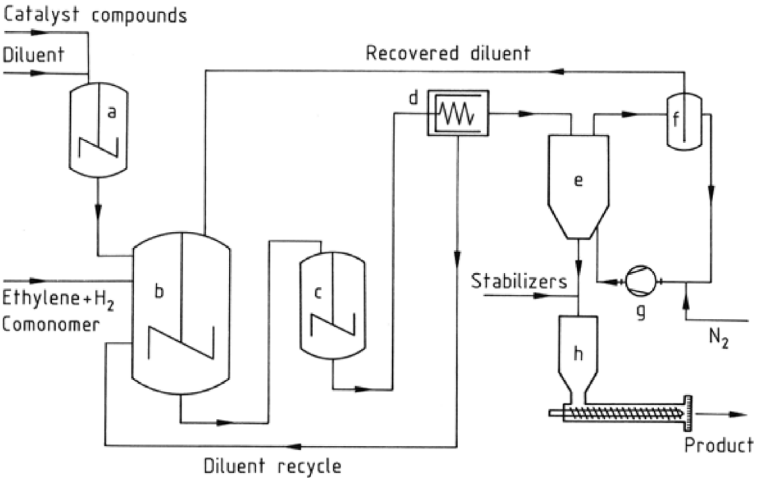


Figure 23. Hoechst suspension polymerization process
a) Catalyst preparation vessel; b) Polymerization reactor; c) Run-down reactor; d) Centrifuge; e) Fluidized-bed drier; f) Diluent condenser; g) Nitrogen circulator; h) Powder-fed extruder

Very often, slurry loop processes contain at least two loop reactors: prepolymerization reactor, which is much smaller in size, and the main reactor. The catalyst is exposed to the limited amount of monomer, usually at somewhat lower temperature, to grow 5–20 times in weight before it is transferred into the main reactor. Both of these reactors are operated in the continuous mode. The purpose of the prepolymerization step is in initiating the polymerization under mild conditions under which the particles start forming rather slowly and the risk of creating fines is smaller. At the same time, some catalysts become even more productive because of the controlled particle growth achieved by the prepolymerization.

Most slurry loop reactors are equipped with the settling legs, extension traps for sedimentation of the solid polymer material resulting in more concentrated slurry. Removal of the product then occurs from the settling legs, so that a limited amount of the diluents leaves the reactor and needs to be flushed out.

Slurry loop reactors are operating in the CSTR mode and the mixing should be effective in both radial and axial direction. This, however, holds true only to a certain extent. It is known that under the conditions for the production of low-molecular-mass polymer, that is, when concentration of hydrogen and/or of some more active catalysts in the reactor is relatively high, a concentration gradient is established and monomer- or chain-transfer concentration decreases in the parts of the reactor that are further away from the catalyst and or feed stream inlet. The gradient can cause certain broadening of the MMD of the product.

Disadvantages of the slurry polymerization reactors are operability problems typically caused by fouling of the reactor walls as a result of polymer agglomeration and stickiness to the wall. More often, the reactor starts operating in an unstable mode, in which the polymerization rate is oscillating and becomes difficult to control.

Still, slurry loop reactors are among the most used forms of the ethylene polymerization processes in the world.

5.2.2. Gas-Phase Process

Another commonly used process for the industrial ethylene polymerization is the gas-phase or fluidized-bed process. Besides the economic advantages, which are relatively low investment cost, absence of a liquid diluent, and large-scale plants, the abundance of the process is at least partially a consequence of the very successful licensing strategy and implementation of Union Carbide. The company developed the Unipol process and distributed the licence to it more than 120 times worldwide. The Unipol process was introduced in the late 1970s, originally for manufacturing LLDPE, but it is currently often used for manufacturing both HDPE and LLDPE materials. Following Union Carbide, other companies developed their original gas-phase processes. Naftachemie (later BP and INEOS) developed the Innovene G process, and Montell (later LyondellBasell), developed the Spherilene process. Both processes have been successfully licensed as well.

Schematics of the gas-phase polymerization process is presented in Figure 24.

The gas-phase process is the most versatile process in terms of the products that can be manufactured by it. As the polymer particles are in their granular form in the reactor, no solubility and viscosity constraints exist such as in the solution process, and the potential for agglomeration, risk of operating soluble materials, is reduced because of the absence of diluents. Therefore, the density range of the products is broad, from 890 to 970 kg/m^3 with an MFR that varies between nonmeasurable to over 100. The process is also versatile in terms of the comonomers that can be used. 1-Butene and 1-hexene are the most often used comonomers, and BP/INEOS used 4-methylpentene as well. If single-site catalysts are used for initiation of the polymerization, owing to their high comonomer response, high reactivity, and need for very low concentration of comonomers in the reactor, also a high-boiling comonomer such 1-octene can be utilized.

Finally, the gas phase process can be used with all kinds of coordination catalysts: Phillips, Ziegler, and single-site. The catalysts need to be supported on silica or $MgCl_2$, and the particle size needs to be sufficiently large to avoid carryover of the small particles into the process. They are usually larger than 40 μm in diameter. The shape of the particles must be as regular as possible. Sphericity and smoothness of the surface is required to avoid static electricity build up

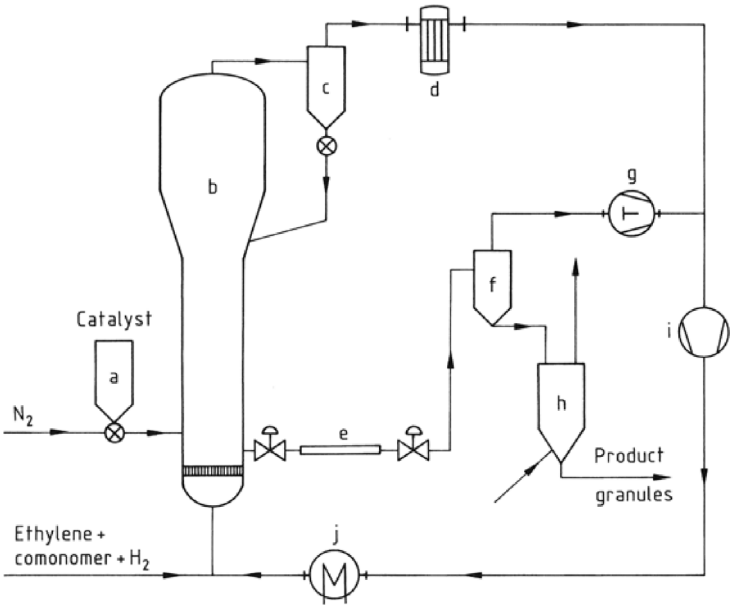


Figure 24. Fluidized-bed process
a) Catalyst hopper and feed valve; b) Fluidized-bed reactor; c) Cyclone; d) Filter; e) Polymer take-off system; f) Product recovery cyclone; g) Monomer recovery compressor; h) Purge hopper; i) Recycle compressor; j) Recycle gas cooler

through the triboelectric effects, and to provide for higher powder bulk density in the reactor.

Most often, the catalyst is injected into the fluidized-bed reactor in its dry form, as powder. This is needed to achieve fast and efficient dispersion of the catalyst into the polymerization bed in the shortest time possible.

The fluidized-bed reactor, which is an essential part of the gas-phase process, is a vertically mounted, rather simple large steel cylinder with the typical widening of the upper area, so-called disengagement zone. Polymerization occurs between a perforated steel plate mounted in the lower part of the cylinder, distributor plate, and the disengagement zone. The polymerization bed of polymer particles is fluidized by the circulation gas traveling from the bottom of the reactor up with the velocity of 0.3–0.8 m/s. When the gas–polymer mixture reaches the disengagement zone, the velocity is reduced because of the volume enlargement and the gas is not capable to carry the particles any longer and they drop back into the main zone of the reactor. The polymer-free cycle gas travels then further to the heat exchanger and compressor, which sends it back into the reactor. Before the circulation gas reaches the distributor plate, the gas composition is rebuilt, the converted monomer, comonomer and chain transfer agent are refurbished to the needed concentrations.

Gas-phase fluidized-bed reactors can have different sizes, and the largest ones are >6 m in diameter and ≥16 m. They can hold more than 100 t of polymer in the polymerization bed, and the production rate in the process can be as high as 80 t per hour.

The fluidized-bed reactors normally operate with the total pressure of about 2 MPa and in the temperature range between 70 and 105°C, depending on the polymer that is produced. C_2 partial pressure in the reactor can be up to 1.5 MPa, and the per-pass conversion of the monomer is between 2 and 10%.

Circulation gas serves a few purposes in the gas phase process and one of them is the heat removal. The gas enters the reactor at the temperature that is up to 20 or more degrees lower than the operating temperature and it absorbs the heat of the reaction almost instantaneously. The gas is cooled down in the heat exchanger.

To further increase efficiency of the heat removal in the gas-phase process, Union Carbide later developed the so-called condensing mode of operating the gas-phase process. In this process, an inert hydrocarbon, pentane or hexane, is injected into the circulation gas, prior to

entering the reactor. The liquid hydrocarbon evaporates in the reactor and absorbs the heat of the reaction. Hydrocarbon vapors are carried over as a part of the circulation gas to the heat exchanger in which they are condensed into the liquid. The liquid is then reinjected in the reactor. By applying the condensing mode of operations, the capacity of the same reactor can be sometimes doubled, which increases the production rate and reduces the residence time.

Mixing in a fluidized-bed reactor is provided by the fluidization and the typical fluidization motion of the polymer powder. The circulation gas travels from the bottom to the top carrying only a part of the polymer powder. The other part of it, separated from the gas in the disengagement zone, falls down along the wall of the reactor, and travels in the other direction, from the top to the bottom. By this, the polymer particles create a certain shear that scrubs the polymer from the wall on which it tends to stick, potentially causing fouling. In addition, the circulation gas tends to create gas bubbles in the reactor. These bubbles coalesce into larger bubbles that burst at the very top of the reactor, placing polymer powder into turbulent motion.

Due to the rather efficient mixing, it is believed that there is little to no gradient in temperature or gas composition throughout a fluidized-bed reactor.

5.2.3. Solution Process

In the solution process, the polymer remains dissolved in an inert diluent throughout the polymerization. As polyethylene is not really soluble in any solvent, the process must be operated at a very high temperature so that melted polymer mixes with the diluent and creates a solution. Because of the high temperature, speed of the polymerization reaction is significantly increased so the residence time in a solution process reactor is rather short, from 90 to 1000 s. This is also very well in line with the decreased stability of most coordination catalysts at the temperatures higher than 150°C sometimes reaching 200°C or more. The solution process, same as the high-pressure process, operates in the adiabatic regime. Per-pass conversion of ethylene is high and it reaches 95%. Schematics of the solution process is presented in Figure 25.

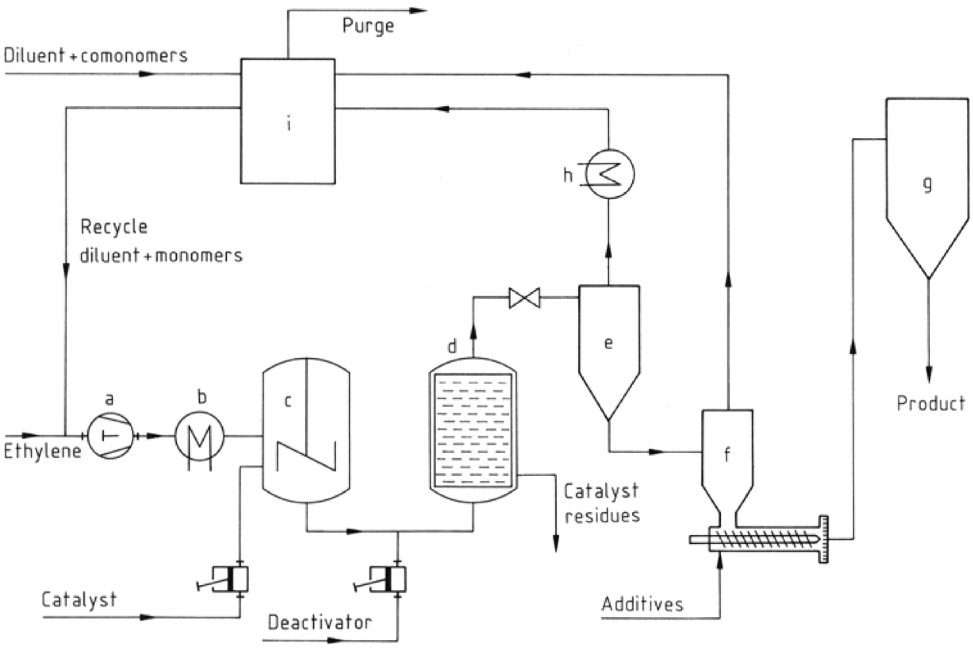


Figure 25. Solution polymerization process
a) Reactor feed pump; b) Temperature control; c) Reactor; d) Catalyst adsorber; e) First separator; f) Low-pressure separator and melt-fed extruder; g) Purged product hopper; h) Recycle cooler; i) Diluent and monomer purification unit

The range of products that can be manufactured in solution is constrained by the viscosity of the melt solution that needs to flow through the process. Depending on the branching of the product that can decrease the viscosity to some extent, the MFR of the material manufactured in solution must be higher than 0.2.

Products of the widest density range can be produced in the solution process, form the lowest at 860 kg/m^3 to homopolymers. The process is also very versatile in terms of comonomer choice. It can produce butene, hexene, or octene copolymers, and it is also used for manufacturing EPDM rubber.

Catalysts used for polymerization in solution are Ziegler and single-site and they are typically formulated by mixing solutions of the individual components of the catalyst system immediately before or after they are injected into the reactor. If operated with the $VOCl_3$ or Ziegler catalysts, the catalyst must be deactivated after the melt solution leaves the reactor, so that the polymer remains well defined and no uncontrolled side reactions in the downstream piping takes place. If the vanadium catalyst is utilized, residuals of the heavy metal need to be removed from the polymer by passing the melt solution through an alumina column. Finally, the melt solution is depressurized and the unreacted monomer and comonomer are collected and sent for purification and recycling in the process. Residual product is then extruded into pellets.

One of the advantages of the solution process is its short residence time and the short time needed to transition from manufacturing one product grade, or using one catalyst, to the other. The size of the reactor and low material inventory in it increase the flexibility of the process so that the transition time becomes on the order of couple of hours, whereby a gas-phase process, for example, might need up to 12 or more hours for the same type of change. This and the versatility of the materials that can be produced in the solution process make the technology interesting for manufacturing speciality products, needed in relatively smaller quantities, in a still economically viable manner.

5.2.4. Combined or Multimodal Processes

MMD of polyethylene chains and distribution of branching in them are the two most important factors that influence the physical performance of the material. The manufacturing processes described so far, in which polymerization occurs in one single reactor, are by themselves providing only very limited possibilities to influence the distribution and the product quality depends mostly on the catalyst used. Different catalysts, depending on the number and nature of the types of active centers, produce different products in terms of molecular mass and comonomer distribution, but that cannot be controlled very easily, especially because plants are typically limited to using only few catalysts and it is not reasonable to switch the catalyst whenever a different grade is needed to be manufactured.

To increase the number of freedom degrees and enable effective tailoring of the polymer so that some enhanced performance is obtained, several companies have developed processes that include two or more polymerization reactors, typically in series, that can, but do not have to, be different in their nature. These processes and/or plants are often called bimodal (or multimodal) processes and/or plants because they can produce bimodal (or multimodal) polymers.

By combining the reactors, polymerization conditions can be chosen so that different materials are produced in each of them so that the combination, the final product, obtains the desired molecular mass broadness and the comonomer is placed in the polymer chains of the chosen length. This is typically achieved by making two or more distinct polymer components that are substantially different in average molecular mass and/or in the amount, sometimes even type, of comonomer incorporated. If, for example, the material produced in the first reactor contains little or no comonomer and the chains produced are rather short and in the second reactor the conditions are adjusted to make a polymer that has higher molecular mass and contains more branching, the final product will have a bimodal, broad overall MMD providing for a good processability, and will contain a high-molecular-mass component that will provide for melt stability and physical performance. The distribution of comonomer will be skewed toward longer chains, further contributing to the good physical performance.

Although the same or similar effects could also be achieved by blending two materials in a post-reactor step, the bimodal process have substantial

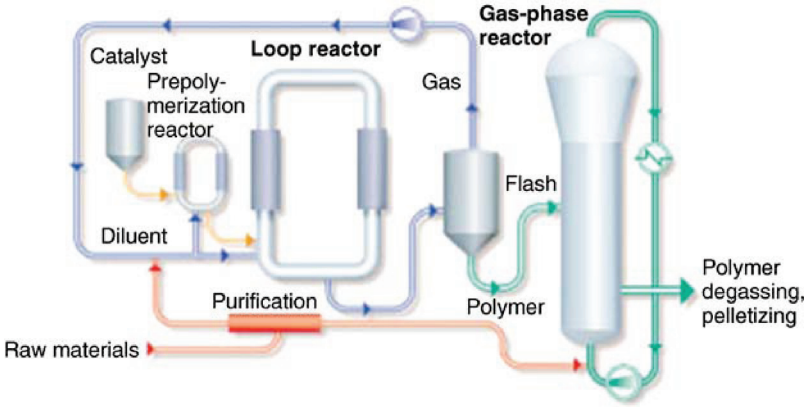


Figure 26. Borstar process

advantages. The "onion" structure that is obtained in a particle-forming process by passing the same catalyst-growing polymer particle through the reactors in series contributes to a substantially better miscibility of the two or more relatively different polymer components, and one avoids the complexity of keeping and managing the inventory needed for the blending step.

The first bimodal plants were developed by combining two slurry-loop reactors in series, and later processes were developed in which different types of reactors are connected. The Borstar process developed by Borealis is a combination of a slurry-loop reactor and a gas-phase reactor. The Borstar process also contains a third step, a smaller slurry-loop prepolymerizing reactor preceding the main slurry loop (Fig. 26).

Most modern solution plants are built with two reactors that can, but do not have to, be operated in series. As the blending occurs in solution, dispersion and mixing works well and one can operate the two reactors also in a parallel configuration.

6. Uses

Polyethylene is one of the most abundant man-made materials overall. It can be found in a very broad range of applications that span from medical prosthesis, artificial joints made of UHMWPE and surgically implanted as replacement for the natural ones, via structural applications that include pipes and cable insulation, to waste bags.

The specific properties of polyethylene including low density, mechanical strength, sealing properties, flexibility, easy processing, low cost, and low environmental impact make the material still increasingly attractive even 80 years after it was industrially manufactured for the first time.

The variety of now well established polymerization and post-reactor treatment processes that are continuously further developed enable the industry to develop specialized products for targeted applications with the properties that are constantly enhanced.

6.1. Films

A large volume of polyethylene production is used in applications in which the material is extruded into thin, flexible foils or films. Film is the preferred material for many forms of packaging, but is also used for other purposes for which separation and/or containment are needed. Typical examples of the nonpackaging polyethylene film applications are agricultural film used for the construction of greenhouses and geomembrane film, thick material that provides containment of the landfill sites and long-term separation of the disposed solids and liquids from the soil.

The two principal manufacturing methods for polyethylene films are blown-film extrusion and cast-film extrusion.

Blown-film extrusion is the method by which molten polyethylene is continuously extruded

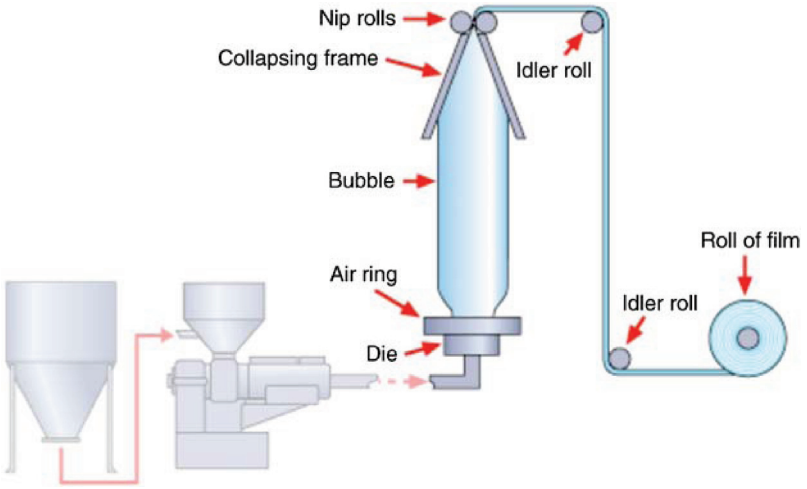


Figure 27. Blown-film line

through a circular die to form a bubble filled with air or nitrogen. The bubble is collapsed at the top by rollers into a two-dimensional tube that is then rolled on the role. The tube is usually further processed into bags by sealing and cutting, or simply cut to create a flat foil (Fig. 27).

The diameter of the bubble can be up to several meters and it is larger than the diameter of the die; the ratio between the two is called "blow-up" ratio. Thickness of the blown film can be between 10 μm and several hundreds of micrometers. Depending on the blow-up ratio, film thickness, and the cooling of the bubble, which is the time allowed for the material to crystallize, the polyethylene chains could be more or less oriented in the final product. The orientation substantially influences the physical performance of the film increasing for example machine direction and decreasing the transverse direction tear resistance.

Most modern blown-film extrusion processes are capable of extruding multilayers from which different materials are coextruded into one film product. This is performed by using multiple extruders and complicated dies that have overlapping openings so that the molten polymers meet and form the bubble all together without mixing with each other. Some of the machines can handle up to eleven layers and the materials that are combined can be very different as long as the adhesive layers are separating two otherwise less compatible layers. The advanced film blowing enables creation of packaging materials that have a combination of properties originating from the polymers specifically designed to provide only some of them. This is particularly important because the properties very often cancel each other and it is not possible to have a certain combination in one polymer only. Consequently, it is difficult to achieve somewhat higher stiffness and improved oxygen and moisture barrier performance in the material that needs relatively low temperature for sealing two layers into one, which is an important requirement for manufacturing bags. Higher density, more crystalline material is stiffer and presents a better barrier, and more mobile polymer chains that are less organized into crystallite, higher branched (lower density) materials, provide easier sealing of the layers.

Cast film is a product of extruding a thin layer of polymer onto chilled rotating rollers (Fig. 28). The material solidifies very fast in the process so that the polymer chains remain largely oriented in the machine direction only. As a consequence, cast films have improved clarity and gloss, can be stretched easily, cling to the surface, and have reasonably high puncture resistance. This makes them an ideal packaging material with which single or more objects need to be protected or held together by wrapping the film material around them. Cast film, also cold-stretch film, is used for industrial packaging of very large objects like vehicles and helicopters,



Figure 28. Cast-film line

but also in common households as food packaging.

All polyethylene grades can be used for manufacturing film materials. LDPE, HDPE, and LLDPE are used for blown-film materials, and LLDPE of somewhat higher density, 930–935 kg/m^3, is used for manufacturing cast films. Manufacturers chose different polyethylene materials depending on the application of the film and the specific properties needed for it.

6.1.1. Extrusion Coating

Very often, a combination of materials is needed to achieve the right combination of properties required for flexible packaging. As in the multilayer film extrusion, in which different polymers are combined, in the extrusion-coating process, polyethylene can be combined with other nonpolymeric materials that are needed for esthetical and traditional reasons, or because polymers cannot provide for the performance that is required.

Mostly, LDPE, owing to its high branching content that leads to a high die swell, is extruded through a thin, wide slit die over a moving layer of paper or other material. The polymer clings to the material and the products are polyethylene-coated cardboard, paper, or metal foils used for packaging of liquids or extremely oxygen-sensitive products.

6.1.2. Blow Molding

Blow molding is a conversion process for forming hollow objects, for example, bottles, in a two-stage process that involves formation of a so-called parison in an extrusion step. A parison is a piece of melted plastics with the hole on the end that is then placed into a mold. In the next step, a gas (usually air) under pressure is injected through the hole into the parison, so that a molten polymer takes the form of the mold and cools down (Fig. 29).

Blow molding is used for manufacturing bottles and containers for packaging of aggressive liquids, household cleaning materials, solvents, or gasoline. HDPE is often used in the process providing for a good environmental-stress crack resistance, a property that is reinforced by higher crystallinity of the polymer.

6.1.3. Injection Molding

Injection molding is one of the more versatile processing methods in terms of the products that are manufactured. Molten polymer is injected under pressure into a mold at one or more injection points at which it solidifies by cooling. The process is used for manufacturing caps and closures of bottles, toys, houseware, containers, and many other objects. The current European beverage market consumes 222×10^9 of bottle

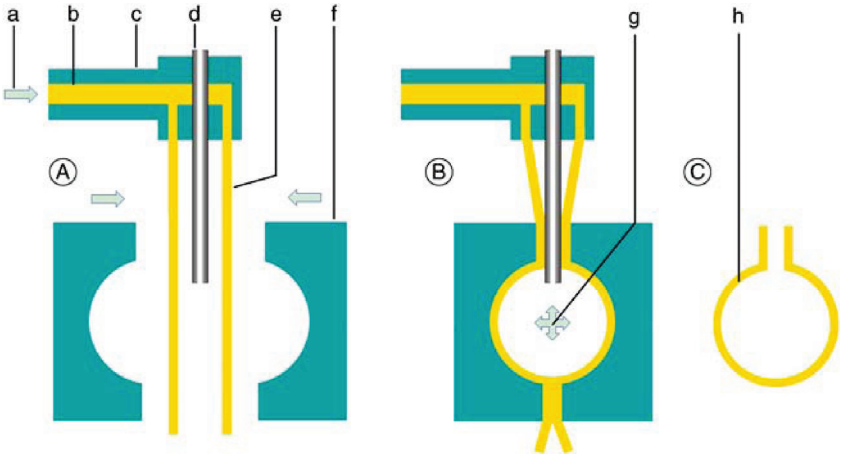


Figure 29. Blow molding
A) Parison formation; B) Blow molding step; C) Final product removal
a) Injection point; b) Molten material; c) Die for parison extrusion; d) Air inlet; e) Parison; f) Mold; g) Expanded gas; h) Final product

caps and closures per year, and most of them are made out of a polymer, very often polyethylene.

Owing to the nature of the process, relatively low molecular mass material that can flow fast through the mold is needed for injection molding. Mostly HPDE and LDPE with the MFR that can be up to 100 or more are used.

6.1.4. Rotational Molding

Rotational molding is the least investment-intensive method for processing of polyethylene, and it is, therefore, used for manufacturing of large hollow parts that cannot be manufactured by using injection or blow molding in an economically viable manner. Molds used for rotational molding are produced out of the inexpensive sheet metal and can be easily modified or reproduced if needed.

The manufacturing process is discontinuous, and it starts with placing a certain amount of polymer powder into the mold that is then closed. The mold is mounted on an arm that rotates and tumbles it in all directions making sure that all inner surfaces of the mold get in contact with the fine polymer powder. The mold is either placed in an oven or is heated by gas flames to the temperature that exceeds the melting point of the polymer. By this, polymer melts still covering the surface. Finally, the mold and the polymer are cooled down so that the object solidifies, and the mold is opened (Fig. 30).

The process is slow and not very efficient in terms of the numbers of objects that can be produced. Still, as molds for injection or blow molding are very costly and even much more so if they exceed certain size, rotational molding is used for small series of objects. Most water-sport crafts, such as kayaks, are manufactured from polyethylene in a rotational molding process.

Single-site polyethylene having narrow MMD is particularly suited for rotational molding processing. The melting point of the polymer is exceptionally sharp so that all material melts at once and the surface of the mold is covered evenly.

6.2. Pipes

Polyethylene is used for manufacturing plastic pipes for water and gas carrying, and as a protection of the steel pipes used for construction of oil and gas long-distance pipelines.

6.2.1. PE Pipes

Polyethylene pipes are increasingly used in the construction industry for hot and cold water and for gas installations. Light weight, flexibility, simplicity of installation, low cost, and good performance of the polyethylene pipes make the material a good replacement for metal or pipes produced from other polymers.



Figure 30. Rotational molding with four molds mounted on the rotating arm

The key feature that is needed for pipes is their long-term pressure resistance. To avoid very costly damages and possible serious incidents, pipes used for gas and water supply need to be able to sustain elevated and constant pressure of up to 10 MPa over a period that is not shorter than 50 years. Materials used for building such pipes are carefully designed, selected, and certified, and the pipes made out of it are tested under stress. To enable development of the materials that, of course, need feedback on the performance, accelerated test methods have been developed that provide sufficient confidence in the data extrapolated from the short-term stress exposure to the 50 years period. Still, developing pipe polymer is a very time-consuming process and changes on the market happen less frequently than in some other applications of polyethylene.

Pipes are produced from the very-high-molecular-mass and high-density polyethylene. To sustain pressure at all, highly crystalline structure organized in thick lamellae is needed not to allow water or gas molecules to pass through the material. Failures that occur short time after pressurizing the pipe because of the insufficient thickness of the crystallites are called ductile failures.

To avoid cracking of the pipes under pressure, longitudinal splits of the material attributable to slippage of the crystallites, long, "free" polymer chains are needed that partially crystallize in more than one lamella, connecting them, and keeping them from slipping. These tie molecules should be branched, containing comonomers, so that the probability of them crystallizing in more than one lamellae is increased.

Pipe materials are normally classified and certified according to the pressure they can resist. PE80 material can resist 8 MPa, and PE100 is good up to 10 MPa. PE80 can still be manufactured by using chromium catalysts in a unimodal polymerization process. To achieve the PE100 performance, bimodality has to be introduced. For bimodal polyethylenes, two kinds of polymer chains can be produced on purpose: relatively long with no branching in one reactor, and very long chains with some comonomer content in the other. By broadening the MMD using two polymerization conditions, processability of the otherwise tough material became possible, and because of the onion structure of the polymer particles, the two components can be homogenized effectively through the extrusion process.

In addition to the described pipe material, postreactor-treated polyethylene can also be used for manufacturing of pipes. In this processing, the material still containing a certain amount of vinyl groups is treated so as to build chemical bonds between the chains that contain the double bonds. This process is also called cross-linking, and it can be achieved by co-extruding initiators, free radical sources, or by irradiating manufactured pipes.

6.2.2. PE used for Steel-Pipe Coating

Steel pipes used for constructing oil and gas pipelines are exposed to the environmental

conditions that can cause severe and rapid corrosion of the metal. Polyethylene is used to coat the steel pipes protecting them from moisture and oxygen.

Steel pipes are typically coated by using three layers of polymers. Already manufactured pipes are first coated with a thin layer of epoxy resin. The pipe is then heated by using magnetic induction, and the epoxy resin polymerizes on the surface of the pipe. The next layer, polyethylene adhesive, is extruded as a tape to the surface of the rotating pipe and it is followed by the layer of top coat, polyethylene material that is the actual protection. The adhesive resin is needed to provide peeling resistance and tight connection between the epoxy layer and the polyethylene top coat.

Alternatively, the two polyethylene layers can be extruded axially to cover the pipe, through a circular die mounted around it.

6.3. Wire and Cable Insulation

With its high purity and outstanding dielectric properties, LDPE has been used for insulation of high-frequency and medium-voltage cables since the beginning of the industrial manufacturing of polyethylene. In the structure of modern electrical and information transmitting cables, for which several metal layers need to be separated by several polymer layers and the entire cluster has to be protected from the environmental influences, polyethylene is still used very extensively as an insulation material and as the top coat for jacketing the cables.

Also in this application, cross-linking is an important method for postreactor modification of the material to secure higher molecular mass of polymer and its higher resistance properties.

6.4. Plastomers

Polyethylene that is highly branched, i.e., it contains large amount of comonomer, and has, therefore, low density, lower than 910 kg/m^3, is distinguished from other typical polyethylene grades through its thermoplastic properties.

Plastomers are usually produced in a solution process by using Ziegler or single-site catalysts using octane, hexane, or butene as a comonomer. They are used for blending with other polymers, polyamide or polypropylene, to enhance the impact resistance of the otherwise brittle matrix. These blends are essential in the automotive industry, for example, for manufacturing bumpers.

Another significant application of plastomers is film. Because of its nonmigrational adhesion properties, so-called clinging, plastomer film is used as a temporary protection of the sensitive surfaces in the electronic industry.

7. Environmental Aspects

7.1. Manufacturing

Polyethylene manufacturing processes are highly sensitive to all kinds of impurities, they operate at high or very high pressure, and the processing conditions need to be very strictly controlled. Most chemicals used in the polymerization process, initiators and catalysts, are temperature, moisture, and oxygen sensitive and need to be stored, transferred, and used with no exposure to the open environment. This also means that the polyethylene production environment is rather well protected from the process itself, because losses of any containment cannot be tolerated at all.

Some limited, controlled emission to the environment could occur during the flaring process, which is controlled burning of excess flammable gases that need to be eliminated from the process. This is, however, avoided whenever possible, for environmental and regulatory reasons, but also because flaring unnecessarily increases the manufacturing costs.

7.2. Polymer Disposal and Recycling

Incineration of polyethylene to recover thermal energy is the most efficient way of its disposal because the products of burning polyethylene are almost exclusively CO_2 and water. In some European countries, as much as up to 76% of heat needed for household heating is generated by alternative fuel, which is collected waste material containing polyolefins as a large part.

Other ways of recycling polyethylene are also practiced and developed, although not

yet to a very large extent. Postconsumer waste is contaminated, and it is difficult to separate polymers effectively, which are not always well miscible. Contamination also renders the recycled material for any packaging use, especially for food packaging, so the number of applications that can tolerate recycled polyethylene is significantly reduced. Examples in which recycled polyethylene can be applied are manufacturing of outdoor urban furniture or composites of polyethylene with wood used for construction of platforms.

Industrial waste is a somewhat better source of recyclable polyethylene. Cast film is used for wrapping shipments of pallets carrying raw materials for many industries, and if collected, the films are relatively clean and narrow in comonomer distribution composition.

Finally, landfills still remain a viable option for polymer disposal for many countries. The environmental impact of polyethylene in landfills is, however, significant, because the material remains solid for a very long time, but it is also limited to the solid polymer, because there are no dangerous decomposition products of polyethylene.

As described earlier, much effort has been made to improve the environmental impact of polyethylene on the monomer level, that is, ethylene generated from renewable sources. The primary source, sugarcane, consumes CO_2 in the photosynthesis, shifting the balance of overall CO_2 emission from using and burning polyethylene. Bio- or green polyethylene, manufactured from such ethylene, has become a significant factor on the polyethylene market with the consumption of approximately 500 000 t/a (2013).

7.3. Material Replacement and Contribution to the Environment

To assess the environmental impact properly, the net result of replacing other materials by polyethylene, which have much higher impact or present other risks to the environment, have to be taken into account. Examples are polyethylene pipes that need no plasticizing and can be burned with no aggressive residuals. In the food industry, polyethylene packaging is essential in the food preservation and for reduction of losses.

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Polyimides

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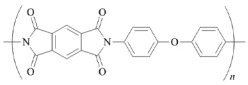
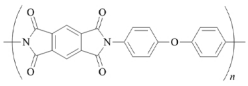
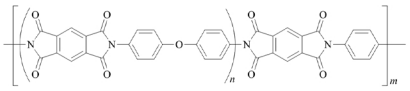
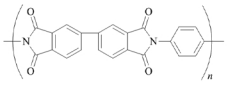
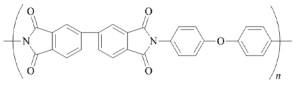
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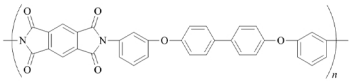
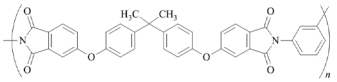
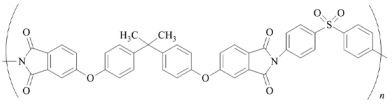
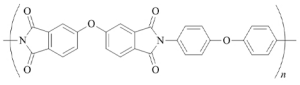
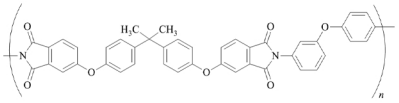
Polyimides are a class of high-performance polymers that contain an imide group, defined as an sp^3 nitrogen bonded to two adjacent carbonyls. This imide structure is most commonly found as part of a five- or six-membered ring. Aromatic polyimides (PIs) polyetherimides (PEIs) and polyimide-amides (PIAs) are noted for their mechanical properties, chemical resistance and dielectric strength. They exist as thermoplastics and thermosets and are available in many formats. Polyimides are used as hot-melt adhesives, matrix resins for composites, dielectric films, photoimageable coatings, flex circuits, foams, wire insulation, thin-walled tubing, molding resins, high-voltage connectors, and high-performance bushings and seals. Although polyimides command a premium price, their versatility, reliability, and demonstrated performance makes them suitable use in high-performance applications where failure and replacement costs are high. As the requirements for lighter weight, broader temperature performance, increased strength, durability, and inertness continue to drive technology, polyimides will play an increasing role in the innovations of the future (Table 1).

The first reported synthesis of an aromatic polyimide was in 1908 [1]. However, most of the initial development and commercialization of polyimide products was performed by researchers at DuPont, who benchmarked this endeavor in the 1960s with the release of Kapton H film, Vespel molded parts, and Pyre-ML wire varnish [2]. This effort inspired other researchers in academia, industry, and government laboratories to pursue the chemistry, fabrication, and applications of polyimides not envisioned several decades ago. There are several excellent books and review articles that address the extensive topic of polyimides [3–8]. Herein, an overview of the field of polyimides is given from synthesis and basic kinetic behavior to fabrication and articles of manufacture.

Ullmann's Polymers and Plastics: Products and Processes
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Table 1. Feedstock commodity polyimide thermoplastic resins and powders (2014)

Polyimide resin manufacturer	Trade name(s)	Polyimide structure
DuPont (USA) http://www.dupont.com/	Kapton Vespel Pyre-ML	
Imitec Inc. (USA) http://www.imitec.com/	I–XXX	PMDA=2XX, BPDA=9XX, ODPA=5XX, and 6FDA polyimide thermoplastics, thermosets, and bismaleimides (BMI)
Kaneka Corp. (Japan) http://www.kaneka.co.jp/kaneka-e/	Apical-AH	
	Apical-NPI	
Ube Industries (Japan) http://www.ube-ind.co.jp/english/index.htm	Upilex-S	
	Upilex-R	

Mitsui Chemicals (Japan) http://www.mitsuichem.com/index.htm	AURUM	
Saudi Basic Industries Corp. (SABIC) (Saudi Arabia) http://www.sabic-ip.com/gep/en/Home/Home/home.html	Ultem	
	Extem	
Shanghai Research Institute of Synthetic Resins (China) http://www.chem-syn.com/en/default.asp	YS-20	
	YS-30	

2. Physical and Chemical Properties

2.1. Electronic Interactions

One of the features of polyimides is that the polyimide macromolecules interact with themselves and each other by either an electronic polarization or charge transfer mechanisms [9–11]. The degree to which these mechanisms play a role depends on the electron affinity of the imide ring (electron deficiency) and the electron donating ability of the N-substituent (ionization potential) [12]. The extent to which these electronic interactions effect neighboring polymer molecules influences the polyimide's color, glass transition temperature (T_g), crystallinity, mechanical properties, and chemical resistance [13, 14]. Clearly, the intrachain electronic polarization affords the yellow to dark orange color that arises in polyimides [13, 14]. The amount of chromophores present can be controlled to some extent by the selection of the cyclodehydration environment, choice of monomers, polymerization conditions, and especially processing methods, and is not related to the presence of unconverted isoimide [13].

2.2. Structural Features

Generally, the bulk structure–property relationships that apply to most polymers apply to polyimides [15]. The thermal transitions are influenced by the selection of monomers and processing techniques [16–19]. Monomers that have kinks, offsets, swivel units, pendent substituents, aliphatic moieties, and bulky units tend to lower the T_g, melt viscosity, crystallinity, and increase solubility, as these units take up more free volume by introducing a more random structure than their symmetric counterparts [20–31]. The proper selection of fluorinated or phenylphosphine oxide containing monomers has produced nearly colorless soluble polyimides [14, 17, 32]. One interesting polyimide developed by NASA, LaRC-SI, does not use the standard approaches to develop solubility. This polyimide starts from a mixture of two dianhydrides, biphenyltetracarboxylic dianhydride (BPDA) and oxydiphthalic dianhydride (ODPA), and a diamine *o*-dianisidine (3,4′-ODA) to afford an amorphous high-molecular-mass polyimide that is soluble in common high-boiling amide solvents [33–35]. Remarkably, the two homopolymers, ODPA/3,4-ODA (LaRC-IA) and BPDA/3,4′-ODA, and the copolymer using ODPA/BPDA/4,4′-ODA are all insoluble and semicrystalline [33, 34]. There have been successful attempts of creating thermotropic polyimides. These liquid crystalline polyimides rely on extended arylene ether-type diamines to create polyimide thermoplastics and blends, or thermosetting polyimides [36, 37]. The advantages of such systems are that they can be more easily melt-processed, the reduced thermotropic melt viscosity, and can undergo shear-induced molecular orientation to gain additional property enhancements.

2.3. Thermal Stability

Aromatic polyimides are highly thermally stable because of their degree of aromaticity, ring structure, and packing density, which are also a function of cure cycles [38–40]. Typical decomposition points for polyimides, not subject to thermally initiated retro reactions, are above 450°C in air and above 500°C in nitrogen for short time intervals [5]. Endcapping a polyimide with a stable monofunctional unit enhances thermal stability by protecting chemically active chain ends that are subject to thermal and chemical instability [41, 42]. Treating polyimides at temperatures in excess of 500°C, under nonoxidizing conditions, results in high yields of approximately 60 wt% of carbonaceous material. The main volatile evolved from pyrolysis is the CO from the imide ring [43]. These polyimide-based carbon films and preforms have been derived for use as membranes and carbon/carbon structural components [44–49].

2.4. Environmental Resistance

Polyimides are resistant to chemical attack, radiation and moisture. An exception is the PMDA-containing polyimides that are hydrolyzed under basic conditions [50–52]. The effect of degradation of one imide ring, in PMDA, changes the characteristics of the other ring by resonance through the common aromatic ring. This is also the case with monoaromatic diamines. However, most polyimides are highly resistant to caustics, acids, organic solvents,

specialty fluids, and salts, even at elevated temperatures [26, 53–55].

Polyimides are typically bioinert, that is, they are not toxic or bioactive. However, Material Safety Data Sheets of every single article of manufacture should be consulted for detailed specification.

2.5. Electrical Properties

The electrical properties and temperature range of polyimides have led to their widespread use as dielectrics, flexible substrates, electronic packaging, and wire insulation for the electronics industry [56–64]. An excellent review on some of the issues for reliability in electronic assemblies, from a materials standpoint, was published indicating moisture as one of the main mechanisms of electrical failure [65, 66]. Although the imide ring is polar and electron-deficient, the two dipoles of the carbonyl groups oppose each other and the imide rings along the polyimide backbone also directionally oppose each other. This geometry simulates the bulk effect of a nonpolar polymer making polyimides good dielectric materials, when combining these properties with their high temperature and chemical stability [60, 62–65, 67–69]. Typical dielectric constants range from below 3 to above 6, depending on structure, frequency, temperature, and moisture absorption. As expected, fluorinated polyimides display dielectric constants typically 0.5 lower than the nonfluorinated polyimides, as the fluorine atom imparts low polarizability, water uptake, and surface energy [70–75]. Similar comparisons can be made from the fluorinated olefinic systems (PTFE and PFE) with their corresponding hydrocarbon analogues.

2.6. Mechanical Properties

The bulk mechanical properties of aromatic polyimides are among the highest for commercial plastics [76]. The various processed forms of solid polyimides have excellent mechanical properties with elongations from 3 to 120%, tensile strengths and moduli 170–270 MPa and >3 GPa, respectively, over a wide range of temperatures from cryogenic to well above ambient. This is a result of the interchain interactions of polyimides and their structural integrity imparted by their aromatic character, morphology, and sub-T_g transitions, that may impart additional toughness [77–82]. Those polyimides that can undergo melt processing tend to make excellent hot-melt adhesives.

3. Synthesis

The synthetic approach to the formation of polyimides is divided into three groups. The first group involves the synthesis of the polyimide by increasing the molecular mass of the monomer(s) through the formation of the imide ring through the amic acid/ester route. The second approach involves increasing the molecular mass of a precursor already containing the imide ring. The last method involves the conversion of a polymer into a polyimide. The requirement is that these approaches must be based on high-yield organic reactions.

3.1. Amic Acid Route

The two-step approach to polyimides is the most general approach used in the synthesis of linear polyimides [83–86]. The first step involves the treatment of a diamine either with a dianhydride (the most popular), a tetracarboxylic acid, a diester diacid, a diester diacid chloride, or a trimellitic anhydride chloride (TAC) as in the case of polyamide imides (Amoco's Torlon) [87, 88] (Fig. 1, step 1). The reaction schemes are generally performed in a high-boiling polar protic (phenolic) or aprotic (*N*-methyl-2-pyrrolidinone, NMP; *N*,*N*-dimethyl acetamide, DMAc; *N*,*N*-dimethyl formamide, DMF; etc.) solvent at low to moderate temperatures, resulting in the formation of the poly(amic acid) or poly(amide acid), amic ester, amic acid ester, etc. through nucleophilic attack by the amine on the carbonyl carbon [89]. Next, the imide ring is formed by thermal treatment, chemical dehydration, or both by a second nucleophilic attack occurring at the adjacent carbonyl carbon by the amide nitrogen. This is followed by the elimination of a condensate (typically water or alcohol). Removal of this condensate forces the equilibrium toward the right, driving the polymerization to completion (Le Chatelier's principle) thus forming the imide ring (step 2) [84].

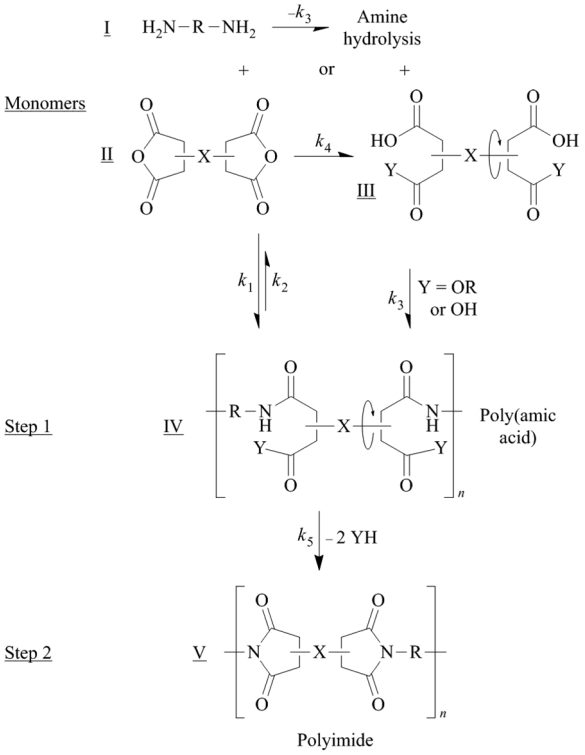


Figure 1. Reaction diagram for thermal imidization via poly(amic acid/ester)

Alternatively, a "one-step" method or direct conversion is used where a diamine and a dianhydride are placed in a solvent and heated to a temperature at which the formation of the amic acid moiety rapidly dehydrates to the resulting imide. Thus, the polyimide is formed in "one step" [90].

3.1.1. Poly(Amic Acid) Formation

To successfully carry out this synthetic approach, the following requirements must be met: chemical purity, the proper type and percent solids of reaction medium (facilitating solubility of the resulting poly(amic acid)), reaction temperature, and a method allowing for the removal of any byproducts of polymerization (heat, condensates, etc.) [91, 92]. Most commonly, linear polyimides involve treating a diamine with a dianhydride or tetracarboxylic acid/ester to afford the amic acid or amic ester, followed by imide ring formation during the final polymerization step. The routes to achieving a high-molecular-mass polyimide, starting from the monomers via the poly(amic acid), are shown in the reaction diagram in Figure 1 [93].

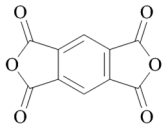
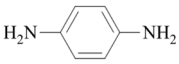
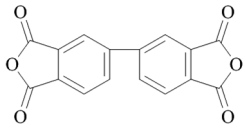
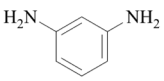
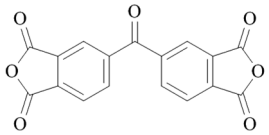
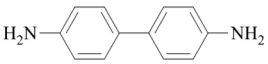
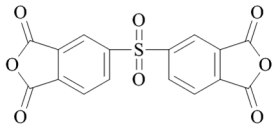
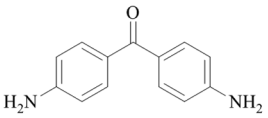
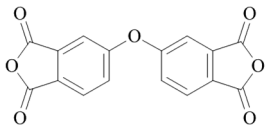
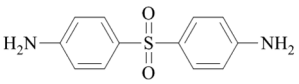
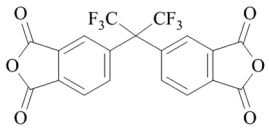
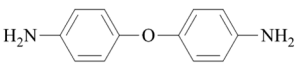
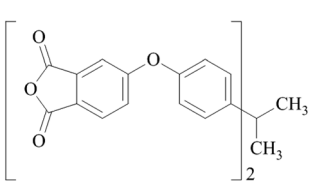
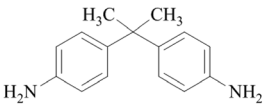
When a diamine (I) is treated with either a dianhydride (II), tetraacid or diacid ester (III), alternative routes may occur depending on the reaction kinetics, in which k_1 and k_3 are desirable and k_2 and k_4 are not. Table 2 summarizes the approximate kinetic k_x values.

The pathway to k_4 depends on: the amount of water or alcohol in the reaction medium; the reactivity (electrophilicity) of the dianhydride or tetraacid/diacid ester; and the nucleophilicity of the diamine (Table 3). Steric hindrance and isomerization; polarity and autocatalytic effects

Table 2. Typical rate constants for poly(amic acid) synthesis [94–96]

Reaction	Rate constants
Propagation (k_1)	0.5–6.01 mol^{-1} s^{-1}
Depolymerization (k_2)	10^{-5}–10^{-6} s^{-1}
Imidization (k_5)	10^{-8}–10^{-9} s^{-1}
Anhydride hydrolysis (k_4)	0.1–0.41 mol^{-1} s^{-1}
Amine hydrolysis ($-k_3$)	0–10^{-6} s^{-1}

Table 3. Electron affinity and basicity values of several common dianhydrides and diamines used in the synthesis of polyimides [13]

Dianhydride	Abbr. name	E_a [eV]	Diamine	Abbr. name	pK_a (H_2O)
	PMDA	1.9		pDA	6.08
	BPDA	1.38		mDA	4.08
	BTDA	1.55		DAB	4.60
	DSDA	1.57		DABP	3.10
	ODPA	1.30		DDSO2	2.15
	6FDA	ND*		ODA or DAPE	5.20
	BPADA or LDA	1.12		Bis-DA	ND*

* ND = Not determined.

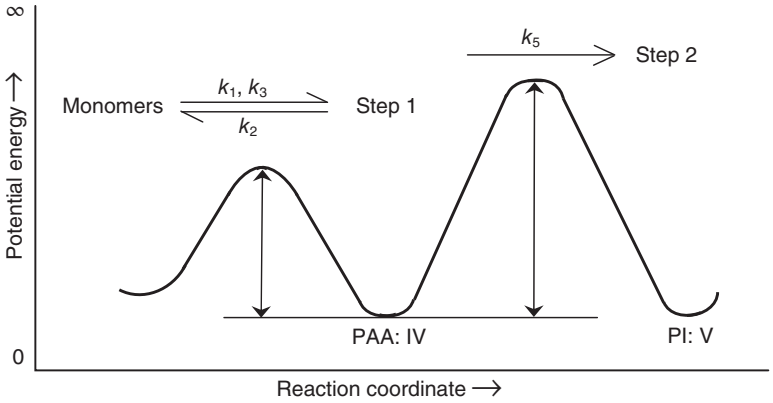


Figure 2. Qualitative reaction coordinate diagram for polyimide synthesis via poly(amic acid) (PAA) [122]

of the solvent; and the time/temperature profile during the poly(amic acid) formation also affect the pathway to k_4 [97, 94, 95]. Conversion of the anhydride moiety, k_4, has the effect of introducing another chemical functionality, with a different reactivity that can affect both k_1 and k_3 through resonance. As shown on the reaction coordinate (Fig. 2), the effect of k_2 competes with k_1 and k_3 when the reaction temperature is raised and the thermal dehydration k_5 conversion to imide is occurring. Once the imide ring is formed, depolymerization is severely limited through removal of the condensate byproduct. The choice of the diamine and dianhydride affects the rate of poly(amic acid) formation both sterically, and through the electronic interactions of the monomers [98–100].

As seen in Table 2, pyromellitic acid dianhydride (PMDA) is the dianhydride with the highest E_a value. Any diamine that is treated with PMDA should polymerize faster than if it is treated with a dianhydride having a lower affinity. However, once one of the anhydride units of PMDA has reacted, the second anhydride will display a lower reactivity because the former anhydride group, now an amic acid, has less electronic withdrawing ability. This effect on other dianhydrides is less pronounced as the anhydride groups are separated by additional moieties that decrease the influence of the reacted anhydrides [97]. A similar trend is seen with diamines. The more basic the amine, the faster it can react with a moiety that is susceptible to nucleophilic attack. Additionally, any chemical groups mitigating the conjugative resonance effects of the amines on each other, the less of an effect the conversion of one amine will have on the reactivity of the other [101].

Solvent effects depend on several factors, including, the polarity of the medium: the percent solids; and the solubility of the reactants. As the polarity of the medium changes with conversion to poly(amic acid), the viscosity and potential autocatalytic effects (kinetic conversion to poly(amic acid)) are observed [102]. These effects are caused by the increasing molecular mass of the poly(amic acid) that results in the buildup of carboxylic acid. The hydroxyl portion of the amic acid can form additional hydrogen bonds to adjacent poly (amic acid) groups, thereby artificially increasing the observed viscosity [86, 91]. These additional carboxyl acid protons can assist nucleophilic attack (on the carbonyl carbon) by coordination with the anhydride carbonyl oxygen increasing the step growth kinetics to poly(amic acid) formation. An accurate kinetic profile has been difficult to obtain as a result of the solvent effects, the changing reaction medium, and the changing pH. Some investigators claim that irreversible second-order kinetics is followed, while others have observed reversible autocatalytic kinetics when tetrahydrofuran (THF) is the solvent. Typically, polymerizations carried out in amide solvents (polar aprotic) do not display autocatalytic behavior [99, 100]. These solvent molecules closely associate with the hydroxyl protons, effectively isolating

them from interacting with other anhydrides and amic acids. The reaction rate generally increases as the solvents become more polar and more basic [103, 104]. A model compound study showed that the acylation rate increased from THF < acetonitrile < DMAc < *m*-cresol. The polar protic solvent, *m*-cresol was claimed to increase the rate because it functions as an acidic catalyst [102, 105]. Similar observations were noted when acids (benzoic acid) were introduced into a poly(amic acid) medium employing an amide solvent. THF, not being very basic, does not associate with the poly(amic acid) and some reversal occurs. This "retro" reaction (k_2) occurs when a proton is transferred from a carboxylic acid to an amide nitrogen (or any other basic species), followed by the subsequent attack of the carboxylate oxygen on the adjacent carbonyl carbon to reform the anhydride or the rare isoimide [103, 104]. This reverse reaction can be suppressed by replacing the hydroxyl proton of the poly(amic acid) with amine salts or esters causing a marked decrease in conversion to monomeric species [86, 106–108].

The effects of adventitious water on both the starting anhydride and poly(amic acid)s has been shown to decrease their molecular mass over time through conversion to the diacid acid and hydrolytic cleavage, respectively [86, 93, 109–112]. This drop in molecular mass appears to be more dramatic the more dilute the solution and may be caused by the apparent increase in water content as the percent poly(amic acid) decreases. Additionally, the conversion from poly(amic acid) to monomeric species is unimolecular, whereas the reverse reaction is bimolecular, shifting the equilibrium to the left towards the reactants [84]. Evidence has indicated that further imidization of the poly (amic acid) occurs upon standing over time, at various temperatures, releasing water into the solution, resulting in further hydrolysis of the poly(amic acid) [86, 93, 113].

Lastly, monomer addition (sequence and rate) has shown to affect both thermodynamic equilibrium, and the resulting molecular mass of the poly(amic acid). This condition is a result of the difference in solubility of the monomers (dianhydride and diamine) in the polymerization solvent [84, 93]. As the dianhydride slowly dissolves in a medium containing the faster dissolving diamine, it maintains an intrinsic stoichiometric balance with the diamine, setting the condition for an infinite degree of polymerization. This "pseudo-interfacial" polymerization generates high-molecular mass poly(amic acid) until one of the monomers is consumed. Thus, near the completion of the reaction, the medium contains a wide bimodal distribution, high polymer and unreacted monomer contents. As the unreacted or excess monomer has time to come in contact with the high-molecular mass poly(amic acid), thermodynamic equilibrium (k_1/k_2) occurs and the molecular masses redistribute towards a unimodal distribution [114–116].

3.1.2. Polyimide Formation

The three methods to form the polyimide from the poly(amic acid) are thermal, chemical, and a combination of both.

Thermal Imidization. The thermal conversion of poly(amic acid) to polyimide requires the removal of the condensate produced during cyclodehydration (Fig. 1). This is achieved by elevated temperatures and, whenever possible, the addition of a solvent that facilitates azeotropic removal of the condensate. A typical solution thermal conversion reaction setup contains approximately 30% solids poly(amic acid) in NMP, 10% solids xylenes (azeotrope to remove water), and the reaction temperature is maintained at about 165°C for several hours with water distilling out rapidly early in the reaction [84, 53, 33]. Thermal conversion of poly(amic acid) in solution is fairly straightforward and only becomes complex when the resulting polyimide precipitates out of solution prior to complete imidization. The kinetics is more complex when the poly(amic acid) is isolated as a powder, spun as fiber, or cast as a film prior to imidization [117]. Generally, the azeotropic cosolvent is not present in these "solid-state" preforms, and the effects of the advancing T_g, solvent evaporation rate, the percent solids, steric effects, side reactions, cure temperature, and surface-to-volume ratio of the polymeric preform effect the overall kinetics [85, 118, 119, 16]. Thus, attempts to follow the imidization rates using spectroscopy have been confusing as these factors are difficult to account for. One reaction that does not appear to

occur during thermal imidization is cross-linking between diamide groups [120–122]. This is not surprising because there are soluble polyimides cited in the literature, and no spectral evidence exists that supports this mechanism. However, thermal aging above 350°C for a period of time may result in cross-linking, but this is most likely the result of a free radical mechanism (thermal degradation) and is influenced by film thickness, atmosphere, and the casting surface [123–125].

Two pathways of thermally induced imidization are (1) the loss of the proton on the carboxylic acid group after cyclization or (2) removal of the proton on the carboxylic acid prior to or during ring closure. As the conjugate base of the amide is more nucleophilic than the amide itself, ring closure should be faster in the latter case [85].

When thermal imidization occurs in the presence of an amide solvent, the conversion to polyimide proceeds more readily, as the loss of the amic acid proton is facilitated through solvent hydrogen bonding. In some cases, the rate of thermal imidization occurs in two steps [85, 118]. The first step is the rapid conversion to imide above 150°C, and the second step is a slower process during the latter stages of imidization. The following scenario can explain this. During the early stages of imidization, more solvent is present to assist ring closure and the T_g of the polymer is low [85]. As the thermal conversion continues, the T_g is increased and the solvent content decreases [118]. Chain mobility and solubility is decreased with increasing conversion, especially if the growing polyimide is semicrystalline [96]. Further depletion of solvent decreases the amount of solvent–polymer complexation that normally facilitates the rate of ring closure [85]. This two-step rate effect is seen for fibers (high surface area) and cast films for which solvent is lost during thermal processing. It has been shown that thicker films form imides at faster initial rates. These thicker films retain solvent longer, because of the extended migration/evaporation time, allowing the chains more mobility and increased solvent–polymer complexation allowing for additional conversion at temperature [126]. However, the effects of the surface imidizing faster (skinning) than the bulk must be taken into account for thermal convection curing [93]. The resulting molecular mass of the polyimide depends on the molecular mass of the poly(amic acid) [93]. Although the kinetics follows that in Figure 2, the resulting physical properties of the polyimide films are different as displayed in Figure 3.

Three molecular-mass divisions are plotted as a function of temperature versus qualitative physical properties, demonstrating the effect of the poly(amic acid) molecular mass on the polyimide during conversion. This effect can be rationalized knowing that the amount of chain scission is independent of the molecular mass, resulting in a more dramatic effect on lower molecular mass poly(amic acid)s. The lower molecular mass poly(amic acid) can be reduced to monomers, where these units may

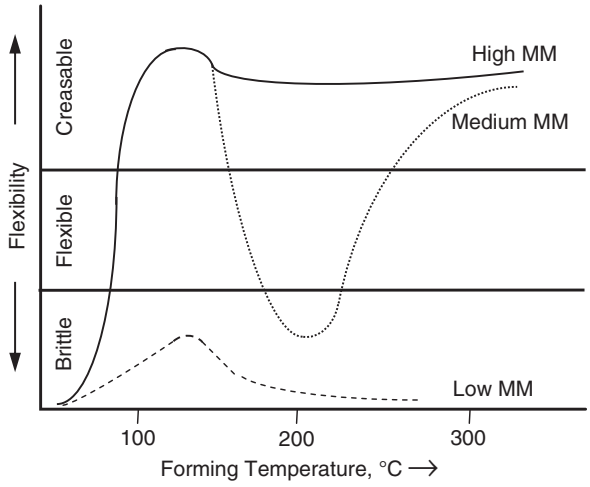


Figure 3. Qualitative physical properties of thermally formed polyimide films of different molecular masses (MM) [93]

be thermally unstable and susceptible to oxidation. When this occurs, the adulterated monomers upset the stoichiometric balance resulting in low-molecular-mass polyimide. Higher molecular mass poly(amic acid)s are less likely to be converted down to monomeric levels, and the oligomers will repolymerize to form medium- or high-molecular-mass polyimide thereby maintaining their desired physical properties.

An interesting reaction sequence, parallel to the two-step synthesis of polyamides through the amide-salt process, has been outlined [7, 20, 127]. Here, the diamine and tetracarboxylic acid are first mixed in water to form the salt precipitate that is collected and dried. The resulting amine salt is placed in water and heated under pressure to 130°C for 1 h, then to 180°C for 2 h and cooled to ambient temperature. The resulting polyimides have molecular masses and physical properties equivalent to those made by the conventional two-step methods.

Chemical Imidization. Chemical imidization is not widely used, except in gel processing, as it employs additional reagents. However, it has the advantage of low-temperature imidization and can be used to directly form fine polyimide molding powder or uniquely structured materials [93, 128, 129]. A typical chemical imidization reaction employs a 20–30% solids poly (amic acid) in an amide solvent with a slight molar excess of acetic anhydride and a molar equivalent of a triamine (triethyl amine, pyridine, or β-picoline) [130–133]. The percent conversion for chemical imidization is a function of polyimide solubility. If the polymer crystallizes and/or precipitates from the reaction medium, imidization will be incomplete [93, 128]. Those systems that remain soluble must undergo thermal treatment to convert any isoimide, and remove residual solvent. The mechanistic routes of chemical imidization are shown in Figure 4, and involve using a triamine to form

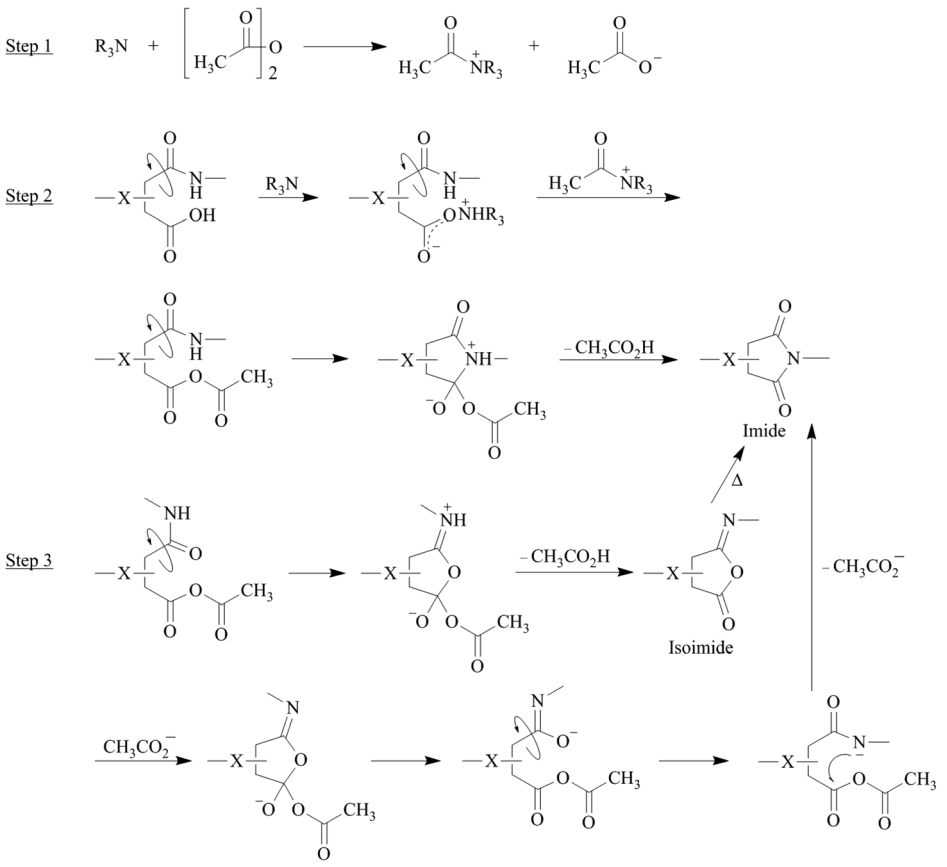


Figure 4. Reaction diagram for chemical imidization via poly(amic acid)

the amine salt from acetic anhydride, step 1, and the amine salt of the poly(amic acid), step 2. Next, the salt is replaced with the acetyl group (from the dianhydride salt) to form a mixed anhydride. The acetate group from the mixed anhydride group leaves as the amide nitrogen attacks the carboxylic acid carbonyl. The acetate group picks up the amide proton to form acetic acid resulting in the formation of the imide ring. If the poly(amic acid) is not in the proper conformation (i.e., the amide group may be rotated out of position) the carbonyl oxygen may attack the mixed anhydride to form the corresponding isoimide, step 3. The isoimide is converted to the imide thermally or by the presence of acetate ions that attack the ester carbonyl carbon, closely following the later stages of Step 2. The important step is the conversion of the poly(amic acid)'s hydroxyl group into a better leaving group, the acetate [134, 135].

Combinational Process. One system that takes advantage of both the chemical and thermal imidization is the gel casting of non-melt-processable polyimide film. These systems start as poly(amic acid) in NMP or DMAc to which is added β-picoline and acetic anhydride. This mixture starts to imidize and forms a gel as it is coated onto a rotating heated drum. The swollen gel film has the mechanical integrity allowing it to be stripped off the drum and gripped by a tenter frame. Final conversion and solvent removal is achieved thermally (infrared and convection) while the film is undergoing mechanical orientation [136].

3.1.3. One-Step Formation of Polyimides

Polyimides that are soluble in high-boiling organic solvents can be directly converted from their corresponding monomers. This is done by mixing a diamine and a dianhydride into a solvent above 180°C. Typically, solvents such as *m*-cresol with catalytic isoquinoline, benzoic acid, nitrobenzene, or NMP are used depending on the polyimide formed [137–139]. This system is useful for diamines and dianhydrides having low reactivity and those that are sterically hindered, such as perylenic dianhydrides [140, 141]. The conversion of monomer to polyimide proceeds rapidly with the intermediate poly(amic acid) being short-lived to the point that it is virtually undetectable. The degree of imidization is nearly 100% [142–145].

3.2. Synthesis Using Imide-Containing Monomers

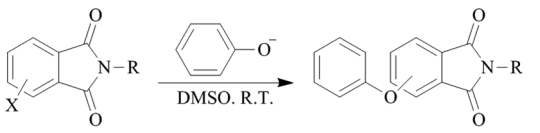
Two methods may be employed to form a polyimide when the imide ring is intact. The first method uses a high-yield organic reaction by which imide-containing monomers polymerize by a different mechanism (aromatic nucleophilic displacement, addition, and free-radical reactions). The second approach involves thermosetting imide oligomers.

3.2.1. Polymerization Processes

Aromatic Nucleophilic Displacement. Aromatic nucleophilic displacement is used in the synthesis of polyarylene ethers. Halogenated bisimides are polymerized with bisphenolates and activated A–B phthalimides to form polyetherimides [146–150]. The reaction proceeds through the Meisenheimer-type transition by lowering the activation energy of the displacement reaction. Table 4 shows the relative rates of displacement on substituted phthalimides with phenoxide. Remarkably, the displaced nitro group may affect the growing polyimide chain if not handled properly [146, 151].

A related synthetic method has been employed specifically for both bisphenols and halogenated

Table 4. Relative reactivities of substituted phthalimides with phenoxide in DMSO at room temperature [152]



Position–X	R = $-CH_3$	R = 
3-Ci	1	–
3-F	4	20
3-NO_2	37	130
4-F	–	65
4-NO_2	170	520

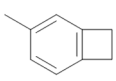
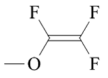
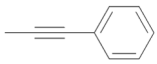
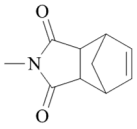
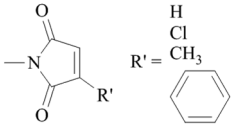
diimides or the halogen-containing A–B-phenolated phthalimide monomers. Bisphenol or the N-phenol unit of the fluorinated phthalimide is converted to its corresponding trimethylsilated analogue. Polymerization of these silated monomers into polyimides are achieved in the melt at high temperature by using cesium fluoride as a catalyst [152].

Addition Reactions. This approach involves using maleimide-terminated monomers (bismaleimides, BMIs) in equal molar ratios with a dinucleophile such as a diamine, or a diene such as dibenzocyclobutane (BCB) and substituted dicyclopentadienes to form the corresponding linear polyaspartimides through Michael-type addition or the polyimides by a Diels–Alder [4+2] cycloaddition (Table 5) [153–162].

Linear polyimides can be synthesized directly from the A–B maleimidobenzocyclobutane monomers [175]. These reactions proceed without volatile evolution, but undergo thermally initiated retrograde reactions that lead to change in physical properties, chemical cross-linking and aromatization of the cyclohexene ring (BCBs) [176].

Reactions involving BMIs with dicyclopentadieneones also proceed by a cycloaddition mechanism [177, 178]. This has the same advantage inherent to all Diels–Alder reactions in that no volatiles are generated. However, with these pentadieneone dieneophiles, CO is eliminated forming a cyclohexadiene moiety. The cyclohexadiene can undergo further addition reactions or aromatize with the abstraction of two hydrogen atoms depending on the reaction

Table 5. Chemical groups used for functionalizing or reacting with polyimides [163–174]

Reactive group		Onset cure temp., °C	Comments on long-term stability at 177°C
—O—C≡N	cyanate	200–230	poor thermal stability
	benzocyclobutene	200–250	co-reacts with maleimide, poor long-term stability
	trifluorovinyl ether	250	small processing window, unknown thermal stability
—C≡CH	ethynyl	200	small processing window, unknown thermal stability
	phenylethynyl	320–370	excellent thermal stability
	nadimide	300–350	cyclopentadiene evolution, low toughness
	maleimide chloromaleimide methylmalimide phenylmaleimide	200–230 200–230 220–250 340–370	poor thermal stability poor thermal stability poor thermal stability unknown thermal stability

conditions, and the added stability of any pendent substituents [177, 178]. This type of chemistry can be used to create photosensitive polyimides for imaging.

Free-Radical Polymerization. The last approach utilizes free-radical polymerization of substituted maleimides to afford ethylenic-type imide polymers [154, 179]. Maleimide groups are copolymerized with unsaturated monomers such as styrene and other maleimides to afford copolyimides [180]. Polymerization of these systems is typically carried out with azobisisobutyronitrile (AIBN) in polar solvents such as THF [181]. These types of polyimides can be used for a variety of applications from optical and photosensitive resins to structural materials, depending on the selection of the N-substituent [175, 180].

3.2.2. Thermosetting

Thermosetting systems involve the placement of reactive moieties with the polyimide, terminal, pendent, or blended as copolymers with the reactive imide monomer (Table 4). These systems contain maleimide, norbornene (nadic), vinyl and allylic, acetylenic, phenylethynyl, or other types of unsaturated groups that react to cross-link the polyimide [182, 163–172]. When bismaleimides are used alone or in excess with a difunctional (at least) nucleophilic monomer, the resulting system is thermosetting with chain extension (through Michael-type addition) occurring prior to the thermal cross-linking of the maleimide functionality (via Michael addition) [117, 183–186]. Although the cross-linking of the maleimide group is thermally initiated, it is catalyzed with both free radicals and bases [180, 164, 165]. Typical synthesis involves 30% (or more) total solids diamine and two equivalents of maleic anhydride in acetone at ambient temperature. After the bismaleamic acid precipitates (several hours), triethylamine is slowly added to the mixture until dissolution occurs (approximately 0.5 equivalents). Acetic anhydride (slightly over 1 equivalent) is added and the mixture is heated at reflux for several hours and the crude product is isolated by water precipitation. The intermediate maleamic acid is susceptible to isomerization during cyclodehydration resulting in the production of the less desirable acetanilide [178, 164]. Metal acetate catalysts have been known to increase the yields of BMI [187]. Blends of BMIs with aromatic allyls and phenylpropenyl oligomers, such as a bisallylphenol, have been used as thermosetting systems that undergo complex reaction involving Ene addition followed by Diels–Alder addition, respectively [117, 183–185, 188–194].

The nadic group has been extensively explored for creating polyimide thermosetting resins including the PMR-type composite materials. These materials include the nadic-endcapped LaRC 160, PMR-15, PMR-II, RP-46, Superimide 800 and others, and the nadic/amine terminated systems which includes AFR-700B. The nadic functionality is similar to the maleimide functionality in that it can undergo similar addition-type reactions and can form the maleimide upon rearrangement and release of cyclopentadiene. A study comparing the thermochemistry of these two moieties is described wherein time, temperature, and free-radical initiation were detailed [191]. These nadic-terminated oligomers are formed from nadic anhydride (NA), a diamine and a dianhydride [195–203]. These systems (like their aromatic counterparts) do not exhibit the same behavior as maleamic acid during imidization as structural conformation remains in place. Unfortunately, the nadimides generate cyclopentadiene at the elevated temperatures required to cure them. Hence, these systems must be cured under pressure to avoid volatilization of the cyclopentadiene that copolymerizes with itself, other nadic moieties and the resulting maleimide [204–206].

In an attempt to create a high-temperature thermosetting imide system that can be handled as a room-temperature liquid, the polymerization of monomeric reactants (PMR) approach was developed. Here, the dianhydride and nadic anhydride are treated with molar equivalents of an aliphatic alcohol and allowed to form the liquid diacid ester isomers. The diamine and the diacid esters are then dissolved in methanol, and the liquid system is solution-cast or coated onto a preform to create a prepreg that is dried and cured under pressure to form a composite part. The advantage of this system is that the monomers remain intact at or below room temperature [207–210]. The molar ratios of the diacid-methylester of BTDA, 4,4′-methylenedianiline

(MDA) and the acid methylester of NA of 2.087:3.087:2 are used to make a 1500 g/mol imidized reactive oligomer referred to as PMR-15. There are several studies that characterize the reactive monomers, the cure chemistry and kinetics, cure cycles, and the resulting thermomechanical stability of the various nadic systems made by the PMR approach [205, 206, 208–216]. Acetylenic groups on polyimides are used to induce thermal cross-linking [169, 217]. The actual chemical structures developed during the acetylenic cross-linking can vary, because the reactivity of these groups is high enough to allow attack on chemical moieties other than acetylenic units [218]. National Starch's Thermid IP-600 is an acetylene-terminated thermoset that has enhanced solubility, as it is an isoimide that thermally converts to imide when cured [219, 77]. The highest temperature thermosetting matrix resin/structural adhesives were those based on phenylacetylene (phenylethynyl) [220–222]. NASA's phenylethynyl-terminated imide (PETI) series are systems that cure at temperatures above 320°C [223–230].

3.3. Polymer Conversion

One method has already been introduced through the chemistry of isoimide synthesis and conversion (Section 3.1.2 polyimide formation). If the isoimide is desired directly, a poly (amic acid) is dissolved in a solvent system that facilitates removal of the byproduct and a molar equivalent of dicyclohexylcarbodiimide or similar cyclodehydrating agent. These isoimides are then converted by thermal conversion to the corresponding imide at elevated temperatures [231]. Other methods involve transimidation and treatment of dianhydrides with diisocyanates. Transimidiation involves the exchange of one imide nitrogen functionality (as the amine) for another. This type of reaction is favored when the attacking amine is more basic than the amine that comprises the imide ring. Because of the lower reactivity of aromatic amines, in comparison to aliphatic amines, this type of reaction offers certain advantages. When the less basic 2-aminopyridine terminates imide oligomers, this amine can be readily exchanged for other aromatic diamines to form a high-molecular-mass polyimide through proper stoichiometric control [232–235]. This scenario allows for the formation of otherwise infusible polyimides, by melt processing techniques, and also permits the incorporation of chemical moieties that are susceptible to hydrolysis via the poly(amic acid) route. Another conversion route involves the reaction of diisocyanates with dianhydrides to form the polyimide followed by elimination of CO_2 [236–243]. There is no general consensus on the mechanism of this reaction. Some researchers contend that the isocyanate reacts with water to form the amine or alcohol to form the urethanes that react with the dianhydride to form the polyimide [238]. Others postulate a seven-membered ring formation that liberates CO_2 forming the imide ring [239]. Metal salts have catalyzed these imide-forming reactions, and some have been polymerized in the melt [244, 245].

4. Uses

Polyimides are manufactured in a variety of forms, finding utility ranging from electronics and medical to structural and adhesive applications. The major forms of polyimide are films, molded and extruded stock, fiber-reinforced adhesive tape, varnish, foam, and composite prepreg.

4.1. Films

One of the more prevalent forms of polyimides is thin films. The most popular films are Kapton by Dupont, Upilex by Ube Industries, Ultem by SABIC, and Apical by Kanekafuji, to name a few. In film form, some of these materials do not display a T_g, have good radiation resistance, and are used as bagging materials for composites, belts, insulative wire wrapping, and flexible circuits. They are coated with acrylics and silicones to make pressure-sensitive tape [246]. Polyimide film is also adhesively bonded to metal foil (copper) to one or both sides, and sold to PCB manufactures for flexible cabling and circuits (examples include DuPont's Pyralux and clad derived from Kaneka's Apical series of PI films). Metal is also vapor-deposited onto polyimide film for applications requiring thin copper or other metals (less than 0.5 oz/12 μm, i.e., 14 g/12 μm) for which the additional adhesive is undesirable. As these films and clads serve as dielectric materials, they are tested

under IPC TM-650 tests and display breakdown voltages above 200 V/μm (5 kV/mil, where 1 mil is 0.001 inch or 25.4 μm) and 1 MHz dissipation factors of 3.2 on average [13]. Several methods to create metallic coatings in situ involves the introduction of silver organic salts (complexed silver(I) acetates) or other metallic complexes into the poly(amic acid). Through thermal imidization, which may be photoassisted, the silver metal is reduced and migrates to the surface to form a reflective coating [247–252]. Another method involves chemically etching the polyimide surface forming the carboxylic acid groups and exchanging these protons with silver ions followed by UV radiation [253]. This has the advantage of not depositing metal ions throughout the film thickness. The latest trend in polyimide dielectrics is the introduction of nanotechnology in order to improve the insulative properties or electrical conductively. A nanoporous polyimide film was developed by blending the poly(amic acid) with PEO and POSS, followed by thermal imidization and thermal oxidation, resulting in a nanoporous silicon oxide polyimide film with a reduction in the dielectric constant [254]. A 3D flex circuit was created by embedding nanowires into polyimide film by heavy-ion implantation followed by surface etching and gold deposition to create conductive patches. The goal was to develop *Z*-axis conduction for flex circuitry and magnetic sensing applications [255]. Polyimide films and coatings have been used for space applications involving thermal and electrical insulation, reflectors and proposed for clear overcoats structures exposed to the space environment. Their inherent aromatic structure affords radiation and UV resistance. However, as organic materials, they suffer from the effects of atomic oxygen (AO), which is more prevalent in low earth orbit. In order to combat the effects of radiation and UV in the vacuum of space, studies of the effect of imide group location, using fluorinated monomers or phenylphosphine oxide (PPO) and silicon oxide (SiO) containing monomers, for optical clarity and AO protection, and nanoparticles have been studied. The results being that polyimides that have the imide units in direct aromatic coupling (e.g., PMDA) are more susceptible, and those polyimides with inorganic filler particles tend to form an in situ barrier when exposed to AO [32, 256–258].

4.2. Coated Wires

For years, the electrical and aerospace industry has used polyimides as high-performance wire insulation. These coatings are used in combination with other materials and may either be biaxially wrapped onto the wire, solution coated and dried in multiple passes to form a varnish, or directly extruded over the wire. The polyimide insulation must survive tight radial bends, chaffing, and electrically induced oxidation and carbon tracking [259–267]. Since polyimides possess high dielectric strength, thermal stability, radiation resistance, and are self-extinguishing, they are employed in both air and spacecraft [263–267]. The low-earth-orbit conditions are especially devastating for organic polymers because of the presence of atomic oxygen and UV radiation [268–270]. This has led to the incorporation of silicone and phosphine oxide units in the polyimide that resists the atomic oxygen degradation [256]. The NASA LaRC-TOR series polyimides, which contain phosphine oxide units in the backbone, have been one of the leading polyimides for low-earth-orbit satellite and vehicle applications [271, 272].

4.3. Membranes, Tubes, Fibers, and Foams

The fabrication of microporous membranes, thin-walled tubes, fibers, and films is performed by solution-casting or dry-jet spinning followed by heat treatment. These asymmetric flat or hollow fiber membranes are used for the selective separation of gas and liquid mixtures. The main parameters for polymeric-based membrane material selection are the free volume, the molecular distance, which relates to porosity, the shape of the molecules, the burst pressure, temperature range, and, of course, the mixtures that require separation. Here, polyimides, with bulky substituents, display the highest fluxes and selectivity when compared to other glassy polymeric materials including polyphenylene oxides [273]. The asymmetry is introduced by selective solution blending of solvent/nonsolvent mixtures to generate a porous gradient, during polymer precipitation, across the membrane wall. This is followed by thermal evaporation techniques to set the

final microstructure [274–282]. In some cases, the surface wettability is improved by treating the polyimide surface with acids to increase the hydrophilicity without sacrificing thermal stability, which is especially important for fuel cells [283, 284]. Lastly, one surface may consist of porous ceramic coating to facilitate ion transport [285]. Thin-walled polyimide tubes created from PMDA and BPDA–ODA polyimides cannot be made by melt processing and are created by successive layering and drying to build up thickness on or inside a fused silica tube [286, 287]. These polyimide-coated tubes find use as GC columns for chemical separation and as catheter medical tubing [288, 289]. Continuous fibers, solution-spun and dried from poly(amic acid) or as the polyimide, present a challenge as the solvent, cyclodehydration and shrinkage problems associated with curing the fiber result in a technical challenge. Although the properties of these fibers are excellent when the proper draw ratio is used, they have not achieved a high-performance niche market able to economically compete with polyesters or polyaramides [289–292].

The extensive processing methodology and physical characteristics make polyimides excellent resins for the design of foamed preforms. The thermal range, density variance and char characteristics make polyimide foams choice candidates for structural insulation, flexible gaskets, acoustical insulation and thermal protection for aerospace and naval vessels [293]. These foams can be created from momomer solutions, amic acid gel or powder with blowing agents and solvent complexation. These components may undergo volatile release on thermal conversion to help develop and control the resulting cellular structure [294–299]. These methods are used when creating open-cell polyimide foams of varying density. The final cell size and type depends on both the thermal cycle and the diffusion rate of the agent out of the particle cell [300]. One of the leading candidate polyimide foams for future cryo-tankage insulation is NASA's TEEK series that have applications for the next generation of aerospace vehicles [301–303]. A more recent development is the synthesis of polyimide aerogels made by using chemical imidization followed by solvent extraction-replacement prior to the final step of CO_2 critical fluid extraction [129, 304, 305]. The physical properties of these aerogels can be controlled by monomer selection and processing conditions.

4.4. Melt-Processable Polyimides

Polyimides that display a T_g and T_m well below their decomposition or thermosetting temperatures are candidates for melt-processing techniques that include extrusion, injection, and compression molding. Several other factors play into the selection of melt-processable polyimides and include melt viscosity, work time, or pot life at temperature and the ability to carry fillers or blends. Melt viscosity is crucial as it directly relates to molecular mass, affecting the processing temperature [241, 306–308]. The higher the molecular mass, the higher the temperature and pressure needed to create the part. As the polymer's molecular mass increases, the mechanical properties increase until a critical molecular mass is obtained, at which the melt viscosity increases while the mechanical properties start to level out. This "knee" or bend in the mechanical and physical properties versus molecular mass curve is where any further increase in molecular mass increases the complexity of the melt forming without a significant improvement in the overall properties of the neat resin [306–308]. The influence of molecular mass and its relationship to melt viscosity are affected by the structure of the polyimide in a fashion similar to the basic structure–property relationships discussed above. Several resin systems developed at GE, NASA Langley, Furon, Mitsui, and others have found utility as thermoplastic molding resins. The T_g for these thermoplastic polyimides are in the range of 210–270°C and the polymers are processed 50–150°C above their glass-transition temperature [306, 307]. The molar masses of these resins range from several thousand to above 30 000 g/mol. These systems display excellent fracture toughness and high modulus and have been extruded, compression molded, machined and polished neat, or filled with graphite, PTFE, metal, and ceramic powders. These thermoplastic polyimides are sold as rod, sheet and film stock or as final stock parts and composites [49, 309–317].

Thermosetting polyimides solve the molecular mass effect on melt viscosity, but add the additional problems associated with curing

exotherms and time–temperature-limited processing windows. Thus, a wide processing window from the melt flow of the monomer(s) to the onset cure temperature should be selected. The melt-processable thermosetting systems are typically BMIs, PMRs, or BCB-maleimides, and these can be blended with chopped fibers or other fillers, ground or extruded, and pelletized for moldings [318–324]. These imide oligomers are then cured into high-performance PCB substrates and composite forms. NASA Langley has developed and commercialized several PETI-based low viscosity (LV) thermosetting resins, PETI-298 and 330, that can be injection-molded or resin-infused into carbon fiber preforms and then cross-linked at elevated temperatures [324, 325].

4.5. Direct-Formed Polyimides

There are several polyimides that do not undergo melt flow, but are directly formed into parts requiring performance under extremely harsh conditions [326–328]. These direct-formed polyimides include DuPont's Vespel (includes the SP product line), Ube's Upimol-S and Imitec's I-903 and I-772. These polyimides undergo a forming process similar to that of ceramic sintering. The starting fine-particle polyimide powder is either hot isostatically pressed (HIPed) or ram-extruded and hot-formed to generate a polyimide stock shape that is machined to size, with a density in the range of 1.4–1.5 g/cm^3 for the neat system [329]. These polyimide powders or films have also been blended/impregnated with graphite, PTFE, and boron nitride for dry lubrication for which tribology and abrasion issues are important [330–332]. These parts have a very low coefficient of thermal expansion and do not smear under load at elevated temperatures, making them excellent choices for high-temperature pressure–velocity requirements [333–337]. These molded parts have found utility in rotating equipment, silicon wafer and chip processing, machine tooling, and chemical and material processing.

4.6. Matrix Composites and Adhesives

(→ Composite Materials; → Adhesives, 1. General) Polyimides display properties that make the resulting advanced composites excellent choices as primary structural members for aerospace applications [338–340]. The fibers in the composite are the load-carrying members and the resin serves to transfer the load to the fibers and hold them in place. Thus, the composite is only as good as the resin [341]. Therefore, the selected matrix resin must have excellent thermal, chemical and mechanical toughness, high compressive strength and adhesive properties. One of the key elements in creating a strong composite is the wetting out of the fibers with the proper amount of resin. This is achieved by two methods, dry and wet (or solution) prepregging [342]. The dry-coating method may consist of coating the fibers with fine polyimide powder and melt shearing the powder to form a film about the fibers [343, 344]. Another dry process involves melt infusing a polyimide film into a fiber matrix affording prepreg tape. Solution prepregging involves the coating of the fibers with a solution containing the polymer or reactive monomers and removing the solvent at a later stage to form the prepreg tape. The resulting prepreg should display tack and drape, i.e., tack to allow it to remain in place prior to and during consolidation, and drape to allow it to contour to the tooling surface. These prepregs are then cut into the desired shapes, stacked, and laminated together on a tool in a hot press or autoclave to form the composite part. In order to achieve excellent consolidation, these polyimide laminates must undergo melt flow and adhere [332]. Hence, the polyimides must display high adhesive strength under a variety of conditions [345–348]. Initial criteria for screening the hot-melt aerospace polyimide adhesives is the Titanium–Titanium or Aluminum–Aluminum Lap Shear test (ASTM D-1002), and for the electronic industry the T-peel and 180° peel tests are used (ASTM D-1976 & D-3330). Well prepared titanium lap shear strengths for polyimide adhesives range from 2000 psi (~138 bar) to more than 8000 psi (550 bar) under ambient conditions. It is worth noting that surface preparation plays a key role in determining the adhesive strength of the resin system. The polyimide resin systems that have been used for aerospace composite programs include BMIs, PMR-15, DuPont's Avimide series (based on the PMR approach) and NASA's PETI-5 (developed under the HSR program) that exceeds the performance criteria for the High Speed Civil

Transport as a structural adhesive and matrix resin for this advanced composites program [340–351].

5. Photoimageable Polyimides

Photoimageable polyimides are mainly used in microelectronic processing as solder masks, protective coatings, and negative and positive photoresists for the selective etching and layering of complex circuitry on multilayered printed circuit boards (PCBs) and silicon wafers [352]. For such applications, these resins must have good substrate adhesion and wettability, a long storage life and high quantum yields upon exposure, undergo changes in solubility without swelling, and serve as a thermal protective coating, which is an inherent characteristic of polyimides. There are several ways (Fig. 5) in which polyimides (PIs) have been used in

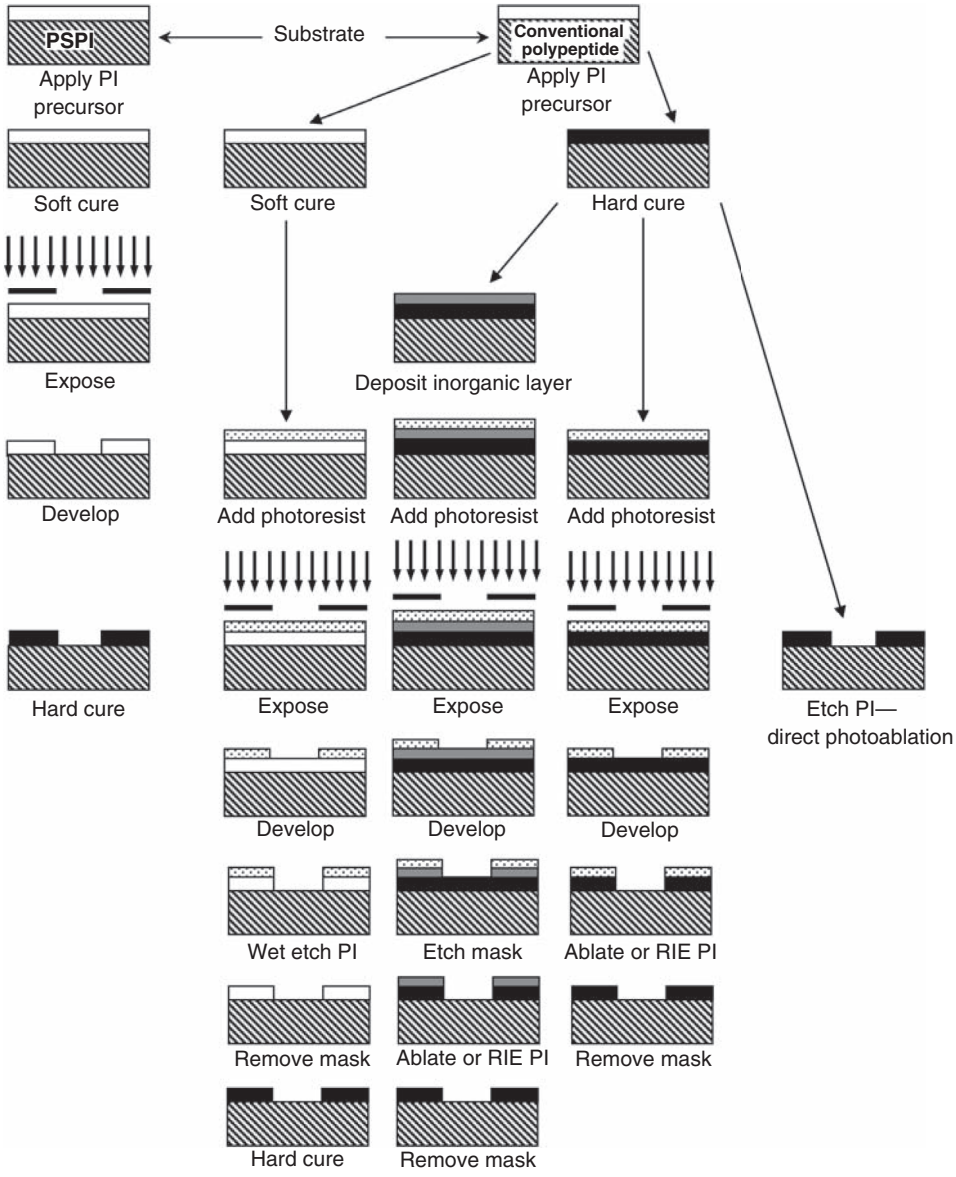


Figure 5. Chart of various photoimaging processes (reproduced from [352])

applications where "photoimaging" is required to produce a pattern on a substrate (typically silicon, or other materials including polyimide itself [352]. The first method is reactive ion etching (RIE, includes plasma etching) or photoablation. This method does not require a photosensitive material, only a mask that can withstand the reactive ion gas or photons and the material to be patterned, that is protected by the mask. In RIE, the reactive ions, generated by a radiofrequency field, attack the exposed polyimide to etch out the pattern of the mask. This process can be used with conventional polyimide film and requires few steps, but is not highly accurate and requires a hard (metal, silicon, etc.) mask. The other methods involving the conventional polyimide, as a dielectric, require an additional photosensitive material as the overcoat. The method also uses a mask, but higher degrees of accuracy are obtained as the photosensitive material's exposure is performed with coherent short-wavelength light. The combination of step reduction, increased accuracy, and less complexity while maintaining good dielectric, mechanical, and thermal properties have spurred the development of photosensitive polyimides, (PSPIs) used with these photoimaging methods [352–354].

5.1. Negative Photoresists

The two types of photoimageable resists are positive and negative. The negative resist undergoes a reaction when exposed that typically decreases solubility, in comparison to the unexposed region, that remains in place during solvent development (a negative image is produced). Negative PSPIs are often used in their soluble poly(amic acid) form with photosensitive units either attached to the polymer backbone, in conjugation with the carboxyl unit of the poly (amic acid), or incorporated into the polyimide structure. Specific areas of the cast photosensitive film are exposed to light, thereby becoming insoluble through a cross-linking mechanism, and the masked portions (unexposed areas) are washed away with solvent. The remaining cross-linked (exposed area) is then baked to thermally cure the poly(amic acid), releasing the cross-linked portion. Subsequent washing removes these cross-linked photocured regions. There are several approaches used to create negative PSPIs, with the more popular being those of the covalent, ionic, and intrinsic types [355].

The covalent type was one of the first and still widely used commercial approaches. A photosensitive unit is attached to the carboxyl group of the starting dianhydride prior to polymerization with a diamine (Fig. 1, k_4 followed by k_3). The resulting sensitized poly(amic acid) is then exposed and the resulting sensitized ester unit photo-cross-links. The exposed film is then developed and baked (Fig. 1, k_5). Such photosensitive units are of the acrylate or cinamyl variety [356, 357]. A system that uses a soluble fluorinated polyimide involves the chloromethylation of the aromatic ring on the arylether portion, followed by treatment with cinnamic acid to form the pendent photosensitive cinnamate group. This resulting PSPI was photo-cross-linked, and the unexposed portion was washed away with solvent [358]. The ionic type is similar to the covalent type with the pre-made poly(amic acid) sensitized by using a tertiary amine having a photoreactive group and a photoinitiator. The interaction of the tertiary amine and the poly(amic acid) hydroxyls form a photosensitized salt that is ionically bound to the poly(amic acid) (similar to Fig. 4, Step 2). The ionic PSPI is then exposed, washed, and baked to develop the image. The last type is the intrinsic PSPIs, meaning that they are photosensitive as made. These PSPIs are generally based on BTDA and *ortho*-alkylated diamines. When these intrinsic systems are exposed to 365 nm wavelength, the hydrogen atoms of these pendent alkyls are abstracted through the excitation (C=O diradical formation) of the benzophenone radicals inducing cross-linking of the pendant methylene radicals. Recently, a hyperbranched PSPI was synthesized terminated by 3-aminophenylacetylene. This system takes advantage of the charge-transfer complex developed between the electron-acceptive imide group and the electron-donating phenylene terminal units. When exposed to 365 nm UV light, a clear negative image is resolved [359]. Overall, resolution of negative PSPIs is controlled by several factors including film thickness, exposure wavelength, and the selectivity of the developer, but the typical resolving limit that can be obtained is a 3:1 width to resist thickness ratio [82]. These drawbacks of the negative PSPIs manifest themselves through pattern distortion, shrinkage,

pinhole formation, and thermal stability effects during wafer processing.

5.2. Positive Photoresists

The positive PSPIs undergo a chemical change in solubility on exposure, versus a molecular-mass change. Typically, the masked positive PSPI is exposed to light and a pendent photosensitive unit is converted into a carboxylic acid or hydroxyl unit that allows the exposed portion polyimide to be removed under aqueous conditions (producing a positive image). The advantage at this point is that since the exposed and unexposed PSPI are close in structure, there is reduced physical swelling on exposure, and the unexposed areas can be re-exposed with a different mask. Hence, these positive PSPIs lead to more accurate patterning and tighter line widths. Lastly, the positive PSPIs are baked to volatilize the pendant photosensitive units to afford the polyimide dielectric. Most of the chemistry of these positive resists use variations of the Wolff rearrangement of diazo systems [82]. As an example, a polyimide with pendent hydroxyl groups was synthesized and blended with diazonaphthoquinone (DNQ). Here, the DNQ complexes with the pendant hydroxyl portion of the polyimide, decreasing the solubility of the polyimide towards aqueous base. Upon exposure, the DNQ undergoes the Wolff rearrangement, forming the indenecarboxylic acid and decomplexing from the polyimide. This results in increasing the solubility of the exposed polyimide mixture towards aqueous base solution [360, 361]. Other methods involve PSPIs made with acetal-containing diamines. These are photocatalytically depolymerized in the presence of *p*-toluenesulfonic acid, resulting in derivatives of benzaldehyde and hydroxyphthalimides that are readily removable [362]. PSPIs with pendent nitrobenzylester groups can be photodegraded to the corresponding aryl–acid functionality to enhance the resulting converted polyimides solubility in caustic solutions, with the additional advantage of subsequent thermal removal of the nitrobenzylester group form the unexposed portion [363]. Most of these post-thermally developed PSPIs, negative and positive, have mechanical properties close to that of standard polyimide film, from which they are derived, thus demonstrating excellent planarity (surface flatness), high-voltage breakdown resistance, and low dielectric constants.

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Polymethacrylates

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1. Introduction

Poly(methyl methacrylate) [9011-14-7] (PMMA) has been produced industrially since the early 1930s. The history and development of this polymer are very closely associated with the chemist Otto Röhm [1, 2]. In 1932, Röhm and his collaborator W. Bauer were the first to polymerize methyl methacrylate [36426-74-1] (MMA) into transparent sheets [3]. Almost parallel to these developments at Röhm & Haas in Germany, corresponding activities were in progress at Rohm & Haas and Du Pont in the United States and at ICI in England. A few years later, the first processable thermoplastic molding compounds based on PMMA were available.

PMMA occupies an intermediate position between "commodities" and "engineering plastics"; its market has in the meantime developed greatly. In 2010, the PMMA production worldwide exceeded 1.6×10^6 t/a with roughly 60% of the market in Asia and 20% each in NAFTA and Europe [4]. Acrylic glass and molding compounds amount to a consumption of about 50% of produced MMA; the other half is used for the synthesis of other monomers, dispersions, paints, binders, adhesives, additives, etc.

PMMA is the main representative of this polymer class; polymers and copolymers of higher alkyl methacrylates are of minor economic importance.

2. Properties

The properties that make PMMA an attractive polymeric material are its good mechanical strength, its outstanding optical properties (clarity, brilliance, transparency), and its extremely good weather resistance [5, 6]. This favorable profile can be supplemented by the surface modification of semifinished products (e.g., scratch-resistant or antistatic coating), coloring or pigmenting, and treatment with flame retardants to open up a wide variety of potential uses for this polymer (see Chap. 5).

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Table 1. Physical properties of PMMA (standard values at 23 °C and 50% R.H. for Plexiglas GS 233 and Plexiglas XT 7H)

Property	Cast (extruded)*	Test procedure
Density, g/cm^3	1.19	DIN 53 479
Charpy impact strength, kJ/m^2	15	ISO 179/1 D
Izod-test value, kJ/m^2	1.6	ISO 180/1 A
Tensile strength (1/1 test bar 3, $v = 5$ mm/min), MPa	80 (72)	DIN 53 455
Elongation at break (1/1 test bar 3, $v = 5$ mm/min), %	5.5 (4.5)	DIN 53 455
Flexural strength (standard bar 80 × 10 × 4 mm), MPa	115 (105)	DIN 53 452
Long-term tensile strength (1/1 test bar 3, $t = 10\,000$ h), MPa	38 (30)	DIN 53 444
Modulus of elasticity (short-term value), MPa	3300	DIN 53 457
Shear modulus (ca. 10 Hz), MPa	1700	DIN 53 445
Ball indentation hardness $H_{961/30}$, MPa	200 (190)	DIN-ISO 2039–1
Degree of transmission (3 mm thickness, illumination D 65, visible region, $\lambda = 380$–780 nm), %	92	DIN 5036
Refractive index n_D^{20}	1.491	DIN 53 491
Linear thermal expansion coefficient (0–50 °C), K^{-1}	70×10^{-6}	DIN 53 752-A
Shrinkage onset temperature, °C	> 80	
Vicat softening point (method B), °C	115 (102)	DIN-ISO 306
Heat distortion temperature (at flexural stress of 1.8 MPa), °C	105 (90)	ISO 75
Water absorption (compared with dry state after 24 h, specimen 50 × 50 × 4 mm), mg	30	DIN 53 495

* Extruded from molding compound.

Pure PMMA is an amorphous polymer, which can exhibit a high surface gloss, high brilliance, and crystal-clear transparency. It is classified as a hard, rigid, but brittle material with a maximum use temperature of just below 100 °C. The tensile, compressive, and flexural strengths are considered satisfactory; scratch resistance is also good and can be improved further by the use of special coatings. The most important physical properties of PMMA are summarized in Table 1; a distinction is made between cast PMMA ($M_r > 10^6$) and PMMA extruded from molding compounds ($M_r < 5 \times 10^5$). The properties listed in Table 1 were determined according to the so-called basic value table [7]; further data can be found in the CAMPUS database [8, 9]. This data base also includes information about commercial copolymers of MMA with small proportions of acrylate esters (e.g., < 10% methyl acrylate). Incorporation of acrylate allows the rheological properties of the thermoplastics to be varied within a wide range to satisfy the processing requirements during injection molding and extrusion.

PMMA is resistant to aliphatic hydrocarbons, nonpolar solvents, aqueous alkalis, and aqueous acids. Aromatic hydrocarbons, chlorinated hydrocarbons, esters, ketones, and other polar solvents attack PMMA, causing it to dissolve or swell. Whereas alcohols and water alone are regarded as nonsolvents, their mixtures may have a solubilizing effect (cosolvency). Detailed information on solvents and precipitating agents for PMMA can be found in [10]. Stress cracking is an important failure mode when molded parts are being exposed to poor solvents, such as ethyl acetate or nonsolvents, such as methanol.

Most physical properties E of polymers depend on the molecular mass. For example, the viscosity of a polymer melt increases continuously with the molecular mass. Some other properties (e.g., glass transition temperature, density, refractive index) show an asymptotic behavior, which can be described by the following equation:

$$E = E_\infty + \frac{k}{\bar{M}_n}$$

For sufficiently high number-average molecular masses $\bar{M}_n$, a polymer-specific limiting value E_∞ is accordingly reached (typically at ca. $\bar{M}_n > 50000$); the constant k is influenced by the terminal groups of the polymer.

Table 2 summarizes some physical properties of the most important polymethacrylates. The values were obtained at sufficiently high molecular mass (i.e., E_∞), so that the influence of the alcohol residue of the ester group is apparent.

The glass transition temperatures, T_g, decrease sharply with the length of the linear, aliphatic side chain. Whereas PMMA, the first member of this homologous series, is a hard, rather rigid material, the polymers with residues larger than *n*-hexyl are rubberlike. The glass transition temperature decreases until poly(*n*-dodecyl methacrylate). With longer linear ester residues, side-chain crystallization occurs,

Table 2. Physical properties of the most important polymethacrylates

Polymer	CAS registry no.	ρ (20 °C), g/cm^3	n_D^{20}	T_g, °C	δ, (J/cm^3)$^{1/2}$	References
Poly(methyl methacrylate)	[9011-14-7]	1.190	1.490	125	18.6	[11, 12, 15]
Poly(ethyl methacrylate)	[9003-42-3]	1.119	1.485	66	18.3	[11]
Poly(*n*-propyl methacrylate)	[25609-74-9]	1.085	1.484	35	18.0	[11]
Poly(isopropyl methacrylate)	[26655-94-7]	1.033	1.4728	81		[11, 12]
Poly(*n*-butyl methacrylate)	[9003-63-8]	1.058	1.483	27	18.0	[11]
Poly(isobutyl methacrylate)	[9011-15-8]	1.045	1.477	53	17.7	[11]
Poly(*sec*-butyl methacrylate)	[29356-88-5]	1.052	1.480	62		[11, 12]
Poly(*tert*-butyl methacrylate)	[25189-00-8]	1.022	1.4638	122	17.0	[11, 12]
Poly(*n*-hexyl methacrylate)	[25087-17-6]	1.007 *	1.481	−5	17.6	[11]
Poly(cyclohexyl methacrylate)	[25768-50-7]	1.100	1.5065	92		[11, 12]
Poly(*n*-octyl methacrylate)	[25087-18-7]	0.971 *		−20	17.2	[11]
Poly(2-ethylhexyl methacrylate)	[25719-51-1]			−10		[11]
Poly(*n*-decyl methacrylate)	[29320-53-4]			−70		[13]
Poly(dodecyl methacrylate)	[25719-52-2]	0.929 *	1.4740 **	−55	16.8	[11]
Poly(hexadecyl methacrylate)	[25986-80-5]		1.4750 **			[11]
Poly(octadecyl methacrylate)	[25639-21-8]			−100	16.0	[11, 15]
Poly(bornyl methacrylate)			1.5059			[11]
Poly(isobornyl methacrylate)	[28854-39-9]	1.060	1.500	110	16.6	[11, 15]
Poly(menthyl methacrylate)	[30847-50-8]	1.010	1.4890	90		[11]
Poly(phenyl methacrylate)	[25189-01-9]	1.210	1.5715	120		[11]
Poly(1-naphthyl methacrylate)	[31547-85-0]		1.6410	75		[11]
Poly(benzyl methacrylate)	[25085-83-0]	1.179	1.5680	54	20.3	[11]
Poly(2-hydroxyethyl methacrylate)	[25249-16-5]		1.5119	55		[11]
Poly(ethylthioethyl methacrylate)	[27273-87-6]		1.5300	−20		[15]
Poly(furfuryl methacrylate)	[29320-19-2]	1.2603	1.5381	60		[11, 12]
Poly(tetrahydrofurfuryl methacrylate)	[25035-85-2]		1.5096	60		[11]
Poly(3,3,5-trimethylcyclohexyl methacrylate)	[75673-26-6]		1.485	79		[11]
Poly(tricyclodecyl methacrylate)				150		[14]
Poly(2,2,3,3-tetrafluoropropyl methacrylate)	[29991-77-3]	1.4934	1.4215	64		[12]

* At 25 °C.
** n_D^{30}.

which masks the glass transition. Polymers with linear alkyl ester residues always have a lower glass transition temperature than their branched and alicyclic isomers. Large bulky residues considerably restrict the mobility of the polymer main chain, particularly if they are joined directly to the ester group.

When discussing the data in Table 2 one has to keep in mind that the properties of a polymer, in particular the glass transition temperature, also depend on its tacticity. If a tactic polymer is regarded as a terpolymer of isotactic, syndiotactic, and heterotactic triads, then its glass transition temperature can be described by the following linear combination:

$$T_g = x_{ii}T_{g,i} + x_{is}T_{g,h} + x_{ss}T_{g,s}$$

where $T_{g,i}$, $T_{g,h}$, and $T_{g,s}$ denote the glass transition temperatures of the (imaginary) polymers constructed purely from isotactic, heterotactic, or syndiotactic triads, respectively, and x_{ii}, x_{is}, and x_{ss} denote the associated mole fractions of these triads in the relevant real polymer. In the case of PMMA, the values $T_{g,i}$ = 42 °C, $T_{g,h}$ = 139 °C, and $T_{g,s}$ = 124 °C were determined by fitting experimental T_g values to x_{ii}, x_{is}, and x_{ss} mole fractions as obtained from NMR analysis [16]; data for other polymethacrylates can be found in the literature [15]. The mole fractions x_{ii}, x_{is}, and x_{ss} depend on the polymerization temperature and the polymerization mechanism (and are possibly influenced by any solvent used in the polymerization). These relationships have been investigated in detail in the case of PMMA [17].

Not all the influences on the glass transition temperature described above have been taken into account in Table 2. Most of the listed T_g values were measured on atactic polymers synthesized by radical polymerization. This explains to some extent the considerable differences researchers find in one and the same polymethacrylate. In addition, variations also arise due to the use of different methods to measure T_g (dilatometry, differential scanning

calorimetry) and evaluation procedures (e.g., "midpoint" and "on-set" evaluation in differential scanning calorimetry).

The presence of low molecular mass molecules, such as residual monomer in the polymers represents a large source of errors in the determination of T_g; even relatively small proportions can lead to considerable reduction of the glass transition temperature. Bulk synthesis of polymethacrylates with bulky side groups (e.g., isopropyl, *tert*-butyl, or cyclohexyl methacrylate) is especially critical because even in the case of a very sharp end polymerization they yield products that still contain a few percent of residual monomers [18]. The values listed in Table 2 were obtained on reprecipitated, carefully dried material and are considerably higher than previous literature values.

Polymers used as materials for optical application require good transmission behavior; the refractive index and Abbe number are other important parameters. Polymethacrylates cover a considerable range of refractive indices; plastics with a particularly low refractive index have been in demand for polymer optic fibers (POF). Fluorinated polymethacrylates are particularly suitable in this connection. A summary of relevant data (T_g, n_D^{20}) is given in [19].

The influence of tacticity on the refractive index and density should also be taken into account, but up to now, little information has been available.

3. Raw Materials

The starting material for PMMA is the monomer methyl methacrylate (MMA). One important route to this monomer (as well as to methacrylic acid) is methanolysis (or hydrolysis) of methacrylamide sulfate. The latter is produced from acetone and hydrogen cyanide via the intermediate acetone cyanohydrin. Alternative synthesis pathways have also been adopted: the C-4 route involves two-stage oxidation of isobutene (or *tert*-butanol) to methacrylic acid and MMA. In the C-3 route, propene is reacted with carbon monoxide to give isobutyric acid, from which methacrylic acid is then obtained by oxidative dehydrogenation. The C-2 pathway involves condensation of propanal (or propionic acid) with formaldehyde to methacrolein (or methacrylic acid). Propanal can be obtained from ethylene by hydroformylation. New routes include the fermentation of sugar by modified *E. Coli* bacteria where 3-hydroxyisobutyric acid is an important intermediate. For further details of the synthesis of methacrylic acid and MMA, see → Methacrylic Acid and Derivatives.

MMA for polymerization is usually available with a purity of >99.9%; impurities are mainly water, methanol, methyl formate, and traces of acid.

MMA is stabilized for storage or transportation with phenol derivatives (e.g., hydroquinone or hydroquinone monomethyl ether) in amounts of 10–100 ppm; the stabilizing action of these compounds requires the presence of oxygen. Nitrogen oxides or aromatic nitro compounds can be used in the absence of oxygen. MMA should be stored under exclusion of light and at a temperature as low as possible (<10°C).

To obtain higher methacrylate esters, methacrylic acid is esterified with the relevant alcohols. Longer-chain methacrylate esters are also synthesized by transesterification of MMA.

4. Production Processes

Methyl methacrylate can be polymerized by a free radical mechanism [20, 21] or an anionic mechanism [22–25]. Anionic polymerization is of little industrial importance because the monomer has to be subjected to extensive purification and polymerization has to be performed at low temperatures. The group transfer polymerization technique (GTP) is mechanistically very similar to anionic polymerization, and is less complicated [26, 27], but has only found little applications. Atom transfer radical polymerization (ATRP) as a form of living radical polymerization is gaining industrial importance [28].

Radical polymerization of MMA may be carried out homogeneously (bulk or solution polymerization) or heterogeneously (suspension or emulsion polymerization). It can be initiated with radiation (light, γ-radiation), heat, or radical-forming chemical agents. Spontaneous thermal initiation of MMA polymerization is extremely slow [29] and is therefore of no industrial relevance. Photoinitiation of MMA polymerization can be performed without sensitizers, but photochemically labile compounds

are generally added. On exposure to light these compounds form radicals either directly (e.g., azo compounds, disulfides, derivatives of benzoin or acetophenone) or are converted into an excited state and then form radicals after abstracting a hydrogen atom from the monomer or solvent (e.g., derivatives of benzophenone or anthraquinone) [30–34]. Initiation of polymerization by γ-rays (e.g., ^{60}Co source) may be of interest if the addition of a thermal initiator is undesirable and a conventional light source cannot be used because the polymerization batch absorbs too strongly (e.g., colored solutions, porous materials, such as wood or stone impregnated with monomer [35]).

The polymerization of MMA is most commonly initiated by using thermal radical-forming agents (i.e., initiators). Azo compounds [36, 37] and organic peroxy compounds [37] (diacyl peroxides, dialkyl peroxides, alkyl peresters, peroxy dicarbonates, perketals, alkylhydroperoxides) are often employed. A wide range of initiators is available so that an initiator can be selected with an appropriate half-life for the relevant polymerization temperature. Redox systems also play an important role in the formation of initiating radicals, particularly in polymerizations in aqueous solution [38].

The polymerization of MMA up to high conversion (particularly in bulk polymerization) is governed by the gel (Trommsdorff) effect [39, 40]. The extremely large increase in the viscosity of the reaction medium during polymerization hinders diffusion of the polymer radicals considerably. Thus, bimolecular chain termination becomes increasingly difficult and the concentration of the growing radicals increases by several orders of magnitude. As a result, the polymerization rate and mean molecular mass increase sharply [41], leading to a further increase in the viscosity of the reaction batch. Under these circumstances, removal of the heat of polymerization (57.7 kJ/mol for MMA [42]) may become a serious problem or even a potential hazard in a batch bulk reaction as it is done for the production of cast sheet.

The considerable decrease in volume associated with polymerization of the monomer may create additional problems. For the bulk polymerization of MMA shrinkage is 25.6% at 60 °C and 100% conversion. Shrinkage decreases with an increase in size of the alcohol residue of methacrylate.

The method selected for the industrial polymerization of MMA (e.g., bulk, suspension, emulsion, or solution polymerization) is generally governed by the form in which the polymer is finally used.

4.1. Bulk Polymerization

Bulk polymerization can be carried out to produce sheets, rods, and tubes of PMMA or can be used to produce molding compounds by extrusion or injection molding processes.

4.1.1. Casting of Acrylic Glass

The conventional casting process is still the most important method for producing high-quality acrylic glass with a mirror-smooth surface (e. g., Plexiglas GS, Perspex, Lucite, Altuglas, Shinkolite, Sumipex). Casting molds consist of two plane-parallel silicate glass plates (e.g., float glass with a typical length, width, and thickness of 3 000, 2 000, and 8–12 mm, respectively) that are held apart by an elastic spacer (gasket) and clamped together with metal clamps. The elastic gasket runs around the edge of the plates and is usually made of poly(vinyl chloride) or ethylene–vinyl acetate copolymer. It must have sufficient compressibility to allow for the shrinkage occurring during polymerization so that the acrylic sheet does not become detached from the glass plates. The thickness of the resulting sheets is between a few millimeters and up to 30 cm.

The reaction mixture consisting of monomer, initiator, and other additives (e.g., comonomers, cross-linking agents, stabilizers, flame retardants, dyes, or pigments) is introduced into the chamber through a small hole in the gasket. Care must be taken to avoid formation of air bubbles; if necessary, the solution should first be evacuated. A monomer–polymer solution (syrup) may be used instead of the monomer solution. This syrup contains 5–20% PMMA and can be obtained by polymerization of MMA in a stirred-tank reactor. The benefit is the reduced shrinkage and heat of polymerization in the chamber and the reduction of polymerization time. Furthermore, the viscous syrup helps to avoid pigment sedimentation and leakage from the chamber.

The contents of the sealed cells are polymerized in horizontal support racks mounted in hot-air ovens with a high air circulation rate,

in autoclaves using spray water (90–100 °C), or in water tanks (20–60 °C) with circulating pumps. The residence time may range from a few hours to several days depending on the sheet thickness. However, conversion only reaches 80–90%, because the glasslike solidification of the reaction mixture that occurs during polymerization below the glass transition temperature of the pure polymer prevents further reaction (glass effect). Subsequent polymerization at 110–120 °C is therefore necessary to obtain maximum conversion [18, 44]. After cooling to room temperature, the polymer sheet is separated from the glass plates and can be removed manually or by handling robots. The glass plates can be reused.

Because the casting process is labor-intensive and time-consuming, alternative methods have been developed for more efficient production of cast PMMA glass. One approach is to stack several plane-parallel glass plates and spacers together. The simplest case is a double cell (three plates with two spacers). Constructions that are more complex have been known for a long time and include a process patented in 1933 in which several glass plates with intermediate seals are stacked in vertical rows. The plates are enclosed on both sides by heatable and coolable metal chambers through which a heat-transfer agent flows and are held together by a screw press [45, 46]. The heat-transfer agent flowing through the metal chambers allows accurate temperature control. Shrinkage is compensated for by compression of the packet, resulting in tighter thickness tolerances of the cast sheets.

In a special variant of this process, the entire apparatus is tightly encapsulated to facilitate degassing of the reaction batch by evacuation. The system is then pressurized to suppress the formation of boiling bubbles caused by local overheating during polymerization. The advantages of this method are the smaller space requirement and reduced workforce. A disadvantage is that the use of metal chambers limits the sheet sizes. The process is still used on a small scale in Europe (Rostero) and in the United States (Polycast Corp).

The production of molding compounds in a casting operation similar to the above described process but in cells made from metal an polyester film pouches has been used in the past but has been abandoned for cost reasons.

4.1.2. Continuous Production of Cast Acrylic Glass

Not all improvements in the conventional chamber process described in Section 4.1.1 can overcome the fact that it is a batch production with variation and cost limitations. The attempts to develop continuous processes have led to a double-belt process that allows efficient production of large series of sheets up to ca. 6 mm thick [47–50]. The MMA–PMMA syrup is continuously fed between two endless, highly polished steel belts (width up to 3 m, length ca. 250 m). The belts are sealed at the edge with flexible plastic hoses (e.g., of PVC) and guided at a rate of about 1–3 m/min over roller systems through several accurately controlled temperature zones. The continuous product sheet can either be wound on rollers or cut into rectangles. This process was first used in the United States by Swedlow and subsequently by Rohm & Haas, Du Pont, and Mitsubishi. The surface quality of the acrylic glass product depends solely on the quality of the polishing of the steel belt; the brilliance of acrylic glass produced by the cell polymerization process is rarely obtained. Polymerization in the double-belt process is faster than in the conventional casting process, resulting in somewhat lower molecular masses and therefore some minor deterioration of mechanical properties. Besides the production of high quality optical sheets the biggest application is in so-called solid surface materials, such as Corian (PMMA–aluminum hydroxide composite).

4.1.3. Tube Polymerization

Tubes of PMMA can be produced by extrusion from a molding compound, but also by a special type of bulk polymerization, i.e., centrifugal polymerization [51]. Monomer or syrup is fed into tubular molds (e.g., of stainless steel) that are rotated during polymerization. A film is produced on the internal wall of the pipe by centrifugal forces and polymerizes to form pipes of specific diameter (13–650 mm) and wall thickness (1–10 mm). This technique is extremely labor-intensive and requires high-precision apparatus. Centrifugal polymerization is therefore seldom used on an industrial scale.

4.2. Suspension Polymerization

PMMA can be produced in the form of small beads by suspension polymerization [52, 53]. The monomer (with or without comonomer) is stirred with about twice its volume of water and dispersants (distributors). Droplets of monomer are dispersed in the water and are stabilized by dispersing aids preventing the droplets from coalescing. The droplets become increasingly viscous during the course of polymerization. Gelatin, cellulose derivatives, synthetic, water-soluble polymers [e.g., poly(vinyl alcohol) or alkali salts of (co)polymers of methacrylic acid] [54], and finely dispersed inorganic substances (kaolin, magnesium carbonate, precipitated aluminum hydroxide) have proved suitable as distributors [55, 56]. The particle size can be controlled within wide limits (50–1000 μm) by choosing appropriate stirring conditions and distributor systems [57].

Suspension polymerization is preferably initiated by adding radical-forming agents, whose distribution equilibrium between the aqueous and the monomer phases should be in favor of the monomer. This also applies to other polymerization auxiliaries, such as chain-transfer agents. The mechanism of suspension polymerization corresponds to that of bulk polymerization. One of the main advantages of suspension polymerization is the ease of heat removal because of an extremely high surface to volume ratio of the polymerizing phase and the high specific heat of water compared to that of the monomer. This permits higher polymerization rates and thus higher space–time yields than in typical batch bulk polymerizations. Another advantage is the substantially lower viscosity of the suspension and the simple isolation of the polymer by filtration.

After the completion of polymerization, the polymer beads are separated from the aqueous phase, washed with water to remove adhering distributor and salts, and dried.

4.3. Continuous Polymerization of Molding Compounds

While in the production of cast acrylic glass continuous processes play a minor role compared with the batch casting process (see Section 4.1.2). the polymerization processes for the production of PMMA used as injection molding and extrusion material are, however, mostly continuous processes. These molding compounds often contain a small proportion of acrylate ester as comonomer (up to ca. 20%) and have a relatively low mass average molecular mass (100 000–200 000) when compared to cast acrylic glass.

The oldest continuous process for producing molding compounds was similar to the double-belt process described in Section 4.1.2 [58, 59]: syrup is metered into an endless hose of sheet material and polymerized by passage through a water bath (ca. 75 °C) and an annealing oven (ca. 110 °C). In a plant with a total length of ca. 50 m the residence time was about 1 h.

Today, there are two main types of processes for the production of thermoplastic PMMA. One type uses the monomer as solvent for the polymerization process in a continuous stirred-tank reactor. Depending on the reaction control scheme, reaction times vary between 45 min and several hours. The typical temperatures are always significantly above T_g and in the range of 130–170 °C. The conversions reach 40–80%. The highly viscous polymer is fed into flash chambers with gear pumps or extruders for degassing of unconverted monomer, which is recovered and reused after refining. In older processes, the aim was to achieve maximum polymerization in the extruder [60, 61]. These techniques are, however, relatively complex and the high polymerization temperatures cause problems with the ceiling equilibrium [42] and thus result in a lower efficiency. More economic processes [62–69] dispense with high conversion in the extruder. The second type of process uses an inert solvent, such as toluene or butyl acetate to reduce the viscosity of the reaction mixture at higher conversions. The polymer separation is carried out in the same way as described above.

The polymer melt can be extruded and pelletized. In order to produce colored pellets, dyes or pigments are mixed with the polymer melt before it is fed into the degassing extruder. Further additives, such as UV-absorbers, lubricants, and stabilizers are added either to the melt or to the stirred-tank reactor.

To avoid fouling of the reactors, it is necessary to operate them hydraulically filled because MMA has a strong tendency to form deposits on reactor walls [70].

4.4. Batchwise Solution Polymerization

The continuous two-stage polymerization of MMA described in Section 4.3 can be carried out both in bulk and in solution. Batchwise solution polymerization of MMA and in particular of longer-chain methacrylates is also of interest, especially if the resultant polymer solutions constitute the form in which the polymer is used. Typical examples include adhesives and paint resins (see also → Adhesives, 1. General; → Paints and Coatings, 2. Types, Chap. 5; → Polyacrylates) or additives for the mineral oil sector. Criteria for the choice of solvents include price, solvent quality, toxicity, flammability, boiling point, and the chain-transfer action during polymerization. Solution polymerization is performed batchwise or with a continuous feed. In order to remove the heat of polymerization, it may be advantageous to operate under evaporative cooling conditions.

4.5. Emulsion Polymerization

Methacrylates play an important role as comonomers for acrylates (see → Polyacrylates) and other vinyl compounds (e.g., vinyl acetate) in the production of aqueous plastics dispersions, which are used as paint resins, paper coating agents, textile binders, paper processing agents, and auxiliaries for leather treatment (→ Leather, Section 8.5). Colloidal dispersion and film-forming properties can be widely varied by adding small amounts of methacrylic acid, methacrylamide, or its methylol or methylol ether derivatives. However, dispersions of pure polymethacrylates do not form films.

Emulsion polymers with a core–shell structure that contain methacrylates as monomers have become important. Such emulsion polymers are used as impact-resistant modifiers [71] for PMMA [72–74] or other thermoplastics [75, 76]. The polymers can be isolated as solids from dispersion by spray drying, chemical or freeze coagulation, or direct coagulation in an extruder [77].

5. Uses

The price of PMMA polymers depends significantly on the cost of the monomer and therefore is somewhat higher than that of other plastic materials. Thus, the materials are used where their specific advantages including low density, resistance to fracture, and, above all, excellent optical properties (transparency, gloss) and weather resistance play a role. PMMA also has favorable processing properties (especially good thermoforming) and can be modified in many ways (e.g., coloring, pigmenting, or surface treatment with scratch-resistant coatings).

PMMA has a wide range of applications, particularly in glazing, roofing, vehicles, machinery, and instruments. Pipelines and vessels made of acrylic glass are also of interest for the storage and transportation of food due to their transparency and lack of smell and taste. Optical components, such as lenses, reflectors, prisms, and spectacle lenses are also made from polymethacrylates. The advent of LCD flat panel displays has become a dominant application with demands for PMMA light guides illuminated with LEDs.

5.1. Molding Compounds

In comparison to the cast sheet products, which can only be mechanically formed, the application and uses of PMMA molding compounds are much more versatile. The thermoplastically deformable polymers can be processed by injection molding and extrusion. The molecular masses (M_r) of PMMA molding compounds are in the range $1–2 \times 10^5$. The recommended processing temperatures are generally between 200 and 280 °C.

5.1.1. Standard Molding Compounds

Standard molding compounds consist of MMA homopolymers and copolymers containing up to 20% acrylate esters. The comonomer permits variation of the softening temperature and thus the melt flow rate of the polymers.

Standard molding compounds are processed by injection molding. As a fully amorphous polymer, PMMA shows very little shrinkage during the molding process. Typical uses

include precision parts, such as dials, rulers, and other drawing instruments; optical components, such as lenses or spectacles; plastic optical fibers (→ Fiber Optics, Section 3.2.3); and domestic and household articles. Colored injection-molded parts (e.g., covers for automobile rear lights) represent a very important market. The development of LED edge-lit light guides to illuminate large flat panel displays has increased the demand. The absence of chromophores together with an unsurpassed light transmission is extremely important. These sheets are being extruded and injection molded in dimensions of up to 53.3 cm diagonal. During injection molding a surface pattern can be embossed for control of the light outcoupling, which is achieved on extruded sheet mainly by screen printing.

Standard PMMA molding compounds are also extruded on a large scale into flat sheets (width up to 3 m, thickness up to 25 mm), sinusoidally profiled sheets and rods, as well as hollow shapes, multiwall-sheets, and tubes (up to 30 cm diameter). If necessary the extruded sheets are also subjected to surface treatment by coating or coextrusion (e.g., scratch-resistant, antistatic, or nondrip water spreading coating or antialgae growth). After cutting to size and covering with a protective masking film (e.g., polyethylene) they are marketed as semifinished products.

Trade names of standard PMMA molding materials include Acrylic/Acrycal (Continental Polymers); Acrylite (Evonik CYRO); Acrypet, Shinkolite (Mitsubishi); ; Delpet (Asahi); Diakon (Lucite); Oroglas (Altuglas, in the US: Plexiglas); Plexiglas (Evonik); Lucite (Lucite).

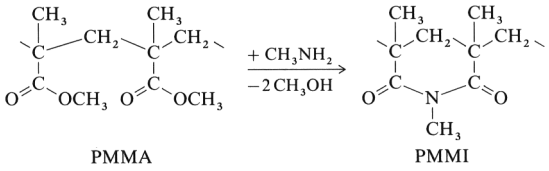
The worldwide market for PMMA standard molding compounds is ca. 500 000 t/a, of which Western Europe and the United States each account for ca. 90 000 t/a.

5.1.2. Heat-Resistant Molding Compounds

A limiting factor in use is that the long-term service temperatures of articles made of standard molding compounds are considerably below 100 °C. Heat-resistant molding compounds can have service temperatures of up to 150 °C. They consist of copolymers of MMA with monomers that stiffen the polymer chains. Examples of such comonomers include maleic anhydride [78] (trade names of copolymers: Acrypet ST, Mitsubishi; Oroglas HT 121 Altuglas; Delpet 980 N, Asahi; Plexiglas hw 55, Evonik) or also methacrylates with bulky ester groups, such as tricyclodecyl methacrylate [14] (Optorez OZ 1000, Hitachi Chemical).

Chain stiffening can also be achieved by polymer-analogous reaction of the functional groups in the PMMA-(co)polymer. For example, adjacent acid groups of a copolymer of methyl methacrylate and methacrylic acid are converted into polymethacrylic anhydride structures under the influence of a strong base [79]. The resulting polymers have Vicat softening temperatures of up to 150 °C, depending on the degree of cyclization. These products have only reached a niche status due to their relatively high cost.

Poly(*N*-methyl methacrylimide) [119499-71-7] (PMMI), also known as poly(*N*-methylglutarimide), a thermoplastic molding compound, is obtained by reacting PMMA with methylamine, → Polyimides, Chap. 5, [80–82].



PMMA PMMI

PMMI, marketed under the trade names Kamax (Rohm & Haas), or PMI resin (Mitsubishi Rayon) is now only produced by Pleximid (Evonik). The product has a favorable combination of optical properties, light resistance, and stiffness (modulus of elasticity, ca. 4.8×10^3 N/mm^2). The Vicat softening temperature of PMMI can be selectively varied via the degree of imidation and exceeds 170 °C in highly imidized products.

The imidation reaction can be performed in the melt or in solution. Other primary amines besides methylamine can be used. In addition to the glutarimide units resulting from the cyclization and unreacted methyl methacrylate groups, PMMI may also contain varying proportions (depending on the reaction conditions) of structural elements derived from methacrylic acid and methacrylic anhydride.

The market volume for heat-resistant methacrylate molding compounds is estimated at ca. 2 000 t/a worldwide and remains limited. The

most important customers for heat-resistant molding compounds are the automobile and lighting industries. In combination with high intensity LED lighting, there is an increasing interest in such polymers.

5.1.3. Impact-Resistant Molding Compounds

Impact-resistant PMMA molding compounds are multiphase polymer blends based on a soft elastomer phase dispersed in the rigid PMMA matrix. The elastomer phase may consist of EPDM rubbers, poly(butyl acrylate), polybutadiene, and, in rare cases, polysiloxanes. The choice of rubber is especially important for the notched impact resistance at low temperature and weathering performance. Most widely used are acrylic rubbers [poly(butyl acrylate], which have a good weather resistance.

The bonding of the disperse elastomer phase to the rigid matrix and its morphology play an important role in determining the mechanical properties of impact-resistant thermoplastics [71]. If the impact-resistant thermoplastics are to be transparent, the refractive indices of the rigid and soft phases must be identical (as long as the domain size of the elastomer phase does not remain below a critical value, e.g., significantly below the wavelength of visible light).

Various methods can be used to produce impact-resistant PMMA: in older processes, a suitable type of rubber was grafted with MMA (and comonomers to adjust the refractive index) by bulk or solution polymerization. Increasing conversion leads to phase inversion, whereby the elastomer phase, which frequently includes PMMA (or, in the presence of comonomers, the corresponding copolymer), becomes the disperse phase. This desired morphology and the size of the elastomer particles can be controlled by the viscosity of the reaction medium and the shear forces resulting from stirring. They are then fixed by cross-linking when conversion is nearly complete. Graft polymerization by two-stage suspension polymerization is carried out on an industrial scale, too [52].

Emulsion polymerization is particularly effective if particle size and particle morphology have to be selectively modified (see Section 4.5). Impact-resistance modifiers with a core–shell structure have therefore been developed for PMMA [72–74].

Block copolymers of acrylates and methacrylates have been introduced into the market by Altuglas (Nanostrength) and Kurary (Kurarity). Their claimed advantage is that the transparency does not vary with the temperature due to the domain size of dispersed rubber [83, 84].

Worldwide demand for impact-resistant PMMA is estimated to be ca. 65 000 t/a. Products in which butadiene constitutes the tough phase include methacrylate–butadiene–styrene (MBS) [25053-09-2] (e.g., Plexalloy-F-PAB, Evonik; Cyrolite G 20, Evonik-CYRO) and methacrylate–acrylonitrile–butadiene–styrene (MABS) [9010-94-0] (e.g., Terluran, BASF; Cyrolite XT Polymer, CYRO). PMMA modified with butyl acrylate is commercially available under the trade names Delpet SR (Asahi), Diakon TD (Lucite), Oroglas DR (Altuglas), Plexiglas zk (Röhm), and Shinkolite (Mitsubishi Rayon Corp.).

5.1.4. Molding Compounds for Special Optical Uses

PMMA is mainly used because of its very good weather resistance, outstanding optical quality, hardness and good processability (e.g., by injection molding). Optical components (e.g., lenses, prisms, mirrors) represent an important area of use for PMMA [85, 86]. The relatively high water absorption of PMMA (ca. 2% when immersed in water) causes dimensional changes and change in refractive index. This disadvantage can be overcome by using cycloaliphatic methacrylates, such as cyclohexylmethyl methacrylate [87] or tricyclodecyl methacrylate [14] as comonomers. Hydrophilic methacrylates such as poly(2-hydroxyethyl methacrylate) are used in soft contact lenses [88, 89].

The excellent optical properties of PMMA (especially its low orientation birefringence) seem to have favored its use as a substrate for optical data storage media. However, in asymmetric, single-sided audio compact discs the relatively high water absorption of the polymer and the associated warpage may detract from these advantages [90, 91]. This problem did not arise with the two-sided video disc; PMMA molding materials were therefore used for these products [92]. See also → Information Storage Materials.

Extremely pure PMMA is used as plastic optic fibers (POF) [93, 94] → Fiber Optics, Section 3.2.3. The theoretical limiting values of transmission loss of PMMA in the 650 and 567 nm minima of the damping spectrum are 100 and 27 dB/km, respectively [95]. Limits of 5–6 dB/km at 680 and 650 nm can be achieved with special deuterated or fluorinated methacrylates [96]. Fiber to the home (FTTH) projects in Asia and United States drive the demand for POFs, which are only made by three Japanese companies in significant quantities. There are a number of Chinese manufacturers trying to enter this market as well. They also produce POF for decorative purposes.

PMMA is also employed in lithographic materials in semiconductor technology. Use as a high-resolution positive resist is based on the depolymerization of this polymer by radiation, see → Imaging Technology. The irradiated regions are accurately dissolved out with suitable solvents. Sensitivity to electron beams and UV light can be increased further by copolymerization with suitable monomers [97, 98].

5.2. Semifinished Products

5.2.1. Extruded Acrylic Glass

A substantial proportion of standard PMMA molding compounds (and in the United States particularly impact-resistant PMMA) is extruded into semifinished products (sheets, multiwall-sheets, corrugated profile sheets, tubes) [99]. Reference has already been made to possible surface modifications of these extrudates (see Section 5.1.1). Cast acrylic glass with a matt surface requires matt glass for production and is difficult to produce; extruded semifinished products with matt surface structures are therefore an interesting alternative. It would be desirable if such products could also be thermoplastically formed without losing their matt structure. This can be accomplished by adding highly cross-linked bead polymer to the extrusion compound in total or only to a coextrusion layer. These materials show interesting light diffusing properties and are being marketed for application in furniture and lighting. One advantage is their reduced sensitivity to scratching.

Besides extruded semifinished products, illuminated advertising signs and glazing (including lighting domes) dominate the European market with a volume is ca. 70 000 t/a. Trade names include Acrylite FF (Evonik CYRO), Altuglas (Altuglas), Perspex TX (Lucite), Plexiglas XT and Plexiglas SDP (Evonik). The backlight unit (BLU) has become the single biggest application for extruded sheet in Asia. With tens of millions of TV sets being manufactured, the capacities for sheet grew dramatically in Asia making Asia the dominating region for PMMA consumption.

5.2.2. Cast Acrylic Glass

The substantially more economic production of extruded acrylic glass has led to a considerable decline in the production of cast semifinished products. Nevertheless, cast material has retained its position in applications with stringent requirements with regard to surface quality and optical properties. For example, cast acrylic glass has kept a significant position in the sanitary ware sector (e.g., baths, shower units, and washbasins). Due to certain deficiencies revealed by the hot water alternating test (DIN EN 198), (co)extruded products have not found broad acceptance in this sector.

Another application of cast acrylic glass (optionally with flame retardants) is in noise protection walls on motorways. This market sector grows due to the increasing motorization all around the globe. Large sheets ($\geq 2 \times 4$ m) are needed to prevent drivers from being disturbed by the frames used for mounting. Very large size thick-wall (up to 120 mm) aquarium glazing is another domain of cast acrylic.

Semispherical lenses for touristic submarine is another interesting application.

Aviation glazing, one of the oldest applications of cast acrylic glass, has become increasingly important because of the enormous increase in air traffic. Acrylic glass has the advantages of low mass and outstanding resistance to extreme weather conditions (high UV radiation intensities at high altitudes). It receives the required strength by biaxially stretching [100]. This step also increases dramatically the resistance to crack growth. The extremely stringent optical requirements [e.g., freedom

from optical distortion, low deflection, lack of internal defects (e.g., bubbles, inclusions), lack of surface defects (e.g., pimples)] predestine cast acrylic glass for aviation glazing. Aviation standards prohibit the use of extruded material.

The total market volume for cast acrylic glass in Europe is ca. 53 000 t/a. Important trade names and manufacturers include Acrylite (CYRO); Altuglas, Casocryl, Paralinx (Kyowa Gas); Perspex (Lucite); Plexiglas GS (Röhm); Plexiglas (Altuglas); Shinkolite (Mitsubishi); Sumipex (Sumitomo Chemical).

5.3. Binders and Paints

Methacrylates are used in large amounts as comonomers in the production of acrylate–methacrylate copolymers for binders and paint resins (→ Paints and Coatings, 2. Types, Chap. 5). Methacrylate is used to obtain the desired glass transition temperature.

The use of such copolymers in the form of solution polymers, aqueous dispersions, or solid products extends over a wide field (e.g., weather-resistant paints, textile binders, paper coating materials, and adhesives); further details are given elsewhere, see → Polyacrylates.

5.4. Additives for the Petroleum Industry

Long-chain poly(alkyl methacrylates), PAMA, are used as additives in the petroleum sector for many purposes [101–104]. The best-known application is probably their use as viscosity index improvers in engine and gear oils (→ Lubricants, 2. Components, Section 3.2). At low temperatures viscosity index improvers increase the viscosity of the mixture only slightly. At high temperatures, however, they compensate for the sharp decrease in viscosity of the base oil by virtue of their intrinsically high contribution to the solution viscosity of the whole system [105, 106].

This is because the mineral oil becomes an increasingly better solvent for PAMA at higher temperatures and the polymer coils expand greatly. Viscosity index improvers thus prevent destruction of the lubricating oil film and resultant damage to the engine. Viscosity index improvers are generally constituents of an extremely complex additive formulation and interact with other components not only in improving flow behavior, but also in cleaning the engine, dispersing dirt and contaminants, and preventing oxidation of the oil. This dispersing effect can be achieved by incorporating polar comonomers (e.g., *N*-vinylpyrrolidone) into the PAMA chain.

PAMA-based additives also act as pourpoint depressants (→ Lubricants, 2. Components, Section 3.3). The pour point denotes the temperature at which oil solidifies as a result of precipitation of paraffin. At concentrations of less than 1%, PAMAs hinder the growth of paraffin crystals and thus prevent the formation of aggregates of crystal needles. The oil remains free-flowing and the oil pump is able to function during cold starting.

5.5. Miscellaneous Uses

Polymethacrylates are also used in many other applications.

Most poly(vinyl chloride) processing auxiliaries consist of high molecular mass polymers based on MMA. They are generally marketed in powder form as spray-dried emulsion polymers [107]. Important examples of such products include Diakon APA (Lucite), Kane ACE (Kanegafuchi Chemical), Metablen (Mitsubishi Rayon), and Plastistrength (Altuglas) Paraloid K (Dow Chemical).

Methacrylate reaction resins (monomer–polymer systems) are used in the building industry in mortars and concretes, and in synthetic floor screeds [108, 109].

Alkali-soluble suspension polymers, e.g., Rohagit (Evonik), are used as thickeners for aqueous dispersions and cosmetics, as sizings and finishes in the textile industry, and as dispersion and stabilizing auxiliaries in suspension polymerization. Cation-exchange resins can be obtained by hydrolysis of PMMA, thus producing weakly acidic carboxylic functions (→ Ion Exchangers).

Polymethacrylates are used as dental materials for fillings, false teeth, and prostheses [110], and in surgery as bone cement for implants. Examples of such products include Kallodoc (ICI) and Plexidon (Evonik).

Coatings of polymethacrylate copolymers, such as Eudragit E-30 D [9010-88-2] or

Eudragit RS [39316-06-8] (Evonik) are used as galenic auxiliaries for controlled-release tablets [111, 112].

6. Toxicology

No toxic effects of PMMA have been described, and the polymer is regarded as inert and nontoxic. In individual cases, however, contact of the mucous membranes with polymer powders or dusts may cause allergic and irritating reactions. Skin reactions (presumably due to residual monomer) and asthma have also been noted [113, 114].

Because PMMA is used as bone cement, its potential carcinogenic effect has been monitored in animal implant tests. Malignant tumors were found in some cases at the implant site, but also occurred with inert materials of the same shape. Such tumors are therefore most likely to be foreign-body carcinoma resulting from mechanical irritation. Tumors have not yet been observed in humans after many years of use [113].

7. Environmental Aspects

In contrast to most other polymers, pure PMMA can be almost quantitatively depolymerized to the monomer at high temperatures (ca. 450 °C). Conversion of production waste and waste from semifinished product blanks to MMA by cracking had already been investigated at the start of large-scale industrial production in the 1930s [115, 116]. In these earlier processes, the polymer was mixed with sand and depolymerized batchwise in retorts or with superheated steam (to avoid local overheating and thus uncontrolled pyrolysis). Continuous processes now operate with an indirectly heated fluidized bed and are substantially more economical [117–119].

In 2010, the first fully transparent blends of PMMA with PLA were commercialized following a trend to build chemical products on renewable resources [120].

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Polyoxyalkylenes

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ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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1. Introduction

This article deals with polyoxyethylene, polyoxypropylene, and polytetrahydrofuran or poly(1,4-epoxybutane). Other names include poly(ethylene oxide), PEO; poly(propylene oxide), PPO; and poly(tetramethylene oxide), PTMO. Strictly speaking, the latter polymer is not derived from an alkene and thus is not a poly(alkylene oxide); however, it is included here, and the term poly(alkylene oxides) is used as a collective term for these three polymers. The poly(alkylene oxides) have an ether linkage in their main chain backbone and thus are polyethers. They are described by the repeat unit

$$-[(CH_2)_x - CHR - O]-$$

Poly(ethylene oxide):	R=H, x=1
Poly(propylene oxide):	R=CH_3, x=1
Poly(tetramethylene oxide):	R=H, x=3

Many details about the alkylene oxides and their polymers are given in [1].

2. Properties

Physical Properties. Typical physical properties of PEO, PPO, and PTMO are presented in Table 1. Except for PTMO, these polyethers can be linear or branched and are commercially available in a broad range of molecular masses from less than a few hundred to several million.

Low molecular mass polymers of ethylene oxide are clear, essentially colorless liquids and become partially crystalline solids at a molecular mass of ca. 800. As the molecular mass increases, they change from soft waxy solids to hard waxes. At high molecular mass, they are tough thermoplastics. Polyoxyethylenes of less than ca. 20 000 number-average molecular mass are usually referred to as poly(ethylene glycols). The crystalline polymer is spherulitic, has a unit cell (see Table 2) with four molecular chains, and has a fiber identity period of seven repeat units in two helical turns. The molecules are in an array of dihedral symmetry with twofold axes. One axis bisects the carbon – carbon bond and the other passes through the ether oxygens.

The glass transition temperature of PEO is listed as − 52 °C in Table 1; however, this is the value for a high molecular mass, partially crystalline polymer. This parameter is complicated by crystallinity in the molecular mass range 10^3 –10^5 [22], and abnormal values as high as − 17 °C are found for the polymer with $M = 6000$, which is known to have the highest crystallinity (ca. 95 %). Macrospherulites or spherulites that can be seen without magnification have been prepared [23].

PEO is soluble in water, chlorinated hydrocarbons, aromatic hydrocarbons, methyl ethyl ketone, 2-ethoxyethyl acetate, butyl acetate, cyclohexanone, esters, dimethylformamide, and

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Table 1. Selected physical properties of the poly(alkylene oxides)

	Poly(ethylene oxide)	Poly(propylene oxide)	Poly(tetramethylene oxide)
Density, g/cm^3			
Amorphous	1.127–1.128[a] [2]	ca. 1.01–1.025[a] [3]	0.975 (25 °C) [4]
Crystalline	1.21 (20 °C) [5]	1.096 (25 °C) [6]	1.07–1.08 [7]
Melting point, °C			
High molecular mass	65 [5]	75 [8]	58–60 [9]
Oligomeric[b]	30–50 [10]	[c]	10–45
Glass transition temperature, °C	− 52 [11]	− 73 to − 78 [12]	− 86 [4], [12]

[a] d_{20}^{20}.
[b] M_n ca. 400–3000.
[c] Liquid under ambient conditions.

other solvents [1]. It has a solubility parameter of 10.3 [24]. It is insoluble in ethers and aliphatic hydrocarbons. Mark – Houwink constants for the intrinsic viscosity/molecular mass relationship $[\eta] = KM^a$ are given in Table 3. In water, PEO exhibits an inverse solubility – temperature behavior, becoming less soluble as the temperature is increased.

Intermolecular or association complexes between PEO and other compounds are readily formed due to the strong hydrogen bonding character of the ether oxygens. These complexes, which involve PEO and polymeric acids such as poly(acrylic acid) [35], urea, and thiourea [36], as well as various other inorganic and organic compounds [1], [37], have potential applications in mechanochemical energy conversion systems [38], chemical valves for altering the porosity of membranes [39], and biosensors and carriers for controlled drug delivery [40]. Alkali-metal salt complexes have electrical properties that make them of interest as battery electrodes [41].

Polymers of propylene oxide remain clear, almost colorless liquids or amorphous solids over broad ranges of molecular mass. They can be prepared as amorphous or stereoregular polymers, with stereoregularity resulting in crystallinity. Polyoxypropylenes with $M <$ ca. 20 000 are usually referred to as poly(propylene oxide) polyols, and these polymers are by far the most important products from a commercial standpoint. They are usually marketed as di- and trihydroxyl polyols that are available in a broad range of molecular mass. (The third hydroxyl group comes from the initiator; for example if glycerine, which is the most common initiator for PPO polyols, is used, the PPO grows off all three hydroxyl groups and a trifunctional polyol results.) High molecular mass PPO polymers are used as specialty rubber and represent only a small worldwide demand of about 1000 t/a. The crystalline polymer has a unit cell (see Table 2) that contains two chains in a bowed zigzag conformation, with the methyl group of one molecule located between the ether oxygen and methylene group of the adjacent molecule.

PPO is soluble in most organic solvents. Very low molecular mass polyols (<1000) are insoluble in aliphatic hydrocarbons such as hexane due to the high hydroxyl content. However, polyols with such high hydroxyl contents do have some solubility in water. Mark – Houwink constants for the intrinsic viscosity/molecular mass relationship $[\eta] = K M^a$ are given in Table 3.

Although not so thoroughly studied as those of poly(ethylene oxide), association complexes

Table 2. Crystal data for poly(alkylene oxides)

	Poly(ethylene oxide) [13–15]	Poly(propylene oxide) [16], [17]	Poly(tetramethylene oxide) [18–21]
Unit cell	Monoclinic	Orthorhombic	Monoclinic
a, nm	0.796	1.04	0.548–0.561
b, nm	1.311	0.467	0.873–0.892
c, nm	1.939	0.716	1.207–1.225
β	124.8°		134.2–134.5°

Table 3. Mark – Houwink constants for poly(alkylene oxides)

Solvent	Temperature, °C	$K \times 10^5$	a	Approximate molecular mass range	Average molecular mass	Reference
Poly(ethylene oxide)						
Water	30	12.5	0.78	10^4–10^7	Weight	[25]
Water	35	6.4	0.82	10^4–10^7	Weight	[26]
Aq. 0.45 M K_2SO_4	35	130	0.50	10^4–10^7	Weight	[26]
Aq. 0.39 M $MgSO_4$	45	100	0.50	10^4–10^7	Weight	[26]
Benzene	25	39.7	0.69	8×10^4–5×10^6	Weight	[27]
Carbon tetrachloride	20	69	0.61	200–10 000	Number	[28]
Toluene	35	145	0.70	400–4000	Number	[29]
Poly(propylene oxide)						
Acetone	25	75.5	0.56	1000–4000	Number	[30]
Benzene	20	11.1	0.77	700–3300	Number	[31]
Benzene	25	11.2	0.77	3×10^4–7×10^5	Weight	[32]
Toluene	20	20.8	0.72	700–3300	Number	[31]
Toluene	25	12.9	0.75	3×10^4–7×10^5	Weight	[32]
Poly(tetramethylene oxide)						
Benzene	30	131	0.60	3×10^4–10^6	Weight	[33]
Cyclohexane	30	176	0.54	3×10^4–10^6	Weight	[33]
Ethyl acetate	30	42.2	0.65	3×10^4–10^6	Weight	[33]
Toluene	28	25.1	0.78	3×10^4–10^5	Number	[34]

of poly(propylene oxide) are also known. These complexes are formed with a variety of salts such as lithium perchlorate [42] and metal halides, particularly chlorides [43]. Complexes of propylene oxide – ethylene oxide block copolymers with sodium and lithium salts exhibit marked increases in electrical conductivity [44] as compared to the uncomplexed copolymers.

Tetrahydrofuran can be polymerized to high molecular mass, but the commercially available poly(tetramethylene oxide) diols have molecular masses of ca. 650–3000 and a narrow molecular mass distribution. Although these polyols are usually crystalline in nature, their narrow molecular mass distribution [45] makes them easy to use, since even partial melting yields a product with effectively the same molecular mass distribution as that of a completely melted product. The crystalline polymer has a monoclinic unit cell whose characteristic dimensions are given in Table 2.

Solvents for PTMO, which has a solubility parameter of 17.3–17.6 [46], include aromatic hydrocarbons such as benzene and toluene, chlorobenzene, dichloromethane, chloroform, carbon tetrachloride, esters such as ethyl acetate, and nitrobenzene. Low molecular mass products are soluble in acetone, alcohols, and similar polar solvents. The polymers are insoluble in aliphatic hydrocarbons such as heptane, hexane, pentane, and petroleum ether. Only cursory studies of association complexes of PTMO have been conducted [43].

Chemical Properties. Poly(alkylene oxides) are chemically characterized as usually having primary (PEO and PTMO) and secondary (PPO) hydroxyl end groups [47]. PEO and PPO have been prepared with a variety of end groups including allyl or propenyl ethers, which arise during polymerization of ethylene oxide and propylene oxide through the termination reaction [48]; carboxyl [49], [50]; amine [51]; cyano [52]; and vinyl ether [53]. Alkyl or aryl ester terminated PEOs are used as nonionic surfactants [54], [55], and alkoxy-terminated PEOs prepared from alcohols or other monohydroxyl compounds are used for similar purposes as well as in cosmetic and pharmaceutical preparations. In addition to primary hydroxyl termination, PTMOs have been prepared with a majority of primary amino terminal groups [56]. Isocyanate-terminated poly (propylene oxides) and poly(tetramethylene oxides) are known as isocyanate-terminated prepolymers for preparation of polyurethanes.

Copolymers of various types can be prepared from the alkylene oxides. The best known of these are the polyurethanes, though they are not normally prepared from the poly(ethylene oxides). Polyurethanes are formed in a rearrangement

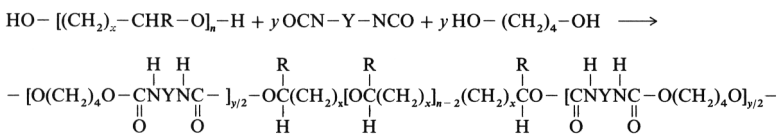


Figure 1. Formation of polyurethanes

reaction from poly(alkylene oxide) polyols, short chain diols such as 1,4-butanediol and ethylene glycol, and multifunctional isocyanates. The reaction takes place at relatively low temperatures, including room temperature, as depicted in the general, idealized manner (Fig. 1) where Y represents the residue of a polyfunctional isocyanate without its isocyanato groups. (In this generalization, it should be noted that the starter molecule for the poly(alkylene oxide) is omitted. If the alkylene oxide involved were propylene oxide, on the average both end groups would have been secondary hydroxyl groups.)

This unit would be the average repeating unit in the final polyurethane. A wide variety of isocyanates are used, including toluene-2,4-diisocyanate, 4,4′-diphenylmethane diisocyanate and its polymeric forms, 4,4′-dicyclohexylmethane diisocyanate, and isophorone diisocyanate. The latter two isocyanates are used when light-stable polyurethanes are required.

Urethane acrylates are formed by preparing an isocyanate-terminated prepolymer and then capping it with a hydroxyalkyl acrylate. These acrylate-terminated oligomers are widely used in radiation curable coatings.

Isocyanate-terminated PTMO polyols have been marketed as Adiprene (Du Pont) and Vibrathane (Uniroyal) precursors. Block copolymers of poly(tetramethylene oxide) and poly (butylene terephthalate) are marketed as Hytrel (Du Pont) for a variety of end uses.

Other copolymers include the very important ethylene oxide – propylene oxide copolymers [57], which occur in random, block, and graft form. Random copolymers are usually prepared from mixtures of monomers, and block copolymers by alternately feeding the two monomers. Block copolymers are often used as surfactants, metal lubricants, and functional fluids. Most of the block copolymers have poly(ethylene oxide) as the hydrophilic block and poly(propylene oxide) as the hydrophobic block. Other hydrophobic blocks include poly(styrene oxide), poly (tetramethylene oxide), and polystyrene [58]. ABA block copolymers of poly(1-proline) and amine-terminated PEO [59], as well as those of poly(ϵ- caprolactone) [60] and polyesters [61] grown onto hydroxyl-terminated PEO, have been prepared. A well-known graft copolymer, hydroxyethyl cellulose (→ Cellulose Ethers) [62], [63] is formed by swelling cellulose in a caustic solution and then adding ethylene oxide to the hydroxyl groups of the anhydroglucose units. Silica [64], gelatin and collagen [65], and chitin [66] are other polymeric substrates to which ethylene oxide has been grafted. Low molecular mass PEOs terminated with 1,2,4-triazoline-3,5-dione have been grafted onto polybutadiene [66].

A particularly useful class of grafted poly (propylene oxide) polyols was discovered in 1966 [67], [68]. These so-called polymer polyols are composed of vinyl polymers (e.g., acrylonitrile, styrene) and copolymers which are grafted to PPO or to PEO- capped PPO. They are produced by adding the vinyl monomers to the PPO polyol and dispersing them by agitation. A catalyst is then added to polymerize the vinyl monomers, which are believed to graft or partially graft to the polyol. The polymer polyol retains the end-group hydroxyl functionality, which is thus available for reaction with, for example, isocyanates. The vinyl polymer, which is incompatible with the polyol, is present in the form of a stable dispersion that acts as a reinforcing filler. These polymer polyols are used to manufacture polyurethane foams that have enhanced moduli while maintaining other desirable characteristics. Commercial products contain either grafted polyacrylonitrile or acrylonitrile – styrene copolymers, and they are used in high-resiliency automotive seating [69], microcellular elastomers [70], and other high-performance applications.

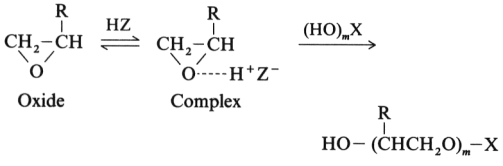
A deficiency of polyethers is their susceptibility to oxidation. PEO degrades by an autoxidation mechanism that is associated with formation and cleavage of intrachain hydroperoxides [71], [72]. Mechanical actions such as high shear can also cause degradation [73].

Hydroperoxide formation is facilitated by heavy metal ions, strong acids, and ultraviolet light. PPO and PTMO degrade by both chain scission and cross-linking [74], [75]. A number of investigations indicate that aromatic compounds such as substituted phenols, cresols, and quinones [76–78], mixtures of aliphatic amines and dihydric phenols (e.g., hydroquinone, *tert*-butylhydroquinone) [79], carbamates [80], and similar compounds function as stabilizers. A prime stabilizer for the poly(alkylene oxides) is 2,6-di-*tert*-butyl-4-methylphenol. Stabilization during storage is usually effected with 200–300 ppm of the stabilizer. However, in end uses involving solutions or slab stock polyurethane foam produced in bun form [1, p. 237] from poly(propylene oxide) polyols, 1000–5000 ppm are used to compensate for the long times at high temperature that are encountered due to retention of the heat of polymerization caused by the excellent insulation properties of the foam.

3. Production

Ethylene oxide was first polymerized in 1863 by WURTZ [81], who heated the oxide with water in a sealed tube. Earlier, in 1859, LOURENÇO [82] had obtained the polymer from ethylene glycol and ethylene bromide. Seven decades later STAUDINGER and LOHMANN [83] prepared a number of polymers with a variety of catalysts, including alkali and alkaline earth metals.

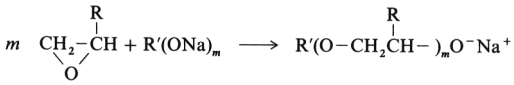
There are three main ring-opening reactions for the polymerization of ethylene oxide and propylene oxide: acid, base, and coordinate initiation. Acid or cationic initiation [84–86] with an acid, HZ, involves addition of an active-hydrogen compound such as an alcohol or glycol, $(HO)_mX$ ($m = 1 - 4$), to the 1,2-epoxide ring. In the initiation step, an oxonium complex forms and ring opening takes place by cleavage of the oxygen – carbon bond to form an initiated species that is available for propagation.



In the propagation step, n molecules of oxide are added to give a polymer having the formula $HO-[(CHRCH_2O)_n]_m-X$. Termination can occur by proton transfer, which yields an unsaturated product, or by anion transfer, which generates the starting acid.

Brønsted or Lewis acids such as $AlCl_3$, $SnCl_4$, PF_6, and BF_3 are used as initiators. The reaction is very fast, molecular mass is relatively low, and molecular-mass distribution is broad.

Base or anionic initiation [87–89] takes place in the following manner, where R′ is usually an alkyl group.



Propagation takes place in a manner similar to that described above. Termination can be by hydrogen abstraction from the backbone, which results in terminal unsaturation and formation of a new initiation site, or by rearrangement of the active species.

Polymerization rates for the two mechanisms when perchloric acid and sodium methoxide are used are given in Table 4 for a few selected alkylene oxides.

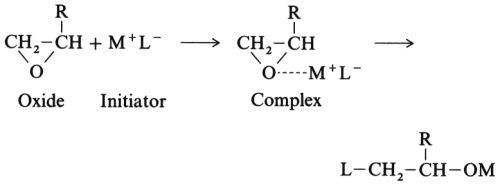
Anionic initiators are usually metal alkoxides such as sodium or potassium methoxide or ethoxide. The reaction is usually slower than that obtained with acid initiation, except for epichlorohydrin and glycidol [90], [91]; relatively high molecular masses can be obtained and the molecular mass distribution is relatively narrow.

Ionic coordinative polymerization [92–95] involves a complex of a metal, M, such as Al, Sn, Fe, Mg, Li, etc., with ligands, L (e.g., OH, OR, Cl) that coordinates in an ionic manner with the oxygen atom of the epoxide. Complexation is followed by nucleophilic attack by the

Table 4. Polymerization rate for selected alkylene oxides relative to ethylene oxide [90], [91]

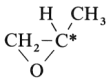
Oxide	Initiator	
	Perchloric acid	Sodium ethoxide
Epichlorohydrin	0.065	4.8
Ethylene oxide	1.0	1.0
Propylene oxide	54	0.5
Isobutylene oxide	5100	0.06

ligand, which results in opening of the oxirane ring to give an initiated species that can undergo propagation to form the polymer chain.

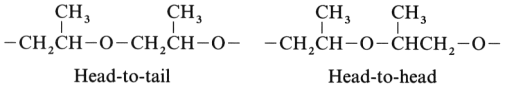


There are two categories of ionic coordination initiators [94], [96]. Initiators in the first category involve the formation of metal – oxygen coordination bonds, and those in the second category are alkaline earth compounds that have an anionic surface capable of coordinating with the oxide monomer.

In the case of propylene oxide, the monomer has an asymmetric carbon atom (C*)



and when the ring is opened this asymmetric center is incorporated in the polymer chain. PPO can contain both head-to-tail and head-to-head sequences.

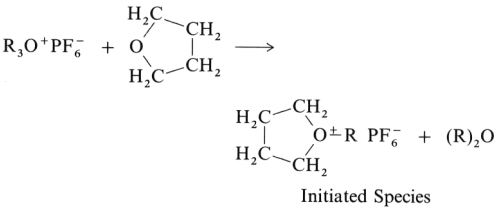


The head-to-tail sequences are formed by the expected carbon – oxygen cleavage between the methylene group and the oxygen atom of the epoxide, whereas the head-to-head sequences occur when unexpected cleavage takes place between the methyl-substituted carbon and the oxirane oxygen. Up to 30 % head-to-head structure has been found in certain polyoxypropylenes [97], [98].

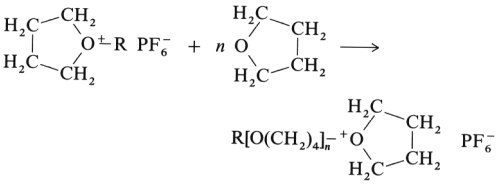
Tetrahydrofuran was first polymerized by MEERWEIN and KRONING in 1937 [99], [100]. An I.G. Farbenindustrie patent [101] indicates that polymers of this monomer were the subject of numerous investigations from 1939 to 1943. Ring strain, a necessity for favorable polymerization, is small in this monomer compared to other cyclic ethers [102], and thus THF has less tendency to polymerize than ethylene oxide and propylene oxide. Although commercial polymers are dihydroxyl functional and low in molecular mass, a high molecular mass polymer with a melting point above 100 °C has been reported [103].

THF is a nucleophilic monomer that forms a tertiary oxonium ion during initiation and only polymerizes by a cationic ring-opening mechanism [104–108]. A variety of mechanisms for formation of the tertiary oxonium ion are known. These include direct alkylation or acylation, in situ formation from reactive organic halides and metal salts or Lewis acids, and direct addition of strong protic acids to the oxygen atom. For example [109], direct alkylation of the monomer by exchange with trialkyloxonium salts illustrates the initiation reaction.

Propagation then takes place by collisions between the initiated species and THF, whereby

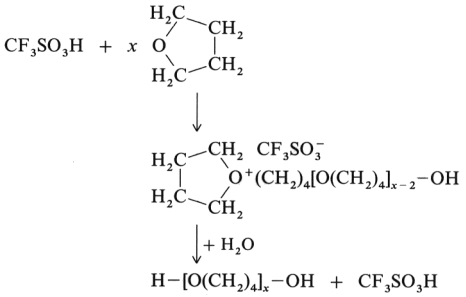


only collisions that occur at the α-carbon atom of the THF molecule result in propagation.



Water, oxygen, and other nucleophilic reagents can be used to terminate the polymerization.

Industrial poly(tetramethylene oxides) are hydroxyl terminated, and control of the termination reaction is important to the process. Hydroxyl groups, which have a profound effect on molecular mass, can be formed if strong protic acids are used to form the initiated species [110], [111]. The proton gives rise to an hydroxyl group on the end of the propagating species, and when water is used to terminate the polymerization, a second hydroxyl group is formed and the initiator acid is regenerated.



4. Toxicity [112]

Poly(ethylene oxides) have a very low single-dose oral toxicity that decreases with increasing molecular mass. Single-dose oral LD_{50} values in g/kg, for polymers of 200, 1000, 2000, and 6000 are, respectively, 34, 45, 45, and > 50 for male rats; 28, 32, > 50, and > 50 for female rats; 14, (not available), > 50, and > 50 for male rabbits; and 34, > 50, > 50, and > 50 for mice. PEOs of 400, 1540, and 4000 molecular mass were fed to dogs at a 2 % level in the diet with no adverse effect. When fed to rats at 2 %, PEO of 400 molecular mass had no effect, and at 4 % PEOs of 1540 and 4000 molecular mass had no effect. Doubling the dietary amounts for rats resulted in weight loss, an increase in liver weight, and slight histologic changes in the liver with the 400 compound, an increase in liver weight with the 1540 compound, and weight loss with the 4000 compound. Feeding of a 4 000 000 molecular mass compound at 5 % (rat) and 2 % (dog) diet had no detectable effect after 24 months. Testing with a radioactively labeled sample of the high molecular mass PEO indicated no significant absorption of the polymer from the gastrointestinal tract of the rat or dog.

PEOs do not appear to cause appreciable irritation to the eyes of rabbits. Skin irritation is apparently absent, which is attested to by the wide use of these compounds in cosmetic preparations. Overall, there are no reported adverse effects or human injuries from handling of PEOs [111].

Poly(propylene oxides) of molecular mass ca. 200 – 2000 have a single-dose oral toxicity that is noticeable, and they have mild eye irritability. They are not irritating to the skin, and even though there is some absorption through the skin, they do not appear to present a serious industrial health hazard. Inhalation of mists, particularly of the low molecular mass compounds (ca. 400 to 1200), could be hazardous. The low molecular mass compounds are rapidly adsorbed from the gastrointestinal tract and are potent CNS stimulants that readily cause cardiac arrhythmia. Excitement and convulsions are apparent within minutes after oral administration. Higher molecular mass compounds (>2000) are very low in toxicity by all administration routes and do not stimulate the CNS. Oral LD_{50} values (rat) in g/kg for polymers of 400, 1200, and 4000 molecular mass are 1.6, 1.4, and >15 for males and 2.1, 1.1, and >15 for females, respectively.

Poly(tetramethylene oxides) are commercially available in four number-average molecular masses (650, 1000, 2000, and 2900) as dihydroxyl functional compounds [113], [114]. Acute oral toxicity (LD_{50} in g/kg) for albino rats was 11.3, 18.8, and >34 for the 650, 1000, and 2000 molecular mass polyols, respectively. Acute dermal toxicity in albino rabbits was 8.37, 10.25, and >10.25 g/kg for the same polyols. The poly-ols are rated as being minimally irritating to the eyes and skin of albino rabbits [112]; however, a Material Safety Data Sheet indicates that the products may irritate the skin and eyes [115].

5. Handling

Most manufacturers and suppliers of poly (alkylene oxides) have detailed, current handling methods available for bulk, drum, and laboratory handling and storage, which should be consulted when working with the chemicals.

The poly(ethylene oxides) range from liquids at low molecular mass to hard waxes at moderate molecular mass, and to tough thermoplastics at high molecular mass (> ca. 100 000). They are not corrosive to most common construction materials. Although not strongly corrosive to copper and its alloys, some discoloration may occur if the compounds are kept in contact with copper- containing materials for prolonged times. Aqueous solutions of PEOs are corrosive to regular carbon steel; hence, stainless steel should be used for their storage. Tanks for bulk storage are usually made of plain carbon steel. For smaller quantities, lined steel drums are used to minimize the pickup of traces of iron [116]. When short storage times of a month or less are involved, storage under air is

acceptable. For prolonged storage, particularly in hot climates or under heated conditions, the products should be kept under an inert (nitrogen) atmosphere. Since PEOs are hygroscopic, dry conditions are important for most uses. PEOs have low vapor pressures and are not fire hazards unless high temperatures are involved. For example, polymers of molecular mass 200, 1000, 4000, and 9000 have Cleveland Open Cup flash points of 171–182 °C, 254–265 °C, 271 °C, and 271 °C, and Cleveland Closed Cup flash points of >148 °C, >177 °C, >177 °C, and >177 °C, respectively.

The poly(propylene oxides) are usually liquid, stable, noncorrosive compounds that have a very low vapor pressure. They are preferably stored at temperatures below 50 °C, usually in carbon steel tanks. However, if there is concern about the pickup of iron, tanks protected with a baked phenolic coating can be used [117]. PPOs should be blanketed with dry air or nitrogen to prevent absorption of moisture during storage. They are usually dried before use in polyurethane manufacture. Nitrogen is preferred for prolonged storage or storage at elevated temperature. They represent fire hazards only at high temperatures. For example, 400, 2000, and 4000 molecular mass polymers have Cleveland Open Cup flash points of 166 °C, 229 °C, and 229 °C, respectively.

The poly(tetramethylene oxides) are liquids or low-melting solids under ambient conditions. Mild steel and phenolic-lined steel tanks are suitable for storage. These products are not considered fire hazards unless high temperatures are encountered, and they have a Tag Open Cup flash point of >163 °C. The compounds are unstable and may decompose at temperatures above 100 to 200 °C or at lower temperatures if in contact with high surface area substrates such as fibrous insulation [115]. When they decompose, very flammable tetrahydrofuran and carbon monoxide can be released.

6. Uses

Low molecular mass poly(ethylene oxides) (M<800) are usually used as intermediates for the manufacture of fatty acid ester surfactants that are used in a variety of formulated products. Illustrative of these products are soap or detergent suds control agents, foam stabilizers, fabric softeners, and optical brighteners. Typical detergents contain up to 20 % of a nonionic or anionic surfactant. Polymers with molecular mass of ca. 1000–2000 are low-melting waxes used in pharmaceutical ointments, cosmetic creams, and lotions. Their low toxicity, nonirritating nature, and smooth, creamy texture along with liquefaction at body temperatures make them particularly useful in cosmetic and pharmaceutical applications such as formulations for salves, suppositories, and ointments. Esters of these compounds are used as thickeners in cosmetic formulations.

The medium molecular mass PEO compounds, up to about 20 000, are hard, brittle waxes. They are used as adhesives, binders, plasticizers, molding compounds, wood impregnants, stiffening agents, and metal-working lubricants. Various PEOs are used in artifact preservation, particularly for items recovered after prolonged water immersion [118], [119]. In particular, copolymers of ethylene oxide and propylene oxide are often used in metal-working fluids and as quenchants, lubricants, and hydraulic fluids.

High molecular mass PEOs are used as textile sizes, as hydrodynamic friction reduction agents, in cosmetics and toiletries, as water-soluble films for seeds, in packaging, in adhesives, and in dentistry. The ability of the high molecular mass polymer to reduce hydrodynamic friction has led to applications in fire fighting and municipal sewage discharge control. The polymer is so effective in reducing the friction of water that it has been banned from use in competitive skiing and boating, where it markedly improved speed when incorporated into waxes and polishes. The association complexes of poly(ethylene oxide) have found use in controlled release of drugs, as adhesives, in artificial kidneys, and microencapsulation.

Poly(propylene oxides) are used as plasticizers, lubricants, solvents, softening agents, antifoaming agents, surface active agents, mold release agents, hydraulic fluid compositions, quenchants, and as intermediates in the production of resins (polyurethanes and alkyds). The largest use of the poly(propylene oxides) and ethylene-oxide-capped PPO polyols is in the production of polyurethane foams

and elastomers. The main polyurethanes are those based on toluene-2,4-diisocyanate and 4,4′-diphenylmethane diisocyanate, although light-stable versions based on cycloaliphatic polyisocyanates are made for specialty end uses. The polyurethanes are used as automobile seating, automotive crash pads, furniture cushioning, insulation, bedding, packaging, carpet underlay, molded parts, and many other applications.

The low molecular mass poly(tetramethylene oxide) polyols are used in coatings, to make block copolymers that are used for fabricated parts, and polyurethanes used as elastomeric fibers (spandex fibers). PTMOs have FDA approval for use in polyurethanes and adhesives that come into direct contact with dry foods [120]. The fibers have low hysteresis loss, very good tensile strength, and good tear and abrasion resistance. They are particularly useful for clothing, support garments, knitwear, swimwear, and other similar end uses. No commercial uses are known for high molecular mass PTMO.

7. Economic Aspects [121]

Estimates of the worldwide production of poly (alkylene oxide) polyols for polyurethanes is given in Table 5. Poly(propylene oxide) polyols account for about 95 percent of the polyols produced for polyurethanes, and poly(tetramethylene oxide) polyols account for about 2 percent of the total.

It is difficult to estimate amounts produced for nonpolyurethane end uses since major companies use the same facilities to produce for both markets. The production for nonpolyurethane end uses is given in Table 5. The majority of the polyol for nonpolyurethane use is for surface active agents (40 %) and for functional fluids and lubricants (31 %). The remainder is used in a wide variety of end uses (see Chap. 6). In the United States, production is about 18.6 % poly(propylene oxides), 31.4 % poly(ethylene oxides), and 50 % ethylene oxide – propylene oxide copolymers. In Western Europe production is about 38 % PPO and PEO, and the remainder copolymers. In Japan production is about evenly divided between PPO, PEO, and copolymers.

The largest manufacturers are:

United States	ARCO, BASF, Dow, E. R. Carpenter, Mobay, Olin, and Union Carbide
Western Europe	ARCO, BASF, Bayer, Dow, Montedipe, and Shell
Japan	Asahi Denka, Asahi Olin, Dow, and Mitsui Toatsu
Republic of Korea	Korea Polyol and Miwon
Taiwan	Chiunglong Petrochemical

Although production of poly(tetramethylene oxide) polyols is included in the production values for polyols as given in Table 5, production of this specialty polyol is delineated by company in Table 6. Polyurethane fibers and elastomers produced from these polyols have tensile properties as good as or better than those of polyesters, together with especially good hydrolytic stability and excellent low hysteresis loss [122].

Table 5. Major worldwide production or consumption of poly (alkylene oxide) polyols [121]

Country	Production, 10^3 t
Production for polyurethane end uses	
Western Europe	931
United States	835
Japan	260
Korea and Taiwan	54
Total	2080
Production for nonpolyurethane end uses	
United States	159
Western Europe	92
Japan	57
Total	308

Table 6. Worldwide production of poly(tetramethylene oxides) [121]

Company	Production, 10^3 t	Trade name
United States		
Du Pont	30	Terethane
QO Chemicals	11	Polymeg
Wesern Europe		
BASF	4	PolyTHF
Du Pont (Netherlands)	30	Terethane
Japan		
Hodogaya Chemical	3	
Mitsubishi Kasei	4	
Sanyo Chemical	1	

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Polyoxymethylenes

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1. Introduction

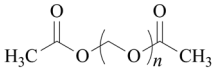
Polyoxymethylenes (POM) are thermoplastically processable plastics, whose structure is predominantly composed of unbranched chains of oxymethylene units:



Polyoxymethylene

The term polyacetals is also commonly used for such products. The first systematic investigations of the production and properties of polyoxymethylenes were carried out by Staudinger and Kern [1] in the 1920s. Basic properties such as the relatively high softening temperature of ca. 175°C, high crystallinity, and the ability to form films and fibers were already recognized at that time. However, the insufficient thermal stability of polyoxymethylenes at processing temperatures prevented any practical use of the products.

Following intensive work begun at the end of the 1940s, DuPont made a breakthrough in 1956 with the production of a high-molecular, thermally stable polyoxymethylene that could be processed thermoplastically [2]. The decisive step consisted of blocking the unstable hemiacetal terminal groups by esterification with acetic anhydride. A production plant with ca. 7000 t/a capacity came on stream in the United States in 1959. The product was introduced on the market under the name Delrin.

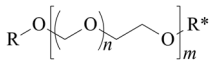


Polyoxymethylene (homopolymer)

A few years later, Celanese in the United States and Hoechst in Europe succeeded in producing

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a thermally stable acetal copolymer [3, 4] by copolymerizing trioxane with small amounts of cyclic ethers or cyclic acetals. Compared with homopolymers with blocked terminal groups, the copolymers have the advantage that they are resistant to alkalies, though they have a somewhat lower crystallinity.



R, R*: $-CH_3$, $-CH_2CH_2OH$ Polyoxymethylene (copolymer)

Production of the acetal copolymer Celcon came on-stream in 1962 in a 7000 t/a plant at the Celanese plant in Bishop, Texas. The year before Celanese and Hoechst in Germany had already established the joint venture Ticona Polymerwerke, which commenced production of the acetal copolymer Hostaform in 1964. In 1962 Celanese and Daicel formed the joint company Polyplastics in Japan and commenced production of the acetal copolymer Duracon. This was followed in the 1970s by Ultraform (established jointly by BASF and Degussa; product name: Ultraform), the Asahi Chemical Industry Co. (product name: Tenac), and the Mitsubishi Gas Chemical Co. (product name: Iupital). Further plants were built in Poland (product name: Tarnoform) and the Soviet Union. In the 1980s and early 1990s new plants were constructed mostly in Asia (Korea Engineering Plastics: Kepital; Lucky-Goldstar: Lucel; Taiwan Engineering Plastics).

New capacities are coming on-stream in the new decade in China, e.g., PTM Engineering Plastics (joint venture of Polyplastics, Ticona and Mitsubishi Eng. Plastics), Shanghai Bluestar New Chem. Materials and from the Yuntianhua Group. It was also announced [5] that Ibn Sina, a joint venture between Celanese and Sabic, is planning to build a production plant in Jubail, Saudi Arabia.

Worldwide demand in the recession year 2009 [5] was at ca. 650×10^3 t, with ca. 25% in Europe, 20% in USA and 55% in Japan and China.

Worldwide ca. 27% of the material are used in automotive applications (biggest single market segment for POM).

Polyoxymethylenes are now widely used in areas that were for a long time the preserve of metals. Their low specific weight (compared with metals) and economic processing together with an advantageous combination of mechanical, thermal, electrical, and chemical properties have led to a wide range of applications. In Asia, especially China, main applications are in consumer articles as well as in electronic areas.

Further details of production, properties, processing, and uses of polyoxymethylenes can be found in [6–8].

2. Physical and Chemical Properties

Important physical properties of homopolymers are summarized in [9], and those of copolymers in [10, 11]. Some physical data for polyoxymethylene are given in Table 1 and [12, 22]. Materials properties can be obtained from the Western European producers (Material Data Bank CAMPUS: Computer Aided Material Preselection by Uniform Standards [23]).

2.1. Morphology

Polyoxymethylene crystallizes in a hexagonal structure with the lattice constants a=474 pm and c=1739 pm. The polymer chains have a helical conformation with an identity period of 9/5 [24, 25].

The crystalline density is 1.49 g/cm^3 [24], and that of the amorphous state 1.324 g/cm^3 (homopolymer) and 1.320 g/cm^3 (copolymer) [15]. The density of the commercially available partially crystalline polyacetals is 1.42 g/cm^3 and 1.41 g/cm^3 for homopolymers and copolymers, respectively [9, 10, 26].

The crystallinity of polyoxymethylenes varies between 50% and 80%, depending on the comonomer content, molecular mass, and sample pretreatment. Crystallinities of 64–69% for homopolymers and 56–59% for copolymers were found for identical thermal histories [15]. The degree of crystallinity can be increased by thermal posttreatment. Considerably higher values for the crystallite melting point and degree of crystallinity have been reported for the as-polymerized virgin polymer [27].

During crystallization from the melt spherulitic superstructures form. The size of the spherulites depends, among others, on the

Table 1. Physical properties of polyoxymethylene

Property	Value	Reference
Activation energy of polymerization, kJ/mol		
of cationic polymerization of trioxane in dichloroethane	79.5	[13]
in the solid state	36	[13]
Ceiling temperature, °C		
polymerization of formaldehyde (gas) → polyoxymethylene (solid) at 1 bar	116–137	[12]
Coefficient of linear thermal expansion, K^{-1} (ASTM D 696)		
copolymer	0.85×10^{-4}	[14]
homopolymer	0.81×10^{-4}	[14]
Crystallinity, %		
Delrin 550, 20°C, from density data	68.7	[15]
Hostaform C 9020, 20°C, from density data	58.7	[15]
Density, g/cm^3		
homopolymer, Delrin 550, 20°C	1.435	[15]
copolymer, Hostaform C 9020, 20°C	1.416	[15]
Dielectric constant at 10^3 Hz (DIN 53 483, ASTM D 150–59 T)	3.6–4.0	[12]
Dielectric loss tan δ at 10^3 Hz	$(15–50) \times 10^{-4}$	[12]
Dielectric strength, kV/mm (DIN 53 481, 50 Hz, 0.5 kV/s, 0.2 mm film)	50–70	[12]
Enthalpy, kJ/kg		
homopolymer, 300 K	222.5	[16]
copolymer, 300 K	211.4	[16]
Entropy, kJ kg^{-1} K^{-1}		
homopolymer, 300 K	1.487	[16]
copolymer, 300 K	1.439	[16]
Heat capacity, J mol^{-1} K^{-1}		
homopolymer, 300 K	42.79	[16]
copolymer, 300 K	41.11	[16]
molten polyoxymethylene, 300 K	57.67	[17]
Heat distortion temperature under load, °C (ASTM D 648)		
homopolymer	124	[12]
copolymer	110	[12]
Heat of combustion of polyoxymethylene, kJ/mol	-511.6 ± 1.7	[18]
Heat of fusion, kJ/kg		
homopolymer	236	[19]
copolymer	181–192	[20]
Heat of polymerization, kJ/mol		
formaldehyde (gas, 1 bar, 298 K)	−55 to −72	[12]
trioxane (liquid → solid)	−22.6	
Melting point, °C		
Delrin 500	175	[9]
Hostaform C 9021	164–167	[10]
Specific volume, cm^3/g		
Delrin 550, at 20°C	0.6968	[15]
Hostaform C 9020	0.7064	[15]
Surface resistivity, Ω		
homopolymer (ASTM D 257)	2×10^{13}	[14]
Thermal conductivity at 20°C (VDE 0304), W m^{-1} K^{-1}	0.292	[21]
Volume resistivity (film 0.2 mm, DIN 53 482/ASTM D 257–61), Ω · cm	$> 10^{15}$	[10]
Water absorption (ASTM D 570), %		
after 24 h immersion		
homopolymer	0.25	[14]
copolymer	0.22	[14]
equilibrium, 50% R.H.		
homopolymer	0.2	[14]
copolymer	0.16	[14]

crystallization temperature and number of nucleation centers. The overall crystallization rate and number of spherulites formed can be increased by adding nucleation agents (see Section 3.4).

2.2. Mechanical Properties

Polyoxymethylenes exhibit high hardness and rigidity, high toughness down to −40°C, high thermal dimensional stability, low water absorption, good electrical and dielectric properties, good elasticity, favorable slip and wear behavior, and are easy to process. This combination of favorable properties means that polyoxymethylenes are widely used construction materials.

The structural difference between homopolymers and copolymers results in a lower degree of crystallinity for copolymers. As a consequence homopolymers have about 10–12% higher hardness, rigidity, and strength [6]. However, copolymers possess advantages with regard to thermal and chemical stability.

Standardized test methods are used to determine the physical properties. Since polyoxymethylenes are generally processed by injection molding, the mechanical properties are usually measured on injection-molded test specimens. Slight differences in test specimen production and mechanical testing can result in changes in the measured values. For this reason it is only possible to a limited extent to make an absolute comparison of the property values given in the manufacturers' product data sheet [9–11]. Further details are given in [22].

The mechanical properties are measured by the conventional methods used for polymer materials (→ Plastics, Properties and Testing). Test methods and values can be obtained from the brochures of the raw material manufacturers [9–11]. See also Table 1 as well as [22] and Chapter 5.

The suitability of a structural component for a given purpose depends not only on the mechanical properties of the selected raw material, but to a large extent on its structural form and shape [28, 29]. In addition there are influences resulting from the production and environmental conditions, as well as time, temperature, and stress level.

2.3. Thermal Properties

The thermal properties of polyoxymethylenes essentially depend on the crystallinity and chemical structure, which are also responsible for differences in the thermal behavior of homopolymers and copolymers.

Homopolymers have higher crystallite melting points (175°C) than copolymers (164–167°C). Further information on structural changes with temperature are obtained from the torsion vibration test (DIN 53 445), from the temperature function of the mechanical shear modulus G', and the mechanical loss factor d. The transition region (relaxation region) at −60°C represents an important embrittlement limit under impact conditions. A second relaxation region exists at 0°C. A third, subsidiary maximum above 100°C is attributed to molecular motion in the crystalline regions [22] and is important for the thermal dimensional stability.

The continuous use temperatures are, depending on the type of stress, about 90–110°C [22] and 80–100°C [30]. According to Underwriters Laboratory, Hostaform is permitted for use up to 80–105°C [10]. Experience shows that short-term thermal loading (several hours) up to 140°C is permissible [30].

The continuous use temperature is largely determined by thermal aging processes, which generally involve thermal-oxidative damage at high temperature. Thermal-oxidative decomposition as well as decomposition caused by acidic degradation products can be suppressed by adding oxidation stabilizers and costabilizers (see Section 3.4 and [31]).

Thermal stability and continuous use temperatures are, however, not accurately definable material-specific properties and must always be considered in the context of the relevant application.

Temperatures of 190–210°C are generally recommended for processing polyoxymethylenes. Higher temperatures can be used with shorter residence times (e.g., up to 230°C for copolymers) [6, 10].

The specific heat of copolymers is 1.47 kJ kg^{-1} K^{-1}, and the thermal conductivity is 0.31 W m^{-1} K^{-1} (at 20°C) [10]. Further thermal data are given in Table 1 and [12, 22].

2.4. Chemical Stability

Owing to their high degree of crystallinity, polyoxymethylenes exhibit good resistance to numerous chemicals. Copolymers are also resistant to strong alkalies. Polyoxymethylenes are not resistant to strongly acidic and oxidizing substances.

Only hexafluoroisopropanol and hexafluoroacetone sesquihydrate are suitable as solvents at room temperature. Most other solvents dissolve polyoxymethylenes only when the temperature is approaching its melting point; solvents include polar substances such as benzyl alcohol, dimethylformamide, γ-butyrolactone, and phenol [32].

Various investigations on the stability towards numerous chemicals have been published, for example [9–11].

Conventional organic solvents such as alcohols, esters, ethers, ketones, aliphatic and aromatic hydrocarbons, as well as perhalohydrocarbons do not attack polyoxymethylenes at room temperature even under prolonged contact. The mechanical properties are only slightly affected, and the degree of swelling is small.

The good resistance to all common fuels (regular, premium, also fuels containing 15–20% methanol, diesel), as well as to oils and greases, coolants, and brake fluids means that polyoxymethylenes are widely used as construction materials in the automotive sector [10, 33].

Polyoxymethylenes swell only very slightly in contact with water; the water absorption is 0.6% at 20°C, and 1.6% at 100°C [10]. Copolymers in particular are extremely stable at high temperatures. For example, the tensile strength decreases by only 25% after two years in boiling water. The copolymers are therefore widely used in washing machines and dishwashers, as well as in water boilers. Alkaline detergents and rinsing agents do not affect the stability of the copolymers. Polyoxymethylenes are generally not subject to stress-cracking.

As regards use in the sanitary sector, varying chlorine contents in tap water, as well as temperature and pressure fluctuations mean that the suitability must be individually assessed in each case.

2.5. UV and Weather Resistance

Polyoxymethylenes can be protected to a certain extent against UV radiation by the use of additives. Suitable UV absorbers include those based on benzophenone or benzotriazole derivatives. In practice, they are combined with HALS stabilizers, which give a synergistic effect. A further improvement can be achieved by adding carbon black or pigments such as titanium dioxide (see Section 3.4).

Weathering results in a loss of surface gloss, followed by so-called chalking, caused by a layer of degraded, low molecular mass polyoxymethylene. This layer protects deeper-lying layers, so that the reduction in the mechanical properties is greater at the start of weathering, but then decreases. The damage to thin-walled parts is thus greater than to thick-walled parts. The behavior of non-light-stabilized copolymers under natural and artificial weathering is described in [34]. Investigations of the mechanism are given in [35–38].

Various tests are used to evaluate the UV and weathering resistance. Artificial irradiation in the Xenotest and in the Fade-O-Meter produces similar results to natural weathering [37]. Weathering in the Florida test can, depending on the intended use, be performed in the open air or behind window glass. It is not possible to interconvert the various results.

Polyoxymethylenes are only moderately stable to γ-radiation. Medical equipment can be sterilized by using conventional radiation doses of 2.5×10^4 J/kg [10]. The deterioration in the mechanical properties increases with increasing radiation dose [39].

2.6. Permeability

Polyoxymethylenes are only very slightly permeable to many gases and solvents. In particular, the very low permeability to propane; butane; aliphatic, aromatic, and halogenated hydrocarbons; alcohols; and esters should be emphasized. The permeability to hydrogen, CO_2, water, and methanol [21, 33, 40] is higher. A comparison with other plastics is given in [22].

Numerous uses have accordingly been found for polyoxymethylenes; for example, cigarette

lighters, aerosol containers, and automotive parts in contact with fuels.

2.7. Fire Behavior

Polyoxymethylenes burn slowly with a pale blue flame, forming droplets. The external ignition temperature is 350°C, and the self-ignition temperature is 360°C.

According to Underwriters Laboratories polyoxymethylenes are classified in Class HB (UL Safety Standard 94). According to the U.S. Federal Motor Vehicle Safety Standard FMVSS 302 and DIN 75 200, the combustion rate does not reach the maximum permitted combustion rate of polyoxymethylenes at wall thicknesses of ≥1 mm, and accordingly use in automobiles is permitted. Further information on flammability can be found in [11].

A formulation with the classification V–0 is not known.

2.8. Optical Properties

Polyoxymethylene moldings are translucent to opaque-white, depending on the thickness. The light transmission of 2 mm thick injection-molded plates is 50%. The refractive index n_D^{20} is 1.48. The gloss depends mainly on the surface quality of the mold.

2.9. Electrical Properties

Polyoxymethylenes have good electrical insulation properties and a favorable dielectric behavior. This, together with the good mechanical properties, means that polyoxymethylenes are useful materials in electrical engineering.

The specific resistivity is $>10^{15}\ \Omega \cdot \mathrm{cm}$, and the surface resistance is $>10^{13}\ \Omega$. The relative dielectric constant ϵ_r is 3.6–4.0. Since the loss factor tan δ is low, high-frequency heating and high-frequency welding are not possible [10].

The dielectric strength describes the behavior under short-acting stress produced by high voltages. Values of 600–700 kV/cm have been measured for polyoxymethylene sheets [10].

Polyoxymethylenes generally do not accumulate static charge. Antistatic and electrically conducting grades have been developed for specialty uses (e.g., Hostaform C 27021 AS and Hostaform EC 140 XF or EC 270 TX [10]).

3. Production

3.1. Polymerization of Formaldehyde and Trioxane

The polymerization of formaldehyde and trioxane proceeds according to an ionic mechanism. Whereas formaldehyde can be polymerized anionically as well as cationically, trioxane, being a cyclic acetal, can be polymerized only under cationic conditions. Polymerization can be performed in the gas phase, liquid phase, in dispersion, and in solution. Trioxane also polymerizes in the solid state.

In practice homopolymers are produced by anionic polymerization of formaldehyde, while copolymers are mainly produced by cationic copolymerization of trioxane with cyclic ethers or cyclic acetals. Processes for producing copolymers that use formaldehyde as starting material have also been described [41].

A review of the historical development of polyoxymethylenes is given in [42–44]. Comprehensive summaries of the homopolymerization and copolymerization of trioxane can be found in [45–47].

For information on the most important process steps in the production of homopolymers and copolymers, together with numerous literature and patent references, see [48].

3.2. Homopolymers

Terminal-group-stabilized homopolymers of formaldehyde with adequate thermal stability were first developed by DuPont [2, 48–50].

The production process can be divided into the following steps:

1. Oxidation of methanol to formaldehyde
2. Purification of formaldehyde
3. Polymerization
4. Terminal group capping
5. Homogenization of the polymer in the melt; addition of auxiliaries

The production of formaldehyde from methanol is described in → Formaldehyde. The formox or silver catalyst process is usually used; see also [51]. The Asahi process, in which formaldehyde is prepared by oxidation of methylal rather than methanol [52] leads to higher formaldehyde concentrations [53].

High-purity formaldehyde is required for the polymerization step. Purification on an industrial scale can be performed, for example, by absorbing the reaction gases from the formox or silver catalyst process in cyclohexanol [54, 55]. Cyclohexanol hemiformal is formed from formaldehyde and cyclohexanol; water and other impurities are then removed by vacuum distillation. Vacuum distillation is followed by thermal cracking. The resultant formaldehyde gas can then be passed after further purification (e.g., removal of reactive impurities by partial polymerization [56, 57]) to the actual polymerization process [49]. Amines [57]; alkoxides [58]; ammonium and sulfonium salts [59]; metal carbonyls [60]; and phosphines and arsines are suitable initiators for anionic polymerization.

The high heat of polymerization (ca. 60–70 kJ/mol [12, 61]) must be removed. Suspension polymerization has proved convenient in practice. Aliphatic or cycloaliphatic hydrocarbons are suitable suspension agents, for which the same purity requirements apply as for the monomer.

The purified formaldehyde is added to a reaction vessel containing the suspension agent (e.g., cyclohexane) and initiator (e.g., tri-*n*-butylamine). The polymerization can be carried out at room temperature and under normal or reduced pressure. The polymer is formed as a fine suspension.

In the next step the thermally unstable hemiacetal terminal groups of the polymer are converted into alkyl or acyl groups. In particular esterification with acetic anhydride has become industrially important [2]. The reaction can, for example, be carried out in the presence of small amounts of sodium acetate as catalyst in boiling acetic anhydride.

This conversion stage is followed by several purification steps. Finally, the polymer powder is melted in extruders with the addition of antioxidants, costabilizers and other additives, and converted into granules.

Asahi has proposed a modified process in which acetic anhydride is used as a chain-transfer agent. Acetate-terminated polymers are obtained directly in the polymerization process [62].

3.3. Copolymers

The copolymer production process is divided into the following steps:

1. Oxidation of methanol to formaldehyde
2. Trimerization of formaldehyde to trioxane
3. Purification of trioxane
4. Copolymerization of trioxane with cyclic acetals
5. Removal of unstable terminal groups
6. Homogenization of the polymers in the melt; addition of auxiliaries

The production of formaldehyde is described in → Formaldehyde, Chap. 4.. The trioxane must satisfy strict purity requirements for the subsequent cationic polymerization. The concentration of compounds that are chain-transfer agents such as water, methanol and formic acid should be below 80 ppm. The final purification to polymerization grade trioxane is generally carried out by crystallization [63, 64] or distillation.

3.3.1. Polymerization of Trioxane

The production of POM copolymers can best be understood by a brief look at the mechanism of trioxane polymerization. A detailed discussion of the mechanism is given in [47].

Polymerization of trioxane takes place through a series of chemical reactions which can be categorized into initiation, chain propagation and chain termination.

3.3.1.1. Initiation

A large number of compounds may be used as initiators for the cationic polymerization. Important catalysts include

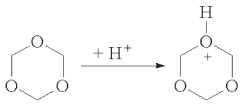
1. Lewis acids, such as BF_3, and their complexes (e.g., $BF_3 \cdot Bu_2O$) [65]

2. Protic acids such as perchloric acid, perfluoroalkanesulfonic acids, as well as their alkyl esters or anhydrides [66]
3. Heteropoly acids such as tungstophosphoric acid [67, 68]

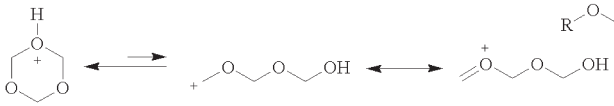
Carbenium salts such as triphenylmethyl hexafluoroarsenate [69], or oxonium compounds, and metal complexes [70].

The following describes the initiation process using protic acids:

Initiation starts with the formation of an acetal-oxonium ion:



Acetal-oxonium ions have the unique feature of isomerizing to oxocarbenium ions in a ring-opening reaction:



This reaction is made possible by the resonance stabilization of the oxocarbenium ions. Nonetheless the equilibrium of reaction (2) is shifted far to the left [71]

Oxocarbenium ions are the decisive species of all chemical reactions taking place during trioxane polymerization. They first react with the counterion and form an acetal ester [72]:



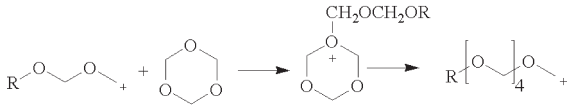
The equilibrium of this strongly exothermic reaction is far on the right side. At very low concentrations however a part of the ester dissociates. The order of magnitude of the oxocarbenium ion concentration can be estimated at 10^{-10} mol/L; the formation of the oxocarbenium ion is an entropy-driven process.

Reaction (3) can explain the strong influence of the counterion (X^-) of the acid as the equilibrium constant of reaction (3) strongly depends on the nature of X^-. Due to the high enthalpy of reaction (3) the equilibrium concentration of the oxocarbenium ion increases strongly with temperature.

Reaction (3) can be used to influence the activity of the initiator. Addition of X^- as salt of the corresponding acid reduces the concentration of the oxocarbenium ion and the speed of polymerization slows down. The activity of the initiator can be varied over a wide range in two ways: by changing the acid concentration and the salt-to–acid ratio. This "two-dimensional" initiator has proven valuable in the industrial production of POM [73].

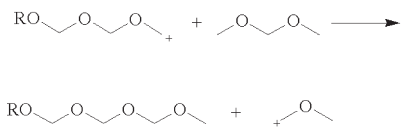
3.3.1.2. Chain Propagation

Again, the reactive species in the polymerization process is the resonance-stabilized oxocarbenium ion which reacts with trioxane to form an oxonium ion. The polymerization process continues via isomerization to an oxocarbenium ion.



3.3.1.3. Chain Termination by Chain Transfer

The molecular mass of POM is controlled by chain-transfer reactions. This is accomplished by the addition of acetals like methylal or butylal to the polymerization mixture [74]. Nearly all chains (>99.9%) are terminated by chain-transfer reactions. The oxocarbenium ion of the growing polymer chain reacts with methylal to form a polymer with a stable methoxy end group and another oxocarbenium ion which starts a new chain:



If all chains were terminated by chain transfer with methylal then all polymer chains would have stable methoxy end groups and the resulting polymer would be perfectly stable. But due to impurities in the monomer (water, methanol and formic acid) and because of a certain side reaction ("hydride shift") some chains have

unstable hemiacetal and formate end groups that are removed in a separate step by heat treatment (in a process called "hydrolysis").

A special case of chain transfer involves the polymer itself as chain-transfer agent. This transacetalization results in a Schulz–Flory distribution for polymer chain lengths and a statistical distribution of comonomer units in the copolymers.

POM copolymers are produced by adding comonomers to the polymerization mixture prior to polymerization. Suitable comonomers include cyclic ethers and cyclic acetals. In particular 1,3-dioxolane, diethylene glycol formal [75], and 1,4-butanediol formal are used. The comonomers are generally used in amounts of 2–5 wt%.

The polymerization of trioxane can be performed in bulk, solution [76], or suspension [77]. Bulk polymerization is the preferred method in practice. It is generally carried out in self-cleaning kneaders or double-screw reactors [78, 79] at 70–115°C. Polymerization is complete within a few minutes, and a very hard, crystalline polymer is formed. The heat of polymerization, ca. 23 kJ/mol [80], leads to evaporation of trioxane and formaldehyde.

Other polymerization processes have been reported, including solid-state copolymerization of trioxane/1,3-dioxolane [81], homogeneous-phase polymerization [82], polymerization in an open vessel [83], and a drum process [84]. After polymerization, the acid catalyst is deactivated and the unstable hemiacetal and formate terminal groups are removed by heat treatment. In practice, both solution [85, 86] and melt [87, 88] processes have proved suitable. Solution processes are generally carried out at 150–200°C, and melt processes at 170–250°C. Amines or phosphines, for example, are added to deactivate the acid catalysts. They also catalyze the removal of unstable end groups. The objective of all the processes is to completely remove unstable terminal groups and residual monomers from the polymer.

The solution processes are very efficient but have the disadvantage of high energy consumption and higher capital cost. After thermal treatment, the product is precipitated in powder form by lowering the temperature. The adhering residual solvent is removed mechanically and thermally. The dry powder, together with stabilizers and other optional additives, is melted and homogenized in extruders and processed into granules. The melt processes do not achieve the efficiency of the solution processes, but require less energy. After addition of stabilizers, the melt can be processed directly into granules.

A large number of patent applications have been filed by various companies for the polymerization as well as the work-up process, e.g., [89–97].

3.4. Additives

3.4.1. Stabilizers

Polyoxymethylenes can be decomposed by the action of high temperatures, oxygen, shear forces, and/or acidic substances. These influences are especially important in the processing of the products in the melt. Further influences may also occur when using the finished parts.

In the case of terminal-group-stabilized polyoxymethylenes, decomposition begins by chain scission. Above the melting point, chain scission is followed by depolymerization with elimination of formaldehyde. For copolymers, this involves elimination of formaldehyde units until the next stabilizing comonomer unit is reached. In the case of homopolymers complete decomposition of the polymer chain occurs. Formic acid, which can initiate an acidolytic chain scission, is formed as byproduct of the decomposition by oxidation of formaldehyde or by disproportionation. Acidic catalyst residues can also produce chain scission [98, 99]; for further details, see [100].

Only multicomponent systems are used to stabilize polyoxymethylenes. Sterically hindered phenolic compounds in particular have proved suitable against thermal-oxidative decomposition (antioxidants). Alkaline-earth metal salts and nitrogen-containing compounds, among others, are used to prevent acidolytic decomposition (acid trapping agents). Formaldehyde trapping agents (scavengers) can be used to further improve the stability.

The following compounds are used as antioxidants:

1. 4,4′-Butylidenebis(6-*tert*-butyl-3-methylphenol) [101]
2. Triethylene glycol bis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate] [102]

3. 1,6-Hexamethylene bis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate] [103]
4. 2,2′-Methylenebis(4-methyl-6-*tert*-butylphenol) [104]

The following compounds, among others, are used as acid trapping agents:

1. Dicyanodiamide, melamine [105]
2. Calcium carbonate, stearate, or montanate [106]
3. Polycondensates of formaldehyde, isophthalamide and 2-imidazolidinone [107]
4. Polyamides [108]
5. Triazine derivatives [109]

The nitrogen-containing compounds also act as formaldehyde scavengers. Other formaldehyde scavengers include polyhydroxy compounds such as poly(vinyl alcohol) [110], hydantoins [111], glyoxyldiureide compounds [112], hydrazides of carboxylic acids [113] or guanamine compounds [114].

The aforementioned classes of stabilizers can be combined in numerous ways. Optimum utilization of the possible synergistic effects can be achieved only by carefully matching all the components.

Damage caused to polyoxymethylenes by UV radiation and weathering is described in Section 2.5. The addition of organic light stabilizers and special pigments has proved useful in improving the resistance to UV radiation and weathering.

Compounds from the following classes are used as light stabilizers [115–117]: benzotriazoles, benzophenones, benzoates, oxanilides, and sterically hindered amines (HALS stabilizers). Synergistic effects can also be achieved here by suitable combinations of stabilizers of different classes of compound, in particular combination with HALS stabilizers. Titanium dioxide and, in particular, carbon black are suitable pigments.

All the above-mentioned stabilizers and pigments are added during compounding.

3.4.2. Nucleation Agents

The following are suitable as nucleation agents for polyoxymethylenes:

1. Branched or cross-linked polyoxymethylenes [118]
2. Trioxane block copolymers [119]
3. Special melamine–formaldehyde resins [109, 120]
4. Boron nitride [121]
5. Talc [122]
6. Antimony trioxide [123]

Even in amounts of less than 1 wt% these compounds accelerate crystallization of the melt. Nucleated polyoxymethylene molding compounds often allow earlier removal from the mold, and thus a reduction of the cycle time, in injection molding processing. The resulting spherulite structure is finer and more uniform, which results in increased strength and toughness [22, 124].

3.4.3. Release Agents

The addition of release agents may be advantageous for the production of complicated molded parts. Suitable additives include, for example, polyethylene waxes, montan acid esters and salts, *N*,*N*′(bis-stearoyl)ethylenediamine, fatty alcohols, and fatty acid salts.

3.5. Impact-Resistant Types

Polyoxymethylenes are materials that already have a high basic toughness, without the need for further modification. However, the toughness can be improved further by impact resistance modification with elastomers.

The first commercial impact-resistance-modified polyoxymethylenes were introduced in 1982, and in the meantime several manufacturers have developed products of this type. The various products differ according to their flow behavior and degree of impact resistance modification. Compared with the unmodified products the impact-resistant types have slightly reduced rigidity, hardness, and thermal dimensional stability, though this is compensated by a substantially higher energy absorption under impact and tensile stress.

The conventional types are based on blends of polyoxymethylene and thermoplastic polyurethane (POM-TPU) elastomers [125–129].

Products in which cross-linked rubbers having a particularly low glass transition temperature and a defined particle size are used for the impact strength modification have been developed as well [130].

Further development of POM-TPU blends with significantly improved impact resistance and weld-line strength, without sacrificing other key properties, has been commercialized by Ticona. This grade, manufactured by a special backbone-modified POM, exhibits increased impact-performance, excellent friction and wear properties. It also makes possible overall optimized part designs as well as reduced part costs. Speed-up of cooling cycles in injection molding of up to 30% has been reported [131]. In most recent developments, these grades are penetrating areas that were once preserved of impact-modified PA66.

Impact-resistant polyoxymethylenes are produced by mixing the components in the melt, using single-screw or double-screw extruders. Processing into moldings is performed by the same methods as are used for unmodified polyoxymethylenes. Whereas polyurethane-modified products have, depending on the extrusion and processing conditions, a variable morphology of the impact-resistant component (size, shape, and distribution of the particles), the rubber-modified products have a uniform particle morphology. In addition to the particularly high low-temperature impact resistance, these products have further advantages, including the extremely good weld line strength and the absolute absence of delamination during processing [132].

3.6. Low Volatile Organic Carbon (VOC) Grades

Due to higher requirements in the automotive interior, low-emission and high-performance materials are in high demand (especially in Europe and Asia). All major POM-manufacturers have now added special low-emission grades to their range of high-quality products. This helps the car industry to implement its emission minimization strategy.

Most recent developments have shown, that special grades are at least 50% lower than the self-imposed limits specified in the guidelines (VDA 275 and VDA 270) of the German Association of the Automotive Industry [133]. These improvements were achieved by optimized manufacturing technologies as well as the use of new additives.

3.7. High-Strength POM Copolymer

As discussed in Section 2.2, POM homopolymer grades have advantages in mechanical properties, while the copolymer grades are superior in thermal stability and chemical resistance. This is mainly due to differences in polymer structure, molecular-mass distribution and end groups between the two families. Because of more ether-type end groups of copolymers, they typically exhibit greater thermal and chemical (hot water and alkaline) stability. The development of a new POM copolymer grade with a unique combination of the best in mechanical properties and the best in thermal and chemical stability has recently been accomplished. The enhancement was achieved by improvements in the cationic polymerization reaction used to make the POM copolymers. A more detailed comparison between the different materials in regards to mechanical properties, creep resistance and flex fatigue of the materials was presented [134].

4. Economic Aspects

Table 2 lists producers of polyoxymethylenes, together with their capacities and trade names [135]. A demand for polyoxymethylenes of about 700×10^3 t/a can be compared with a nominal capacity of ca. 1000×10^3 t/a for 2008. Homopolymers accounted for about 25% of the total market.

5. Quality Specifications and Analysis

Residual monomer content, molecular mass, thermal stability, and mechanical properties are important quality criteria for polyoxymethylenes. For the copolymers there is in addition the comonomer content.

Table 2. Major world producers of polyacetal resins in 2008 [135]

Company and plant location (Trade name)	Annual capacity as of August 2008, 10^3 t	Share of world capacity, %
North America		
DuPont, DuPont Engineering Polymers Parkersburg, WV, United States (Delrin)	73	6.8
Ticona LLC Bishop, TX, United States (Celcon)	102	9.5
Western Europe		
DuPont Performance Elastomers BV Dordrecht, Netherlands (Delrin)	107	9.9
Ticona GmbH Frankfurt am Main, Germany (Hostaform)	100	9.3
Asia		
Korea Engineering Plastics., Ltd Ulsan, Kyongsangnam-do, Republic of Korea (Kepital)	80	7.4
Polyplastics Co., Ltd. Fuji, Shizuoka Prefecture, Japan (Duracon)	100	9.3
PTM Engineering Plastics (Nantong) Co., Ltd. Nantong, Jiangsu, China	60	5.6
Thai Polyacetal Co., Ltd. Rayong, Thailand (Iupital)	60	5.6
Total	682	63.3

The so-called lutidine or acetylacetone method [136], which is specified by the BfR (Bundesanstalt für Risikoforschung, Berlin, Germany) to evaluate the formaldehyde content of plastic molded parts that come into contact with foods [137, 138], is generally used to measure the content of extractable formaldehyde in granules or in molded parts. Formaldehyde can also be determined with chromotropic acid or by titration with sodium sulfite solution. The tests are normally performed on aqueous extracts of the materials.

The molecular mass is monitored in practice via the melt viscosity (melt flow index, MFI). Various η–M relationships are given in the literature for molecular mass determination by means of the solution viscosity. Usual solvents are dimethylformamide and hexafluoroacetone–water mixtures [139, 140].

The weight loss that occurs in the melt at a specific temperature over a certain time and in a defined atmosphere (air, nitrogen) can be used to evaluate the thermal stability [141, 142].

NMR spectroscopy is suitable for monitoring the comonomer content in the end product [143]. When the comonomer is ethylene oxide, the frequency of occurrence of mono-, di-, and triethylene glycol units can also be determined with this method.

IR-spectroscopic methods have been described for the determination of terminal groups in acetylated homopolymers [144, 145].

Conventional analytical techniques such as UV, IR, NMR, and ashing, optionally in combination with suitable separation methods, can be used for the qualitative and quantitative determination of additives, fillers, and reinforcement agents in the end product.

6. Product Range and Processing

Polyoxymethylenes are produced in various degrees of polymerization. The individual types differ as regards their flow behavior (melt index) and in the choice and concentration of additives and colored pigments. Reinforced types, types with improved slide and wear behavior and impact resistance, and products with anti-UV additives are also available [9–11]. The usual supply form is granules of about 3 mm grain size.

Polyoxymethylenes can be processed with all conventional machinery for thermoplastics, such as injection molding machines, extruders, injection and extrusion blow units, as well as by compression → Plastics, Processing, 1. Processing of Thermoplastics. Temperatures between 190°C and 210°C are generally recommended for processing. The temperature in the melt should not exceed ca. 230°C [10, 11].

Posttreatment of injection moldings is generally not necessary. Machining, in which parts are fashioned from the bulk plastic (semi-finished product), has, however, become important. Machining is economically practicable up to medium-size production runs, particularly if computer numerical control techniques are used.

The "outsert" technique has found widespread use in the past. With this technique a wide range of polyoxymethylene functional components can be bonded to a metal blank in a single step in an injection molding process [146]. Such components include guiding and sliding elements, bearings, axles, columns, snap connections, and spring components. They are used, for example, in compact disc drives and in cassette and video recorders.

Further information on processing is given in [6, 7, 22].

7. Uses

Polyoxymethylenes have a balanced combination of favorable properties for technical use, such as hardness, rigidity, toughness, spring elasticity, and resistance to fuels. The range of uses has been broadened further by a large number of modified special grades. Polyoxymethylenes are used in almost all sectors of industry and technology. The main areas of polyoxymethylene consumption in Western Europe are the automotive sector (36%), consumer goods, industrial applications, fluid handling and household appliances (36%), and in electrical engineering and the electronics industry (17%) [5]. Further uses include mechanical engineering, medical technology, toys, and cosmetics.

Utility articles and parts fabricated from polyacetals vary widely as regards their range of application and are accordingly so numerous that it is only possible to list the most important uses. Some examples of applications are as follows [6]:

Automotive Sector: parts for gasoline pumps, gasoline gauges, carburetor floats, brake boosters, chain wheels, clips, tank closures, water separators, lock housings, fan blades, loudspeaker grills, fuel tank module and safety belt parts.

Electrical Industry: gearwheels, bearings, springs, radial cams, lifters, tappets, axles, pinions, gears, transmissions, worm gears, computer keyboards, water boilers, and parts for leakage current protection circuits.

Mechanical Engineering: valves, pistons, sliding bearings, and ball-type nipple cages.

Sanitary Sector: dispenser, fittings, control flaps for WC flush units, and functional parts in water and gas meters.

8. Recycling

On account of the high commercial value of polyoxymethylenes a functioning material reuse recycling system for polyoxymethylenes already exists. Many plastics processors use material residues directly themselves and contribute substantially by means of this internal recycling process to reduce waste. Polyoxymethylene waste is also processed by compounders into regranulate. This regranulate is, however, of poorer quality than the original material.

Hoechst has developed a closed-loop recycling process, in which polyoxymethylene waste is decomposed into the monomer starting materials. The recovered monomers are purified and polymerized [147]. The cycle can be repeated as often as desired without affecting the quality.

9. Toxicology and Occupational Health

Polyoxymethylenes are odorless and tasteless. Feeding tests have not produced any positive clinical results. Skin compatibility investigations showed that polyoxymethylene does not irritate intact skin [40, 148].

There are no objections to the use of polyoxymethylene moldings that come into contact with foods, as long as the regulations of the licensing authorities (BGA [137], FDA [149, 150]) are satisfied and the parts are suitable for the intended use. The regulations cover the nature and amount of monomers, comonomers, catalysts, deactivators, regulators, stabilizers, lubricants, and fillers, and specified contents of fluorine, boron, zinc, and amines must not be exceeded. A maximum permissible upper limit is specified for formaldehyde traces that can be extracted from finished parts.

The maximum permitted workplace concentration for formaldehyde should also be observed when processing polyoxymethylenes.

In Germany the MAK is 0.3 ppm (0.37 mg/m^3) [151], and in the United States the PEL-TWA is 0.75 ppm (0.9 mg/m^3) [152]. These limits may be exceeded for a short period only if certain preconditions are satisfied. For further details see → Formaldehyde.

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Poly(Phenylene Oxides)

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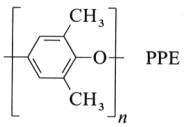
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ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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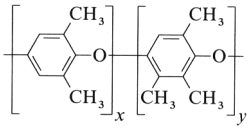
1. Introduction

Poly(phenylene oxides) [*9041-80-9*], also known as poly(phenylene ethers) or polyoxyphenylenes, refer to a class of polymers made by the oxidative polymerization of substituted phenols. A large variety of polymers have been investigated based on differently substituted phenols (Table 1). However, only poly(2,6-dimethyl-1,4-phenylene ether) [*25134-01-4*] (PPE) has significant utility, albeit in blends with other polymers such as polystyrene or polyamide:



PPE

History. The discovery of poly(2,6-dimethyl-1,4-phenylene ether) in 1956 by Hay (General Electric) [1] marked the introduction of the catalyzed oxidative coupling of phenols as a means of obtaining engineering resins. This poly-(phenylene oxide) made from 2,6-dimethylphenol can be regarded as amorphous for all practical purposes [2], and possesses a high glass transition temperature (T_g 211 °C) in addition to an extremely high melt viscosity, which requires high processing temperatures that lead to side reactions [3],[4]. Only through the exceptional miscibility of PPE and polystyrene (PS) [5] could acceptable processing temperatures and melt viscosities be achieved. This development led to the marketing of the first commercial poly(phenylene oxide) in 1964—Noryl, a blend of PPE and impact modified PS (HIPS). These PPE – HIPS blends are unique because their ultimate use temperature can be easily adapted to application requirements by adjustment of the PPE – HIPS ratio. GE Plastics was the sole supplier of modified PPE until 1983 when its original patents expired; other companies (e.g., BASF with Ultranyl and Hüls with Vestoran) have now introduced their own PPE grades. A blend of HIPS and a PPE copolymer with a similar property profile to poly(2,6-dimethyl-1,4-phenylene ether) was introduced in the early 1970s under the trade name Prevex (Borg – Warner and Mitsubishi Chemicals):



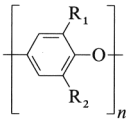
Today, over 200 000 t/a of modified PPE are sold worldwide, mainly for applications in the automotive, electronics, and electrical industries.

2. Production

The synthesis of PPE from 2,6-dimethylphenol, using an amine complex of a basic cupric salt as a homogeneous oxidation catalyst, follows a

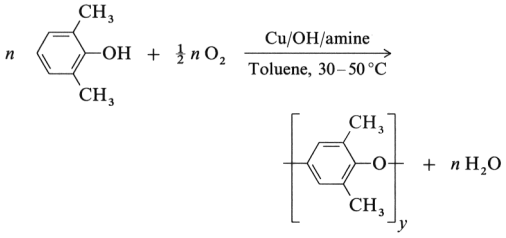
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Table 1. 2,6-Substituted aromatic polyethers formed by oxidative coupling of di- *ortho*-substituted phenols

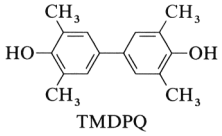


R_1	R_2	Polymer	Diphenoquinone compounds	CAS registry no.	T_g, °C	T_m, °C
H	H	branched	branched	[*25667-40-7*]	82	298
H	CH_3	branched	branched			
CH_3	CH_3	X		[*25134-01-4*]	211	268
CH_3	C_2H_5	X		[*26635-16-5*]		
CH_3	$CH(CH_3)_2$	X		[*31985-12-3*]	144	
CH_3	$C(CH_3)_3$		X	[*35916-68-8*]		
CH_3	$CH_2C_6H_5$	X		[*26545-37-9*]	99	
CH_3	C_6H_5			[*25805-39-4*]	169	
CH_3	OCH_3	X				
CH_3	Cl	X		[*26498-58-8*]		
C_2H_5	C_2H_5	X			120	
$CH(CH_3)_2$	$CH(CH_3)_2$		X			
$C(CH_3)_3$	$C(CH_3)_3$	X				
Cl	Cl	X		[*26023-26-7*]	228	269
OCH_3	OCH_3		X	[*25667-13-4*]	167	
C_6H_5	C_6H_5	X		[*24938-68-9*]	225	460 (decomp.)
C_6H_5	3-$CH_3C_6H_4$	X		[*79569-12-3*]	219	
C_6H_5	4-$CH_3C_6H_4$	X		[*79569-09-8*]	218	
C_6H_5	4-$(CH_3)_3C_6H_4$	X		[*79569-10-1*]	240	
C_6H_5	2-naphthyl	X		[*79569-11-2*]	234	

complicated polymerization mechanism which has not been completely resolved [6],[7].



The main byproduct of the polymerization is 3,3′,5,5′-tetramethyldiphenoquinone (TMDPQ):



TMDPQ

The oxidative coupling chemistry is very versatile because different di-*ortho*-substituted phenols can be used for the formation of 2,6-sub-stituted aromatic (co)polyethers (Table 1). However, only PPE is of commercial importance.

Commercial PPE production can be performed batchwise or continuously. Different reactor designs are possible depending upon the choice of the solvent and introduction of oxygen (pure oxygen or air – oxygen mixtures). A gas – liquid reactor is used to avoid low reaction rates associated with diffusion of air into the liquid. Reaction temperatures are typically 20–65 °C. At higher temperatures, formation of TMDPQ increases and should be avoided. The solubility and viscosity of the final polymer solution depend on the solvent, temperature, polymer concentration, and its molecular mass. Commercial PPE is produced with a weight-average molecular mass of 32 000–40 000.

The following stages can be discerned (Fig.1):

1. Preparation of the catalyst solution
2. Preparation of reaction mixture
3. Polymerization using oxygen or oxygen – air mixtures
4. Termination of polymerization at a certain degree of polymerization

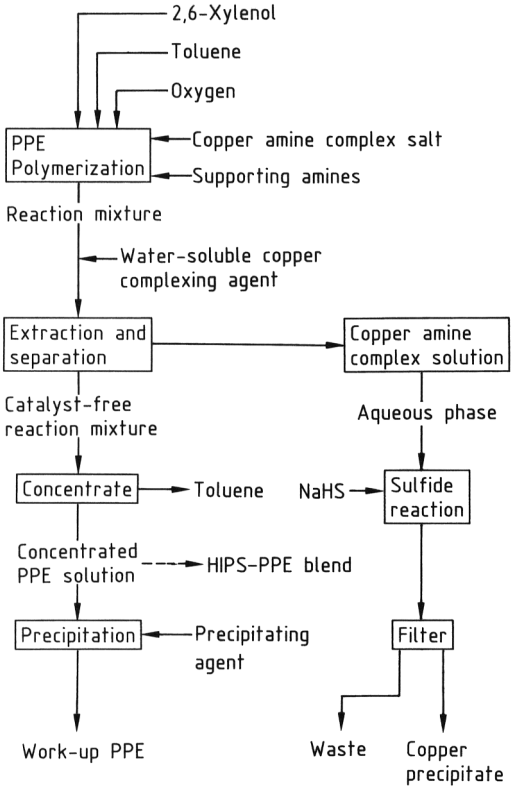


Figure 1. Commercial production of PPE

5. Removal of copper catalysts from the reaction mixture using a copper complex as complexing agent and liquid – liquid extraction
6. Concentration of PPE solution
7. Precipitation of PPE in a nonsolvent
8. Repeated washing and drying (purification of resin)

3. PPE Blends

3.1. PPE – PS Blends

A processible, commercially attractive material is obtained by blending PPE with PS (Fig. 2). The unique, complete miscibility of this blend presumably results from interaction between the π-electron donor PS and the electron-deficient methyl groups of PPE [8]. The T_g of the blend can be varied almost linearly between 100 and 215 °C over the complete composition range of PS and PPE (Fig. 3). Table 2 shows some important properties of PPE – HIPS blends.

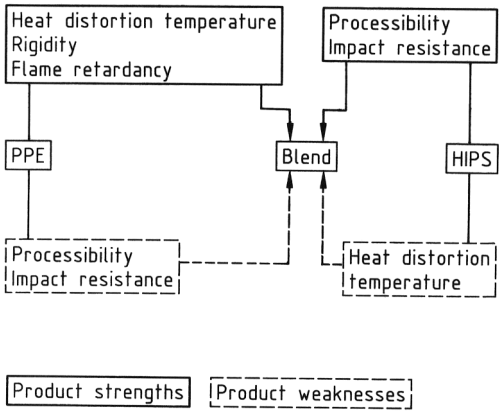


Figure 2. Blending criteria for PPE – PS

Commercial blends such as Noryl (GE Plastics) or Luranyl (BASF) make use of PS impact-modified with polybutadiene (high-impact polystyrene, HIPS). Impact modification of these blends comprising a ductile resin (PPE) and a brittle one (PS) poses an interesting problem because the two components require different rubber particle sizes for optimal impact modification (Fig. 4). Diluting HIPS with PPE yields a more ductile matrix in which smaller rubber particles (diameter 0.5–2 μm) are more effective in impact modification than the larger particles (2–12 μm) [9],[10]. The larger particles are more effective at higher HIPS levels [11]. Processing temperatures of PPE-rich compositions above 80 °C cause additional cross-linking of the polybutadiene rubber phase, rendering it less effective.

PPE – HIPS grades offer relatively constant mechanical properties over a wide temperature

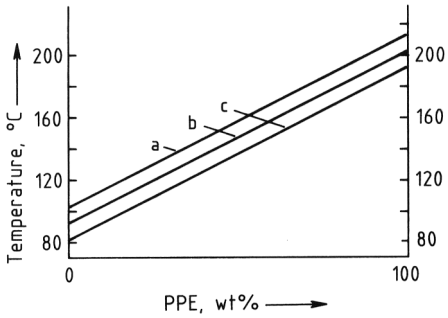


Figure 3. Thermal properties of PPE – HIPS blends
a) Glass transition temperature, T_g; b) Vicat B softening temperature; c) Heat distortion temperature

Table 2. Selected properties of PPE – HIPS blends (Noryl, GE Plastics)

Property	Standards		Unreinforced blend[a]	Unreinforced flame retardant[b]	Glass-reinforced blend[c]	Glass-reinforced flame retardant[d]	Structural foam[e]
	ASTM[f]	DIN[f]					
Mechanical							
Tensile strength (break), MPa	D 638	53 455	50	45	90	77	22
Tensile elongation (break), %	D 638	53 455	50	50	3	2	8
Tensile modulus, MPa	D 638	53 457	2500	2400	6500	7300	1600
Flexural strength (yield), MPa	D 790	53 452	98	90			
Flexural strength (break), MPa	D 790	53 457			140	120	46
Flexural modulus, MPa	D 790	53 457	2500	2500	6000	5000	1800
Hardness (H 358/30), MPa		53 456	100	87	122	147	
Hardness, Rockwell	D 785		R 115	R 115	L 106		
Flexural creep (300 h, 6.9 MPa), %	D 674						0.60
Impact strength							
Charpy impact (notched), kJ/m^2		53 453	15	15	9	9	5
Izod impact (notched), J/m	D 256		200	250	80	60	
Izod impact (notched, – 40 °C), J/m	D 256		140	120	70	50	
Thermal							
Vicat softening point (rate B), °C	D 1525		148	105	145	148	
Vicat VST/B/120, °C		53 460	135	100	140	135	
Deflection temperature under load (0.45 MPa), °C	D 648	53 461				133	96
Deflection temperature under load (1.82 MPa), °C	D 648	53 461	130	90	132	126	83
Thermal conductivity, W m^{-1}K^{-1}	C 177		0.22	0.16	0.24		0.12
Linear thermal expansion coefficient (flow), K^{-1} (7 – 8)×10^{-5}	D 696	VDE 0304/1	6×10^{-5}	7×10^{-5}	4×10^{-5}		2.4×10^{-5}
Physical							
Relative density	D 792	53 479	1.06	1.10	1.21	1.45	0.88
Water absorption (24 h), %	D 570		0.07	0.08	0.06	0.05	
Water absorption (equilibrium), %	D 570		0.14	0.37	0.14		
Water absorption (equilibrium, 100 °C), %	D 570		0.30	0.55	0.32		
Mold shrinkage (flow), %	D 955		0.5 – 0.7	0.5 – 0.7	0.2 – 0.4	0.1 – 0.3	0.6 – 0.9
Electrical							
Volume resistivity, Ω · m	D 257		$>10^{15}$	$>10^{15}$	$>10^{15}$	$>10^{15}$	
Dielectric strength (3.2 mm), kV/mm	D 149		22.0	16.0	17.0		7.5 (6 mm)
Dielectric constant (50 Hz)	D 150		2.70	2.70	2.90		2.30
Dielectric constant (1 MHz)	D 150		2.60	2.60	2.90		2.20
Dissipation factor (50 Hz)	D 150		0.0004	0.0004	0.00008		0.0047
Dissipation factor (1 MHz)	D 150		0.0009	0.0009	0.0014		0.0039
Arc resistance (tungsten), s	D 495						
Flame characteristics							
Oxygen index, %	D 2863		24	33	26		28
Flame retardancy (mm thickness)	UL-94		HB (1.65)	V-0 (1.52) 5 V (3.12)	HB (1.47)	V-0 (1.60) 5 V (3.20)	V-0 (6.29) 5 V (6.29)

[a] Noryl 731.
[b] Noryl N 190, V – 0 rating according to UL 94; V-1 and V-2 grades also available.
[c] 20 wt% glass-filled grade Noryl GFN 2; 10, 20, and 30 wt% glass-filled grades also available.
[d] V-0 rating according to UL 94; 35 wt% glass-filled grade Noryl VO 3525.
[e] Noryl FN 150 D.
[f] Unless otherwise stated.

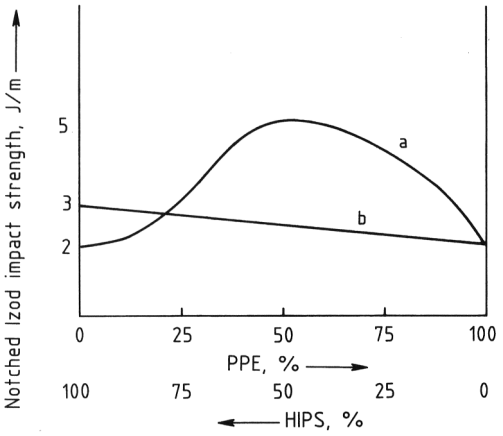


Figure 4. Notched impact strength of PPE – HIPS blends impact-modified with polybutadiene rubber (10 wt %, content in HIPS)
a) 0.5–2 μm polybutadiene rubber; b) 2–12 μm polybutadiene rubber

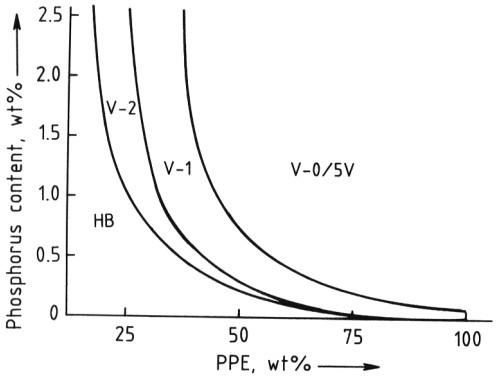


Figure 5. UL-94 flammability ratings of PPE – HIPS blends with different triaryl phosphate contents

range. Ultimate use temperatures of PPE – HIPS blends, as estimated from UL temperature ratings, are between 90 and 100 °C (see Table 2).

The very low water absorption of PPE –HIPS blends and their favorable mechanical properties contribute to a high dimensional stability under load, the most important property of engineering thermoplastics.

Polymer miscibility is not restricted to the PPE – HIPS system, but also holds for combinations of other substituted poly(1,4-phenylene oxides) (see Table 1) with styrene homopolymers such as poly(α-methylstyrene), poly(4-methylstyrene), and styrene copolymers in which the comonomer content is limited to maintain full miscibility with PPE.

Adjustment of the maximum use temperature offered by blend technology also applies to the UL-94 flammability ratings of the PPE – HIPS grades (Fig. 5). For a description of UL-94 ratings, see → Flame Retardants. PPE is intrinsically flame extinguishing as exemplified by its high limiting oxygen index (LOI) value of 29. HIPS, on the other hand, has a LOI of 17 and burns easily and completely [12]. Blending these two miscible polymers provides an intermediate flammability behavior which can be further improved by adding triaryl phosphates to produce flame-retardant PPE – HIPS grades that meet required industrial specifications without utilizing halogen-containing compounds [13]. Since the organic phosphate also functions as a plasticizer, a higher percentage of PPE is required to maintain a given heat distortion temperature (HDT) (Fig. 3). This leads to a well-balanced relation between flame retardancy behavior, composition, and HDT. The flame-retardant PPE – HIPS grades also have excellent melt processibility.

Enhanced flame retardancy, however, decreases the comparative tracking index (CTI), a criterion used for applications in the electrical and electronics industry (→ Insulation, Electric, Section 2.1.). This problem can be solved by the addition of inorganic fillers (e.g., glass fibers) and has led to the development of special grades.

PPE – HIPS blends are, like most polymers, excellent electrical insulators. The dielectric loss factor, a measure for the loss of electrical energy through heat buildup, is <0.002 in the range 1 – 16 MHz over a wide temperature span [14]. For other electrical properties of poly(phenylene oxides), see → Insulation, Electric.

Chemical resistance of PPE – HIPS blends is summarized in Table 3. Temperature, strain level, contact time, and the chemical nature of the contact liquid strongly affect the related environmental stress cracking phenomena. PPE –HIPS blends have an intrinsically high resistance against hydrolysis under acidic and basic conditions.

3.2. PA – PPE Blends

PPE can also be used as an organic filler in semicrystalline matrices such as polyamides (PA 66 or PA 6). PA – PPE blends have

Table 3. Chemical resistance of PPE – HIPS (Noryl) and PA – PPE (Noryl GTX) blends

Chemical	PPE – HIPS blend	PA – PEE blend
Water and aqueous solutions		
Cold water	excellent	very good
Hot water	excellent	good
Cleaning agent	very good	satisfactory/good
Salts	very good	good
Acidic solutions	good	good
Basic solutions	good	satisfactory
Concentrated bases	good	satisfactory
Concentrated acids	satisfactory	bad
Organic solvents		
Alcohols	very good	very good
Ketones	very good	satisfactory
Aliphatic hydrocarbons	swelling	very good
Aromatic hydrocarbons	bad	good
Chlorinated hydrocarbons	bad	bad
Esters	bad	satisfactory
Miscellaneous		
Gasoline	bad	(very) bad
Fats	type-dependent	(very) good
Oils	type-dependent	(very) good
Freon	type-depentent	(very) good

been specifically developed for on-line painted exterior automotive parts with excellent ("class A") surface quality.

The favorable processibility properties, chemical resistance, and impact resistance of PA are combined with the high-temperature performance of PPE. PA – PPE blends were the first commercial blends of two completely incompatible polymers and are different from the fully miscible PPE – HIPS system. Blends of immiscible polymers are thermodynamically unstableand lack morphological stability, which leads to phase separation and delamination. This can be overcome by the use of compatibilizers (concen-tration usually $\geq$ 10 wt%), which are frequently A–B block copolymers. The compatibilizers reduce the interfacial tension between the constituent polymers, resulting in greatly improved dispersion of PPE in PA. They also provide strong bonding between the dispersed and the continuous phases (important for mechanical properties), and increase morphological stability by preventing agglomeration of dispersed particles. The latter is important as it allows processing of the blends under practical shear conditions such as exist in injection-molding equipment.

Compatibilization is achieved either by adding PA – PPE block copolymers or by in situ formation of these block copolymers. The latter is achieved by addition of PPE end-capped with functionalized maleic anhydride (Fig. 6A) or by addition of PS grafted with maleic anhydride (Fig. 6B). The anhydride groups react with the amine end groups of the PA polymers and form a compatibilizing linear PA – PPE block copolymer (Fig. 6A) or a grafted PS – PA block copolymer (Fig. 6B). Figure 7 shows the effect of compatibilization as determined by scanning electron microscopy[15]. Higher concentrations of PA – PPE copolymers reduce the dimensions of the dispersed PPE phase.

PPE is a ductile material which can be impact-modified to form extremely tough blends. The high glass transition temperature of PPE also increases the strength, rigidity, and dimensional stability of the PA – PPE blends up to the temperature required for automotive lacquering. The blends are usually impact-modified phase selectively with various rubbers located in the PPE or PPE – PS phase dispersed in the PA phase. Two-phase impact modification of the PPE (or PPE–HIPS) and the PA phases is also possible by appropriate selection

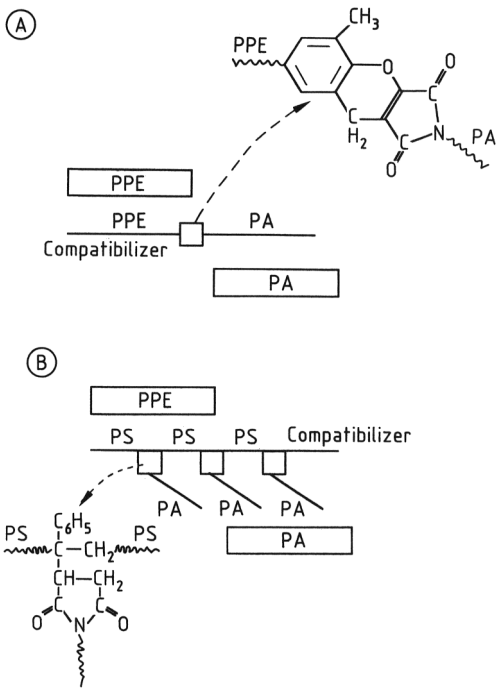


Figure 6. Schematic representation of compatibilization of PA – PPE using PPE end-capped with functionalized maleic anhydride (A) or PS grafted with maleic anhydride (B)

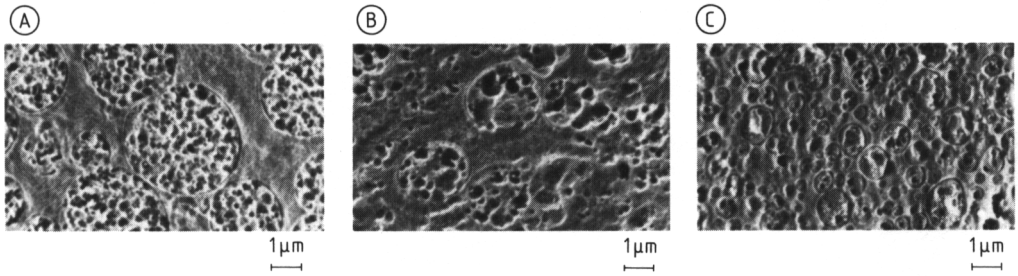


Figure 7. Effect of compatibilization on PA – PPE morphology as determined by scanning electron microscopy with PA as the continuous phase (courtesy of S. Y. Hobbs, General Electric)
A) No compatibilizer; B) 8 wt % compatibilizer; C) 15 wt % compatibilizer

of the rubbers. The PA – PPE blends can thus easily be adapted to give the ultimate use temperatures and impact levels required for specific lacquering and painting applications of exterior automotive parts (see Fig. 8). Ranges of temperature requirements for various coating techniques are indicated.

Table 4 shows important properties of PA –PPE blends. Polyamides are known for their high moisture absorption which reduces their dimensional stability. Addition of PPE to PA lowers the water absorption but, remarkably, PA – PPE blends absorb less moisture than that calculated from their PA volume fraction (Fig. 9). The resulting blend thus has a greater dimensional stability than PA, providing a more constant mechanical property profile with temperature and relative humidity. This dimensional stability can be further enhanced by reinforcing the material with glass fibers. Special grades exist for bumper beams that combine high-temperature paintability with low-temperature impact performance.

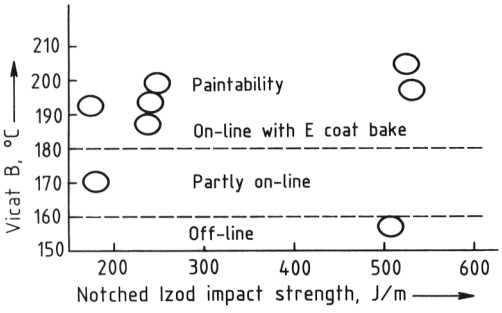


Figure 8. Ultimate use temperature plotted against impact strength of commercially available PA – PPE blends (Noryl GTX, GE Plastics), ranges of possible coating techniques are indicated

Advantages of PA – PPE blends over PPE – HIPS blends are their better chemical resistance (see Table 3), improved environmental stress cracking resistance, and a higher ultimate use temperature range.

3.3. PPE – Polyolefin Blends

In 1989 GE Plastics introduced a blend series (Noryl Xtra) containing ≥ 90 % PPE. The high melt viscosities of PPE (see Chap. 1) were reduced using plasticizers and olefinic components of proprietary composition as flow promoters. The resins combine good processibility with high dimensional and temperature stability up to 195 °C as well as an UL-94 V-0 flammability rating. The materials have a high surface gloss and can be used as light reflectors.

In addition to excellent intrinsic flame retardancy properties, the special-grade Noryl Xtra LS generates an extremely low amount of smoke during burning because it contains PPE-specific char promoters. This feature is extremely important for its use in electrical insulation applications in enclosed or inaccessible areas (airplanes, ships, public buildings).

4. Processing

Melt viscosities of all PPE – HIPS and PA – PPE grades conform to the processing capabilities of conventional melt-processing equipment (injection molding, extruding etc.). However, PA – PPE blends require a more stringent drying procedure, and care should be taken with PPE – HIPS blends not to exceed the recommended

Table 4. Properties of PA – PPE blends (Noryl GTX, GE Plastics)

Property	Standards		Unreinforced[b]	30 wt % glassfiber-reinforced[c]
	ASTM[a]	DIN[a]		
Mechanical				
Tensile strength (yield), MPa	D 638	53 455	55	
Tensile strength (break), MPa	D 638	53 455	50	160
Tensile elongation (yield), %	D 638	53 455	5	
Tensile elongation (break), %	D 638	53 455	100	3
Tensile modulus, MPa	D 638	53 457	2000	9000
Flexural stength (yield), MPa	D 790	53 452	85	
Flexural strength (break), MPa	D 790	53 452		220
Flexural modulus, MPa	D 790	53 457	2100	7000
Hardness (H 358/30), MPa		53 456	115	141
Impact strength				
Charpy impact (notched), kJ/m^2		53 453	15	7
Izod impact (notched), J/m	D 256		240	85
Izod impact (notched, – 20 °C), J/m	D 256		190	75
Thermal				
Vicat softening point (rate B), °C	D 1525		220	240
Vicat VST/B/120, °C		53 460	190	240
Deflection temperature under load (1.82 MPa), °C	D 648	53 461		225
Thermal conductivity, $Wm^{-1}K^{-1}$	C 177		0.23	0.26
Linear thermal expansion coefficient (flow), K^{-1}	D 696	VDE 0304/1	9×10^{-5}	$(2-3) \times 10^{-5}$
Physical				
Relative density	D 792	53 479	1.10	1.31
Water absorption (24 h), %	D 570		0.40	0.50
Water absorption (equilibrium), %	D 570		3.50	3.60
Mold shrinkage (flow), %	D 955		1.2 – 1.6	0.3 – 0.5
Flame characteristics				
Oxygen index, %	D 2863		20	29
Flame retardancy (mm thickness)	UL-94		HB (1.60)	HB (1.60)

[a] Except where otherwise stated.
[b] Noryl GTX 900.
[c] Noryl GTX 830.

drying time of 4 h at 110 °C, since this leads to loss of impact resistance. Processing temperatures of standard grades are typically 220–270 °C for PPE – HIPS, 280–300 °C for PA – PPE, and 320–340 °C for PPE – olefin blends. Injection molding and glass-filled grades require slightly higher temperatures.

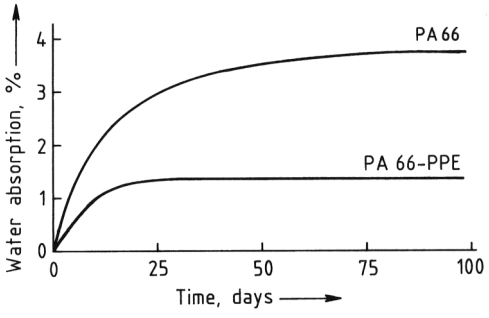


Figure 9. Water absorption of PA and PA – PPE at 23 °C and 50 % R.H.

5. Uses

The most important application areas for PPE blends are in the automotive industry (35 %), in electric and electronic appliances (25 %), office equipment (15 %), and (hot) water distribution and environmental applications (8 %) [13].

Interior Automotive Applications. The development of PPE – HIPS blends marked the break-through of plastics for interior automotive applications. The most significant applications are dashboards of PPE – HIPS (Fig. 10), a development that started in Europe and was followed worldwide. Other applications include radio housings, loudspeakers, and heating and ventilation systems. A recent development are the so called "anti-squeak" materials used for handgrips and ventilation grills.

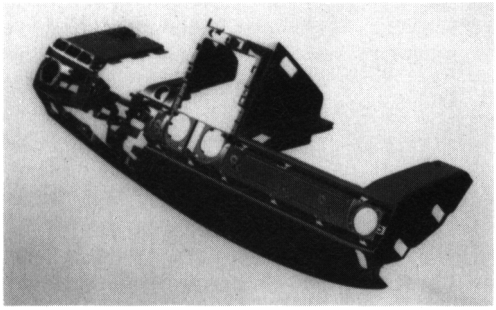


Figure 10. PPE – HIPS dashboard (Noryl, GE Plastics)

Exterior Automotive Applications. The on-line and off-line paintability of PA – PPE blends provided by their high-temperature performance, their "class A" surface with excellent dimensional stability, and good mechanical properties in combination with low-temperature impact resistance makes them suitable for vertical body panels, bumpers, petrol filling caps, wheel trims, grilles, spoilers, electromechanical systems (EMS) and, most recently, fenders for the 1991 Renault Clio 16 S (Fig. 11). These applications allow for easy styling changes, weight savings, and, most importantly, cost savings. The latter is particularly important for "small" production series of 50 000 vehicles per year.

Electrical and Electronics Industry. Flame-retardant PPE – HIPS grades are used mostly on account of their good processability, good mechanical properties, and flame retardancy behavior without using halogens. Typical applications are housings for electrical equipment (Fig. 12), connectors, switches, and interior parts in laundromats. PA – PPE blends can be used in paintable extrusion and blow molding parts.

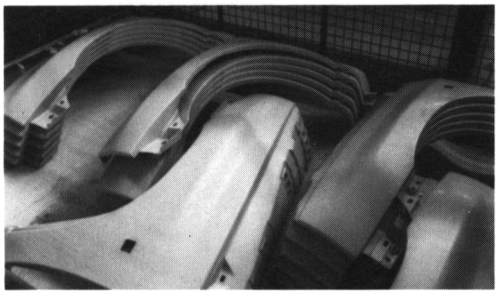


Figure 11. Fenders of 1991 Renault Clio 165 (Noryl GTX, GE Plastics)

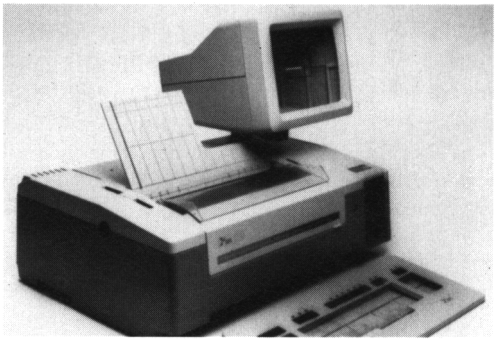


Figure 12. PPE – HIPS housing (Noryl, GE Plastics)

Data Processing and Office Equipment Industry. Flame-retardant PPE – HIPS blends or, alternatively, painted structural foams are used for in-house appliances such as computer housings. These materials are provided with a UV-stabilizing system to comply with the most stringent demands for color stability.

The hydrolytic and dimensional stability of PPE – HIPS blends and the reduced stress – crack sensitivity provided by glass fiber reinforcement makes them suitable for applications in water and air purification systems. All blends in applications involving food contact or drinking water are approved by the FDA.

Building and Construction. This industry segment constitutes a new market for PPE blends. Current low sales percentages result from the fact that traditional materials are still used in potentially large-volume applications such as insulation systems or solar collectors.

New Developments. A few promising new developments can be mentioned. In situ PPE – PS blends used to make expandable beads give strong foams with a low density (to 0.02 g/cm^3) and a heat distortion temperature above 100 °C, a sterilizable and reusable material (Fig. 13).

The use of PPE as an organic, highly heat-resistant, flame-retardant filler that does not affect mechanical properties at high filling ratios, as demonstrated for PA – PPE blends, will be applied to other blend systems (Section 3.2). These new blends include a blend of PPE and poly(butylene terephthalate) which has an even lower moisture absorption than PA – PPE blends and thus higher dimensional stability. Blends of chemically modified PPEs will

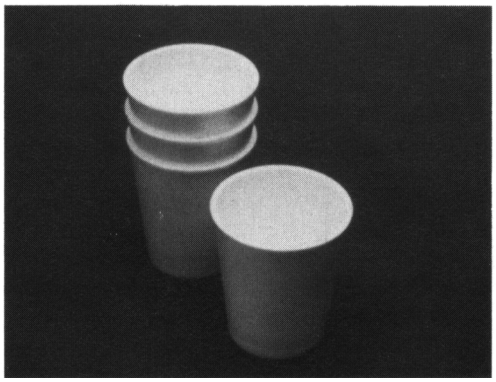


Figure 13. Beakers made from PPE – PS expandable beads (Caril, Shell)
Bead size 300 – 500 μm, density 60 g/L, T_g 110 °C

also find increased use, aimed at applications with specific requirements.

6. Acknowledgement

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Polypropylene

ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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1. Historical Overview

The history of polyolefins effectively started with the discovery of high-pressure ethylene polymerization at ICI in the UK in 1933, which initiated the development and production of low-density polyethylene (LDPE). In the search for a more energy efficient route to polyethylene and the development of fully linear polymers of this monomer, Karl Ziegler discovered in 1953 new catalysts based on the combination of transition metal halides (e.g., titanium chloride) with aluminum alkyls (e.g., triethylaluminum) [1]. With these he demonstrated that ethylene could be polymerized to a high molecular mass, crystalline polymer at moderate pressure and temperature and laid the foundation of a revolution for the plastics industry. Before that, propene could not be polymerized to high molecular mass products with the catalysts then available, namely, free-radical, anionic, and cationic systems. Even the most favorable of these yielded only liquids consisting of many isomers and greaselike materials unsuitable for making hard plastic products.

Ziegler's group at the Max-Planck-Institut für Kohlenforschung in Germany had for some years been using aluminum alkyls to convert ethylene to a range of oligomers having an even number of carbon atoms. Unexpectedly, almost total conversion to butenes occurred in one experiment. The cause was eventually traced to nickel-ion contamination in the autoclave. Tests with many other metal compounds revealed that titanium ions were even more active in producing polyethylene (PE) with a

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high molecular mass, resulting in a first patent [2]. Such combinations of transition metal compounds with an aluminum alkyl later became known as Ziegler–Natta (ZN) Catalysts, thereby acknowledging the immense contribution of Giulio Natta to discovering and characterizing polypropylene (PP) and other (stereoregular) α-olefin polymers in 1954.

Natta, Professor and Director of the Milan Institute of Industrial Chemistry, was a consultant to Montecatini, to whom he assigned his patents. The close collaboration between Ziegler and Natta was acknowledged in 1963 by the joint award of a Nobel Prize in Chemistry for their outstanding contributions to polymer science (a fascinating account of these discoveries is provided by McMillan [3]). Natta's discovery of the stereospecific polymerization of propene to produce isotactic (and hence crystalline) polypropylene (iPP) [4] resulted first in products with an isotacticity of only around 40%. This regularity was increased to 80% within one year through modification of the catalyst, allowing the first Montecatini production facility for iPP with a production volume of 6.10^3 t/a to go into operation in Ferrara, Italy, in 1957.

In retrospect, it is clearly recognizable that with the chain branching of PE and the stereostructure of PP, two crucial general control factors for the crystallinity and mechanics of polymers had been discovered [5]. Finally, the crystallization structures of the polymers were also elucidated around the same time; Andrew Keller presented his concept for chain folding in PE crystals in Bristol in 1957 [6].

The patent dispute over crystalline polypropylene in the USA between Natta and Montecatini on the one side and Phillips Petroleum Company on the other was clearly a result of different legislation between the USA and Europe. The dispute started in 1958 and became one of the longest in industrial history, only ending 20 years later [7]. Phillips' polymerization catalyst, consisting of chromium-ion-promoted silica–alumina, has not been used in any commercial plant to manufacture iPP.

New applications for the polymer with the impressive combination of a melting point of 165°C and a density of 900 kg/m^3 were constantly being found, in 1959 with the production of the PP fiber Meraklon, and in 1962 with first attempts at PP suitcases made by Hoechst. The ZN catalysts also proved to be suitable for the production of elastomers based on ethylene and propene [8]. For a polymer having its glass transition around 0°C this turned out to be a decisive factor for evolving into technical applications requiring mechanical stability over a wide temperature range. Together with the availability of an initially cheap monomer, this resulted in a rapid growth of the production volume from less than 100×10^3 t/a in 1960 to 6.1×10^6 t/a in 1980 to more than 53×10^6 t/a in 2012, making it the most produced single thermoplastic material (see Fig. 1) [9]. In the same period, the production volume of new plants

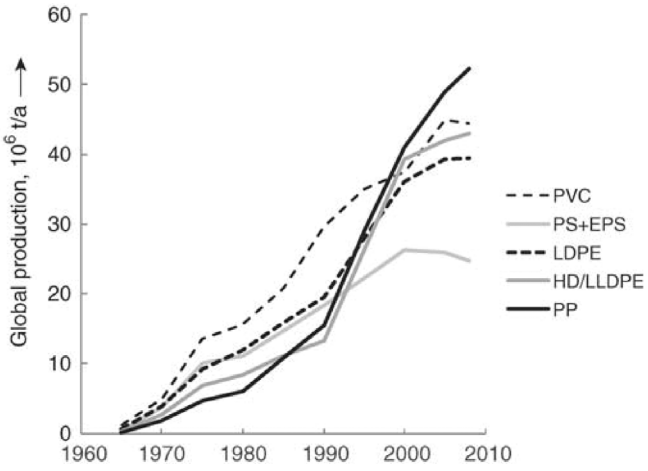


Figure 1. Production-volume development of standard thermoplastics (redrawn after [9])

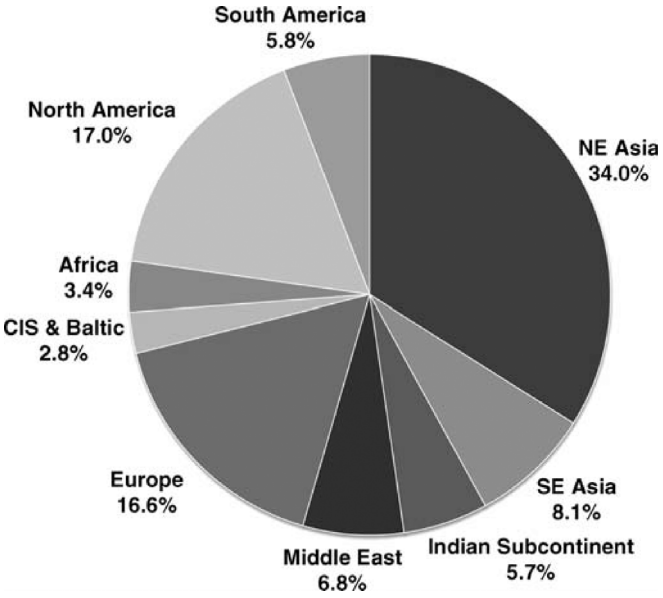


Figure 2. Regional distribution of global PP production (2012, data from [10])

increased to $200–400 \times 10^3$ t/a. A massive regional shift to Asia has occurred in recent years, with Northeast Asia and especially China now having the biggest share in production (see Fig. 2) and fewer than ten companies producing more than 60% [10].

Technical factors for this massive volume increase are numerous, but mostly related to a clever combination of catalyst chemistry and polymerization technology. A key step in terms of application range was certainly the development of products long referred to as "block copolymers". These combine a crystalline PP matrix with embedded particles of ethylene–propene rubber (EPR) and PE, which determine impact resistance and low-temperature resistance [11], and should more correctly be referred to as heterophasic copolymers (HECOs) or PP impact copolymers. Important for their development were improved catalysts and the availability of multireactor polymerization plants. With the second generation of ZN catalysts it became possible from the mid-1970s to produce "technical" HECOs, but with only a moderate EPR content. The introduction of the third generation of ZN catalysts at the end of the 1970s together with the breakthrough of bulk processes for polymerization without solvents enabled reliable synthesis of HECOs with high impact strength. Modern ZN catalysts allow the production of reactor-based thermoplastic elastomers with high impact toughness in a temperature range from +80 to −30°C.

In the field of catalysts, NATTA had already discovered the fundamental suitability of metallocenes for the homogeneous polymerization of olefins. In 1975 a crucial step forward in the practical use was taken with the discovery by KAMINSKY in Hamburg of methylaluminoxane (MAO) as a massively reaction accelerating cocatalyst [12]. This enabled MC-based PE, and BRINTZINGER in Konstanz extended the concept with the use of bridged MCs for iPP in 1984. While the market penetration of metallocenes and other single-site catalysts has been significantly slower than anticipated, due in part to the continuous improvement of the traditional—and cheaper—ZN systems, the former have enabled unprecedented fine-tuning of chain microstructure by ligand design.

2. Polymer Structure

2.1. Molecular and Chain Structure

Since PP is the largest single thermoplastic material [9] the structure, morphology, and properties of isotactic polypropylene (iPP) have been studied extensively. As the propene

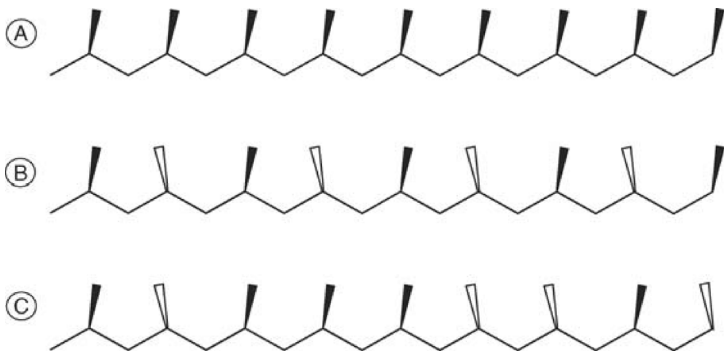


Figure 3. Main polypropylene types
A) Isotactic; B) Syndiotactic; C) Atactic

monomer is asymmetric, polypropylene can be produced with different stereochemical configurations [13]. The different stereoisomers of PP were isolated and characterized by NATTA et al. in 1954–1955. The most common types of PP, shown in Figure 3, are isotactic (iPP), syndiotactic (sPP), and atactic (aPP). In iPP all methyl groups are located on the same side of the backbone, in sPP on alternating sides, and in aPP the methyl groups are arranged randomly along the polymer chain.

Atactic PP is an amorphous material with much less practical importance than its regular counterparts, but it has some niche applications like hot-melt adhesives. The isotactic and syndiotactic stereoisomers of PP are both semicrystalline polymers. The melting points are in the range of 165°C for iPP and 130°C for sPP. Isotactic PP dominates the polypropylene market because it is easily produced with heterogeneous ZN and metallocene catalysts. In addition, it shows easier processing behavior and better mechanical properties. Syndiotactic PP shows a slower crystallization rate and can only be produced with some metallocene catalysts; therefore, it is commercially almost nonexistent.

State-of-the-art ZN catalysts make isotactic PP with only a minor atactic fraction. The industrially used ZN systems favor the 1,2-insertion and head-to-tail enchainment (Fig. 4). Defects such as a 2,1-insertion following a 1,2-insertion create irregularities along the PP chain resulting in a lower melting point and lower crystallinity of the material [14]. With metallocene catalysts it is possible to produce polypropylene with high isotacticity but lower regioregularity, responsible for their lower melting point compared to PP

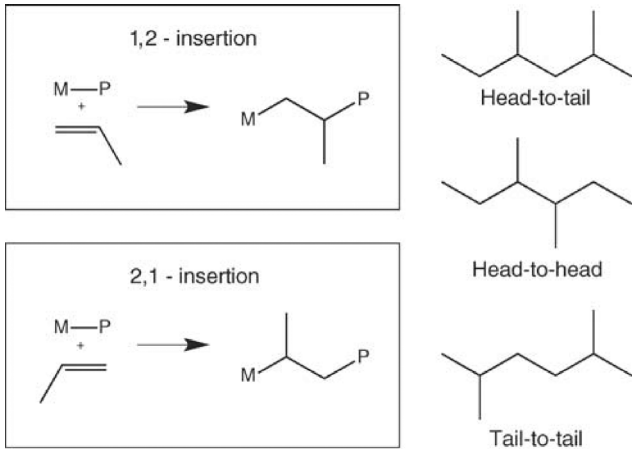


Figure 4. Regioirregularity in polypropylene polymerization

made with a ZN catalyst. With the help of metallocene catalysts also other stereostructures such as block polymers of isotactic and atactic sequences can be obtained, but these materials are not yet in commercial use.

2.2. Crystallization and Morphology

Polypropylene molecules associate to form supramolecular structures when cooled to temperatures below the melting point (crystallization temperature). At the crystallization temperature, the macromolecules begin to arrange themselves into crystals, and ordered crystalline regions and disordered amorphous regions are formed. The growth of the crystals may happen spontaneously (when a highly ordered crystal structure is favorable) or may be induced by the presence of a foreign particle (e.g., a nucleating agent or the metal mold surface). Typically, the onset of crystallization occurs at ca. 110–120°C in a differential scanning calorimeter (DSC) at a cooling rate of 10 K/min. The observed crystallization rate is dependent on the nucleation rate and the rate of crystal growth. Crystallization is generally favored by slower cooling from the melt, and the degree of crystallization can be controlled by the rate of melt quenching and subsequent annealing. Very rapid cooling can even suppress crystallization. The degree of crystallinity can vary and different types of crystal structures depending on the stereochemical structure, processing conditions, and additives exist [15]. The observed morphology of PP exhibits a hierarchy of characteristic scales, as shown in Figure 5. In the cross section of a molded part one can see skin–core structures, which on a finer scale reveal a spherulitic structure on the order of 1–50 μm. The size of these structures can be determined by means of optical microscopy, small-angle light scattering (SALS), and scanning (atomic) force microscopy (SFM). The individual spherulite is composed of lamellar-shaped crystals. The lamellar periodicity is given by the long spacing and is in the range of 10–30 nm, depending on processing and thermal history. Typically used protocols are small-angle X-ray scattering (SAXS), higher-resolution electron microscopy, and SFM. The lamellae are composed of crystallographically ordered regions [16]. The individual macromolecule chains form a helical arrangement packed together in unit cells with specific dimensions. The unit-cell dimensions (0.6–2 nm) are shown in Figure 5 for the α form of iPP. Commonly wide-angle X-ray scattering (WAXS),

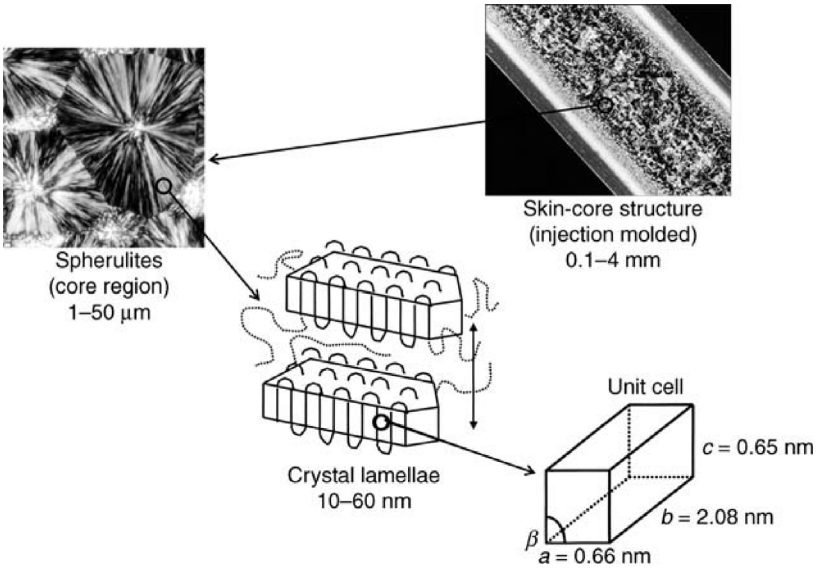


Figure 5. Characteristic hierarchy of morphological scales in PP. The skin–core morphology of an injection-molded specimen is shown to illustrate the morphology on the visual scale (redrawn after [16])

Table 1. Crystal characteristics of PP [17–19]

Crystal form	System	ρ (20°C), g/cm^3	Chains per unit cell	T_m *, °C
i-α	monoclinic	0.932–0.943	4	171
i-β	pseudohexagonal	0.922	9	150
i-γ	triclinic	0.939	1	131
Smectic		0.916		
Amorphous		0.85		
sPP	orthorhombic	0.93	2	138

* The enthalpy of melting for 100% crystalline iPP is variously reported, due to different methods, e.g., 165±18 J/g [17] and 209 J/g [18].

electron diffraction techniques, and SFM are used to evaluate the structure on this scale. The α form of isotactic polypropylene is the primary form of PP obtained under normal processing conditions. Besides the α form, β, γ, and δ crystal modifications are known for PP. The basic features of the crystal forms of PP are given in Table 1 [17–19]. The β form of polypropylene exhibits a lower tensile strength at a given strain rate and higher impact strength than the α form. The β form can specifically be obtained by the use of nucleating agents [20]. It converts to the α form only on melting and recrystallization.

2.3. Multiphase Copolymers

Commercially PP is available in different forms, dependent on the desired properties. Polypropylene homopolymers only consist of propene monomer units and provide stiffness, but their glass transition temperature T_g is about 0°C and thus are not usable in subzero environments. By addition of an elastomeric phase the impact resistance of the material is increased [21]. The addition of an elastomeric component leads to a multiphase structure often referred to as impact or block copolymer. The achieved impact resistance is dependent on the type, amount, and morphology of the elastomeric phase, while the polypropylene matrix determines the stiffness.

Generally multiphase copolymers are produced in at least two reactors in series. In the first reactor the isotactic polypropylene matrix is made, and the second produces an ethylene–propene (EP) elastomeric copolymer. The dispersed copolymer dissipates energy during impact, increasing the toughness of the material. The dispersion of an elastomeric phase in a PP matrix can also be achieved through melt mixing (compounding) of rubber materials with polypropylene. An example of the achieved morphology is given in Figure 6.

3. Raw Materials

3.1. Propene and Comonomers

Due to the high sensitivity of ZN catalysts to impurities, which lead to a drastic reduction of the reaction rate and also negatively affect the product quality (isotacticity) of the polymer, the used propene and comonomers require high purity [22]. Compounds that will bind strongly to the active centers (Ti) of the catalyst or react with the alumina-based cocatalyst, such as polar and highly unsaturated compounds (e.g., acetylenes, dienes, carbon monoxide and dioxide, carbonyl sulfide, water, alcohols, ammonia, and arsine) can only be tolerated at parts-per-billion levels [23]. In addition, compounds that do not influence the chemistry but negatively affect the process by increasing the reactor pressure also must be avoided. These inert substances, such as methane, ethane, propane, butane, and nitrogen, also accumulate in the process and complicate the monomer recovery section and recycle streams.

For the production of polypropylene materials polymer-grade monomers are used as feedstock, which can be further refined by passing the monomers through special purification columns. A typical design consists of four purification steps to scavenge and absorb impurities [22].

Table 2 lists the typical specification for propene quality. Certain catalyst systems may require the lower levels listed for carbonyl

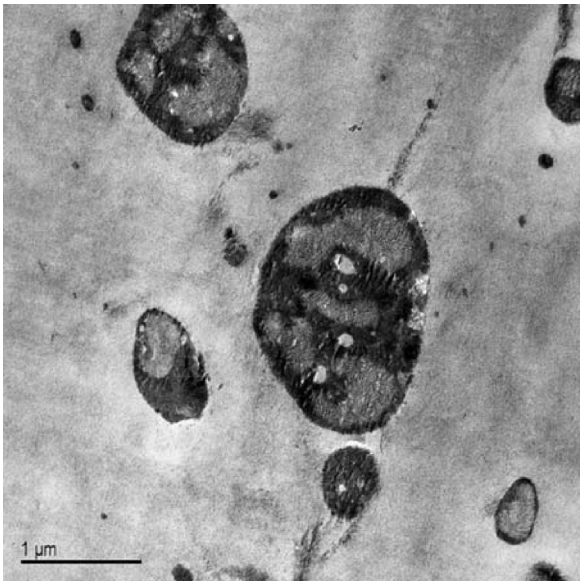


Figure 6. TEM image of the morphology of a commercial high-impact EP copolymer with 16.5 wt% elastomer (Borealis BD310MO). Dark regions correspond to the elastomeric phase with crystalline PE inclusions; contrasted with RuO_4 (scale bar = 1 µm)

sulfide, carbon monoxide, and oxygen (this quality is said to be suitable for metallocene catalysts) [24]. Propene properties relevant to PP production are listed in Table 3.

To broaden the property window of PP certain α-olefins are used in copolymerization with propene. The commercially most important comonomer is ethylene, but 1-butene and higher olefins are reported as well [25, 26].

Propene is normally produced outside the PP plant by steam cracking of naphtha or gas oil at 700–950°C (→ Propene, Section 3.1.) yielding an ethylene-to-propene weight ratio of approximately 2:1. The increasing demand for propene derivatives, especially PP, made other routes such as the dehydrogenation of propane from natural LPG fields commercially interesting (→ Propene, Section 3.3.1).

3.2. Polymerization Diluents

The polymerization of propene can be performed under slurry and gas-phase conditions and combinations thereof. The first commercial processes used inert hydrocarbons ranging from butane to dodecane and refined petroleum fractions as diluents. Typically there is twice as much diluent in the reactor as polymer, and consequently the demands on the purity of the diluent are as stringent as for the monomers. The inert diluent helps to transfer the propene to the solid catalyst and to convey the heat of

Table 2. Propene quality requirements

Type of component	Component	Recommended concentration
Monomer	Propene	99.5 wt% min.
Inert	Ethane	500 vol ppm
	Propane	0.5 wt%
	Butane	500 vol ppm
	$N_2 + CH_4$	300 vol ppm
	Ethylene	50 vol ppm max.
	1-Butene	50 vol ppm max.
	Butadienes	10 vol ppm max.
Copolymerizing monomer	Isobutene	50 vol ppm max (estimated)
Poison	Propyne	5 vol ppm max.
	Propadiene	5 vol ppm max.
	Oxygen	2–5 vol ppm max.
	Carbon monoxide	0.3–3 vol ppm max.
	Carbon dioxide	5 vol ppm max.
	Carbonyl sulfide	0.03–0.5 vol ppm max.
	Total sulfur	1 wt ppm max.
	Water	5 wt ppm max.
	Methanol	5 vol ppm max.
	Ammonia	1 vol ppm max.
	Hydrogen	10 vol ppm max.

Table 3. Propene properties relevant to PP production

Property	Value
Heat of polymerization	2514 kJ/kg
Boiling point	−47.7°C
Critical temperature	92°C
Critical pressure	4.6 MPa
Vapor pressure at 20°C	0.98 MPa

polymerization to the water-cooled reactor jacket. Polar impurities, such as alcohols, carbonyl compounds, water, and sulfur-containing compounds, must be kept below 1–5 ppm. The quality of the diluent is monitored regularly by means of standard analytical methods, preferably on-line analytics, to prevent accumulation of oxidized species and catalyst fragments.

At the end of the polymerization process the used diluent has to be removed completely to guarantee compliance of the PP material with food and drug regulations. Since state-of-the-art polymerization plants are based on gas-phase and bulk (polymerization in liquid propene) technologies the used diluents can be removed more easily.

3.3. Catalysts [27]

Heterogeneous ZN catalyst systems still largely dominate commercial production of highly isotactic PP. The catalyst system consists of a solid transition metal halide, usually $TiCl_4$, a Lewis base (referred to as internal electron donor, e.g., 1,3-diethers) on a support (mostly $MgCl_2$), and an organoaluminum alkylating agent such as triethylaluminum (TEA), and a second Lewis base (usually called external donor, e.g., alkoxysilanes) added separately to the polymerization mixture. An overview on the development phases of propene polymerization catalysts is given in Table 4.

3.3.1. $TiCl_3$-Based Catalysts

$TiCl_3$ can form four different crystalline modifications (i.e., α, β, γ, and δ) dependent on the preparation method used. The α, β, and δ forms are purple, while the fourth is brown (β) and not used for PP production due to its poor stereospecificity. All purple forms have a layer lattice consisting of chlorine atoms with hexagonal (α), cubic (γ), or random succession of hexagonal and cubic close packing (δ) (Fig. 7).

The most important process of industrial $TiCl_3$ production has been the reduction of $TiCl_4$ by means of Al metal or Al alkyls. A major refinement in Al alkyl-reduced $TiCl_3$ systems has been made by Solvay [28, 29] in their three-stage process, which gives a four- to fivefold increase in activity:

1. Preparation of a reduced solid by reducing $TiCl_4$ with diethylaluminum chloride (DEAC) at 0–2°C, and then heating the mixture to 65°C. The obtained brown solid is a β-$TiCl_3$ ($TiCl_3 \cdot x\ AlCl_3 \cdot y\ AlEtCl_2$, where $x \approx 0.15$ and $y \approx 0.20$).
2. The brown β-$TiCl_3$ solid is treated with diisoamyl ether to dissolve out most of the Al compounds.
3. The above solid is treated with excess $TiCl_4$ diluted in hydrocarbons at 60–70°C to give a

Table 4. Performance development of ZN catalysts for PP [a]

Year	Catalyst system	Productivity, $kg_{PP}/g_{Cat.}$	I.I.[b], %	mmmm[c], %	M_w/M_n	H_2 response[d]
1954	δ-$TiCl_3 \cdot 0.33\ AlCl_3$ + $AlEt_2Cl$	2–4	90–94			low
1970	δ-$TiCl_3$ + $AlEt_2Cl$	10–15	94–97			low
1968	$MgCl_2/TiCl_4$ + AlR_3	15	40	50–60		
1971	$MgCl_2/TiCl_4$/benzoate + AlR_3/benzoate	15–30	95–97	90–94	8–10	low
1980	$MgCl_2/TiCl_4$/phthalate + AlR_3/Silane	40–70	95–99	94–99	6.5–8	medium
1988	$MgCl_2/TiCl_4$/diether + AlR_3	100–130	95–98	95–97	5–5.5	very high
1988	$MgCl_2/TiCl_4$/diether + AlR_3/silane	70–100	98–99	97–99	4.5–5	high
1999	$MgCl_2/TiCl_4$/succinate + AlR_3/silane	40–70	95–99	95–99	10–15	medium

[a] Polymerization conditions: liquid propene, 70°C, 2 h.
[b] Isotactic index (% insoluble in boiling heptane).
[c] Content of isotactic pentads.
[d] Melt flow rate change as function of H_2 concentration.

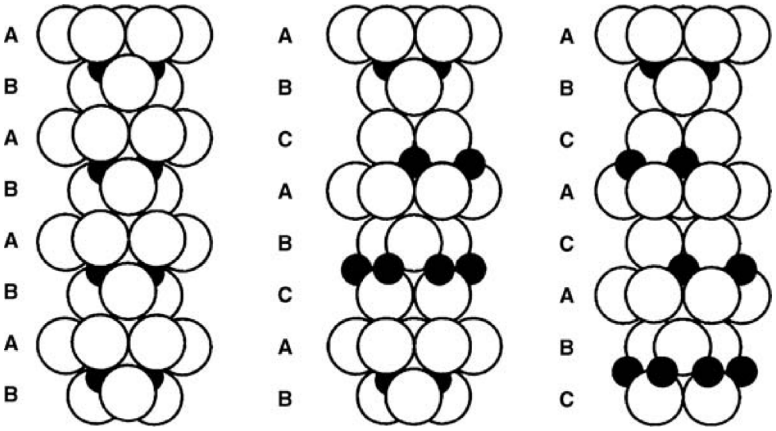


Figure 7. Models of chlorine packing in the different $TiCl_3$ modifications: α (left), γ (center), δ (right) (adapted from [27])

violet δ-$TiCl_3 \cdot x$ ($AlEt_nCl_{3-n}$)$\cdot y$ (i-Am_2O) composition ($n = 0$–2, $x < 0.2$, and $0.01 < y < 0.11$). After washing with hydrocarbons to remove adsorbed $TiCl_4$ and other byproducts, a catalyst with high surface area (150–200 m^2/g), high porosity (> 0.2 cm^3/g), and very high activity is obtained.

Similar catalysts have also been described by other companies, e.g., the Chisso Corporation, Japan. Adding a Lewis base (benzoic esters, alkoxysilanes) is claimed to afford high isotacticity and activity.

3.3.2. $MgCl_2$-Supported $TiCl_4$ Catalysts

A decisive step in the research on ZN PP catalysts was the development of supported titanium catalysts by Montedison (now LyondellBasell) in Italy and Mitsui Petrochemical Industries (now Mitsui Chemicals) in Japan [30]. Collaboration and cross-licensing between these two companies eased the commercial success and avoided incipient interference claims. Starting with finely milled $MgCl_2$, which has a similar structure to violet $TiCl_3$, in 1968, routines were identified to create highly active and stereoselective catalysts. Though other supports with layered structures (e.g., $MgBr_2$, $MnCl_2$, and others) in principle can also be used to make stereospecific catalysts for PP, $MgCl_2$ has been used almost exclusively because it gives catalysts the highest activity and stereospecificity.

For the preparation of particle-form supported catalyst three main procedures have been developed:

1. Mechanical routes: the different catalyst components (usually $MgCl_2$, $TiCl_4$, and a Lewis base) are milled together in suitable ratios.
2. Combined mechanical and chemical routes: $MgCl_2$ or precursors of $MgCl_2$ are co-milled with the Lewis base, followed by one or more treatments with excess $TiCl_4$ at temperatures > 80°C and washing with hydrocarbons to remove unconverted $TiCl_4$.
3. Chemical routes: the active $MgCl_2$ is formed simultaneously with the incorporation of the Ti compound and the Lewis base.
   a. $MgCl_2$ and the Lewis base (e.g., an alcohol) react to form a complex, which is subsequently treated with the internal donor (D_i) and excess $TiCl_4$ at temperatures > 80°C, followed by washing with hydrocarbons.
   b. Solid $Mg(OR)_2$ or Mg(OR)Cl is treated with D_i and excess $TiCl_4$. The $MgCl_2$ is formed by the reaction of the Mg compound with $TiCl_4$, and the byproducts (Ti alkoxides) are eliminated by subsequent washing.
   c. MgR_2 or MgRCl (optionally dispersed on SiO_2, Al_2O_3, or other carriers) react with a chlorinating agent to form active $MgCl_2$, followed by hot treatment with D_i and excess $TiCl_4$ (as above).

d. First a solution of $MgCl_2$ or other Mg compounds (e.g., $Mg(OR)_2$, $Mg(OCOR)_2$, MgR_2, or Mg silylamide) in suitable solvents such as ROH, trialkyl phosphate, $Ti(OR)_4$, epoxychloropropane, and others is prepared. The solution is then either treated with a chlorinating agent to precipitate $MgCl_2$, which is then loaded with Ti and D_i as described above, or directly treated with D_i and excess $TiCl_4$.
e. In a recent development, Borealis described a method [31] for in situ formation of the catalyst carrier particle and the actual active species by solidifying the catalyst from solution. A solution of a complex of a group 2 metal (Mg compound) and an electron donor in an organic liquid is mixed with a transition metal compound (Ti) to produce an emulsion. By changing temperature and stirring conditions solid catalyst particles with regular spherical shape are obtained.

3.3.3. Single-Site Catalysts

Metallocenes have been used for 30 years as model compounds for ZN reactions. They were quite unsuitable for commercial reactors because of their extremely low activity and poor stereocontrol. During the mid-1970s several groups discovered accidentally that traces of water improve the catalyst activity of metallocene-based homogenous catalysts in the presence of trimethylaluminum ($AlMe_3$). Sinn and Kaminsky first identified the potential of $AlMe_3/H_2O$ activators for metallocene-catalyzed ethylene polymerization [32]. Since the 1980s the performance of metallocene-based catalyst systems been improved substantially to produce isotactic, syndiotactic, and stereoblock PP on an industrial scale [33]. Metallocenes suitable for isotactic PP manufacturing generally seem to be based on zirconocenes supported on inert solids to preserve particle size and shape. This makes them more compatible with the advanced process technologies of the major operators, who refer to them as "drop-in catalysts". The concept of single-site catalysts has been expanded to bridged half-sandwich Ti amide complexes, which became known as constrained-geometry catalysts [34]. For many years the focus of metallocene catalyst development was on group 4 transition metals such as Ti, Zr, and Hf. Today the potential of late transition metal complexes of Ni, Pd, Co, and Fe is recognized as well, with heavy patenting in the field. With the development of single-site catalysts it became possible to specifically design polyolefins with narrow molecular mass distribution (polydispersity $M_w/M_n = 2$), well defined regio- and stereoregularity, and molar mass independent random or sequenced comonomer incorporation (see Fig. 8).

Although isotactic PP remains the polypropylene with the highest commercial interest, the opportunities of controlling the microstructure by catalyst design have helped to achieve a better understanding of basic structure–property correlations of PP and to expand its property range.

3.3.4. Aluminum Alkyl Cocatalysts and Donors

The cocatalysts used with $MgCl_2$-supported catalyst systems are preferably Al trialkyls, triethylaluminum (TEA), and triisobutylaluminum (TIBA). Al alkyl chlorides afford a much poorer performance and can only be used in combination with trialkyls. TEA is made commercially from aluminum, ethylene, and hydrogen. Trimethylaluminum is available as methyl aluminoxane (MAO), made through controlled addition of water to the trialkyl.

The external donor (D_e) that can be used is dependent on the type of internal donor (D_i). In the early 1980s alkyl phthalates were introduced as D_i together with alkoxysilanes as D_e, affording improved productivity and isotacticity (see Table 4). These catalysts are still in use in many industrial PP manufacturing processes. Later 1,3-diethers were introduced as internal donors providing even better activities and isotacticities without the need for any external donor. The most recent developments use succinates as D_i; as in the case of phthalates, also here alkoxysilanes are used as D_e. The performance of these catalyst systems is comparable to that of the phthalate systems, but they lead to much broader molecular weight distributions.

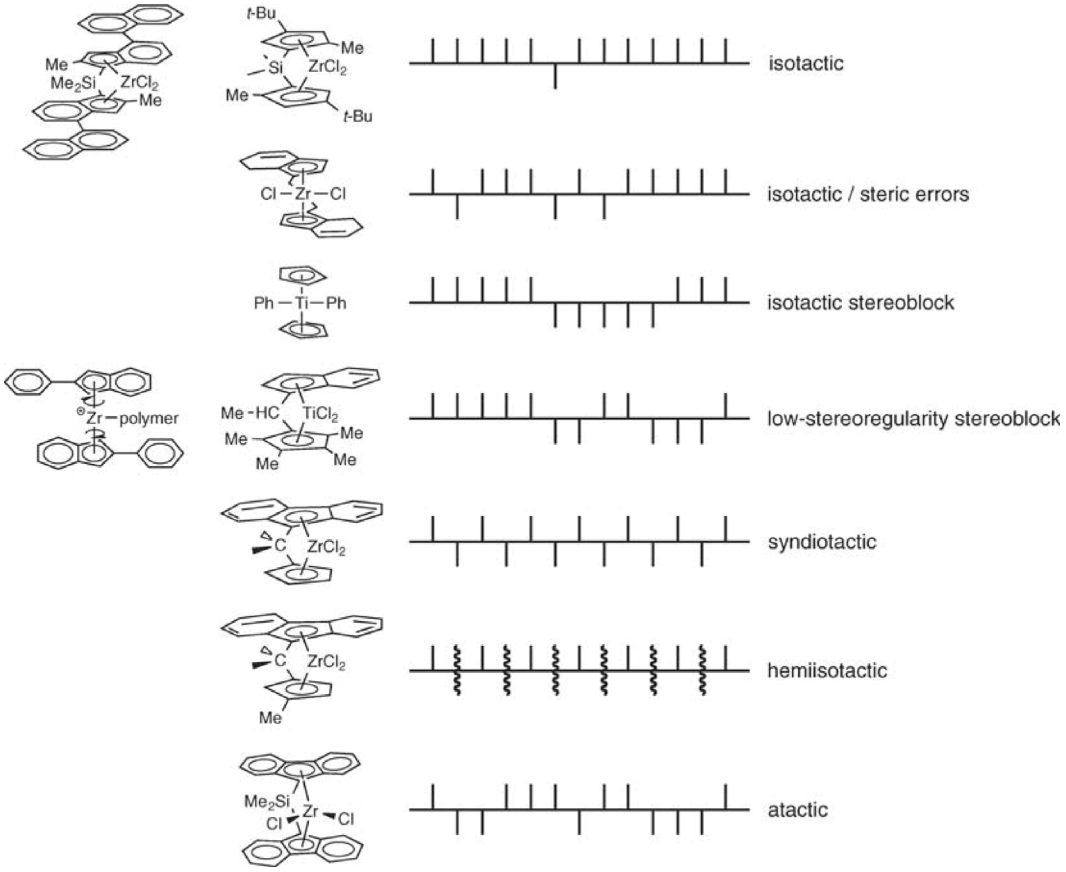


Figure 8. Correlations between metallocene structures and PP architecture (adapted from [32])

3.4. Hydrogen

Hydrogen is used as molar mass regulator in the reactor and its concentration must be accurately controlled.

4. Polymerization Mechanism [35]

For the catalytic polymerization of α-olefins different models and reaction mechanisms were developed. COSSEE [36–38] developed a model to explain the catalytic polymerization process of ethylene or 1-alkenes at a titanium center. The catalytic cycle is shown in Figure 9. It starts with the side-on complexation of the α-olefin, which activates the C–C double bond. This is followed by insertion into the Ti–C bond through a cyclic transition state, by which the polymer chain grows by one monomer unit. Simultaneously, the vacant site becomes free again for complexation of a monomer molecule.

Together with ARLMAN, COSSEE explained how the active sites are formed at the surface of $TiCl_3$. The chloride anions form a closely packed array with gaps where the much smaller Ti cations are located. Each Ti cation is then surrounded octahedrally by six chloride anions. At the surface, the titanium centers and the chloride anions are exposed (Fig. 10), and thus accessible to other components. In the proposed mechanism one chloride ion reacts with the alkyl aluminum compound and is replaced by an alkyl group. In this way, a Ti–C bond is generated at the surface of the $TiCl_3$ particle. The propene (olefin) can insert into this Ti<C->C bond provided there is a vacant site for olefin complexation. This incoming propene molecule approaches the active site, whose immediate crystal geometry controls

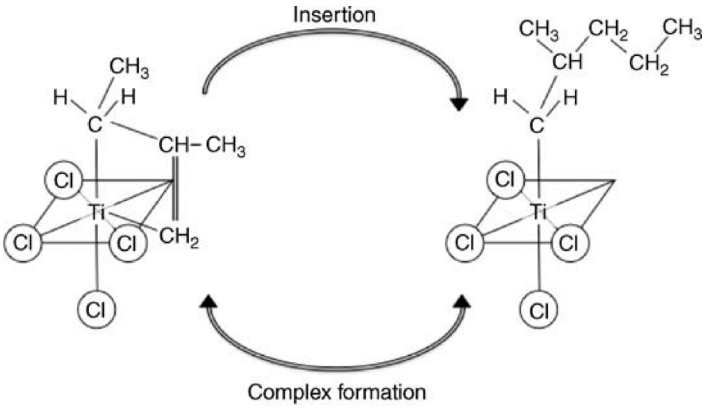


Figure 9. Catalytic cycle for propene polymerization at a heterogeneous $TiCl_3$ catalyst according to Cossee and Arlman (adapted from [35])

both the initial coordination and the configuration as the monomer inserts into the titanium–alkyl σ bond. Accordingly, this is a template-type polymerization controlled by the surface shape, and not by the previously inserted monomer unit. Atactic polymer is formed at more open surface sites having two vacancies or two weakly bonded chlorine atoms. On complexation of one propene molecule to the Ti center, the complex shown in Figure 10 (the figure shows ethene complexation) is formed. In Figure 10, the three chlorine ions at the surface of the $TiCl_3$ particle are shown together with the CH_2 group of the growing chain; the nearest-neighbor chlorine ion inside the crystal cannot be seen. A propene molecule occupies the sixth Ti coordination site. Starting from this transition state, propene is inserted into the Ti–C bond. One catalytic cycle, as shown in Figure 9, is thus completed.

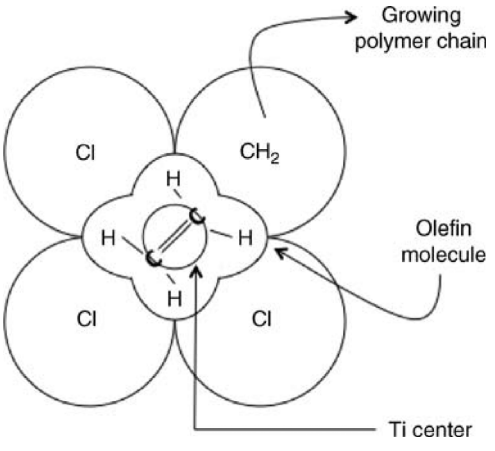


Figure 10. Structure of the active center with a complexed ethylene molecule

In addition to the main reaction, chain propagation (with the monomer as the reaction partner), there are further reactions at the active site, such as β-hydride elimination, which leads to removal of the polymer chain from the active center along with the formation of a vinyl group at the chain end, or chain-transfer reactions with hydrogen and alkyl aluminum compounds.

It is very unlikely that the active sites on the $TiCl_3$ crystal are all uniform, so a distribution of imperfections results. This is why ZN catalysts are referred to as multisite catalysts to emphasize the observed wide distribution of polymer chain lengths and stereoregularities. In $MgCl_2$-supported titanium chloride systems, it is assumed that about 10–20% of the Ti is in the form of active sites. Surface geometry still controls stereoregularity, but Lewis bases are much involved in this regulation [39] (see also Chap. 3).

Metallocene and other single-site catalysts have well-defined structures, which in turn lead to narrow molecular mass distributions and better control of chain irregularities, including new types of chain defects obtained with selected combinations of metallocenes and aluminoxanes. Metallocenes can be used in solution, but for better control of particle size and shape, heterogenized systems are preferred. Supported single-site catalysts can be used as

so-called drop-in catalysts to emphasize the ease of using these systems in existing plants without spoiling catalyst or plant performance.

5. Industrial Polymerization Processes [40]

Since the start of industrial PP production in 1957 the advances in catalyst technology and the demand for improved product performance have been the main drivers for the development of propylene polymerization processes [41]. The processes can be grouped into three main categories: gas-phase, bulk, and improved slurry. All state-of-the-art process technologies employ a gas-phase or bulk reactor system for the production of homopolymers and random copolymers. For the polymerization of impact copolymers (heterophasic copolymers) an additional gas-phase reactor is connected in series. The typical current PP processes are listed in Table 5.

Polyolefin production lines have been developed to extremely efficient and large machines, starting with annual capacities of about 5×10^3 t in 1963 to more than 400×10^3 t for the newest plants being built now.

Historically the suspension processes are the oldest ones; three facts are decisive for the design:

1. The limited polymerization yield of the catalyst, which on the one hand resulted in the necessity to remove the catalyst residues. On the other hand, it implied the use of serial reactors for improving productivity.
2. The necessity to remove amorphous fractions (atactic PP, which is found at ZN catalysts in low molecular masses and waxy form) because of the limited stereocontrol in the polymerization.
3. The fact that complex copolymers with multiphase structure and various solubility were soon considered as important products to expand the application range of PP.

Table 5. Some typical PP processes (homopolymer reactor)

Regime	Process (technology supplier)
Gas phase	Unipol (Dow)
	Innovene PP (Ineos)
	Horizone (JPP)
	Spherizone (LyondellBasell)
	Novolen (Novolen)
Bulk	Spheripol (LyondellBasell)
	Borstar (Borealis)
	Hypol II (Mitsui)
	ExxonMobil
Slurry	Several

In Figure 11 the block design for an early PP process is compared with a fourth-generation ZN catalyst setup. Especially the advances in catalyst technology led to the design of more efficient processes, and thus the elimination of some process steps.

For slurry- and gas-phase reactors the polymer is formed around heterogeneous catalyst particles. Slurry technologies can be divided into diluent and bulk processes. In diluent technologies, an inert diluent (typically a C_4–C_6 alkane) is used to disperse the growing polymer particles, while the monomer (propene and ethylene as comonomer) is introduced as a gas and other comonomers (higher α-olefins) are fed as liquids. In bulk technology the polymerization takes place in the liquid propylene monomer. Slurry technology can be used for the production of PE and PP, while bulk technology is restricted to polypropylene and its copolymers. In slurry polymerizations autoclaves and loop reactors are used. Ethylene, propene, and higher α-olefins can also be polymerized in gas-phase reactors. They can be classified into fluidized-bed reactors (FBRs) and stirred-bed reactors (SBRs). In FBRs a gaseous stream of monomer and an inert gas (nitrogen) fluidizes the polymer particles, while mechanical stirring is responsible for suspending the polymer particles in gas-phase SBRs. This reactor type can be subdivided into horizontal and vertical reactors.

5.1. Liquid-Phase Processes

The first commercial PP production processes were based on slurry technology. The main advantage of using slurries rather than the gas phase is the far better heat-transfer capacity when the polymer particles are suspended in a liquid. However, slurry processes require a workup section for the diluent, leading to extra costs in the investment and operation of the plant.

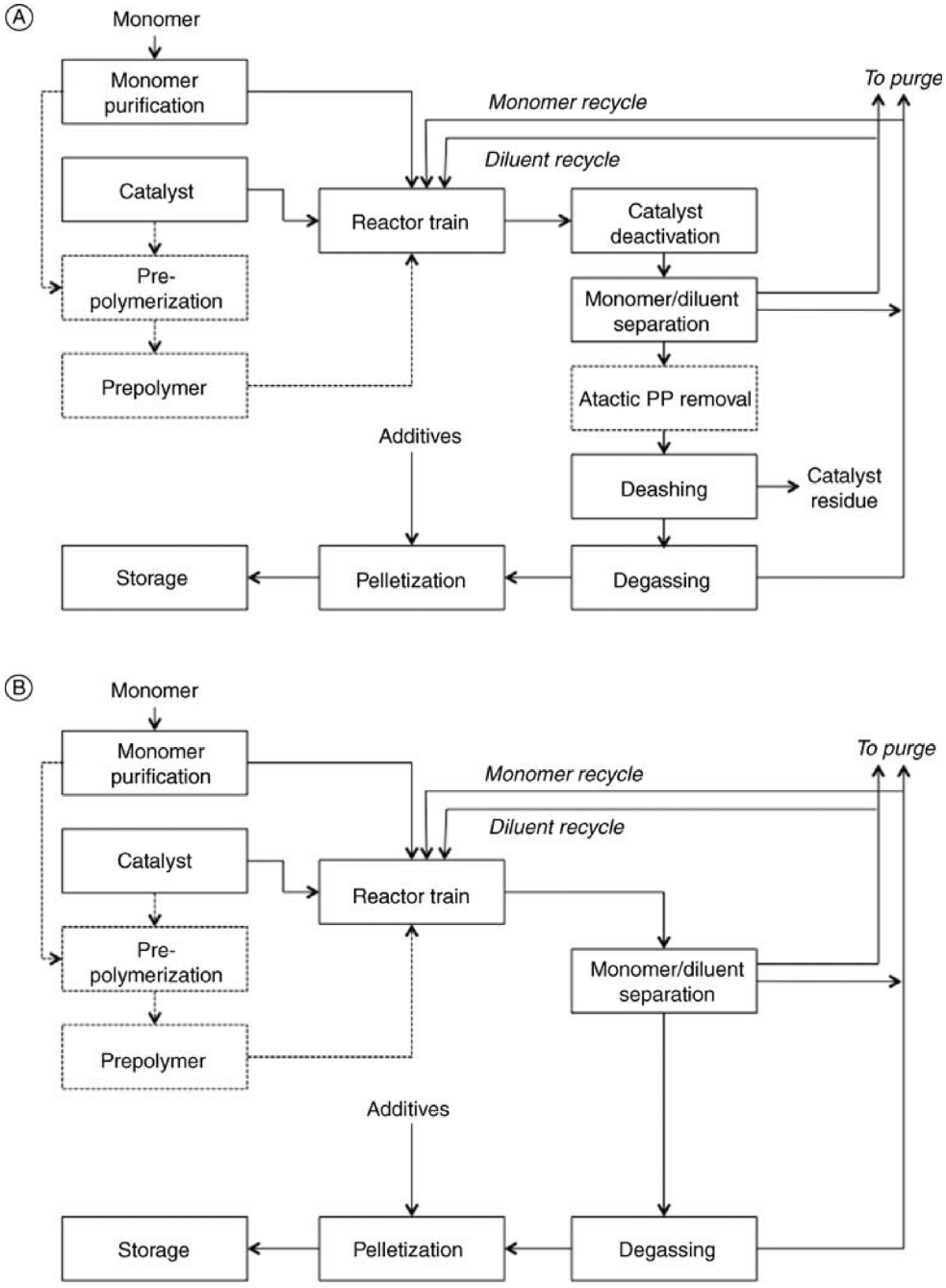


Figure 11. Polyolefin plant designs
A) Early PP process; B) State-of-the-art PP process

Most first-generation PP processes used slurry conditions (Hercules and Montecatini) with hexane as diluent. Two to four stirred tank reactors (autoclaves operated at 60–80°C and 5–15 bar) not only allowed good monomer conversion, but also the production of copolymers with multiphase structure. The limits are defined here by the copolymer solubility but also the available heat-transfer surface per unit volume compared with loop reactors.

The workup of the reaction mixture in these early processes was rather tedious. Both the atactic fractions and the catalyst, which is still used today for producing PP grades with very high purity, which are, for example, required for producing capacitor films, had to be removed. The catalyst is decomposed with a mixture of alcohol and $NaOH/H_2O$, followed by separation of the organic and aqueous phases. The aqueous stream is distilled, leaving the catalyst residue in the wastewater. The organic stream is then sent to a centrifuge for removing the iPP part. From the diluent stream the aPP is recovered in a thin-film evaporator, while the iPP is purified with steam and dried.

Polymerization in liquid propene as polymerization medium (bulk process) can be performed in continuous stirred-tank reactors or loop reactors. In both cases the use of liquid monomer as polymerization medium maximizes the polymerization rate due to the high monomer concentration. Bulk processes are used to produce homopolymers and random copolymers with less than 5 wt% of ethylene (or other comonomers). Higher concentrations of the comonomer or the production of rubber phases (ethylene–propylene rubber) in heterophasic copolymers are not feasible due to the solubility of the rubber in the liquid monomer. For the production of these materials hybrid processes (see Section 5.3 or multistage gas-phase reactors) are used.

Loop reactors account for production of about 50% of all commercial polyolefins (PE and PP) and many different reactor configurations are used in industrial processes. The loop reactor can be placed in the vertical (*Phillips*, *Spheripol*, *Borstar* processes) or horizontal position (*USI process*). The loops can have up to 12 legs (the loop shown in Fig. 12 has four legs), and each leg can be up to 60 m tall. The volume of a typical loop reactor is on the order of 100 m^3, which corresponds to a capacity of roughly 250×10^3 t/a. The solid content is in the range of 40–50 vol%, mainly limited by the viscosity of the slurry. A pump provides for circulation of the slurry at the bottom of one of the legs. High fluid velocities (10–30 m/s) create a turbulent flow, which helps to prevent particle settling and also improves the heat-transfer coefficient.

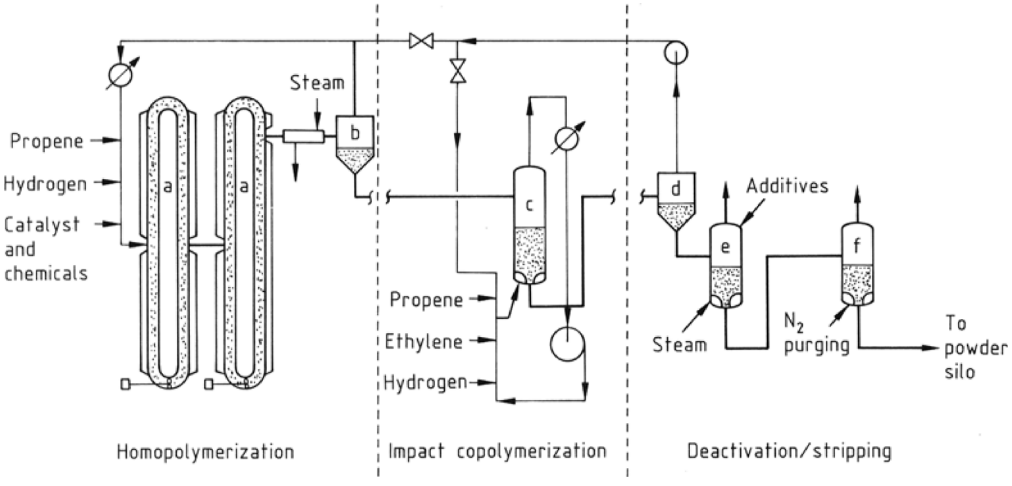


Figure 12. Spheripol process
a) Loop reactors; b) Primary cyclone; c) Copolymer fluidized bed; d) Secondary and copolymer cyclone; e) Deactivation; f) Purging

5.2. Gas-Phase Processes

Gas-phase processes are an economical and energy-efficient alternative to liquid-phase polymerization. Separation of polymer from the unconverted monomer is easy, since the monomer is in the gas phase. There is no need to flash off large amounts of liquids, which means a significant cost reduction compared to slurry processes. Another advantage of gas-phase processes is their potentially broader product window, as there are no solubility limits for hydrogen and monomers in the reaction medium. Polypropylenes with very high melt flows (low viscosities) and high comonomer contents can be produced. However, the actual flexibility of the process depends on the reactor size and the residence-time distribution (RTD). A drawback of gas-phase reactors is their limited heat-transfer capability. To enhance the thermal characteristics of these reactor types special actions must be taken. One possibility is to inject small amounts of liquid components below their dew points or the use of inert gas-phase compounds with a higher heat capacity than nitrogen.

From a process design perspective gas-phase reactors are available as FBRs and SBRs in vertical and horizontal configuration, as well as the multizone-circulating reactor (MZCR) introduced by LyondellBasell.

The *Unipol process* by Dow was initially developed for PE production in the late 1970s and later adapted for the polymerization of PP by introducing Shell high-activity catalysts (SHAC) [23]. The process is based on a large FBR for the production of homopolymers and random copolymers and can be extended by a second, smaller, gas-phase reactor for the production of heterophasic copolymers. The basic design of the process is shown in Figure 13. The expanded upper section in the reactor is designed to reduce gas velocity and powder entrainment. Reaction conditions are reported as 60–70°C for the homopolymer reactor and a pressure in the range of 25–30 bar. The residence time per reactor is typically 1 h. Thus, the grade transition times are comparable with those of loop reactors. The Unipol process has a unique product discharge system, using a cyclone separator.

The *Innovene* and the Japan Polypropylene (JPP) *Horizone process* technology are based on a horizontal stirred gas-phase reactor. The reaction conditions are 65–85°C for the homopolymer reactor and a pressure in the range of

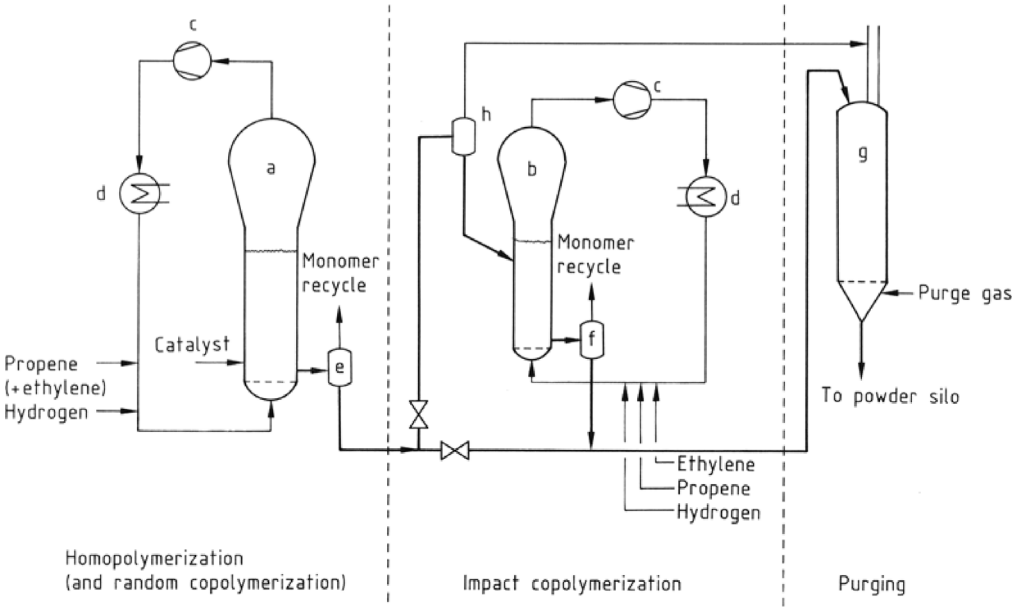


Figure 13. Unipol fluidized-bed process
a) Primary fluidized bed; b) Copolymer fluidized bed; c) Compressors; d) Coolers; e), f) Discharge cyclones; g) Purge

25–30 bar. The residence time per reactor is typically 1 h. The spacing of the injection points for the catalyst and cocatalyst appear to be critical for this type of reactor. If they are to close one encounters lump formation in the feed zone; if they are too far apart the catalyst is not properly activated. Adding the ethylene–propene rubber in a second gas-phase reactor can make heterophasic copolymers.

Vertical stirred gas-phase reactors were developed first by BASF, *Novolen technology*, and put into operation in 1967. Originally the design was that of a stirred autoclave with a bottom-mounted helical stirrer. This stirrer is designed to convey the particles up the reactor wall and let them fall down through the center of the bed. The special design of the agitation system is considered to be responsible for forming subsegments in the reactor. Thus, it is claimed that the reactor behaves like a cascade of a large number of CSTRs. The heat is removed by circulating monomer gas through an external heat exchanger. For impact-modified PP, a rubber phase is polymerized in the second gas-phase reactor connected in series. Figure 14 shows the design of the Novolen process.

The *Spherizone* multizone circulating reactor (MZCR), presented in Figure 15, was developed by Basell and first commercialized in the early 2000s. This reactor concept builds on the riser-tube design known from fluid catalytic cracking. The Spherizone technology consists of two interconnected reaction zones—a riser and a downer—separated by a cyclone. In the riser (the first reaction zone) the gas velocity is high and thus this zone acts like a fast-fluidized bed. In the connected cyclone the polymer particles are separated from the gas and then enter the second reaction zone (downer). The downer can be characterized as a moving packed bed [42]. The two different sections of the reactor can be operated at different concentrations of hydrogen and comonomer, leading to bimodal polymer qualities (with respect to molecular mass and/or comonomer concentration). This is achieved by separating the composition of two reaction zones with the help of a barrier fluid introduced

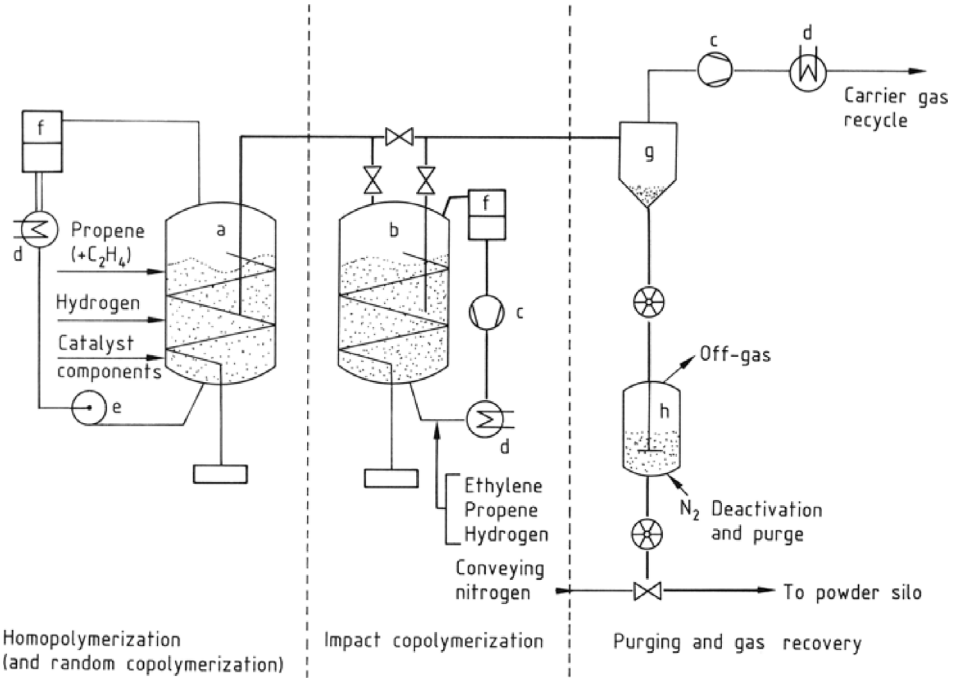


Figure 14. BASF gas-phase Novolen process
a) Primary reactor; b) Copolymerizer; c) Compressors; d) Condensers; e) Liquid pump; f) Filters; g) Primary cyclone; h) Deactivation/purge

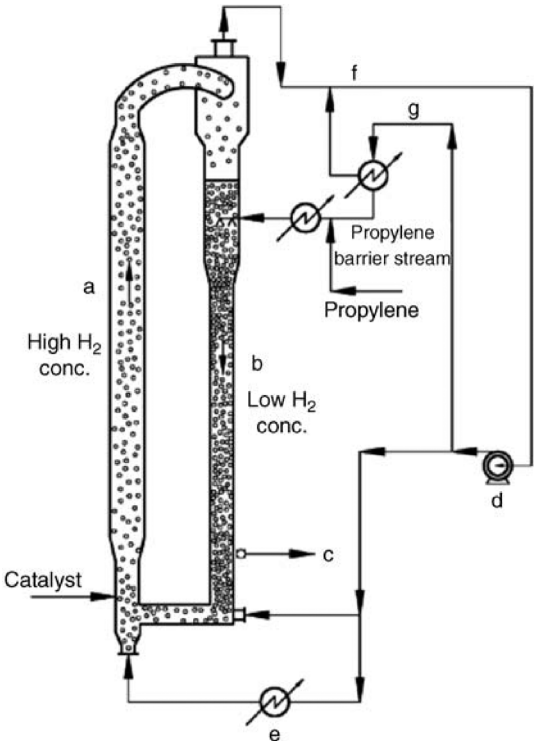


Figure 15. LyondellBasell Spherizone multizone circulating gas-phase process (adapted from [42])
a) Riser: upward pneumatic transport; b) Downer: packed bed moving downward; c) Product discharge; d) Gas fan; e) Heat exchanger; f) Internal gas/solid separator; g) Condenser

at the top of the downer. The fast circulation of the growing polymer particles between the different reaction zones makes the residence time per pass in each zone one order of magnitude smaller than the overall residence time. This leads to a very good homogeneity of the final product even for bimodal compositions.

The multizone circulating reactor can be connected with an additional gas-phase reactor (FBR) for producing heterophasic copolymers.

5.3. Hybrid Processes

Hybrid processes combine the production of a homopolymer or random copolymer with low ethylene content in liquid propene with the production of a rubber phase (ethylene-propene rubber) in a sequential gas-phase reactor.

The dominant hybrid process is the *Spheripol process* by LyondellBasell. Figure 12 shows a two-loop and single-FBR Spheripol design. Roughly one-third of today's world PP production is based on this technology. In this process monomer and catalyst components are fed into the first loop reactor for homo- and random copolymerization. Due to the large surface-to-volume ratio of loop reactors, the heat-removal capacity is high and enables high specific outputs exceeding 400 kg h^{-1} m^{-3} of PP. The shape of the spherical catalyst particles, consisting of many microscopic $MgCl_2$ single crystals with active surface, is replicated to give spherical polymer particles with a narrow particle size distribution. Coupled with the high liquid velocities in the loop reactor, reactor fouling can be avoided. Operating conditions are in the range of 60–80°C and 35–50 bar.

For impact (heterophasic) copolymers, a gas-phase reactor is required. Upon exiting the loop reactors, the propene–PP slurry is depressurized and flashed. The pressure must be adjusted to allow recycling of the vaporized monomer by condensation and to be sufficient for gas-phase copolymerization. The ethylene–propene rubber needed for impact copolymer is produced in an FBR at temperatures up to 100°C and a pressure of 15 bar. A second (or even third) FBR can be added to the process for tailoring the rubber phase with respect to molecular weight and comonomer concentration.

The Mitsui *Hypol* bulk polypropylene process was originally based on two stirred autoclave reactors in place of the loop reactors shown for the Spheripol process in Figure 12, followed by two stirred FBRs. In the Hypol II process loop reactors replace the stirred autoclaves. The gas-phase reactors are also used to produce homopolymers, enabling a broader polymer-property window.

The design and operation of the ExxonMobil PP process technology was originally based on the Hypol design but has been modified with respect to gas-phase reactor operation.

Borealis has developed the *Borstar* polyolefin process technology for the production of PE and PP. A basic design of the Borstar PP technology is given in Figure 16. The platform for making homopolymers and random copolymers is based on a loop reactor followed by an FBR. The loop reactor allows polymerization under sub- or supercritical conditions. For PE this is done in propane and PP is

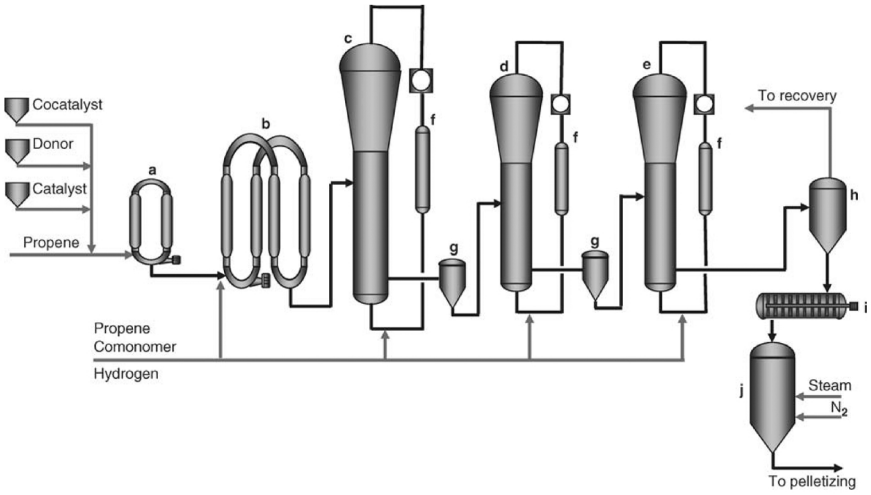


Figure 16. Borstar PP process scheme (four-reactor setup)
a) Prepolymerizer; b) Loop reactor; c) First gas-phase reactor; d) Second gas-phase reactor; e) Third gas-phase reactor; f) Coolers; g) Separators; h) Low-pressure degasser; i) Dryer; j) Purge bin

polymerized in liquid propene. The advantage of running the loop reactor under supercritical conditions is the possibility of increased hydrogen and comonomer concentration without the formation of gas bubbles. In the next section an ethylene–propene rubber is made in an FBR for producing impact copolymers. Powder transfer from the homopolymer FBR to the rubber gas-phase reactor allows complete gas separation for better design of the rubber. An additional rubber FBR can be added to the reactor train if high elastomer contents are required.

The hybrid processes are the workhorses of the polypropylene industry. Loop reactors dominate the bulk polymerization processes due to the better heat-transfer capacity and thus higher production rates. Hybrid processes contain up to six reactors split between a sector dedicated to homopolymers and random copolymers and a second sector used for the production of a rubbery phase (ethylene–propylene rubber) to increase the toughness of the polymers. This second block contains only FBRs. The two blocks are almost always separated by a kind of gas lock/flash in order to better control the properties of the different phases. With the described process design PP manufacturers can produce a wide range of product qualities, but this must be balanced with the capital investments needed for full-fledged reactor train.

6. Product Finishing

The so-called dry end of a polymerization plant starts at the discharge point from the last polymerization reactor and involves deactivation, powder purification, and in most cases melt compounding. Even if the polymer is planned to be sold as powder, it must be stabilized, as PP is far more susceptible to radical attack and degradation than PE. In any case, the transport and sale of PP can be handled both in bulk form (silo trucks or railway cars) and in packages of various sizes, ranging from 25 kg bags to big-bags and octabins (corrugated cardboard containers with PE-film inlays) containing up to 1000 kg.

Melt homogenization can provide several functions for the final product, ranging from homogenization (especially relevant for polymers with a bimodal or generally broad molecular mass distribution (MWD) and heterophasic copolymers [43]) through the dispersion of stabilizers and other functional additives to generating a product with homogeneous particle (pellet) size. With increasing plant size, the respective equipment has also increased in throughput from 15–20 t/h in 1990 to 50–75 t/h in 2010. In addition to cost, extruders are selected according to the following factors: powder morphology, product melt flow rate (MFR) range, melt filtration needs, devolatalization options, throughput flexibility, temperature control, mixing needs, and additive feeds. Single-screw machines are hardly used any more, while twin-screw extruders with co-rotating and segmented screws dominate the market because of their high flexibility and good mixing efficiency. A balance between mixing quality and polymer degradation must always be kept, with temperature (220–260°C) and specific energy input (SEI) as decisive factors. A gear pump between the die plate and the discharge end of the screw can be used both to reduce the SEI and to increase the throughput.

Pelletization is possible in strand form or in underwater systems. Modern polymerization plants are, however, too big for the former in which several melt strands from the die plate are quenched in water for solidification and then chopped by high-speed cutters into 2–5 mm long cylinders. In underwater systems, high-speed knives rotate against the extruder die plate to cut off short lengths of the molten extrudate. The insulated die plate is immersed in water, which solidifies the lens-shaped pellets and also transports them to a sieving and drying device. While nitrogen must be used for powder conveying up to the extruder, air can be used for pneumatic pellet transport afterwards.

The direct sale of nonstabilized or (mostly) spray-stabilized PP powder is very limited. While in the 1990s Himont (presently LyondellBasell) still assumed that the spherical powders resulting from fourth-generation catalysts and the Spheripol process would be suitable in nonpelletized form for large parts of the market, applications are largely limited to rotomolding, melt-blown fiber spinning, and use as supports for liquid additives like peroxides. While energy-intensive extrusion and pelletization operations could be saved, the limited choice of additives and the homogenization problems more than compensate these advantages in most areas.

6.1. Additives

Nonpolymeric additives generally allow further modification of the properties of polyolefins. An approximate distinction is drawn between additives (up to 1 wt% addition, typically ca. 0.05–0.3 wt%) and fillers or reinforcements (5–40 wt% addition). The most important additives [44] are antioxidants and UV stabilizers.

More than PE, PP must be protected against oxidation, particularly above 100°C. The dominant reaction is chain scission by free-radical attack at the tertiary carbon atoms of the backbone. The different types of *antioxidants* can be divided into:

- H donors/primary antioxidants (e.g., sterically hindered phenols; active mostly at application temperatures)
- Hydroperoxide decomposers/secondary antioxidants (e.g., phosphites; active mostly at processing temperatures)
- Radical scavengers [hindered amine light stabilizers (HALS); specific against UV-induced radicals)

In Figure 17 the autooxidation process and the principle of antioxidants in polymers is illustrated. The reaction starts on the left-hand side of the scheme, where scission of the chain (R) initiated by, e.g., heat and shear to give the alkyl radical ($R^{\bullet}$) is shown. The alkyl radical can be directly deactivated with a radical scavenger or forms the peroxy radical ($ROO^{\bullet}$) in the presence of oxygen. Both the H donor (primary antioxidant) and the radical scavenger can work as antioxidant here. Otherwise, $ROO^{\bullet}$ will react with other chains by hydrogen abstraction (cleavage of the weakest C–H bond). This leads to the formation of hydroperoxide (ROOH), which is relatively unstable and decomposes into the reactive alkoxy radical ($RO^{\bullet}$) and the hydroxy radical ($^{\bullet}OH$). $ROO^{\bullet}$ reacts with the H donor to form stable ROOH. Hydroperoxide decomposers (secondary antioxidants) are used to induce (from ROOH) the formation of inert alkoxy ($RO^{\bullet}$) and hydroxy radicals ($^{\bullet}OH$) to avoid chain fracture, which otherwise results in discoloration and brittleness.

A further contribution to long-term stability is the use of acid scavengers for neutralizing decomposition products of ZN catalysts, especially HCl. The most common is Ca stearate (0.05–0.1 wt%), which also prevents equipment corrosion. It behaves as a mild slip agent and suppresses attack of HCl on certain antioxidants. Stearates or oxides of zinc and magnesium are also in use, and synthetic hydrotalcite (a hydrated magnesium aluminum hydroxycarbonate) is the latest addition to this class.

Besides the thermomechanical loading to be expected for a specific application, additive packages are also defined by critical environmental interactions, e.g., NO_x with fibers or detergent solutions with appliance components. The choice of stabilizer is further influenced by regulatory constraints such as global or specific migration limits.

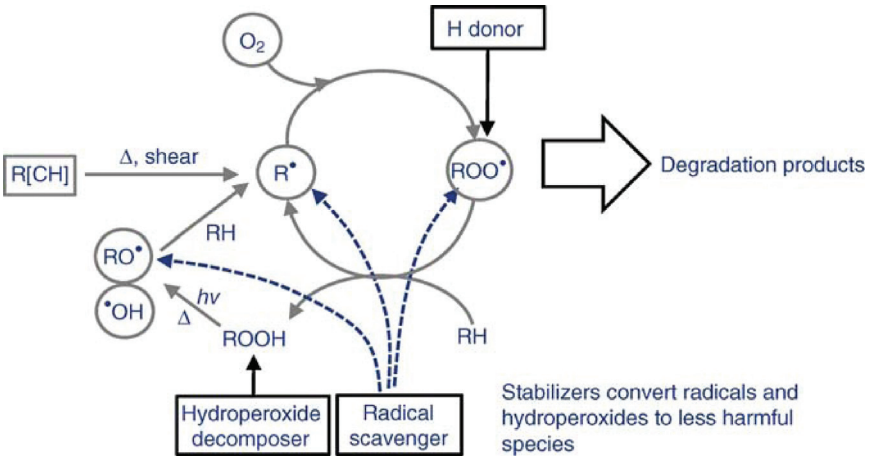


Figure 17. General scheme of inhibition of thermo-oxidative degradation of PP

Continuous outdoor exposure also requires protection from the damaging effects of UV radiation, for which UV absorbers (in the simplest case carbon black or TiO_2) or radical scavengers are used. Polymer photooxidation results from the combined action of light and oxygen. First, the polymer chain is excited by the absorption of light ($h\nu$), and UV absorbers act in this stage of degradation. In the presence of oxygen and further light, an alkyl radical ($R^{\bullet}$) is formed, and radical scavengers (HALS) are used to scavenge radicals. In contrast to UV light, the effect of high-energy radiation like electrons or γ rays cannot be prevented by additives alone; polymer design measures must be considered here.

Antistatic agents act against static charges and resulting dust deposits on many plastics; 0.2–1.0 wt% of polar additives such as polyether fatty amide and fatty amine condensates, but also simple glyceryl monostearate, reduce the surface resistivity from $>10^{13}$ to ca. 10^7 Ω. The mechanism involves slow diffusion of the additive to the surface, where it picks up atmospheric moisture. Time and humidity are important, and while at 50% RH most of the recommended additives are satisfactory, dryer environments require the use of fatty amine derivatives.

Slip and antiblocking agents are mainly used in film production where high-speed handling requires a controlled reduction in frictional forces; 0.1–0.5 wt% of oleamide, erucamide, or mixtures thereof is usually sufficient. Fine, spherical particles of silica or other minerals prevent layers of film adhering to each other during storage.

Nucleating agents for PP crystallization [45] are applied both for improving processability and final performance. The combination of moderately slow crystal growth at large undercoolings together with the practical absence of sporadic nucleation makes iPP, which melts at 160–170°C but crystallizes at 100–130°C, an ideal material for controlled nucleation. In addition, the different crystal modifications of iPP (α, β, and γ) can be controlled in their respective expression, and thus affect the mechanical and optical profile of the material. A wide range of chemically very different substances (see Fig. 18) can be used; decisive is the crystalline and not the molecular structure, because nucleation happens by epitaxy and "lattice matching". These additives must be distributed very well. Different routes can be applied here, and the Borealis nucleation technology (BNT) has a special position: Because the dispersion occurs already during the polymerization step, a very low concentration of a polymeric nucleating agent is sufficient for optimum performance [46]. Improvements of stiffness (modulus) and the related heat deflection temperature by selectively nucleating the α modification is one of the key targets. Another target of α nucleation is improved transparency and clarity; here nucleation will even help to prevent haze increase during steam sterilization (normally caused by postcrystallization at the elevated temperature

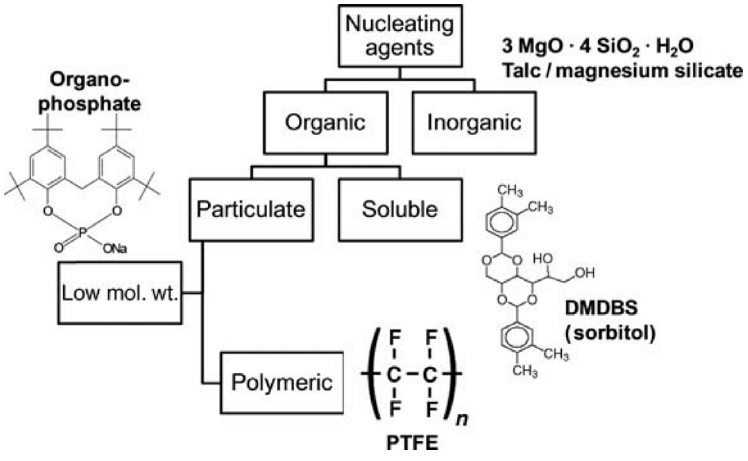


Figure 18. Classification of nucleating agents for PP

used). As crystallization is also accelerated, nucleation also helps to reduce cycle times in injection molding and to allow higher speed in extrusion processes. Specific β nucleation is a useful tool for improving impact strength and reducing crack growth in pipe materials, where it has already been used for many years [20]. Careful balancing of the overall additives recipe is essential in any case, because both adverse and beneficial interactions occur between some of the components.

6.2. Compounding and Blending

For PP, modification after the polymerization process plays a major role in expanding the property range. Besides the already mentioned co-rotating twin-screw extruders with special mixing elements for improving the quality of dispersion and resulting phase structure, other kneaders and mixers are used for special requirements. The Farrel kneader, for example, has a large blending chamber for adding EPR, EPDM, and other elastomers in form of a bale, while the Buss co-kneader allows more gentle dispersion of glass fibers by combining rotating and pulsating melt movement.

Modifications of mechanical properties as well as shrinkage and thermal expansion are possible through the addition of fillers and reinforcements of mostly mineral nature. The respective effects are determined by the properties of the base polymer as well as by the quantity and nature of the filler [47]. Talc with an average particle size of 0.6–10 μm is the most important filler, while calcium carbonate, kaolin, wollastonite, and mica are used to a lesser extent.

When using glass fibers (GF), which give the highest strength, further improvements are possible by modifying the fiber surface (sizing) and using compatibilizers (adhesives). Both short (S) GF having an initial fiber length of 3–5 mm and long (L) GF are applied. While SGF compounds are produced in normal melt mixing, LGF–PP is produced by impregnating continuous GF rovings with a high-MFR matrix and cutting the resulting strand after solidification to 10–15 mm length. Special processing operations are required in the latter case to avoid excessive fiber breakage [48], but the resulting material is well suited for metal replacement, especially in the automotive area.

Organic reinforcing fibers are obtained from natural (regenerative) sources such as hemp, flax, sisal, and wood, including high-crystallinity man-made cellulose fibers [49]. The strength of glass fiber reinforced materials is not achieved with such additives and the lot-to-lot variations of natural fibers are a problem; the full combustibility and improved sustainability of such composites are, however, seen as an advantage.

Modification or blending with elastomeric or polymeric components for further expanding the property range of PP is discussed in Section 7.4.

6.3. Reactive Modification

An even broader variety of structural modification is possible by reactive post-reactor processes. The earliest version was targeted at modifying the molecular mass distribution, whereby the preferential splitting of PP chains in radical reactions allows tailored production of narrow molecular mass distributions [50]. This process, known as visbreaking or (controlled rheology) CR process, is best applied to PP homopolymers or random copolymers, leading to products with higher MFR and broader Newtonian region of the viscosity curve. Often liquid peroxides are in use, which are sprayed under nitrogen onto the warm reactor powder before it is fed to the pelletization extruder. In large-scale plants, visbreaking also allows the production of a multiplicity of grades from one reactor setting. While for reactor grades of PP (with broad MWD), stiffness increases with increasing MFR, it remains constant or is reduced for visbroken (narrow-MWD) grades. At the same time, transparency and surface gloss are rather improved, and these grades have significant advantages in fiber spinning and cast-film processes.

Other reactive modification steps for PP are also mostly based on radical-initiated grafting reactions [51]. The potential applications of this technology range from the production of long-chain branched PP with high melt strength (strain hardening) offering advantages in foaming [52] and other processes with strong extensional flowlike extrusion coating, via the stabilization or partial crosslinking of phase structures (to the point of thermoplastic

vulcanizates, TPVs) up to polar modifiers (e.g., by grafting with maleic anhydride).

7. Properties

7.1. Homopolymers

For PP homopolymers (PP-H), the mechanical and optical performance is determined by:

- The average molecular mass and molecular mass distribution
- The chain structure, i.e., the presence of stereo- and regiodefects
- Nucleating additives (see Section 6.1) [53]

As for all semicrystalline polymers, processing history and component geometry will play a further role in affecting the final properties, and the evolution of performance over time will depend on a proper stabilization.

While a proper parameter for the average chain length is the weight average of the molecular mass distribution M_w in industrial practice polymers are normally defined by their melt flow rate (MFR), which in the case of PP is determined at 230°C and 2.16 kg load. The two parameters are related via the melt viscosity, where the zero-shear viscosity η_0 is proportional to the 3.4-th power of M_w [43]. At higher shear rates normally encountered in processing and more characteristic for MFR determination, the dependence is still greater than a power of two because much chain entanglement still exists. The exact correlation, however, also depends on the broadness (polydispersity, defined as ratio between M_w and the number average of the molecular mass distribution M_n) and shape of the molecular mass distribution. PP-H grades are commercially available in an MFR range of 0.3–1000, corresponding to an M_w of 500–20 kg/mol and covering applications from sheet and pipe extrusion to high-speed fiber spinning.

With modern ZN catalysts a single-step reaction gives a polydispersity M_w/M_n of 4–6, while with older catalyst types ($TiCl_3$, used in diluent-based slurry processes) M_w/M_n can be up to 8. Broad or bimodal molecular mass distributions are achieved by multistage polymerization with varying hydrogen feed and/or temperature, while narrow molecular mass distributions with M_w/M_n down to ca. 2 are mostly achieved by visbreaking (see Section 6.3). Both versions have specific advantages: High polydispersities deliver higher crystal orientation through flow-induced crystallization [54, 55], especially in injection molding, which results in higher stiffness and heat resistance and is consequently of interest for technical applications. Narrow-MWD grades crystallize more slowly [53] and have advantages in film casting and fiber spinning, but also for special molding applications like film hinges.

The chain structure of PP homopolymers is affected by stereo- and regiodefects, the latter only being relevant for single-site catalysts (SSC). An absolute quantification of stereoregularity is only possible by ^{13}C NMR spectroscopy in solution, with isotactic triads (mm) or pentads (mmmm) being used for quantification. Commercial PP has a pentad regularity of >92%, and very high stereoregularity of >97% is achievable with modern ZN catalysts and suitable external donors, even without removing any soluble (atactic) byproduct. Besides a broad MWD, high isotacticity is a further tool for reaching highest stiffness [54]. Alternative measures for isotacticity are FTIR spectroscopy (in the solid state, where sample preparation must be considered) and the content of heptanes-soluble fraction. For some applications like nonwovens with thermobonded fibers or biaxially oriented PP (BOPP) film, processing can be facilitated by reduced isotacticity or chain regularity in general. This is readily achieved by lowering the donor feed in polymerization, or by introducing small amounts of copolymerized ethylene.

When isotactic PP is produced by SSC or, more specifically, metallocene catalysts (MC), three major product-related differences over ZN catalysts are evident [56, 57]:

1. The polymers have a much lower polydispersity, with M_w/M_n in the range of 1.8–3. Also, the amount of solubles, measured both in cold xylene (XCS) and in boiling hexane (C6) is reduced significantly, as is the level of hydrocarbon emissions. All of these advantages can be explained by the reduced amount of oligomers generated in SSC-based polymerization.
2. Besides the stereoregularity, the presence of regiodefects (misinsertions of monomers)

must be considered. Most relevant are the 2,1 regiodefects commonly defined as the sum of 2,1-*erythro* and 2,1-*threo* regiodefects, which can be present up to 2 mol% depending on the MC type. While MC-based PP-H types can have a high isotacticity, these defects cause a significant reduction of the melting point and limit both heat resistance and stiffness [57].

3. All chain defects, but also the insertions of comonomers—and specially ethylene—are much more randomly distributed along the chain. At the same time, higher α-olefins like 1-butene and 1-hexene can be copolymerized more easily.

A very special case of PP-H is syndiotactic polypropylene (sPP), which is characterized by significantly lower crystallinity and stiffness [58]. It can be polymerized with specific SSCs, both MC and constrained-geometry types, and varied over a wide range by controlling the relative content of isotactic, syndiotactic, and atactic sequences. Its commercial relevance is, however, so far rather limited, largely as a consequence of the high solubility in various organic solvents.

An overview of the most relevant properties of different PP product families can be found in Table 6.

7.2. Random Copolymers

Similar to the variation of density and mechanical properties when moving from high density polyethylene (HDPE) to linear low density polyethylene (LLDPE) by copolymerization with higher α-olefins like 1-butene (C4) and 1-hexene (C6), the properties of PP can be modified already in one-step polymerizations. Incorporating ca. 2–5 wt% of ethylene (C2) into the chain lowers the overall crystallinity, gives a broader softening range with reduced melting points (see Figure 19), lowers the glass transition temperature, increases the fraction of soluble polymer, and improves transparency and surface gloss [59]. Ethylene–propene random copolymers (EP-RACOs) are somewhat tougher than homopolymers, and do not exhibit the familiar stress-whitening behavior of the tougher copolymer impact grades. These changes for EP-RACOs are determined by the amount of comonomer and its distribution along the chain, with significant differences resulting from catalyst and donor type. The randomness or rather the probability for isolated C2 units in the chain decreases with increasing amount, leading to phase-separation phenomena in case of ZN catalysts at contents >5 wt%; higher values can be achieved with metallocene catalysts.

All changes in mechanical properties and optics are related to a reduced crystallization speed and a lower lamellar thickness caused by the comonomer-related chain defects [60]. This also results in a better quenchability of EP-RACOs to the mesomorphic state, making them ideal materials for highly transparent cast films, where also the broader melting or sealing range is an advantage.

The increased amount of XCS- and C6-soluble material in EP-RACOs is, however, limiting their applicability in this and other areas, especially when packaging of food or pharmaceutical products is the intended use. A better balance between softness and solubles content is possible with C4 copolymers, perhaps because the solubles are produced at semi-exposed catalyst sites more easily accessible to ethylene [59]. The higher T_g and lower toughness of C3/C4 copolymers can be compensated by producing terpolymers with C3, C4, and C2, for which also other advantages like improved processability are found [61]. Typical applications for these specialty grades are sealing layers in coextruded films.

Common to all random copolymers is a shift in crystalline structure from the predominant monoclinic α modification to the orthorhombic γ phase. A new crystal modification was identified in MC-based copolymers with higher α-olefins [62]. The trigonal δ modification allows better incorporation of side chains resulting from these comonomers in the crystal lattice. While for the γ phase some advantages regarding transparency and ductility can be found and promotion by α-nucleating agents is possible [45], no specific technical benefits of the δ phase have been identified so far.

7.3. Impact Copolymers

Sections 5.2 and 5.3 describe multistage copolymerization systems for producing

Table 6. Overview of most relevant PP properties for various grade families

		Unmodified PP grades*					Compounds		
		Soft (1)	**Standard (2)**	**Random (3)**	**Impact (4)**	**HCPP (5)**	**Talc**	**Glass fiber**	**Filler & elastomer**
Filler content, wt%		0	0	0	0	0	20–40	20–50	10–25
MFR (230°C/2.16 kg), g/10 min		0.5–15	0.3–1000	0.3–100	0.5–100	2–50	0.5–15	1–10	0.5–50
Density, g/cm^3	ISO 1183	0.900	0.905	0.900	0.900	0.905	1.05–1.25	1.04–1.22	0.95–1.15
Melting point, °C	ISO 3146	135–150	160–167	135–150	160–167	165–169	164–168	164–168	164–168
Glass transition, °C	ISO 6721-7	−10 to 0 −60 to 35	0–4	−10 to 0	0–4 −60 to 35	0–4 −60 to 35(5)	0–4	0–4	0–4 −65 to 45
Flexural modulus, MPa	ISO 178	300–700	700–1500		1200–1900	>1900	2500–5000	5000–9000	1000–2000
Yield stress, MPa	ISO 527	15–25	25–40	20–30	25–40	40–50	25–35	70–140	15–30
Extension at yield, %	ISO 527	15–25	5–15	15–25	5–15	4–10	2–4	2–4	5–15
Extension at break, %	ISO 527	>300	20–800	30–1000	20–200	5–40	15–30	3–5	6–10
Charpy IS**, kJ/m^2	ISO 179 1eU								
+23°C		n.b.	10–n.b.	15–n.b.	50–n.b.	30–n.b.	10–n.b.	25–50	n.b.
−20°C		30–n.b.	3–80	5–n.b.	10–n.b.	3–40	2–20	20–40	20–n.b.
Charpy NIS**, kJ/m^2	ISO 179 1eA								
+23°C		10–n.b.	2–25	5–50	10–n.b.	2–4	2–12	7–20	15–35
−20°C		5–50	1–10	2–15	5–60	1–3	1–5	4–15	5–25
Vicat softening temperature, °C	ISO 306								
Vicat A		80–120	100–140	85–110	140–150	150–160	150–160	140–160	100–130
Vicat B		30–60	50–90	35–65	70–100	100–120	80–100	100–130	40–60
Heat deflection temperature, °C	ISO 75								
HDT-A		35–45	40–60	40–55	50–70	60–80	60–90	130–150	40–60
HDT-B		50–70	70–100	55–75	100–120	110–130	120–140	150–160	70–100
Gloss 20°, %	ISO 2813	30–60	60–80	60–80	70–80	70–80	5–30	20–40	20–40
Ball indentation hardness, N/mm^2	ISO 2039-1	20–40	30–80	30–50	80–90	>90	80–90	100–120	40–60

* 1: High-EPR heterophasic and random-heterophasic copolymers; 2: Homopolymers; 3: Random co- and terpolymers; 4: Heterophasic copolymers; 5: Homopolymers and low-EPR HECOs.
** IS: impact strength; NIS: notched impact strength; n.b.: not broken.

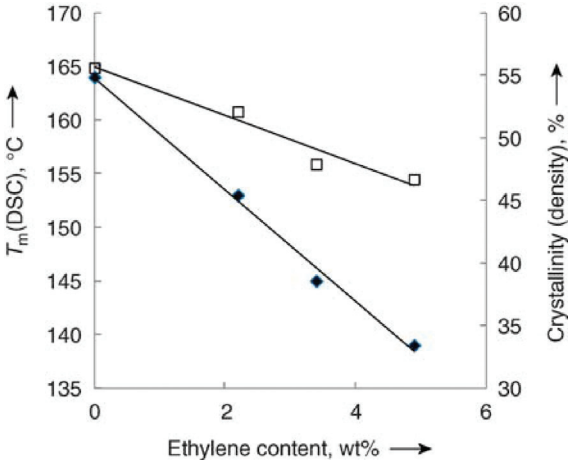


Figure 19. Effect of comonomer effect in EP random copolymers on melting point (♦) and crystallinity (□) (data from [60])

high-impact copolymers of PP. These combine a crystalline PP matrix (produced in the first 1–2 reactors) with embedded particles of EPR and PE (produced in one or more following reactors) giving impact and low-temperature resistance [63]. While often still referred to as block copolymers, the correct term for such products is heterophasic copolymers (EP-HECOs) or PP impact copolymers.

In-reactor production of EP-HECOs has been found to be more effective than compounding (see Section 6.2) for producing impact-modified PP. On the one hand, cost and energy are saved by eliminating the external elastomer components and the compounding step, and on the other hand morphology and performance advantages are achieved. The structure of these reactor blends has been shown to be rather complex: Besides the PP matrix and the amorphous ethylene–propene rubber (EPR), they can also comprise crystalline copolymers having both PP and PE crystallizable segments, and even neat high-density PE (HDPE). The elucidation of this complex structure has been progressing by combining cross-fractionation with various thermal, spectroscopic, and chromatographic techniques correlating the molecular structure to the performance of these materials [64, 65].

Since their development in the 1970s [11], these materials have conquered a wide range of applications from seemingly trivial packaging uses to technically complex parts. The matrix consisting of a PP homopolymer or, in the case of random heterophasic copolymers, an EP-RACO is responsible for retaining good high-temperature performance and adequate stiffness, while the particulate EPR/PE phase contributes good toughness. Depending on the composition of the EPR component the respective T_g can be as low as −60°C, resulting especially in improved impact performance at subzero temperatures. While such low glass transitions can be achieved by a high ethylene content in the EPR phase, high propene content in the same will enhance the compatibility to the matrix, allowing better transparency [21]. Overall, the size, shape, internal structure, and spatial packing of the dispersed EPR domains (which generally range from 0.2 to 4 μm in average diameter under equilibrium conditions) are critical parameters affecting not only the mechanical performance but also properties like surface appearance and migration. The morphology is a complex result of the rheological parameters of the single components, the matrix–dispersed phase compatibility, and the processing conditions.

One critical factor is already the catalyst morphology. In the production of EP-HECOs, the morphology of the produced polymer particles replicates the morphology of the employed catalyst particles. Spherical aggregates of microcrystalline $MgCl_2$ are conventionally used as support material for the $TiCl_4$ in ZN catalysts [63], offering a porous structure with large surface area. The maximum amount of

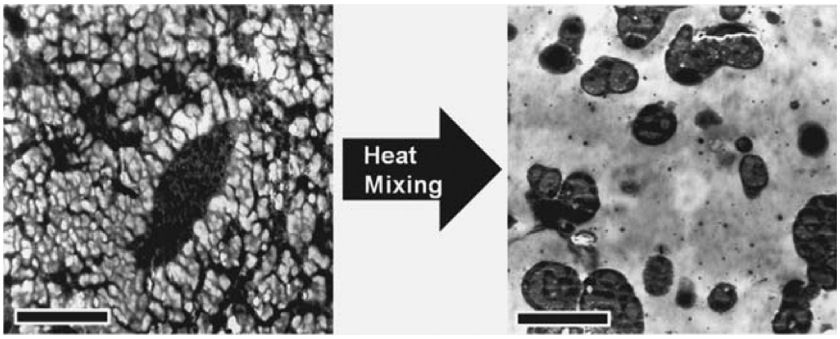


Figure 20. Relation between powder morphology (left) and granule morphology (right), revealed by RuO_4-contrasted transmission electron microscopy (TEM); high-impact EP copolymer type with 26 wt% ethylene and 22 wt% elastomer (EPR; xylene-soluble fraction); EPR is dark because of lower crystallinity; PP matrix and PE inclusions in particles are light; scale bars 2 μm

EPR/PE which can be accommodated in the polymer granule without causing stickiness appears to primarily depend on the porosity of the catalyst particle. Figure 20 shows the difference in distribution of the EPR phase between the original reactor "powder" (defined by the catalyst structure) and the pelletized or processed polymer [66].

While details of the EPR composition and its viscosity ratio relative to the matrix are highly relevant for product design in detail, a key factor for increasing the energy absorption capacity is to increase the EPR weight fraction in EP-HECOs. Here, the toughness is improved by reducing the interparticle distance, resulting in a stepwise brittle-to-tough transition as a function of EPR concentration, combined with linear reduction of tensile modulus (see Fig. 21). The blend concentration at which this transition occurs is determined by the chemical composition of matrix and dispersed phase as well as their viscosity ratio, but also on the geometry and test conditions. For PP/EPR blends the phase transition and the respective development of the mechanical performance has been comprehensively discussed [67].

7.4. Composites and Blends

An extension or even an alternative to multistage polymerization with the production of EPR can be the addition of external elastomers. This was historically the first approach to impact modification of PP, for example, blending of PP-H with 10–20 wt% of polyisobutylene (PIB) elastomer. Nowadays this route is instead used for fine-tuning the property profile. High impact strengths can be achieved with ethylene-*co*-octene or -butene plastomers and elastomers based on polymerization with single-site catalysts in solution [68]. The comonomer content and the molecular mass of these homogeneous copolymers can be varied over a wide range, allowing applicability in a wide range of stiffness and MFR. For special purposes, styrene-based elastomers of the di- or triblock type have found uses despite their higher price. Mostly hydrogenated styrene–butadiene triblock systems (SEBS) are used, which can be designed in a wide range of compatibility and viscosity by varying the molecular mass and individual block lengths.

For the still-used external EPRs or ethylene–propene–diene elastomers (EPDM) based on vanadium catalysts, a two-stage process in which the elastomer is first compounded with PP to give a 50–70 wt% masterbatch of the rubber as free-flowing granules is commonly used. Only rather C2-rich EPR types are sufficiently crystalline to be pelletized in pure form [69]. Also different PE types can be added in minor amounts for property design. In the presence of an EPR phase, preferably reactor-made, the PE will be located inside and towards the center of these rubber droplets [70], and mostly enhances the room-temperature impact strength and limits shrinkage. Addition of HDPE is especially suitable for the reduction of stress whitening or scratch sensitivity.

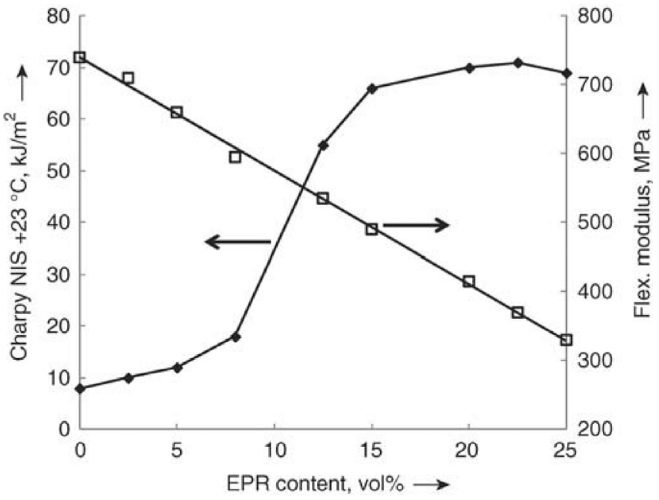


Figure 21. Effect of EPR concentration on stiffness (flexural modulus, ISO 178) and toughness (Charpy notched impact strength, ISO 179 1eA) at 23°C for a series of random-heterophasic copolymers with constant matrix and EPR composition (data from [21])

Blends of PP with other polymers were studied intensely in the 1990s and were even commercialized in some cases. Three blend partners were most studied (in order of increasing polarity): polystyrene (PS), poly(methyl methacrylate) (PMMA), and polyamide-6 (PA-6). In all cases, besides viscosity matching as with other multiphase PP systems, also the use of an appropriate block or graft copolymer as compatibilizer is required for delivering good property combinations [71, 72]. While PS can add stiffness, surface gloss, and print- as well as paintability, PA-6 was shown to deliver a good combination of modulus and temperature resistance, especially when combined with glass-fiber reinforcement. The most relevant example of blend commercialization was the Hivalloy product line of Himont (now LyondellBasell), based on a reactive modification concept with PS and PMMA as blend partners. Introduced on the market in 1994 and produced as pure blends but also reinforced with glass fibers, the product line was stopped in 2001 and finally considered a commercial failure.

8. Processing and Applications

In the global application distribution for PP (see Fig. 22) the extrusion segments (films and fibers, but also coating and pipe extrusion) used slightly more than 50%, while injection and blow molding made up less than 50% of the consumption. In 2010, the global PP market was about 50×10^6 t/a, with more than 50% of this being used in the Asian-Pacific region. Further perspectives for volume growth can be illustrated best with the annual per-capita consumption: The global average in 2010 was 7 kg, with a wide span between developing countries, the BRIC-countries (e.g., India at 2.1 kg), and highly industrialized countries (Western Europe 18.4 kg) [73].

The wide range of PP applications [74] clearly results from the possibility to adapt the polymer structure, its processability, and final performance to many conversion routes and requirement profiles. A general trend towards material substitution has allowed PP to grow by replacing more costly polymers like polycarbonate (PC) and acrylonitrile–butadiene–styrene terpolymers (ABS), but also "traditional" materials like glass and metal. This process, often involving a redesign of the respective application (e.g., going from metal cans to stand-up pouches for food packaging) and can result in a significant overall reduction of raw material and energy consumption (see Chap. 9).

8.1. Injection Molding

Injection molding is used for a wide range of packaging material and general purpose items

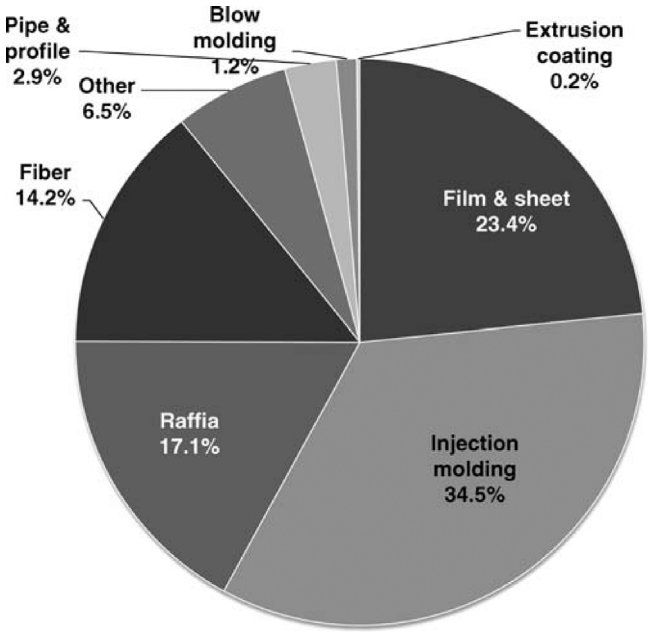


Figure 22. Global application distribution for PP in 2010 (CMAI data, after [73])

with limited requirements, as well as for most of the technical uses of PP. As these two segments require quite different materials and processing considerations, the simpler segment is discussed here, and the technical segment in Section 8.6.

Two main groups of factors define the selection of PP grades for injection molding applications: part geometry, especially the flow ratio (i.e., the ratio of longest path to the section thickness) and the complexity of the part, and the thermomechanical requirements in the respective application. A simple increase of the MFR, for which a range between 1 and 100 g/10 min (230°C/2.16 kg) is presently available for injection molding, will allow thin and narrow cavities to be filled even over longer distances, but the impact strength of such materials will be greatly reduced. Compensating this by moving from PP homopolymers to random or heterophasic copolymers will in turn compromise stiffness, heat resistance, and transparency.

In addition, the formation of crystalline superstructures like shear-induced skin layers [75] is decisive both for the solidification speed and the mechanical strength of the molded parts. The presence of a high molecular mass fraction is decisive here, which makes highly polydisperse grades more prone to skin-layer formation. Further polymer-related factors are anisotropic fillers and nucleating agents [76], but melt temperature and flow speed are also relevant. Thus, like in all semicrystalline polymers, the processing parameters become a part of the final property design. Standard processing conditions used for PP are [77]:

- Melt temperature T_m: 200–265°C
- Injection pressure p_{inj}: 50–150 MPa
- Injection speed v_{inj}: 100–400 mm/s
- Mold (wall) temperature T_w: 30–60°C

As a rule of thumb, lower T_m values are used for higher MFRs, and lower T_w values for thinner parts. This may even lead to partial quenching, a phenomenon which is discussed in Section 8.4. Besides mechanics and optics, the resulting crystalline structure also determines the extent and anisotropy of in- and post-molding shrinkage. Linear post-molding shrinkage of PP is 1.0–1.5%, of which 85% occurs within the first 24 h. Distortion or warpage in molded products results from anisotropic

shrinkage and reflects both internal stresses and crystal orientation. PP grades with high MFR and/or narrow MWD (low polydispersity) can help to reduce this problem [60].

An important practical aspect of PP concerns its ability to form strong integral hinges, such as in a lidded box, where the lid is permanently attached to the base by a thin web of polymer along the whole of one edge (Fig. 23). This web, about 0.25–0.6 mm thick, can be produced directly in the molding process. An initial flexing of the hinge while slightly warm induces the correct molecular orientation to permit repeated opening, even at subzero temperatures. In the laboratory, such hinges have withstood 23×10^6 flexes without failure [74].

Apart from this extreme case, injection-molded parts of PP range in wall thickness from 0.3 mm (e.g., for thin-wall dairy cups) to 10 mm (e.g. for pressurized ion-exchanger cartridges in coffee vending machines). Mostly, however, wall thicknesses above 4 mm are avoided by partial foaming (see Section 8.6) or by gas- or water-assisted injection molding. These seemingly complex processes have been developed to a degree of practical simplicity, making them useful even for mass production of articles like beer crates and toys.

General purpose items injection molded from PP can largely be categorized into three groups [74]:

1. Household articles and general consumer products, covering such diverse uses as kitchenware, garden furniture, toys, and luggage. Kitchen bowls and storage containers were among the first articles produced from PP, and outdoor furniture such as stadium seats also already has a long application history. Nevertheless, the development of highly transparent molding grades and improved UV stabilization concepts have improved the possibilities significantly.
2. Packaging systems, ranging from thin-walled cups and beakers through buckets and pails to folding boxes and crates for transport packaging. The requirements vary broadly, but weight reduction and materials savings have been the main factor in recent years. High-crystallinity PP grades, very often as heterophasic copolymers with a good subzero impact performance, dominate the transport packaging segment, while nucleated random copolymers give the best product visibility.
3. Medical articles and pharmaceutical packaging systems have special requirements in terms of allowed additives and required purity. Disposable syringes were the first PP application here, and already required sterilizability as a further parameter. The entrance barriers for polymer producers are higher here, mostly due to the long approval processes [78].

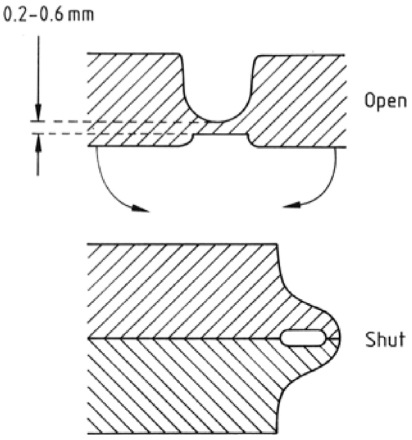


Figure 23. Integral hinge (Courtesy of the "Propathene" Business, ICI Chemicals & Polymers)

8.2. Blow Molding

For producing bottles, canisters, and other containers, blow molding processes have been employed mostly for PE for a long time already. While PP has been slower in the initial market development, advantages of this polymer, such as better heat resistance and transparency, have enabled the gradual development of a significant application volume. Two different processes with different degrees of complexity and different requirements for the material used are distinguished here:

In *extrusion blow molding* (EBM) an extruded molten parison (tube) is transferred to a mold in which the end is clamped and it is inflated with low-pressure air at 0.4–1.0 MPa [79]. High molecular mass polymers having an MFR of ca. 1.0–2.5 g/10 min, combined with low melt temperatures at the die of 200–210°C,

provide a suitably stiff melt. If the melt stress in a heavy PP parison exceeds ca. 20 kPa, then the resulting tension thinning will be troublesome as regards parison stability and uniform wall thickness. EBM is cheaper and simpler to operate, but the produced articles will always show a certain degree of surface roughness limiting the transparency and gloss. In modern processing equipment, control of the final container wall thickness by modifying the parison thickness along its extrusion direction can significantly improve appearance and performance [80]. A variation of the EBM process is the blow, fill, and seal (BFS) process, mostly used in the medical area for ampoules and infusion bottles. While LDPE is mostly used in this process, special PP grades are also gradually becoming available.

Injection blow molding (IBM) and the more common *injection stretch blow molding* (ISBM) are two-stage processes in which first a preform is produced by injection molding. Blowing (in IBM) or a sequence of stretching and blowing (in ISBM) takes place in a second mold which maintains the high-definition neck and thread of the preform. In both cases, the produced bottles or wide-mouth containers are characterized by better optical and mechanical performance, but also by improved dimensional accuracy. Significantly different polymers are required here [81] which have an MFR of 10–25 g/10 min and are preferably nucleated random copolymer types in order to facilitate processing. While PP is used in much smaller volumes than poly(ethylene terephthalate) (PET) for ISBM bottles, it has a number of clear advantages in water-vapor permeability and heat resistance, which enable hot filling and/or steam sterilization.

Products from these processes are mostly used for packaging in the food area (dairy products, fresh juices, still water), the nonfood area (household cleaners, dishwashing liquids, cosmetics, body-care products), and also the medical/pharmaceutical area. EBM processes can also be used for technical applications like fluid containers for cars, dishwashers, and other household equipment. A special use for PP-based ISBM bottles are sterilizable baby bottles, as well as reusable sports bottles.

Like in films or injection molding, multilayer constructions resulting from coextruded parisons (EBM) or two-component preforms can be used as precursors for the bottles when special barrier properties are required. Most commonly, a central layer of ethylene–vinyl alcohol copolymer (EVOH) to reduce oxygen diffusion is combined with moisture-protective outer layers of propene–ethylene random copolymer to give containers suitable for storing oxygen-sensitive food products.

8.3. Fibers and Flat Yarns

One of the biggest application areas of PP homopolymers are fibers and tapes as well as their derivatives. The respective applications cover a wide range of physical forms, including increasing amounts of versatile nonwoven fabrics [82, 83]. Monoaxial orientation in the solid or semisolid state can be applied to conventional spinneret yarns, as with polyamides and polyesters, and to flat tapes made from extruded film. These application forms differ in various respects listed in Table 7.

The three conventional PP fiber operations are continuous filament (CF), bulked continuous filament (BCF), and staple fiber (SF). In any case the formation of the primary molten fiber by extrusion through a die plate perforated by

Table 7. Polypropylene fiber processes

Process	Filament count, tex*	Product
Long spin	0.2–3.0	high-tenacity monofilament; drawing integral or separate; high output
BCF yarn	0.2–2.0	special case of long spin making only bulked continuous fiber
Spunbonded	0.2–2.0	venturi haul off; no 2nd stage draw; bonded mat output
Shortspin	0.2–40	compact unit; tow stretched and cut in line for staple
Melt blown	0.002–0.02	low orientation, very fine fiber; only bonded mat output
Fibrillated yarn	110–500	oriented slit film; fibrillated for baler twine, rope, etc.
Weaving tape	ca. 110	nonfibrillated slit film for carpet backing, sacks, etc.
Strapping tape	500–1000	thick, oriented tape as a steel alternative

* tex = weight in grams of 1000 m of yarn; equivalent cylindrical fiber diameter in $\mu m = 37\sqrt{\text{tex}}$.

many small holes is crucial. High melt temperatures (230–280°C) and melt flow rates (MFR 10–30 g/10 min; preferably combined with narrow molecular mass distribution for high extensibility [84]) are applied on short extruders, mostly combined with manifolds and melt pumps before the 8–20 spinnerets having 50–250 holes each. For the CF process, a long spinline is preferred which can combine spinning and finishing stages as well as out-of-line drawing options. An air-cooling gap of 2–5 m is needed between the die plate and the windup roll. Line speeds up to 1000 m/min at the spinning stage, increasing to 3000 m/min during solid drawing over hot rolls, require complex and expensive haul-off, drawing, and windup sections. The product is preferably sold as continuous yarn or tow.

The BCF process is mostly used for carpet face and upholstery yarns and characterized by the addition of a "bulking" step after spinning or spinning and orientation. The bulking or texturizing at 140–160°C in a jet with compressed air has a similar effect to the crimping process used for other textile fibers, causing fibers to have a wavy to curly structure for higher volume. While the MFR range is the same as for CF, broader molecular mass distribution and higher crystallinity can give advantages here.

In spunbonding, filament spinning and web formation are integrated into one process, yielding a continuous bonded mat of partially oriented yarn as a consequence of some draw in the venturi-type haul-off operating at up to 5000 m/min. There is no further drawing as the fiber is collected as a mat on the take-off belt for conversion into nonwoven fabrics. These are used, for example, in geotextiles, furnishings, and carpet backing [85]. The balance between drawdown rate and orientation in this process is influenced by the polymer molecular mass distribution.

Figure 24 depicts a compact shortspin process for staple fiber production using a die containing ca. 40 000 holes. Cooling air jets freeze the melt within about 20 mm so that godet haul-off rolls can be placed only 1 m away from the die. Orientation is achieved by the in-line stretching of this tow in an air oven, followed by chopping in line to produce staple [82]. Broad-molecular mass distribution polymers again give the necessary melt strength, while MFR

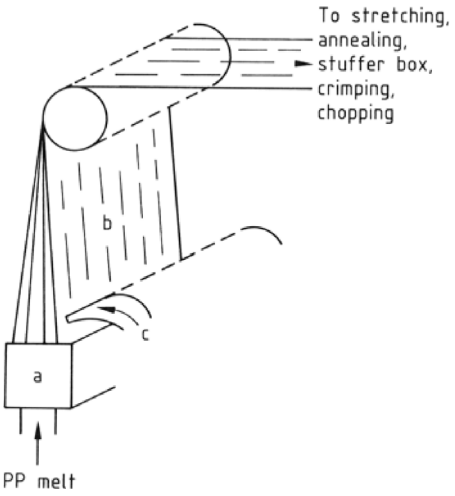


Figure 24. Shortspin process
a) Spinneret; b) Quenched fibers; c) Air-jet cooling; Courtesy of the "Propathene" Business, ICI Chemicals & Polymers

requirements increase from 7 to 20 g/10 min as the filaments become finer. These find use in carpet face fiber, and diaper cover stock applications. A useful feature of PP fabrics made from fine fibers is the ability of underwear garments to reduce clamminess by transferring moisture away from the skin to an outer absorbent layer. Polypropylene-based fabrics are also used for sports clothing and socks, but the low melting point of PP calls for special attention to the heat setting of the average domestic iron.

For the most recent production process (Fig. 25), melt-blown (MB) fibers, air is blown through a very fluid polymer melt maintained at high temperature to assist chain scission in the spinning process itself [74]. Polymer MFR at the nozzle can range from 200 to 800 g/10 min or higher, achieved by visbreaking with some residual peroxide in the polymer before extrusion. The specially designed die, having a row

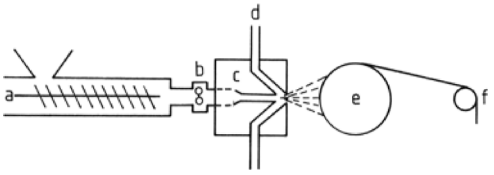


Figure 25. Melt blowing process
a) Extruder; b) Gear pump; c) Heated die; d) Hot air manifold; e) Collector; f) Take-off roll

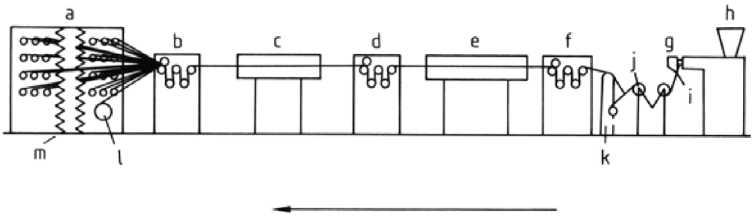


Figure 26. Flat tape/yarn production unit
a) Windup frame; b) Third godet stand; c) Hot-air annealing oven; d) Second godet stand; e) Hot-air orientation oven; f) First godet stand; g) Simple film costing unit; h) Extruder; i) Film die; j) Water-cooled chromium-plated rolls or water bath; k) Slitting unit; l) Starting drum; m) Individual precision flangeless bobbin wind up; Courtesy of the "Propathene" Business, ICI Chemicals & Polymers

of nozzles along its width, sprays a stream of short, low-orientation fibers of very low diameter onto a moving steel-web belt, where they are bonded together and wound onto a roll. This process produces nonwoven fabrics which are of increasing importance for industrial wipes and surgical wrap, and for a variety of filtration applications, such as face masks made from bonded mats of very fine fibers. MB fiber webs have only limited mechanical strength and can be combined with spunbonded webs in a so-called SMS structure.

For producing flat yarns, extruded film is used as the basis. Melt from a conventional slot die is rapidly quenched with cold water or water-cooled steel rolls to give low-crystallinity film, 50–250 μm thick (see Fig. 26). Razor-blade-type knives then slit this broad film into strips 5–20 mm wide, which are oriented in a hot air oven at 120–180°C by drawing between godet rolls at ratios in the range 5 : 1 to 10 : 1. Both film thickness and width diminish in this operation by approximately the square root of the draw ratio. These yarns are preferably woven into cheap textile structures used for bigbags or food transportation like rice or grain bags.

Fibrillated tape is another variety in the "low-performance" area. While flat yarns are quite strong in the direction of draw, they are very weak in the transverse direction. With normal PP homopolymer, simply twisting high-draw-ratio tape induces spontaneous fibrillation. A web of irregular fine fibers is formed as the film splits down its length. The resulting product resembles a coarse sisal twine, for which it is a good substitute. Such fibrillated yarns can be tailored to specific applications by controlling draw ratios, thickness, and polymer. Nowadays, pin fibrillation, in which a co-rotating spiked roll contacts the film just after slitting, offers more precise control over this step. The products are familiar as baler twine, string, and some ropes.

Highly oriented fibers or tapes are also the starting point for the production of self-reinforced PP parts [86, 87]. The ability to reach very high specific strength in fiber spinning processes by post-drawing in the solid or semi-solid state is used in combination with weaving and sintering of such high-strength PP fibers to plates for later thermoforming. These products are marketed under the trade name Curv and can reach modulus values of up to 5000 MPa. The geometrical design is however limited to thermoformed parts.

Thick, 0.3–0.9 mm, oriented tapes are established alternatives to steel bands in many strapping applications. They are generally made by the water-quench process operating at draw ratios of 9–10. Thicker tapes are made from foil or individually extruded film tapes. High molecular mass, MFR 0.4–2.0 g/10 min, PP homopolymers and EP impact copolymers with added chalk and polyethylene largely suppress fibrillation. A further precaution here is to emboss the finished tape with a diamond pattern. A useful aspect of PP strapping tapes is their higher elongation and elastic recovery which helps them to remain tight on packages prone to shrink or settle.

8.4. Films and Sheets

Depending on the processing technology employed, PP can be processed into films and sheets ranging in thickness from 5 to 2000 μm

and converted further to a wide variety of products [88].

The more common processing step is film casting with extrusion from a slit die onto a (relatively) cold roll. The so-called chill roll is kept at temperatures between 15 and 80°C by liquid cooling or heating, depending on the polymer processed and its final destination. If the film is applied directly after solidification in this step, in which only a limited degree of orientation in machine direction is achieved, it is known as cast film, which covers a thickness range of ca. 30–300 μm. The rapid cooling leads to films of low crystallinity and good optics, which can be influenced in performance both by a choice of polymer and additives and by variation of the processing conditions [89].

If the film runs from the chill/take-up roll further through a calendar-like arrangement of rolls for solidifying and annealing, it is known as roll-stack film with a primary thickness range of 300–2000 μm (see Fig. 27). These films or sheets are primarily used for subsequent thermoforming applications. For this process a variety of methods can be used depending on the desired shape and dimension. Both in-line and off-line processes are applied with two essential steps, heating and shaping, the former mostly by infrared irradiation and the latter by mechanical force, air pressure, or vacuum. Thermoforming is the only film processing segment in which nucleation is applied to a significant extent [90].

In the thinner part of this thickness range, special high-efficiency cooling setups can be used to produce the lowest crystallinity and highest transparency. With water-bath or steel-belt technology, the ideal materials for pharmaceutical tablet blisters or transparent folding boxes are produced. The application of non-nucleated PP homopolymers is advisable in these special cases.

The thinnest films (5–30 μm) are produced by postdrawing (postorientation) of a thicker cast film, whereby monoaxial orientation

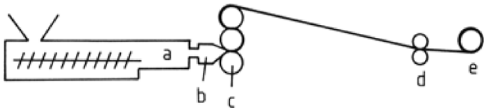


Figure 27. Three-roll stack extrusion
a) Extruder; b) Slot die; c) Polishing stack; d) Nip rolls; e) Wind up

(MOPP) and biaxial orientation (BOPP) is possible [91]. The BOPP films are characterized by a much higher orientation, stiffness, gloss, and transparency in comparison to cast film. While in the packaging area, the low water-vapor permeability and the excellent optical appearance are especially appreciated, the high mechanical and thermal resistance make BOPP also suitable for electrical capacitors.

A similar thickness range to cast films can also be reached by film blowing, which for PP is still of much lower importance than PE. Air-cooled blown films are only possible with specific grades combining a certain amount of melt strength (at a general MFR range of 1.5–3 g/10 min) with fast crystallization, and on modern processing lines. Water-quenched blown film, originally the only processing method suitable for PP, has been making a comeback recently, especially for applications with increased optical performance requirements [92, 93]. Air-cooled blown film is also the first step of an alternative BOPP process, the so-called double-bubble technology with sequential longitudinal and transverse stretching of the film tube (see Fig. 28).

In general, materials with MFR values of 1.5–4 are used for BOPP, thermoforming, and blown film applications, while for cast films polymers with an MFR of 7–20 are preferred (always 230°C/2.16 kg). While the low-MFR grades should have a rather broad molecular mass distribution to have sufficient melt strength, the higher MFR cast film grades preferably have a narrow molecular mass distribution, for example, visbroken or SSC-PP types. The film area is largely dominated by PP homopolymers and random copolymers with ethylene, but for sealing layers also terpolymers with ethylene and butene are used. Impact copolymers are limited mostly to nontransparent applications with low-temperature toughness requirements, unless special polymer designs are applied which allow a combination of transparency and toughness (e.g., “interpolymer” concept with high propene content in the EPR phase [74]).

In any case multilayer constructions are possible and even necessary in case of packaging applications requiring the combination of different requirements, such as sealability, sterilizability, and integration of barrier layers (for this,

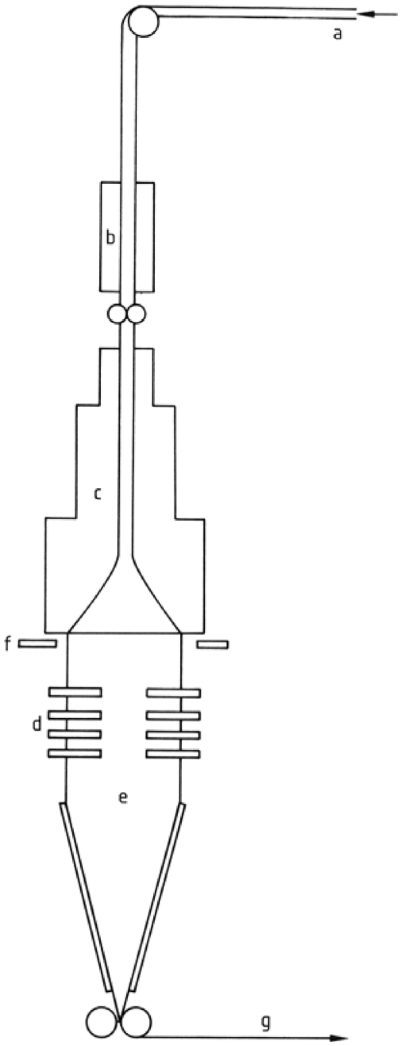


Figure 28. BOPP bubble process
a) Cast tube; b), c) Stretching heaters; d) Bubble guides; f) Air ring; g) Wind up, slitting, etc

polar polymers like EVOH or oriented PA are used) or peel-layers for a more easy opening of a packaging (here multiphase systems like PE–PP blends are applied). Through metallization (e.g., by chemical vapor deposition, CVD) and lamination even more complex structures can be designed. Preferably multilayer co-extrusion with specially design film extrusion heads ahead of the die is used for producing such constructions. Lamination with hot-melt or reactive adhesives is applied whenever nonpolymeric (e.g., paper or metal), specially oriented (e.g., oriented PA) or already printed (e.g., PET) layers are required. In this case, and also whenever printing or gluing of the film is intended, the film surface is activated by corona, plasma, or flame treatment. Corona treatment is the most common process here, but the fact that surface polarity generated with this method will decay over time must be considered when planning production processes [94].

In summary PP films cover an extremely broad area that reaches from textile packaging through medical applications up to electronic components like capacitors. Special requirements can be achieved partly by specific processing or material combinations, but in other areas like sterilizability [95], low-temperature toughness, or resistance to aggressive media, special polymer design is required.

8.5. Foaming and Coating

The foamability of normal PP with linear chain structure is limited and even in specially designed foam injection technologies like the MuCell process only rather high foam densities can be achieved [96]. Good foam cell nucleation, which is always given in fiber or mineral reinforced materials, can improve the situation sufficiently here, in combination with a broad MWD and especially the presence of a high molecular weight component.

A low MFR (0.5–1.5 g/10 min) is also sufficient for particle foaming processes in which, as in the case of polystyrene, massive PP particles are impregnated with a solvent (hydrocarbon or halogenated hydrocarbon). These particles are then foamed and fused under elevated temperatures into the desired shape. Normal pipe or even thermoforming grades can be used here, but an addition of some long-chain branched PP (high melt strength PP, HMS-PP [51, 52] allows for a lower final foam density.

In contrast, HMS-PP is absolutely required for extrusion foaming processes and especially solvent-free processes applying carbon dioxide [97]. Extruded PP foam has excellent mechanical properties including high temperature resistance and can be tailored in its toughness by blending HMS-PP homopolymers with EP impact copolymers. The final application ranges from extruded sheets thermoformed into food

trays or packaging components to pipe insulation layers.

Other processes facilitated or even enabled by HMS-PP are thermoforming at high draw ratios (deep shapes) and especially extrusion coating [98], which is otherwise a clear domain of long-chain branched LDPE. The Recart process of Tetra-Pak, in which sterilizable coated cardboard packages are produced for food packaging, is based on such materials which have a higher MFR than for foaming (8–15 g/10 min as compared to 2–4 g/10 min) and must be free of crosslinked fractions which would form gels in the coating process.

8.6. Technical Applications

As a rule, technical parts from PP and its composites are produced by injection molding or its process variations like inlay, gas-injection, and two-component molding. Elaborate part and mold design are required both to fulfill the requirements to surface quality and to process special materials like short and long glass-fiber-reinforced PP (SGF- and LGF-PP) [99]. LGF-PP can be further diluted to vary the final fiber concentration and the related mechanics in the actual processing step, in which special mold and machine design is required.

Especially in the development of modern cars PP plays an important role due to its combination of density (part weight) and mechanics (strength) [100]; out of the ca. 17% mass fraction of thermoplastics in passenger cars, 70% is polypropylene (see Fig. 29). An overall important contribution of the polymer fraction is the weight reduction compared to metals, which is essential for reducing the fuel consumption. As about 90% of lifespan energy demand of a car occurs in the usage phase; replacing 350–500 kg of other materials in a car with about 200 kg of polymers results in about 750 L of fuel saved in a car's lifespan.

SGF-PP and LGF-PP, targeted at metal replacement and often also component integration, find numerous uses in modern car design, generally supported by modeling [101]. From front-end modules, integrating headlight and bumper support as well as the cooling system, through dashboard carriers and underbody protection elements, the range extends to complete

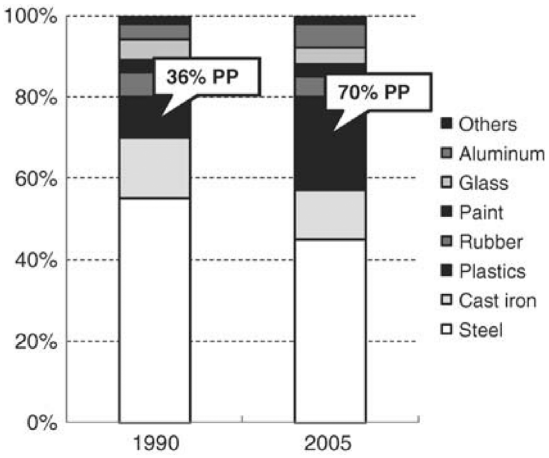


Figure 29. Composition change of a European passenger car from 1990 to 2005 (internal data of Borealis AG)

door and hatch modules, in which LGF-PP frames can be combined with injection-molded cover elements to achieve largely metal free constructions. For the latter, as generally for automotive exterior and interior elements, composites based on high-impact EP copolymers are applied.

Automotive exterior applications started at side trims and door steps, progressed into bumpers, and now include fenders and other parts of the car body. Basically the only part of a passenger car's body which has not yet been designed and produced from a PP-based material is the roof. Base materials for the composites used here are EP impact copolymers with an EPR content of 20–30 wt% and frequently a high-crystallinity matrix, and the mechanical performance is further balanced by external elastomers and mineral reinforcements. Surface quality is important both for painted and the minority of nonpainted applications and it is clearly related to phase structure [102]. Another critical aspect for gap-free combination with metal parts is the thermal expansion of the material, which is normally closely related to shrinkage [103].

For automotive interior applications, slightly lower impact resistance and especially no toughness below −20°C is acceptable, leading to modified recipes for composite design. Here, however, scratch resistance [104] and low levels of emissions and odor are important factors. A variety of techniques ranging from back

injection molding onto foam/textile combinations over metal or modified wood inlays to the application of soft varnishes are used for design; the contribution of these components to overall stability must be considered.

One of the oldest areas of PP application in car design is the under-the-hood segment, where air ducts, battery cases, and fluid containers were already produced from PP homopolymers in the 1960s. The most recent innovation in this segment are air-intake manifolds made of GF-reinforced PP, replacing GF reinforced PA-6 with advantages in water adsorption and sound damping.

Due to its good chemical and electrical resistance PP is inherently suitable also for applications in the electrical and electronics sector. In practice, uses range from housing and internal components in household equipment via connector systems for low voltage up to BOPP capacitor films. For the last-named PP homopolymers with extremely high purity are applied. A common key requirement for housings is the surface quality. As the "reference material" is mostly ABS, a combination of gloss and surface hardness or scratch resistance is required here, which can only be achieved with high-crystallinity PP grades.

The white-goods industry with washing machines and dishwashers as main products is an especially important application area of PP-based composites with mineral fillers and glass fibers [105]. SGF-PP and LGF-PP are used in areas with high dynamic loads, like the tubs of washing machines, and special lye-resistant stabilization systems must be used.

8.7. Pipes

The highest molecular masses of PP are used in the pipe area where, compared to PE, the application volume is rather small [106]. A normal MFR range (230°C/2.16 kg) for PP used in pipe extrusion is 0.3–0.8 g/10 min, while still higher levels of processability are used for injection-molded fittings complementing pipe installation systems. The applied processing temperatures range from 220 to 280°C, the latter mostly occurring in multilayer extrusion heads, and must be controlled rather well both to avoid degradation and to ensure proper crystallization, whereby PP is generally far more sensitive than PE.

For pressure pipes, two polymer modifications play an important role: Random copolymers with ethylene are used for hot-water and underfloor heating installation, while β-nucleated PP homopolymers find use in industrial piping applications and are especially suitable for contact with aggressive chemicals like concentrated acids. Pressure, creep, and crack-propagation resistance of these materials is specified in relation to pipe dimensions in ASTM and ISO standards [107]. Here, also the new material class for hot- and cold-water pipes, known as PP-RCT (RCT stands for random, crystalline, temperature-resistant), is specified. The combination of EP random copolymers with β nucleation allows pipes to be used at higher pressures or wall thickness to be reduced.

Another application area which has experienced significant volume growth in recent years is nonpressurized sewage pipes for domestic and infrastructure areas [108]. Especially in the case of large diameters the external load on a pipe in the ground is bigger than the internal load, a problem that can be solved, for example, by multilayer, rib, or corrugated pipe constructions. High-modulus impact copolymers are nearly exclusively used here, as the toughness requirements are rather high. The development presently continues in the direction of even larger parts like shafts and manholes to achieve full mono-material solutions for sewage systems. For large cross-sectional dimensions fiber-glass-reinforced types are in use here.

Pipe jointing uses all the common techniques, with the exception of solvent welding. Ring seals with rubber inserts allow some movement in domestic waste pipes. Also used are flanged joints, hot-plate butt welding, and socket-fusion welding, the last-named being optionally supplemented with hot-gas bead welding. Compression joints involving copper alloys should not be used at temperatures exceeding 60°C because of reduced life expectancy resulting from Cu ions; the use of metal deactivators in stabilization can only partly remedy this hazard.

9. Environmental Aspects

After some decades of success, polymers have been going through a hard time recently. For the

first time since the oil crisis of the early 1970s, global production decreased in 2008 as a result of the economic crisis. At the same time, public perception of "plastics" deteriorated, with critical views on issues like the release of endocrine disruptors, littering, and waste. While some of these arguments may be justified, many remain superficial like the quarrel about single-use plastic shopping bags. Being less visible as a packaging material, PP has not been affected as much as PE by this discussion, but the widespread idea that all petro-based polymers can and will be quickly replaced by "bio-based" or even biodegradable materials of course affects customers' choices when looking for materials for new applications.

In reality, bio-based polymers account for less than 0.5% of the global polymer production, and besides the widely discussed question of resources for their production and the related competition with nutritional usage there are also technical issues [109]. While bio-based PE (or even PP which may become available as well) will of course not exhibit different properties than its petro-based counterpart, most biodegradable polymers suffer from significant shortcomings in terms of processing stability, mechanical and optical performance but mostly long-term stability. Life-cycle assessments [110] need to include these factors, which frequently lead to heavier and more complex solutions being taken into consideration in order to be realistic.

Even apart from the discussion of bio- versus petro-based materials, the question of long-term monomer supply is clearly an issue for the polymer industry as a whole [111], even though presently only ca. 6% of total crude oil consumption is employed for polymer production. Natural-gas-based production, including olefin conversion steps such as olefin metathesis, will therefore become more important. Feedstock recycling can also contribute, as can improved polymer and component design to reduce the amount of material necessary for fulfilling a certain function. Overall, however, the numerous advantages of polymers over traditional materials must be kept in mind [112].

9.1. Life-Cycle Analysis

When comparing the environmental impact of different materials, numerous factors must be considered. Life-cycle analysis (LCA) is a common and widely used approach for quantifying energy and resource usage as well as gaseous, liquid, and solid waste streams associated with producing a specific material or article, assuming identical boundary conditions [113]. In contrast to a complete LCA, other measures like carbon footprint (essentially specific CO_2 number per unit weight or application; see Fig. 30 for a comparison of standard thermoplastics) or water footprint can only cover some aspects of the situation.

For most standard thermoplastics, PlasticsEurope (the Association of Plastics Manufactures in Europe) publishes LCAs or "environmental product declarations" at regular intervals. For PP, this was last updated in 2008

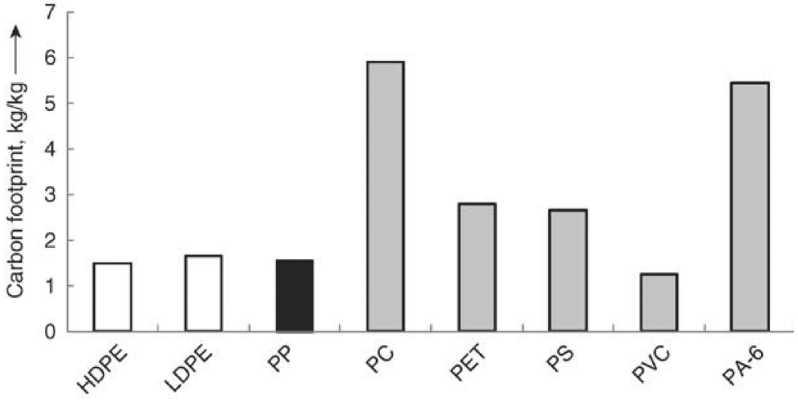


Figure 30. Comparison of the carbon footprint (CO_2 equivalents) of different standard and advanced thermoplastics (data collected from www.plasticseurope.org in July 2013)

[114] and provides an overview of all relevant input and output parameters in PP production, a key figure of which is the average amount of 1.565 kg fossil fuel equivalents needed for producing 1 kg of PP. From an alternative angle the energy demand can be broken down into 52.6 MJ/kg for feedstock and 20.4 MJ/kg for process energy.

Because LCAs should rather be done on an application level, both processing and usage aspects must be considered there. Conversion energy demand is generally lower for polymers than for metals or glass due to their lower melting point and processing temperature, and emissions from conversion are generally not critical for PP, like for other polyolefins [115]. The possibility for saving energy by using PP in automotive applications is discussed in Section 8.6, but also in the packaging area there are numerous positive examples. Realistic LCAs in this area [113, 116] actually conclude that, depending on the boundary conditions, even biopolymers may only offer marginal (if any) advantages over polyolefins.

While the PP base polymer will normally define the major part of energy demand, fillers or reinforcements as well as additives also contribute. For standard additives like the necessary antioxidants this is considered in the PlasticsEurope evaluation [114]. For reinforcing fibers, although glass fibers still dominate the market, the use of organic fibers from renewable sources is increasing in recent years [49]. Whether this improves the LCA and the sustainability in general depends, however, on the achieved thermomechanical performance of the thus-produced composites [117].

Normal LCAs will find their limits of comparability whenever toxic waste streams are involved in the production process. Propene and ethylene monomers themselves are nontoxic asphyxiant gases whose flammable nature calls for the usual extensive fire precautions, as ignition by static electricity is possible with high-pressure leaks and accidental discharges. Monomer recycling is a standard element in industrial production processes, but some waste gas will still end up in traditional flare stacks or modern ground flares. In the latter, the visual impact of flares as well as the noise level is reduced significantly. Since emission certificates for CO_2 are a relevant cost factor in many countries worldwide, producers are working continuously on reducing flaring volumes.

Although catalyst components constitute only a very small proportion of plant materials, both their manufacture and disposal involve noxious substances. Titanium tetrachloride is used for all catalysts, sometimes in considerable excess for high-activity systems. Whereas expensive recycle and recovery stages may be installed as capacities increase, some remaining complex residues will require disposal. Often, this involves hydrolysis with water to generate corrosive HCl and titanium dioxide suspensions. After neutralization with alkali, these slurries are either discharged as aqueous effluent or settled out and used in landfill. Lower aluminum alkyls are pyrophoric, react violently with water, and are intensely aggressive towards exposed skin. Safe handling usually calls for full protective clothing. Disposal can be by burning in special facilities to generate alumina, or quite often, by controlled hydrolysis with water after deactivation with alcohols. Some alkyl manufacturing plants will accept returned waste alkyls for disposal in their own dedicated facilities.

In contrast to those toxic ingredients the catalyst residues in the final polymer are not critical as:

- The Mg, Ti, and Al residues are mostly oxides or hydroxides from the deactivation step with water vapor (free HCl or other residual chlorides are handled by acid scavengers, see Section 6.1)
- The amount is very low (<400 ppm) due to the high productivity of modern catalysts.

9.2. Mechanical Recycling

The chemical structure and inherent properties of PP make it well suited to recycling operations [118]. There is no fear about cross-linking, nor of complications with plasticizers or chlorine-rich species. Re-extruding PP usually lowers its molecular mass and narrows the molecular mass distribution, particularly in aged feedstock. This can be helpful in some applications requiring enhanced flowability, but it negatively affects the mechanical performance and especially the impact strength. Other factors to be considered

in reprocessing and aging are loss of oxidation stability, discoloration, contamination, and odor development.

As a rule, increasing heterogeneity (even within the same polymer class), contamination, and age of the starting material for mechanical recycling will reduce the possibilities for producing high-value secondary grades. Even elaborate cleaning and sorting operations have been generally found to be unable to really purify and upgrade highly mixed waste streams [119].

In PP production, off-specification materials will result from grade transitions, production faults, technical flaws, and test runs for the introduction of new grades. Resulting deviations in MFR, copolymer characteristics, and the like will determine whether the respective material can be added to prime products in minor amounts in a process normally called trimming. Otherwise, these are pelletized separately and re-classified as low-requirement products to be sold to processors or independent compounders.

Recycling in the conversion industry is based on the fact that turning PP into moldings, pipes, film, etc. invariably involves some scrap production. Apart from substandard articles, there are sprues from moldings, edge trim from film and sheet, parison waste, and stamped sheet from thermoforming. These are recovered for recycling by the converter himself if the application allows, or sometimes by an external compounder. Problems may arise here due to stabilizer consumption in multiple melting processes as well as by the presence of foreign polymers like in multilayer co-extrusion.

A quite different situation arises when trying to recycle PP after its service life, as in recycling of post-consumer plastic waste [118, 119]. Unless collected separately, thermoplastic materials make up 8–12 wt% of the municipal solid waste (MSW) stream in industrialized countries and will only contribute positively to the calorific value of MSW if incinerated (see below). Recovery of a useable plastic fraction from MSW after undifferentiated disposal is a hopeless task, but even the recovery and reuse of mixed plastics is quite difficult. The development of specific low-profile applications and fabrication processes for such comingled polymers, which are largely incompatible and contaminated, has natural limits. Using mixed thermoplastic waste for massive products, such as posts, construction boards, and other bulky structures for which resistance to water and decay is more important than high inherent strength is an established process but certainly not the perfect solution for efficient recycling.

Separation of specifically collected plastic waste is possible by a combination of sorting, grinding, density separation, and compounding processes, and specialized recycling companies are able to produce a number of secondary plastic materials. Both mixed polyolefins with a PP content of 40–70 wt% and nearly pure secondary PP materials are available on the European market, but always limited in terms of applicability in a number of respects: The color is necessarily dark (from gray to black), properties can vary significantly from lot to lot, and the smell is frequently problematic [120]. All of these factors limit applicability.

A number of measures appear possible to improve the potential of post-consumer plastic waste recycling. In the packaging area, the development of mono-material solutions or at least a reduction of the nonthermoplastic content will facilitate recycling [121]. Closed-loop recycling systems are another option for large-volume applications and especially helpful in recycling high-performance materials in technical applications.

9.3. Chemical and Energetic Recycling

PP can be cracked to liquid hydrocarbons by thermal pyrolysis at 400–550°C or even lower temperatures in the presence of suitable catalysts. Other thermoplastics, such as PE and PS, can also be pyrolyzed to liquid products, allowing mixed feedstock recycling for MSW fractions not suitable for mechanical recycling processes [122].

Modern MSW incineration technology, with energy recovery in the form of electricity generation, can take advantage of the high calorific value of thermoplastics. Municipal waste calorific values average 10 kJ/g, compared with 30–35 kJ/g for coal. At 44 kJ/g, PP and other polyolefins have the same calorific value as fuel oil. Moreover, PP has an exceptionally low sulfur content, which makes it a very clean fuel with no apprehensions about toxic fluegas emissions.

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Polystyrene and Styrene Copolymers

ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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1. Polystyrene

1.1. Introduction

Polystyrene (PS) belongs to the group of standard thermoplastics that also includes polyethylene, polypropylene, and poly(vinyl chloride). Because of its special properties, polystyrene can be used in an extremely wide range of applications. The annual consumption worldwide in 2004 was ca. 11.5×10^6 t; thus polystyrene is one of the most quantitatively important chemicals.

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Historical Aspects. Styrene [*100-42-4*] (known as styrax) was first isolated in 1831 by BONASTRE from the resin of the amber tree. In 1839 E. SIMON, who also first described the polymer, gave the monomer its name. He observed that styrene was slowly converted into a viscous solution on standing. Around 1925 the development of an industrial production process for polystyrene began; this work achieved success in the plants of the IG Farbenindustrie in Germany in 1930 [1]. In the United States polystyrene was first produced on a commercial scale in 1938 by the Dow Chemical Company.

Polystyrene and Impact-Resistant Polystyrene. Chapter 1 deals with the clear polystyrene molding materials [*9003-53-6*] and rubber modified polystyrene [*9003-55-8*], also known as styrene–butadiene molding material.

Polystyrene molding materials are hard, transparent materials with a high gloss. They are most commonly described as general-purpose polystyrene (GPPS) but terms such as standard polystyrene, normal polystyrene, clear polystyrene, crystal polystyrene, or styrene homopolymer are also in use. In this article the definition polystyrene molding material (PS) is used according to ISO 1622–2.

Below 100 °C PS molding materials solidify to give a glasslike material with adequate mechanical strength, good dielectric properties, and resistance toward a large number of chemicals for many areas of application.

Above its softening point clear polystyrene occurs as a melt which can be readily processed by techniques such as injection molding or extrusion. Small quantities of lubricants can be used internally or externally as processing aids. The addition of antistatic agents, UV stabilizers, glass fibers, or colorants is also common.

The mechanical properties of the relatively brittle PS molding materials can be considerably improved by adding rubbers, generally polybutadiene [*106-99-0*]. Styrene–butadiene molding materials are generally referred to as high-impact polystyrene (HIPS), this term is used here. They are also known as toughened PS or rubber-modified PS; ISO 2897–2 defines them as impact-resistant polystyrene (IPS).

Early production processes for HIPS were based on mixing PS molding materials with a rubber component. Polymerization of a styrene–polybutadiene solution is, however, much more effective. A two-phase system is formed due to the immiscibility of polystyrene and polybutadiene. Polystyrene forms the continuous phase (matrix) and polybutadiene the disperse phase. The globular rubber particles contain small inclusions of polystyrene (Fig. 1).

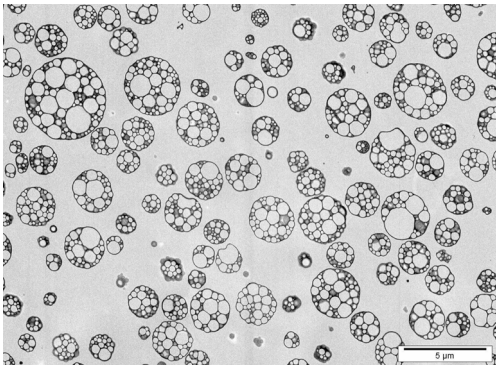


Figure 1. Electron micrograph of HIPS molding material
The dispersed rubber particles (dark as a result of OsO_4 treatment) are embedded in the polystyrene matrix (lighter regions). The rubber particles contain lighter polystyrene inclusions
Courtesy of W. HECKMANN.

The additives commonly used with PS molding materials can also be employed in HIPS. Paraffinic white oil is commonly used as lubricant, zinc stearate as mold release agent. Antioxidants are used for rubber stabilization. Flame retardants, antistatic agents, and other additives are added for special applications.

The rubber particles in HIPS generally have a mean diameter of 0.5–9 µm. They thus scatter visible light and the transparency of the PS molding materials is lost. Sequential anionic block copolymerization of styrene and butadiene allows the production of transparent [3, 4]. Phase separation of the different blocks occurs. Typically lamellar or similar impact resistant molding materials, also called styrene block copolymers (SBC) structures are formed instead of discrete particles (Fig. 2). The thickness of the layers is far less than the particle size in HIPS, so that light scattering does not occur at the phase boundaries.

Styrene Copolymers. Styrene can be copolymerized with many other monomers. Styrene–acrylonitrile molding materials, in particular, have achieved great economic importance in transparent and rubber-modified forms (SAN

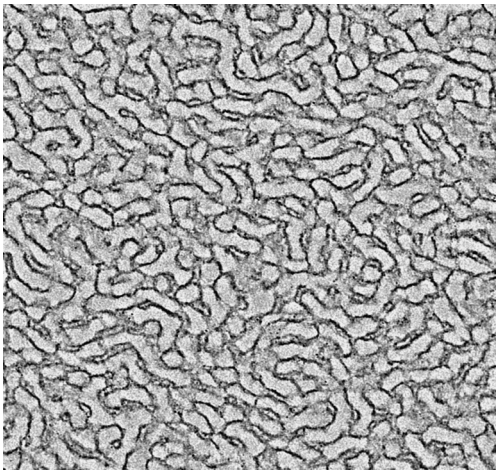


Figure 2. Electron micrograph of a transparent IPS molding material (SBC, contrasting as in Fig. 1). The size of the square is approx. 1.5 μm × 1.5 μm.
Courtesy of W. HECKMANN.

[*9003-54-7*], Chap. 2; ABS [*9003-56-9*], Chap. 5). Compared with the pure styrene polymers they have advantages with regard to hardness, strength, and resistance to heat distortion and environmental stress cracking. However, these advantages are offset by a higher price and more difficult processing.

Copolymers of styrene and maleic anhydride [*9011-13-6*] (Section 4.3) have a softening point that is up to 30 °C higher than that of PS molding materials. These products are used in the form of foams in the automotive industry (e.g, as interior headliners).

Polystyrene Foams. Expandable polystyrene (EPS) is the starting material for PS hard foam materials. It is produced from polystyrene by the addition of ca. 6 % of a low-boiling hydrocarbon (e.g., pentane) as the foaming agent. Extruded polystyrene (XPS) foams are produced from polystyrene and a blowing agent, e.g., carbon dioxide. Foamed polystyrene is discussed in detail elsewhere, →Foamed PlasticsFoamed Plastics.

1.2. Production

Styrene. The properties and production of the raw material styrene are described elsewhere (→ →StyreneStyrene). The styrene used for polymerization should have a purity greater than 99.6 % because the contaminants arising from the production process, mainly ethylbenzene, cumene, and xylenes, affect the molecular mass of the polystyrene. Commonly, purities of 99.9 % or more are used.

For storage and transport styrene is stabilized with inhibitors such as 4-*tert*-butylcatechol to prevent polymerization at low temperatures. These inhibitory radical scavengers must be removed by distillation or adsorption on alumina.

Polymerization. Styrene can function as an electron donor or an electron acceptor. It can therefore be polymerized by radical, cationic, or anionic mechanisms, or by coordination propagation steps.

The industrial polymerization of styrene to PS and HIPS molding materials is carried out exclusively by a free radical mechanism. The chain reaction does not necessarily have to be started by the addition of radical-forming, readily decomposing initiators because styrene itself can form polymerization-initiating radicals [5]. The propagation mechanism for the chain growth proceeds by addition of further monomer to the radical chain end. Growth of the radical chain is mainly terminated by recombination. With increasing temperature, disproportion and back-biting (see → a21_487-sec4-0002 Polyolefins 1.3.1.1. IntroductionPolyolefins, Section 1.3.1.1.) followed by β-scission [6] play an increasing role. The growth of a chain proceeds within seconds; the gross rate is largely determined by the radical initiation reaction. Average molecular masses between 100 000 and 400 000 are obtained within a short time. Molecular masses are mainly controlled by reaction temperature, chain-transfer agents — including solvents — and by initiators. The kinetics of the process are well understood [7] and may be modeled by commercially available software.

Cationic polymerization of styrene (e.g., by strong Lewis acids such as $AlCl_3$, $HClO_3$, or BF_3) is unimportant industrially because control of the molecular mass is difficult. Very small quantities of very low molecular mass polystyrene are synthesized via such routes.

Transparent HIPS (SBC) is, however, produced industrially by anionic block copolymerization of butadiene and styrene. Organolithium compounds (e.g., *n*-butyllithium) are used as initiators. The monomers and solvent used in anionic polymerization have extremely high purity requirements. The polymerization gross rate is higher than that of

the radical chain reaction due to the simultaneous growth of all initiated chains. Polymerization is carried out at low temperature in solution to enable the reaction to be controlled.

The coordination polymerization of styrene with conventional Ziegler catalysts produces a sterically ordered, isotactic polymer. These highly ordered chains can form polymer crystals. The melting temperature of the crystalline zones of isotactic polystyrene is ca. 230 °C. The rate of crystallization is, however, so low that this property cannot be exploited industrially [8].

Syndiotactic polystyrene crystallizes very rapidly and is produced by using special titanium–aluminoxan catalysts [9, 10]. The melting temperature of the syndiotactic sequences is ca. 270 °C. The material has found limited use in heat-resistant applications, often glass-fiber reinforced or blended with polyamide.

HIPS Synthesis. Rubbers used for HIPS synthesis are medium-*cis*-polybutadienes with a glass transition temperature around–85 °C. They are obtained by butyllithium-initiated anionic polymerization of butadiene. Usually the polybutadienes are long-chain branched to prevent cold flow during storage. Other rubbers (e.g., high-*cis* grades, styrene–butadiene block copolymers, EPDM rubbers) may be also employed, but have less significance.

The synthesis of HIPS requires careful control of the rubber particle size and morphology. Initially, the solution consists of polybutadiene rubber dissolved in styrene and further additives such as diluents, chain-transfer agents, or initiators. With the onset of polymerization, the polystyrene forms a separate phase. Styrene and optional diluents are the common solvents for the elastomer and the polystyrene phase (oil-in-oil emulsion). The polystyrene phase grows at the expense of the rubber phase with further conversion. The rubber phase initially is the continuous phase and remains so if unstirred. In a stirred reactor, phase inversion occurs, largely depending on the phase volume ratios and viscosities of the two phases. The reaction conditions during phase inversion determine the rubber morphology and particle size to a large extent.

Simple blending of polystyrene and polybutadiene leads to a mechanically inferior product. The mechanical strength of HIPS is supported by polystyrene molecules, which are grafted onto rubber molecules. Grafting occurs especially at low styrene conversions, when the volume of the polystyrene phase is still small. Quantity and nature of these copolymers have big impact on the particle size and morphology of the HIPS rubber particles [11, 15].

1.2.1. Bulk Polymerization

Currently, PS and HIPS molding materials are mainly produced by continuous polymerization processes. The polystyrene product has consistent quality, high purity, and a low residual monomer content (generally less than 500 ppm monomeric styrene). The most difficult task from an industrial standpoint is the control of the highly viscous melt and the removal of the heat of polymerization (71 kJ/mol).

Solvents such as toluene or ethylbenzene are frequently present in small proportions (typically 5–15 %) to provide better control of the polymerization rate, the viscosity of the polymer melt, and the cross-linking of the rubber phase. This technique is known as *solution polymerization*. Due to the limited quantities of the diluent, the processes are often also referred to as *continuous bulk polymerization*. The solvent and the unreacted monomer must be removed by degassing. They are generally recovered, optionally purified and transferred back to the feed. In a running continuous operation, solvents are in essence introduced via styrene impurities (mostly ethylbenzene).

The plant setup generally comprises a polymerization section, a degassing and solvent recovery section, and a pelletizing section.

The most common reactor for *PS molding materials* is an ebullient single stirred-tank reactor. A second stirred-tank reactor or a tubular plug-flow reactor may be used to increase conversion. PS molding materials may also be produced in more complex reactor configurations like HIPS units.

HIPS plants generally consist of a series of three to five reactors, split into a prepolymerization and postpolymerization section. In the prepolymerization section phase inversion takes place, and rubber morphology and particle size are largely adjusted. Various reactor designs have been proposed for this part of the plant. Common are one or two stirred-tank reactors, tower reactors, loop reactors with static mixers,

or combinations of these. The reaction is typically carried out at 100–150 °C to 15–30 % conversion. The postpolymerization part commonly consists of several plug-flow type reactors to achieve high styrene conversions, but continuous stirred-tank reactors may be used as well. Common temperatures are 140–190 °C in this part of the plant. Figure 3 shows several common reactor configurations.

In the *continuous stirred-tank reactor* part of the heat is removed by means of reflux cooling. The heat of polymerization causes part of the styrene to evaporate. The gaseous monomer is condensed in condensers with large surface areas and recycled back to the reactor. The prerequisite for this type of heat removal is effective mixing of the reactor contents. Anchor stirrers, impellers, or helical ribbon agitators are commonly used. The reaction temperature is the most important parameter affecting the molecular mass of the polystyrene and thus the properties of the product. It is controlled by varying the

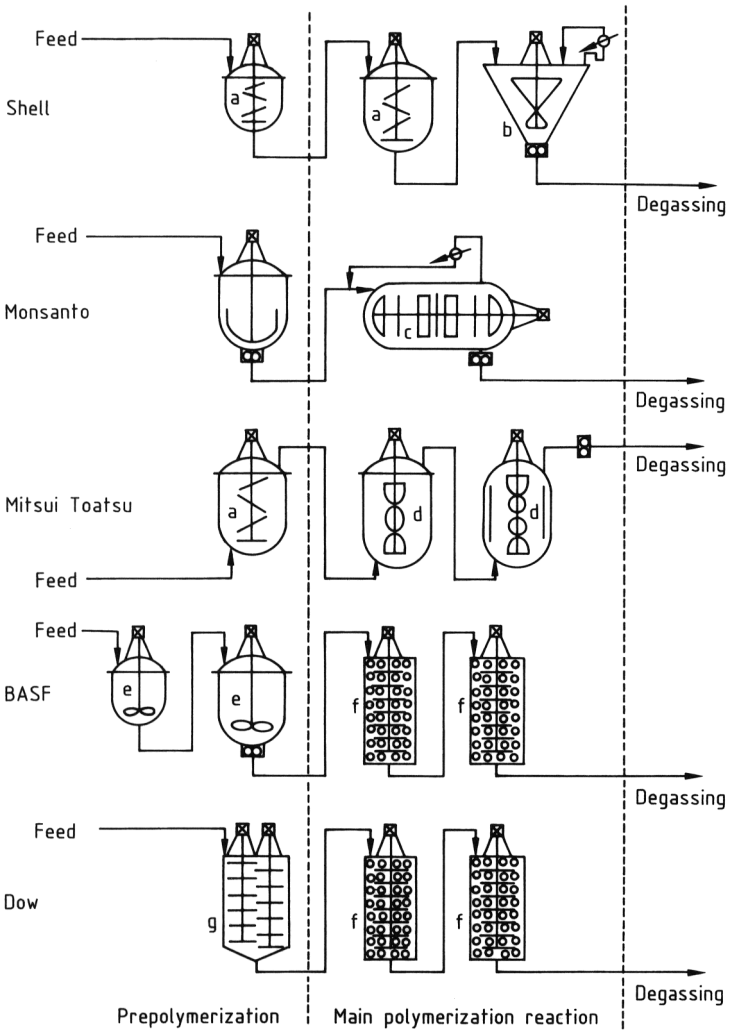


Figure 3. Various reactor configurations for HIPS production a), b), d), e), g) Stirred-tank reactors; c) Horizontal plug-flow reactor; f) Tower reactors
Reproduced from [14] with permission of Hanser Publishers.

pressure and thus the boiling point of styrene in the stirred tank. The temperatures in the reactors are between 100 and 170 °C, corresponding to pressures of ca. 0.5–2 bar.

The reactor feed can also be used to remove heat of polymerization. Reactors converting more than 40 % of the styrene feed usually need additional cooling. The lower solid content of the HIPS prepolymerization reactors, on the other hand, necessitates preheating of the reactor feed.

Tower reactors are equipped with special baffles in which a cooling agent circulates to ensure the removal of the heat of polymerization. Different temperature zones can be set up in a reactor by adjusting the temperature of the cooling agent. The tower reactors are also equipped with agitator blades.

Tubular reactors with static mixing elements and cooling are also in use. Adiabatic or isothermal tubular reactors are sometimes used for high conversions. Also known are axially segmented and agitated tubular reactors operating under reflux.

The polystyrene melt leaving the reactor section has a concentration of 60–90 %. Unreacted styrene monomer and solvent are removed by flash devolatilization. The polymer is fed into an evacuated, heated vessel where the volatile components evaporate, the melt is then pumped out. The styrene–solvent mixture formed is recycled to the first reactor. A small fraction must be discarded, however, to avoid increasing the concentration of styrene contaminants.

A second flash tank or another degassing unit (e.g., falling strand degassers, steam strippers, thin-film evaporators, degassing extruders) may be used to further decrease content of volatile compounds.

The polymer melts can be mixed with additives (e.g., dyes, stabilizers, or lubricants) by using static or mechanical mixing equipment.

Degassing of the polystyrene melt is followed by pelletization. In extrusion pelletization the polymer is forced through a perforated disk in continuous strands. The necessary pressure is applied by means of the discharge pump in the degassing unit or by an extruder. The strands are cooled in a water bath and cut into cylindrical pellets.

Underwater and water-ring pelletizing systems are also used and yield lentil-shaped pellets.

The pellets can be coated with an externally applied lubricant (e.g., zinc stearate or *N,N'*-ethylene-bis(stearamide)) to improve the sliding properties.

1.2.2. Suspension Polymerization

Suspension processes are chiefly used for the production of expandable polystyrene. PS molding materials may be produced by this process when the blowing agent is omitted. The combined bulk–suspension process is sometimes still used for HIPS production.

In suspension polymerization styrene is dispersed in water in the form of small droplets by stirring. The addition of suspension agents such as poly(vinyl pyrrolidone), poly (vinyl alcohol), alkaline-earth phosphates, or celluloses is necessary to stabilize the organic phase. Polymerization must be started with radical-forming initiators because the process temperatures are considerably lower than those of continuous bulk polymerization (80–110 °C).

The main advantage of suspension polymerization is that the heat of polymerization can easily be removed via the aqueous phase. A high degree of conversion can also be achieved.

Generally, however, the polystyrene beads must be repelletized after separation of the water and drying to satisfy market requirements with regard to processing of the molding materials (e.g., injection molding equipment). Additives and dyes can be incorporated during regranulation.

In the case of HIPS, suspension polymerization must be preceded by bulk polymerization to ensure that rubber particles are formed. The reaction can only be carried out in suspension after the formation of the disperse polybutadiene phase. The product has comparable material properties to HIPS produced by the bulk process.

The batch suspension process for styrene polymerization has been gradually replaced by the more economically favorable continuous bulk processes. Very few of the older plants based on batch suspension technology are still run commercially.

1.3. Properties

1.3.1. Chemical Properties

The chemical properties of atactic PS and HIPS are similar.

Under certain conditions oxidizing acids lead to oxidative degradation. However, the molding materials are resistant to dilute acid, alkali, and salt solutions. Exposure to UV radiation in the presence of oxygen causes yellowing and embrittlement, particularly in HIPS modified with polybutadiene. Reactions at the remaining double bonds bring about a gradual loss in elastic properties of the soft components. This damage can be suppressed but not completely inhibited by the addition of light stabilizers. Polystyrene is therefore not generally used in areas of application where weather resistance is required.

The replacement of polybutadiene rubber by EPDM rubber and the addition of special antioxidants lengthen the service lifetime of materials exposed to weathering by a factor of 15–20.

Oils and fats (particularly important in the food packaging sector) produce stress cracking. This can, however, be effectively counteracted by a range of measures [13], for example, by moderately increasing the average particle size to more than 5 μm.

The self-ignition temperature of PS and HIPS is 490 °C. Polystyrene articles are generally classified as being moderately flammable (DIN 4102) and as slow-burning (Underwriters Laboratories UL 94 HB). The flammability of special HIPS molding materials can be reduced considerably with additives (e.g., organobromine compounds) to give products that are classified as having a low flammability. The main area of application for these products is in the electrical sector. They are also increasingly being used for housings for technical appliances (e.g., photocopiers, televisions).

1.3.2. Physical and Processing Properties

Polystyrene, being a linear hydrocarbon chain with phenyl side groups linked, on average, to every second carbon atom, dissolves in aromatic hydrocarbons (toluene, ethylbenzene), halogenated hydrocarbons, aliphatic ethers (tetrahydrofuran), esters (ethyl acetate), and ketones (butanone), but not in aliphatic hydrocarbons (hexane) and alcohols (methanol). A summary of the solubility behavior of polystyrene can be found in [12].

The most important physical data for PS and HIPS are given in Table 1.

Special PS molding materials are available with specific property profiles for different processing technologies such as injection molding, extrusion, or thermoforming.

The mechanical and rheological behavior of polystyrene is predominantly determined by its average molecular mass (normally 150 000–400 000). The strength improves with increasing chain length but the melt viscosity increases making processing more difficult. Lubricants such as butyl stearate or paraffinic oil can be added to lower the melt viscosity of PS and HIPS. However these agents also lower the softening point.

PS grades with very good or good flow properties are mainly used for processing in injection molding machines. High molecular mass grades with higher strength and resistance to heat distortion are preferred for extrusion of films and sheets.

In extrusion and injection molding, the polystyrene melt is forced through narrow nozzles or slits. The polymer molecules orientate themselves parallel to the flow direction due to the high shear rate. The melt often solidifies in the mold so quickly that this initial orientation cannot be reversed by molecular diffusion. Polystyrene end products may therefore display anisotropy of their mechanical properties parallel and perpendicular to the processing direction. Tensile properties are much increased in parallel to the processing direction, while they are generally weakened perpendicularly to it. Biaxially oriented polystyrene has increased mechanical strength over the entire film. It may dissipate mechanical energy by a so-called "shear yielding" rather than the more common and less efficient "crazing" mechanism.

The impact resistance of HIPS is higher than that of PS due to the rubber component, but transparency is lost [exception: transparent styrene–butadiene multiblock copolymers (SBC) produced by anionic polymerization (Section 1.1)]. Processing properties are not altered significantly by the polybutadiene phase. However,

Table 1. Physical properties of PS and HIPS resins

Property	Test method	Typical values	
		PS resins	HIPS resins
Density, g/cm^3	DIN 53 479 ASTM D 792	1.05	1.03–1.05
Melt flow index (200 °C/5 kg), g/10 min	DIN 53 735 ASTM D 1238/G	1–30	2–20
Tensile modulus, MPa	DIN 53 457 ASTM D 638	3000–3400	1600–2800
Yield tensile strength, MPa	DIN 53 455 ASTM D 638	35–60	20–45
Tensile elongation at break, %	DIN 53 455 ASTM D 638	1.5–3	25–70
Ball indentation hardness, MPa	DIN 53 456 ISO 2039	150–160	75–140
Flexural strength, MPa	DIN 53 452 ASTM D 790/1	60–120	35–80
Charpy impact strength, kJ/m^2	ISO 179	10–25	35–no break
Notched Charpy impact strength, kJ/m^2	DIN 53 453	1–2	5–17
Izod impact strength, kJ/m^2	ISO 180/1 A	10–25	35–no break
Notched Izod impact strength, J/m	ASTM D 256/A	15–30	50–150
Vicat softening temperature, °C			
VST/B (50°/h, 5 kg)	DIN 53 460	78–102	75–97
VST/A (120°/h, 1 kg)	ASTM D 1525/B	85–110	80–100
Thermal conductivity, W K^{-1} m^{-1}	DIN 52 612	0.16	0.16
Dielectric constant (1 MHz)	DIN 53 483 ASTM D 150	2.5	2.5–2.7
Dissipation factor (1 MHz)	DIN 53 483 ASTM D 150	$(1–4) \times 10^{-4}$	$(2–8) \times 10^{-4}$
Thermal coefficient of linear expansion, K^{-1}	DIN 53 752	$(6–8) \times 10^{-5}$	$(8–10) \times 10^{-5}$
Refractive index	DIN 53 491	1.59	

the softening point, the modulus of elasticity, and the hardness are lower than those of PS molding materials.

In HIPS, the rubber phase (generally polybutadiene) is distributed in the form of discrete particles in the polystyrene matrix. The most important parameters affecting the properties of the end products are the rubber content, morphology, average particle size, particle-size distribution, and the degree of cross-linking of the polybutadiene phase (Fig. 4).

Rubber Content. The HIPS grades from different producers may be classified according to their polybutadiene (PB) content: semi-impact-resistant (ca. 3 – 6 % PB) and impact-resistant (6–10 % PB). The real criterion is not the rubber content, but the gel content that is obtained with a given rubber content (i.e., the mass fraction of the disperse phase including the polystyrene enclosed within the particles and grafted onto the polybutadiene chains) [14]. The gel content is roughly three to four times the quantity of rubber added.

Rubber Morphology. A wide range of different particle morphologies can be obtained depending on the chemical composition of the rubber and the polymerization conditions. Standard HIPS grades containing polybutadiene usually consist of cellular particles (Fig. 1). If part of the polybutadiene is replaced by styrene–butadiene block copolymers, coils, mazes, shell, or capsule particles are formed [15].

Particle Size and Particle-Size Distribution. The particle-size spectrum of the rubber phase is the factor determining the impact resistance of the molding materials. Commercial grades have average particle sizes in the range 0.5–9 μm. The highest mechanical efficiency is in the range 1.5–3 μm. If the particles are significantly larger, less crazes and less cavitation can be supported by the same rubber quantity [16, 17]. Grades with particles sizes > 5 μm have increased environmental stress crack resistance. Rubber particles smaller than 1 μm are less efficient in craze initiation. Such HIPS

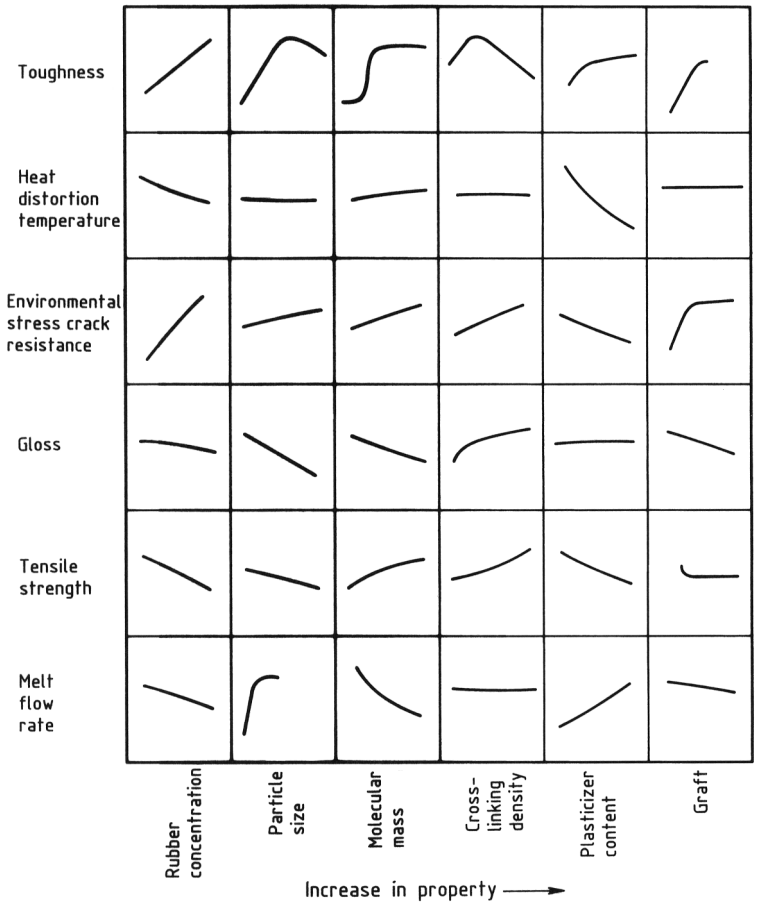


Figure 4. Summary of property relationships of commercial mass-produced HIPS
Reproduced from [12] with permission of The Dow Chemical Company.

grades have reduced impact strength and are used for high gloss applications.

The average particle size depends on the polymerization conditions during phase inversion. The most important parameters listed below can be modified as required:

1. The ratio between the solution viscosities of the disperse polybutadiene and homogeneous polystyrene phases
2. The shear force applied to the polymerizing material via the agitator
3. The surface tension between the two phases [18]—largely affected by the degree of grafting

Degree of Cross-Linking. Another important parameter is the cross-linking density of the polybutadiene phase. The rubber chains must be cross-linked with one another to a certain degree so that they can resist the shear forces used in subsequent processing, thus guaranteeing a stable particle form. However, the cross-linking density must not be too high because this would lead to the loss of the desired rubber-elastic properties. Cross-linking is a thermally initiated radical reaction and occurs mainly at high degrees of conversion and in the degassing section of the polymerization plant. The parameters in this process step (residence time, temperature) must therefore be adjusted to give the desired degree of cross-linking in the end product.

1.4. Processing and Uses

PS and HIPS molding materials are processed using molding processes generally used for thermoplastics (e.g., injection molding, extrusion, or thermoforming). About 50 % of the total quantity is processed with screw injection molding machines at 200–280 °C.

Films and sheets are produced by extrusion at ca. 200 °C with broad-slit dies. Thermoforming is used to produce articles such as refrigerator linings from sheets and yogurt cups and disposable tableware from films.

PS and HIPS molding materials are mutually compatible and can be mixed with one another in all proportions. The properties of the mixtures depend on the proportions of the components.

The main areas of application of PS and HIPS molding materials are in packaging, technical items, household and consumer goods, and refrigeration equipment. Roughly two thirds of PS and HIPS are consumed for packaging and for technical items. Packaging accounts for more than 50 % of the consumption in Western Europe and the United States, where technical items represent 20–25 % of the market. In Asia, 20–25 % of the material goes to the packaging sector, while more than 50 % are used for technical items. Asia accounts for more than 40 % of the total polystyrene consumption, the NAFTA region and the European Union for about 25 % each (2005). Recent annual growth rates have been ca. 2 %.

Technical items include housings for television, computers, printers, air conditioners and the like, electrical appliances, computer accessories, and sanitary ware.

Household and consumer goods include toys, containers, furniture, disposable tableware, and cups for drink vending machines. Polystyrene is used for the packaging of compact discs, audiocassettes, foods and pharmaceuticals. Polystyrene is especially suitable for the packaging of dairy products. Biaxially oriented polystyrene and PS blown film are used for display packaging, wrap film, and envelope windows.

PS and HIPS molding materials do not affect odor or taste and are licensed worldwide for contact with foods. Legal requirements in individual countries specify permitted concentrations of materials used in production and processing. All standard commercial PS and HIPS molding materials comply with these guidelines.

Trade Names and Producers. PS and HIPS molding materials are produced by more than 100 raw materials manufacturers throughout the world who offer an extensive range of products classified according to strength, processing behavior, and dimensional stability when subjected to heat. Total installed capacity is about 15×10^6 t. Examples of trade names are given in alphabetical order by producer below:

Polystyrol	BASF Aktiengesellschaft, Germany
Starex	Cheil Industries, Korea
Polyrex	Chi Mei, Taiwan
-	Chevron–Phillips Chemical Comp.
Styron	Dow Chemical, USA
Edistir	Enichem Polimeri, Italy
-	Estizulia, Venezuela
-	Innova, Brazil
-	Ineos, Great Britain
-	Kumho, Korea
LG	LG Chemicals, Korea
-	Japan Polystyrene
-	Nizhnekamskneftekhim, Russia
-	Nova Chemicals, Canada
-	Resirene, Mexico
-	PS Japan
SC	Supreme Petrochem. Ltd., India
PS	Sabic, Saudi Arabia
-	Secco, China
-	Shantou, China
Lacqrene	Total, France
-	Videolar, Brazil
-	Wuxi Wei Da, China

The producers (and trade names) of transparent HIPS molding materials are Asahi Chemicals, Japan (Asaflex), BASF, Germany (Styrolux); Chevron–Phillips Chemicals, USA (K-resin); Chi Mei, Taiwan (Kibiton), Denka, Japan (Clearen), and Kraton Polymers, USA (Kraton). Total installed capacity is about 0.5 $\times 10^6$ t (2006).

Syndiotactic polystyrene is produced by Idemitsu Petrochemical, Japan, under the trade name Xarec. Installed capacity is 5000 t/a (2001).

1.5. Quality Specifications

Most PS and HIPS molding materials are processed automatically which means that product quality must be as uniform as possible. Quality

assurance systems (ISO 9000–9004) are common in the production of molding materials to guarantee maximum uniformity. The ISO standard specifies the quality of all raw materials, the production conditions, and the properties of the end products.

The rheological, mechanical, thermal, and electrical properties of the molding materials are defined in ISO 1622–2 (PS) and 2897–2 (HIPS). The Vicat softening temperature (VST B/50, ISO 306), the melt flow index (MFI 200/5, ISO 1133), and the impact resistance (Charpy, ISO 179) are among the most important properties. National standards such as ASTM or DIN (Table 1) largely correspond to the ISO standards.

1.6. Storage and Transportation

The storage and transportation of PS and HIPS molding materials do not pose any special problems. They are subject to the general fire protection requirements applicable to solid combustible materials such as wood. Roofed sheds or silos are suitable for storage. Polystyrene is not moisture-sensitive, but must be dry for processing. PS and HIPS molding materials are transported in paper or polyethylene bags, in large cardboard containers (capacity ca. 1 t), in silo vehicles or containers. In the NAFTA region, rail cars (hopper cars, capacity 80 t) are also used.

1.7. Recycling

Waste PS and HIPS can be reutilized in various ways. In *material recycling* the molding materials are broken into smaller pieces, melted, and reprocessed to give finished products. *Chemical recycling* involves the breaking up of the polymer chain into lower molecular mass components which can be used as raw materials for chemical processes. In *thermal recycling* the plastic is incinerated and the liberated energy is used, for example, as process heat or for general heating purposes. See also → → Plastics, RecyclingPlastics, Recycling.

Material Recycling. Recycling of industrial waste, such as trims and scrap, is not problematic. Polystyrene end products can also be recycled after use provided that the material can be cleaned and sorted into grades. In no case, however, should food packaging be produced from this recycled material. Some countries stipulate legal quotas for material recycling of plastics.

Chemical Recycling. Two processes are in the development stage: pyrolysis and cleavage by hydrogenation cracking. Both processes can be applied to pure plastics fractions (e.g., polystyrene) and mixtures of plastics.

Pyrolysis involves the cleavage of long-chain molecules at high temperatures (500–900 °C) with the exclusion of oxygen [22]. In hydrogenating cleavage the polymer chains are broken up under higher pressure at ca. 400 °C, and in the presence of hydrogen, into volatile saturated compounds. Both processes yield a nonspecific spectrum of products (60–80 % of styrene and ethylbenzene, respectively), which can be used as feedstock for other petrochemical processes.

Thermal Recycling. In the presence of sufficient oxygen, polystyrene burns almost completely to give carbon dioxide, water, and a small amount of nontoxic ash residue. The enthalpy of combustion (41 MJ/kg) is close to the energy content of fuel oil (43 MJ/kg). In modern waste incineration plants, polystyrene comprises part of the plastics fraction of household waste, adherence to the necessary combustion conditions is guaranteed.

1.8. Environmental Aspects

PS and HIPS molding materials are not water soluble. No gaseous or liquid components are liberated during transportation and storage. Liquid and gaseous styrene must, however, be handled safely during production processes. Polymerization is therefore carried out in closed systems. The maximum permitted workplace concentration of styrene is between 10 and 50 ppm (42–210 mg/m^3) in all important producer countries.

In bulk polymerization processes, the product only comes into contact with water during the cooling of the extruded strands. Contamination of the water does not occur. In the suspension process, polymerization takes place in an

aqueous medium and the wastewater must be treated by using standard sewage technology.

In the processing of PS and HIPS, small quantities of styrene are liberated above ca. 280 °C as a result of the residual monomer content and of thermal degradation. The styrene can be removed by special ventilation devices; however, normal room ventilation is usually adequate to ensure compliance with workplace concentration limits.

2. Styrene–Acrylonitrile (SAN) Copolymers

Many applications requiring stiffness and transparency are served by polystyrene, a moderately priced commodity thermoplastic (Chap. 1). A mature market has also continued to thrive for resins offering a better balance of optical clarity, rigidity, good chemical and heat resistance, high strength, and flexible processing. One class of thermoplastics having these properties is the styrenic copolymers. The following four copolymers continue to have growing commercial importance:

1. Styrene–acrylonitrile (Chap. 2)
2. α-Methylstyrene–acrylonitrile (Section 4.1)
3. Styrene–methyl methacrylate (Section 4.2)
4. Styrene–maleic anhydride (Section 4.3)

These copolymers are produced commercially by free-radical polymerization [23]. Their specific properties are determined by their molecular mass and composition. The initial concentration of the two monomers (M_1 and M_2) prior to initiation of polymerization must be carefully chosen to give the required copolymer composition for the finished product. Techniques are available for calculating the correct monomer concentration that utilize parameters known as reactivity ratios (r) that reflect the relative reactivity of each monomer with the free-radical end of the growing chain [24]. The dependence of the copolymer composition on the monomer concentration for each of the above styrene copolymers is given in Figure 5.

The styrene copolymers having the greatest commercial importance are the styrene–acrylonitrile (SAN) copolymers [*9003-54-7*].

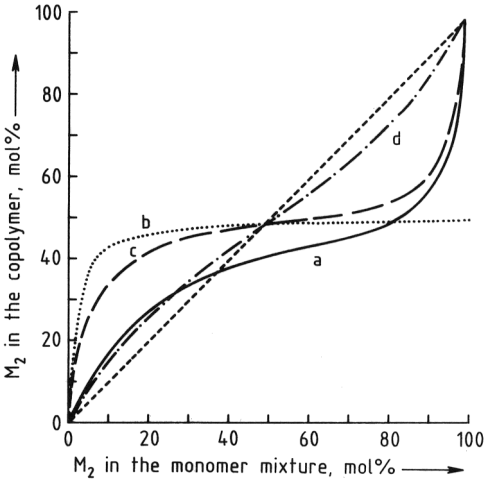


Figure 5. Composition diagram for common styrene copolymers a) Styrene (M_1) – acrylonitrile (M_2) (r_1= 0.40, r_2= 0.04); b) Styrene (M_1) – maleic anhydride (M_2) (r_1= 0.04, r_2= 0); c) α-Methylstyrene (M_1) – acrylonitrile (M_2) (r_1= 0.10, r_2= 0.06); d) Styrene (M_1) – methyl methacrylate (M_2) (r_1= 0.59, r_2= 0.54)

Incorporation of acrylonitrile improves heat resistance, toughness, chemical resistance, and barrier properties when compared against polystyrene. The SAN polymers can be used by themselves in applications requiring transparency, or they can be toughened by incorporation of rubber particles. Use of butadiene rubber gives acrylonitrile–butadiene–styrene (ABS) polymers (see Chap. 5).

The acrylonitrile (AN) levels in commercial SAN polymers fall into two ranges. The lower range (20–35 wt %) covers most injection-molded articles, and the higher range (60–85 wt %) represents a small but growing market for barrier plastics where low gas permeability is needed for packaging of food and beverages (see Chap. 3).

2.1. Production

The relative reactivities of styrene and acrylonitrile differ. Therefore, the polymer composition also differs from the monomer composition, except at the azeotrope (ca. 24 wt % acrylonitrile). This, along with the fact that acrylonitrile is soluble in water, requires special considerations for the various production methods.

Using reactivity ratios [25] and Equation (1) [26] for two monomers M_1 and M_2:

$$C = \frac{P - 1 + \sqrt{(1-P)^2 + 4Pr_1r_2}}{2r_1} \quad (1)$$

C = molar ratio M_1/M_2 in the monomer mixture

P = molar ratio M_1/M_2 in the copolymer

r_1 = reactivity ratio for monomer 1

r_2 = reactivity ratio for monomer 2

the monomer–polymer composition curve can be determined for SAN and other common copolymer pairs (Fig. 5). Reactivity ratios (styrene: $r_1 = 0.4$ and acrylonitrile, $r_2 = 0.04$; Fig. 5.) imply that a mixture of about 75 wt % styrene and 25 wt % acrylonitrile shows no compositional drift ("azeotropic composition").

Reactivity ratios are a function of temperature [27] and the composition curves should be adjusted if the temperature range during manufacture is wide. This is not as critical when the azeotrope composition is approached.

Maintaining tight composition control of SAN is important to obtain acceptable optical and mechanical properties. Differences of a few weight percent in the SAN composition can result in incompatibility [28]. For example, addition of 2 wt % SAN with 32 % acrylonitrile to SAN with 24 % acrylonitrile leads to hazy material. As conversion increases, severe composition drift occurs (Fig. 6) unless corrective actions are taken to replenish the more reactive monomer [29].

Commercially, SAN is produced worldwide by emulsion, suspension, and continuous bulk technologies [30]. These methods are described in detail elsewhere, →Polymerization Processes-Polymerization Processes. The majority (85 %) of SAN is used captively as the matrix component for ABS. Most SANs used for the manufacture of ABS contain 24–32 wt % acrylonitrile. The properties of ABS can be influenced by the composition and molecular mass distribution of the SAN, which are manipulated by the polymerization method employed to make the SAN. This is discussed in detail in Section 5.3.2.

SAN materials sold as finished products are almost exclusively made by continuous bulk methods which results in superior optical properties. Also, continuous bulk technology is the most cost efficient and generates the least waste of the three methods.

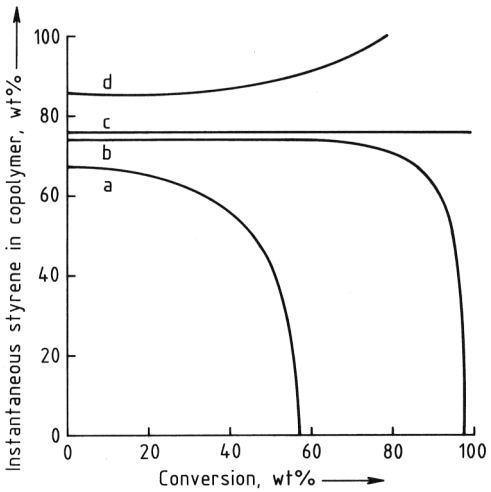


Figure 6. Approximate compositions of SAN copolymers formed at different conversions, starting with various monomer mixtures [29]
Styrene : acrylonitrile weight ratio a) 35/65; b) 70/30; c) 76/24; d) 90/10

Figure 7 shows an example of the manufacture of SAN via continuous bulk polymerization. The process consists of continuous feeds to one or more reactors (a), followed by devolatilization units (f, g) and pelletizer (j). Unreacted monomers and solvent are recycled to maintain conversion and composition at desired levels. The technology is very similar to that employed for PS molding materials (see Section 1.2.1).

The reactor(s) can be plug flow or partially filled types, cooled by jacket and/or reflux [31, 32]. Adequate agitation is critical for proper temperature and composition control. Polymerization temperatures range from 80–170 °C, depending on the process configuration and whether chemical or thermal initiation is used. Conversion ranges from 30 to 70 %.

Devolatilization is usually accomplished via wiped-film or falling-strand type units, but can also be done with a devolatilizing extruder. To achieve the low levels of residual monomer required to meet food contact applications, devolatilization is usually done in a two-stage process with different vacuum levels.

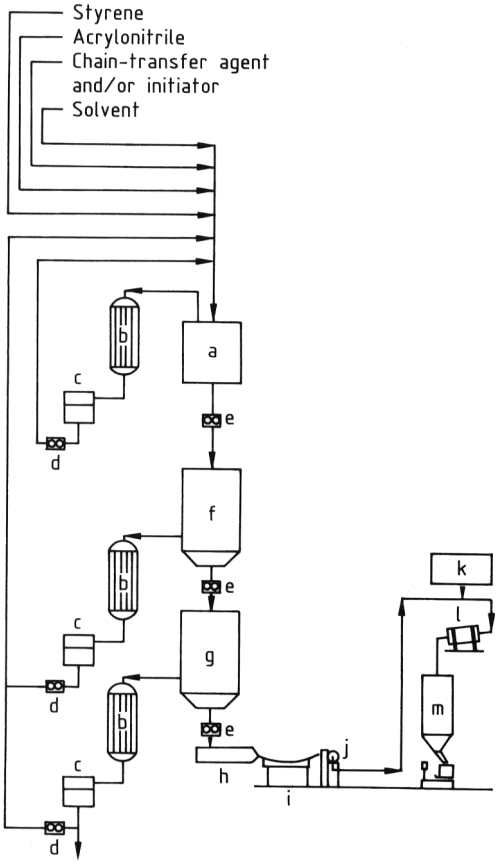


Figure 7. Process for the continuous bulk and solution polymerization of SAN [31] a) Reactor; b) Condenser; c) Condensate receiver; d) Recycle pump; e) Melt pump; f) First-stage devolatilizer; g) Second-stage devolatilizer; h) Discharge screw pump; i) Water bath; j) Pelletizer; k) External lube; l) Screen; m) Silo

2.2. Properties

SAN copolymers with acrylonitrile contents between 20 and 35 wt % are transparent plastics having better mechanical and chemical resistance properties than polystyrene, thus enabling SAN to command a premium price. Properties for commercial grades of polystyrene and SAN are compared in Table 2 [33]. Next to a higher rigidity and impact resistance, the SANs are stronger and more scratch resistant and have a better heat resistance.

SAN can be reinforced with glass fiber to give higher stiffness, breaking strength, and notched impact strength [34, 35]. The effect of adding 20 % glass fiber to SAN is shown in Table 3 [36].

The conventional method for making glass-fiber-reinforced SAN is to mix the polymer pellets and glass fiber in an extruder, followed by injection molding of the glass-filled pellets. This approach suffers from the inadvertent reduction in glass-fiber length (12 mm) to ca. 0.4–0.5 mm.

An alternative approach is to make a glass concentrate (collimate) by polymerizing the SAN in the presence of the glass fibers, and then blending the collimate with SAN pellets. Commercial collimates are available containing 80 % glass [37]. The glass fiber length in the final product is about 1 mm, and superior reinforcing properties are claimed with the collimate approach. The SAN collimate can be added to other thermoplastic resins.

Table 2. Comparison of the physical properties of standard polystyrene and SAN copolymers

Property	DIN test method	Standard polystyrene	SAN copolymers (20–35 wt % acrylonitrile)
Density, g/cm^3	53 479	1.05	1.08
Tensile strength, MPa	54 355	50–65	75–85
Tensile elongation to fail, %	53 455	2–4	5
Flexural strength, MPa	53 452	100–110	110–140
Flexural modulus, MPa	53 457	3200–3400	3600–3800
Impact resistance, kJ/m^2	53 453	15–20	20–25
Notched impact test, kJ/m^2	53 453	2–3	3–4
Heat resistance, °C	53 461, version B	80–100	90–105
Thermal conductivity, kJ m^{-1} h^{-1} K^{-1}		0.71	1.17
Linear thermal expansion coefficient, K^{-1}		$(6–8) \times 10^{-5}$	$(6–8) \times 10^{-5}$
Dielectric constant	53 483	2.5–2.7	2.9–3.1
Dielectric loss factor	53 483	$(1.8–2.1) \times 10^{-4}$	$(6–9) \times 10^{-3}$
Specific resistance, $\Omega \cdot$ cm	53 482	$> 10^{16}$	$> 10^{16}$
Dielectric strength, kV/mm	53 481	> 100	> 50
Water absorption, 24 h, %	53 472	0.1	0.2–0.6
Processing temperature, °C		150–260	175–300

Table 3. Comparison of properties of filled and unfilled SAN

Property	Unfilled	Filled with 20 % glass fiber
Tensile strength, MPa	69–76	74–83
Elongation at break, %	2–3	1.4–1.9
Tensile modulus, GPa	3.3–3.9	8.3–11.7
Notched Izod impact strength, J/m	21.4–32	133–160
Heat deflection temperature, °C at 1.82 MPa load	101–104	99–110
Density, g/cm^3	1.07–1.08	1.22–1.40

The heat resistance (softening temperature) of typical commercial grades of SAN is ca. 5–6 °C higher than that of polystyrene (Table 2), thus allowing SAN to resist softening when exposed to boiling water. The softening of styrene polymers (and copolymers) is a consequence of the glass to rubber transition that occurs when glassy polymers are heated [38].

Addition of acrylonitrile to the styrene chain continuously increases the glass transition temperature (T_g) until a level of approximately 35 wt % acrylonitrile is reached. The T_g then falls with further addition of acrylonitrile [39]. The location and width of the glass transition for any composition is affected by the polydispersity of the molecular mass.

Commercial SANs contain oligomers left from polymerization which lower the T_g via plasticization. Removal of the oligomers in a commercial SAN (24 % acrylonitrile) increases the glass transition from 108.5 to 114.5 °C [40]. Therefore, any commercial SAN that is carefully treated to remove oligomers will benefit by having a higher heat resistance. The oligomers can be reduced by polymerizing at low temperatures (<120 °C) or by stripping them out during devolatization and subsequent purging from the recycle stream. If a large increase in heat resistance over polystyrene is needed, it is preferable to use the α-methylstyrene–acrylonitrile copolymers (see Section 4.1).

SAN has a slight yellow color in comparison to clear plastics such as polystyrene, acrylics, and polycarbonate. This color arises from cyclic chromophores associated with the acrylonitrile segments, and it becomes stronger as the acrylontrile content increases. Some new commercial, "water-white" grades have been introduced for applications requiring minimum yellowness [27, 28]. The reduction in color is brought about by lowering the level of acrylonitrile and fine-tuning the polymerization process to reduce haze and eliminate contaminants.

One negative consequence of the addition of the acrylonitrile to the styrene chain is an increase in melt viscosity. The nitrile groups in acrylonitrile are strong dipoles, and, as the acrylonitrile level increases, the dipolar attraction between the acrylonitrile groups increases the melt viscosity. This can be compensated for by increasing the processing temperature (Table 2). However, raising the temperature also increases the yellow color, so a compromise must be reached between processibility, properties, and color.

The polar nature of the acrylonitrile also results in slight deterioration of electrical properties in comparison to polystyrene (Table 2). SAN still has adequate properties as an insulation material.

Excellent chemical resistance is a very important feature of SAN resins. They are resistant to aliphatic hydrocarbons, nonoxidizing acids, alkali, vegetable oils, foods, some alcohols, and detergents. Many of these materials readily attack polystyrene, but the polarity of the acrylonitrile groups in SAN is responsible for better resistance. SAN resins are attacked by some aromatic hydrocarbons, ketones, esters, and chlorinated hydrocarbons [41]. The moisture absorption of SAN is also slightly higher (Table 2), again because of the polarity of acrylonitrile.

The UV resistance of SAN is not exceptionally good, due to the styrene unit. However, the addition of UV stabilizers improves the UV resistance to the point that some SAN grades are used for glazing and other outdoor applications [41].

2.3. Processing

SAN resins can be processed by all methods common to thermoplastics, with injection molding being the most prevalent [42–44]. The resins are slightly hygroscopic and should therefore be dried prior to processing. Since SAN resins are immiscible with most other polymers it is important that the equipment be thoroughly purged prior to processing.

Injection molding barrel operating temperatures are typically ca. 220–280 °C, which is about 10–20 °C higher than is used for polystyrene. Yellowing and some mechanical property deterioration occurs if the temperature is too high or if too much regrind is used [45].

The mold should be filled as rapidly as possible. This can be accomplished by using large nozzles and gates, high pressure, fast ram, and adequate mold vents. Warm molds are necessary to achieve maximum surface gloss and improve impact strength—the warm mold lowers the cooling rate and allows some of the flow orientation to relax before the part reaches the glassy state. Oven annealing of the part also reduces this orientation and may be required for special applications involving high mechanical stresses and pressures.

Finishing operations applicable to SAN include hot stamping, painting, screen printing, sonic welding, machining, vacuum metallizing, solvent welding, and most other operations used for ABS, acrylics, and polystyrene [46]. The good chemical resistance of SAN facilitates finishing operations requiring chemical exposure. Coloring and provision of antistatic agents, stabilizers, and flame retardants, as well as the reuse of scrap, are handled as with polystyrene (see Chap. 1).

2.4. Uses

The largest end use for SAN is as the rigid component for ABS (Chap. 5). All major ABS producers manufacture SAN for this captive use. SAN is used in the merchant market for a range of applications such as cookware, transparent parts in electronics and electrical appliances, instrument panels, sanitary and medical goods or cosmetic packaging. Chemical resistance and transparency are primary reasons for use [41, 42, 46].

The largest producers of SAN and their trade names are summarized in Table 4.

Table 4. Major producers and trade names of SAN

Producer	Trade name
BASF (Germany)	Luran
Daicel (Japan)	Cevian
Dow Chemical (USA)	Tyril
Techno Polymer Co. (Japan)	Sanrex
Polimeri (Italy)	Kostil

2.5. Blending of SAN

A new resin with unique properties may be obtained by blending (alloying) two or more polymers. Many studies have focused on SAN-based polymers as a major component of the alloy.

Commercial efforts have largely involved blending of ABS with major commercial polymers such as poly(ethylene terephthalate), polycarbonate, poly(vinyl chloride), and polyamide nylon to make resins with improved impact strength, heat resistance, and chemical resistance when compared to the individual polymers (see Section 5.12) [47]. These blends are not transparent because the rubber incorporated into the ABS for impact strength scatters light. The SAN does not become miscible with the other polymer. Rather, distinct domains of ABS and the other polymer phases remain, and the key to developing good mechanical properties is to reduce the domain size and promote good interphase adhesion [48].

Blending of SAN with other polymers to yield a transparent resin would require that the component polymers be thermodynamically miscible, alternatively the domains would have to stay below the critical size for light scattering.

Although polymers are generally not mutually miscible [47], SAN polymers show limited miscibility with poly(methyl methacrylate) [49], styrene–maleimide copolymers [50], styrene–maleic anhydride copolymers [51, 52], polycaprolactone [53], and poly(vinyl chloride) [54].

3. Barrier Resins

Acrylonitrile polymers and copolymers afford efficient barriers to gases, such as oxygen and carbon dioxide. Polyacrylonitrile [*25014-41-9*] (PAN) has the lowest permeability of any polymer, but its inherent rigidity and poor processibility (it degrades upon heating prior to melting) has spurred development of high acrylonitrile copolymers containing 60–85 wt % acrylonitrile.

Rubber-modified acrylonitrile–methyl acrylate copolymers are offered under the trade name Barex by Innovene. The acrylonitrile level in the Barex resin is 74 %. The copolymer is

Table 5. Permeation rates to oxygen and carbon dioxide at room temperature for polymers used in food packaging

Polymer	Permeation rate		
	Oxygen [a]	Carbon dioxide [a]	Ratio CO_2/O_2
Poly(vinylidene chloride)	0.0393	0.118	3.0
Barex 210	0.43	1.22	2.8
AN–styrene copolymer, 70–30	0.39	1.18	3.0
Poly(ethylene terephthalate)	2–4 [b]	4.7–7.8 [b]	
Poly(vinyl chloride) unplasticized	3–6 [c]	7.8–16 [c]	
Cellophane (dry, uncoated)	0.05	0.118	2.3
High-density polyethylene	43	118	2.7
Polypropylene	59	177	3.0
Low-density polyethylene	189	591	3.1

[a] $\frac{cm^3.cm}{m^2.d.atm} \times 10^5$ at 23 °C, 100 % relative humidity.
[b] Depends on crystallinity and orientation.
[c] Depends on compound formulation.

toughened by addition of styrene–butadiene rubber at a level of 10 %. The resins may be processed by all major thermoplastic processing methods.

Permeation of oxygen into food and beverages adversely affects their taste [55], and storage of carbonated beverages requires low permeation of carbon dioxide out of the bottle. The high acrylonitrile resins have much lower permeation rates than other thermoplastic packaging resins (Table 5). These high-acrylonitrile resins are also quite good barriers to moisture, which is another requirement for food packaging.

The effect of acrylonitrile level on permeation rates for SAN copolymers is shown in Figure 8. The highest practical limit for acrylonitrile content is approximately 80 %, at which point the copolymer begins to take on the pseudocrystalline structure of polyacrylonitrile and becomes difficult to process [56, 57].

Barrier resins are produced by suspension or emulsion polymerization [58, 59]. Maintaining constant composition at high acrylonitrile levels requires special techniques. A certain amount of the more reactive comonomer (e.g., styrene) is held outside the reactor and fed in a controlled manner during the polymerization cycle.

As animal tests have shown acrylonitrile to be a potent carcinogen, levels of acrylonitrile in the containers must be kept exceedingly low [60].

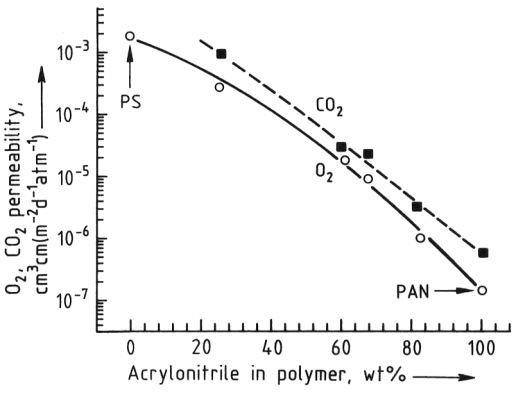


Figure 8. Permeability of oxygen and carbon dioxide through styrene – acrylonitrile copolymers
Values for the two homopolymers, polystyrene (PS) and polyacrylonitrile (PAN), are indicated.

4. Other Copolymers

Producers and trade names of other important styrene copolymers are listed in Table 6.

Table 6. Examples of producers and trade names of common thermoplastic styrene copolymers

Producer (country)	Comonomers	Trade name
BASF (Germany)	α-methylstyrene – acrylonitrile	Luran KR 2556
Nova Chemicals (Canada)	styrene – methyl methacrylate	NAS, Zylar
Arco Chemical (USA)	styrene – maleic anhydride	Dylark
Denki Kagaku Kogyo(Japan)	styrene – maleimide	Malecca
Techno Polymer Co. (Japan)	styrene – maleimide	Superex

4.1. α-Methylstyrene–Acrylonitrile Copolymers

The copolymer of α-methylstyrene (AMS) and acrylonitrile [*25747-74-4*] has a higher heat resistance and softer flow than SAN of the same acrylonitrile content. The heat deflection temperatures of the AMS–AN and SAN copolymers are 104 and 96 °C, respectively [61]. Physical properties and chemical resistance are similar to those of SAN. As with SAN, most AMS–AN copolymers are used as diluents to make high-temperature ABS (Sections 5.1.4 and 5.3.2) and acrylonitrile–styrene–acrylate (ASA) materials. AMS–AN copolymers are extensively compatible with SAN copolymers if they both have an acrylonitrile content of ca. 30 wt % [159]. The AMS copolymer is miscible with poly(vinyl chloride) [62], and could therefore be used to make both toughened and clear blends.

The manufacturing methods used for SAN can also be used for the AMS–AN copolymer. However, AMS reacts more slowly than styrene, greatly increasing the process residence times for a given acrylonitrile content. It is also more difficult to obtain high molecular mass AMS copolymers due to the higher termination rate constant compared with styrene and the strong chain-transfer effect of AMS oligomers and its monomer impurities. AMS-based materials are also yellower than their styrene counterparts.

By utilizing the difference, versus styrene, in reactivity ratio with acrylonitrile, a method for greatly increasing the production rate of AMS–AN copolymer has been developed [63]. Introducing low levels of styrene into the process to make an α-methylstyrene–acrylonitrile–styrene terpolymer is another way to increase reaction rates, with minor sacrifices in heat resistance.

4.2. Styrene–Methyl Methacrylate Copolymers

Methyl methacrylate readily polymerizes with styrene to form a styrene–methyl methacrylate copolymer [*25034-86-0*], SMMA, with similar physical properties to SAN, but with superior optical properties (low haze and glass-like appearance). Off-azeotrope copolymers are much easier to make, due to the similar reactivities of the monomers (Fig. 5). Commercial materials contain 20–60 % methyl methacrylate and are produced by methods similar to SAN [64, 65]. Methyl methacrylate is more commonly used to make clear ABS-type polymers (see Section 5.12.2).

4.3. Styrene–Maleic Anhydride Copolymers

Styrene and maleic anhydride react readily (Fig. 5) to give a copolymer [*9011-13-6*], SMA, with alternating monomer units. Reaction rates are significantly higher than for styrene alone or SAN, so polymerization conditions must be carefully chosen to control heat removal. Polystyrene technology is commonly used to produce thermoplastic SMA resins. The continuous stirred tank reactor technology permits synthesis of SMA copolymers with well defined S : MA ratio. The copolymerization parameters otherwise lead to the preferential formation of alternating copolymers.

The primary benefit of maleic anhydride is the greatly increased heat resistance. Also, the cost of this system is low, as both monomers are commodity materials. The products offer high rigidity, are commonly rubber modified, and are easily reinforced with fillers such as glass.

SMA resins generally fall into two categories. Low maleic anhydride (< 25 wt %), high molecular mass thermoplastic materials are produced for molding or extrusion applications, low molecular mass materials with a high maleic anhydride content (25–50 wt %) are produced for alkali-soluble coatings and adhesives.

Thermoplastic SMA grades span a heat resistance range of 110–135 °C (Vicat softening point). Grades developed specifically for expandable foam applications and blends of SMA and polycarbonate for power tool housings are also available [66, 67].

For structurally demanding parts, rubber-modified SMA is reinforced with glass fiber (typically up to 20 %) by melt compounding. These materials are often used for interior automobile applications [67].

SMA resins are unstable at high temperature, liberating carbon dioxide. They must be adequately stabilized and processed at temperatures below 260 °C, otherwise splaying of parts

results. The resin is stabilized by incorporating up to 1 % of a hindered phenol antioxidant with a thioester synergist.

4.4. Styrene–Maleimide Copolymers

For applications where heat resistance above the levels available from SMA resins is desirable, copolymers of styrene and maleimides can be used. These polymers are produced by copolymerizing styrene with a maleimide comonomer (e.g., *N*-phenylmaleimide) or by imidizing SMA with ammonia or an amine.

Polymerization of styrene and maleimides can be accomplished by any of the methods used for SAN. Imidization of SMA is achieved by injecting ammonia or an amine into a vented extruder, or by direct addition to the polymerization [66, 68].

SMI resins are used in a similar manner as SMA. They are rubber modified, glass reinforced, alloyed, or polymerized with termonomers such as acrylonitrile or acrylates. Unlike SMA, they are thermally stable at high temperatures and do not splay.

4.5. Styrene–Acrylate Copolymers

A recyclable, water-soluble copolymer of styrene and acrylate is available from Belland AG [69]. This copolymer contains carboxyl side groups which give it solubility in basic aqueous media. It is recoverable by precipitation via acidification. End uses include typical coatings applications for packaging laminates, book binding glues, and hygiene products.

5. Acrylonitrile–Butadiene–Styrene (ABS) Polymers

5.1. Definition and Structure

ABS [*9003-56-9*] and HIPS (Chap. 1) represent the industrially most important thermoplastic two-phase systems with an amorphous structure. The ABS polymers are based on three monomers: acrylonitrile (A), butadiene (B), and styrene (S). The polymer components have different chemical compositions and coexist as two separate phases whose compatibility is controlled by their structure and chemical microstructure.

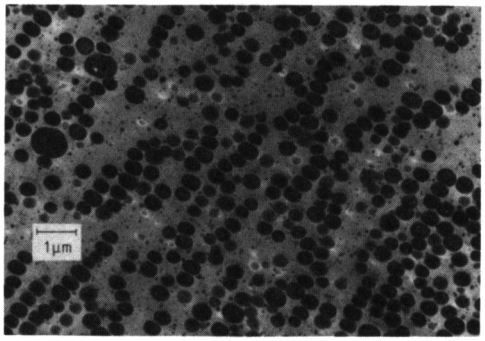


Figure 9. ABS graft polymer showing rubber particles embedded in a styrene – acrylonitrile (SAN) copolymer matrix

In all classical ABS molding compounds the continuous phase (matrix) consists of copolymers of styrene (or an alkylstyrene) and acrylonitrile. An elastomer based on butadiene forms the disperse phase that is distributed in the continuous phase and has a characteristic morphology (Fig. 9).

ABS is mainly produced via two major industrial processes: Emulsion-ABS by compounding of emulsion-made rubbers into the SAN matrix; and solution-ABS via dissolving a rubber (commonly: butadiene homopolymer) in styrene–acrylonitrile and subsequent bulk polymerization, similar to the HIPS process (see Section 2.1). However, process combinations also exist.

Attempts to synthesize styrene-co-acrylonitrile-block-butadiene copolymers via living free radical polymerization have not resulted in commercial products so far [70].

5.1.1. Historical Aspects

The history of ABS polymers began in the mid-1940s. In attempts to produce bulletproof plastic sheets during the last years of World War II, polymer systems were developed from special butadiene–acrylonitrile copolymers and styrene–acrylonitrile copolymers with high molecular masses. These materials had a high impact resistance on account of their low thermoplastic flow, but could only be processed with extruders. Semifinished products (i.e., predominantly sheets, profiles, and pipes) were the first

molded parts to be made from ABS polymers and had dull or matt surfaces.

A drastic increase in the flow of the material allowed processing by injection molding and thus opened up the way for the production of engineering plastics. Improved processibility was obtained by the use of graft polymerization. This technique allowed the production of molded parts with glossy or high-gloss surfaces.

Systematic research into ABS polymers has led to the development of other multiphase plastics with a chemically different make-up. These contain other monomer units in addition to or as a replacement for acrylonitrile, butadiene, or styrene.

Recent developments include modifications of the A, B, and S monomer units as well as complex blend systems, in which the ABS polymers are components of polymer mixtures with an extremely wide range of properties. See also, → Polymer BlendsPolymer Blends.

5.1.2. Structural Principles

A knowledge of the structural principles of ABS polymers and the parameters on which they depend is required in order to understand production processes, their relationship to product properties, and the basis for the development of other ABS polymers.

The most important physical properties for the user are good thermoplastic flow, high rigidity, satisfactory heat resistance, high surface gloss (emulsion-ABS), and good (notched) impact strength down to temperatures as low as ca. − 40 °C.

The simultaneous occurrence of high toughness and high rigidity results from proper bonding between the two polymer phases [71–78].

The elastic properties disappear on cooling to just above the glass transition temperature of the elastomer phase. The two-phase system then behaves as a brittle quasi-single-phase system.

The effect of the elastomer phase dispersed in the resin matrix is seen in plots of the modulus of elasticity as a function of temperature (Fig. 10) and of the stress–strain behavior at constant temperature (Fig. 11) [75, 76].

In Figure 11 the ABS polymer (b) absorbs significantly more energy during deformation up to the breaking point than the SAN resin (a). This is responsible for the high toughness of

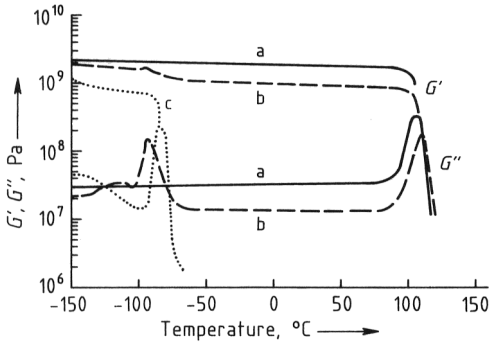


Figure 10. Temperature dependence of the complex shear modulus of ABS graft polymer and its polymer components a) SAN copolymer (matrix); b) ABS graft polymer; c) Polybutadiene (elastomeric graft base)

ABS polymers. The increased deformability in comparison with the pure SAN copolymer and the increased strain in comparison with the pure elastomer component (c) are due to yield processes,in which the applied energy causes the formation of wedge-shaped microcavities (crazes, Fig. 12 A) or initiates shear yielding of the matrix copolymer chains (Fig. 12 B). Both deformation processes are initiated by mechanical loading of the elastomer particles dispersed in the matrix.

The existence of more than one phase is therefore a prerequisite for high toughness. The deformation mechanisms and the effect of different elastomer particles and matrix parameters can be investigated by electron microscopy techniques [79–84].

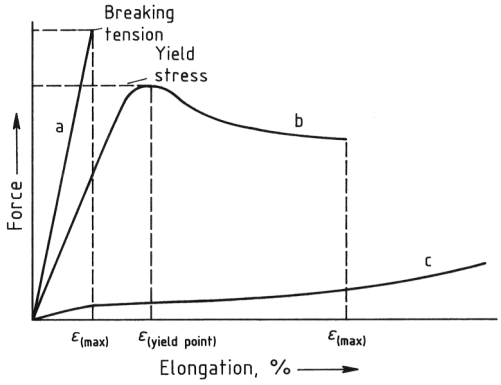


Figure 11. Stress – strain diagram for ABS graft polymer and its polymer components a) SAN copolymer (matrix); b) ABS graft polymer; c) Polybutadiene (elastomeric graft base)

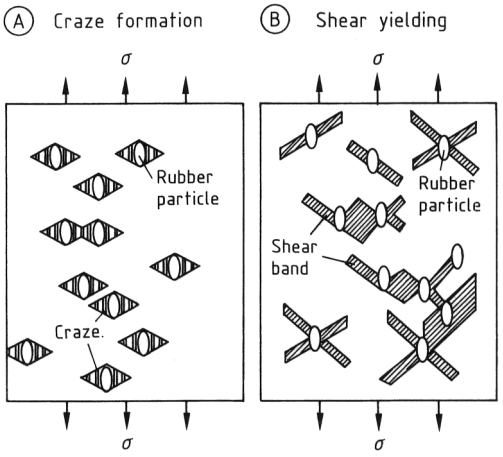


Figure 12. Deformation mechanisms (schematic) in ABS polymers

The glass transition temperature (T_g) depends on the stress frequency (it increases by ca. 30–40 °C after impact). The rubber used as the elastomer phase should therefore have as low a T_g as possible. Apart from special rubbers (e.g., silicone rubbers) polybutadiene is the most suitable. Polybutadiene (T_g – 85 °C) guarantees good low-temperature properties. Copolymers of butadiene with styrene (SBR) or with acrylonitrile (NBR) have much higher T_g values and are mainly used in special types of ABS.

Tough ABS resins require sufficient coupling between the elastomer particles and the resin matrix to ensure that forces can be transferred across the phase interfaces (phase coupling). Optimal phase coupling between the elastomer particles and the matrix is achieved by graft polymerization (Fig. 13). The graft shell surrounding the elastomer particles is synthesized (1) from the same monomers that are used to synthesize the matrix resin or (2) from monomers that produce a copolymer which is miscible (compatible) with the matrix.

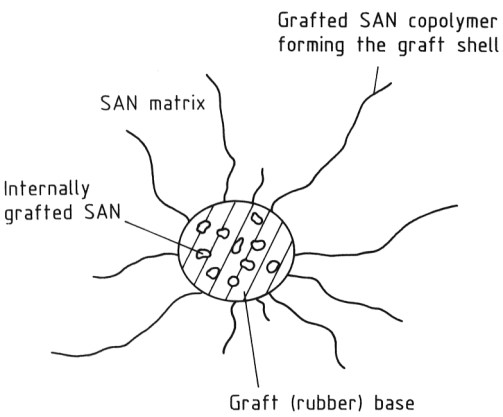


Figure 13. Schematic structure of ABS graft polymers

Various polymerization processes (e.g., emulsion, solution, bulk suspension, and bulk processes) can be used to manufacture ABS molding compounds. These processes are described in detail elsewhere, → → Polymerization ProcessesPolymerization Processes. The producer can also decide whether to use a single-step process involving reaction of polybutadiene and the styrene and acrylonitrile monomers (solution-ABS), or whether to produce the grafted polybutadiene and SAN separately (emulsion-ABS). The second route allows wider variation of individual parameters such as morphology of the elastomer phase (average particle size [85], and degree of cross-linking [75]). The styrene and acrylonitrile can also be copolymerized in different weight ratios [86], and the average molecular mass of the SAN copolymer modified as desired.

Styrene can be replaced partially or completely by α-methylstyrene (AMS). For special requirements (e.g., transparency or high heat resistance), terpolymers are also produced. Monomers used for this purpose, in addition to styrene and acrylonitrile, include methyl methacrylate, maleic anhydride, and *N*-phenylmaleimide.

5.1.3. Synthesis of the Two-Phase Structure

ABS polymers can be divided into ABS blend types and graft types.

In *ABS blend types*, a rubber copolymer is blended with a SAN copolymer. The rubber copolymer contains a matrix monomer (e.g., acrylonitrile in NBR rubber) or a monomer whose solubility parameters resemble those of the matrix [87–89]. These ABS systems have very little importance today.

Graft ABS polymers contain a polybutadiene graft copolymer as the elastomer component. The graft shell is constructed from the same monomer units as the resin matrix to give optimal phase interaction between the cross-linked rubber particles and the thermoplastic matrix [90, 91].

Grafting Reaction. The radical-initiated grafting of vinyl monomers (e.g., styrene,

acrylonitrile, or methyl methacrylate) only produces satisfactory graft yields with a few rubbers. Industrially, butadiene polymers are used almost exclusively as the rubber (graft) base, polybutadiene being the most common because of its low glass transition temperature.

Grafting of vinyl monomers (e.g., styrene) on polybutadiene can take place by two mechanisms [74]:

1. Addition to the double bond

$$-CH_2-CH=CH-CH_2- + R^{\cdot} \longrightarrow -CH_2-\underset{R}{\underset{|}{CH}}-\dot{C}H-CH_2- \quad (1)$$

2. Abstraction of hydrogen.

$$-CH_2-CH=CH-CH_2 + R^{\cdot} \longrightarrow \quad (2)$$

$$RH + -\dot{C}H-CH=CH-CH_2- \rightleftharpoons -CH=CH-\dot{C}H-CH_2-$$

where R· is a polymer or initiator radical.

The polybutadiene radicals (R′·) formed according to Equation (1) or (2) react further with monomeric styrene to give the graft copolymer (3):

$$R'^{\cdot} + H_2C=\underset{C_6H_5}{\underset{|}{CH}} \longrightarrow R'-CH_2-\dot{\underset{C_6H_5}{\underset{|}{C}}}H \quad (3)$$

The allyl radical (Eq. 2) is not very reactive because of its high resonance stabilization. Its resonance energy is comparable with that of a styrene radical [92, 93]. Common polybutadiene rubbers are composed of 1,4-*cis*, 1,4-*trans* and 1,2-vinyl units. Grafting occurs mostly via abstraction of the allylic hydrogen atom of the 1,2-vinyl group.

Recently a copolymerization mechanism has also been proposed for the grafting reaction [94, 95].

The kinetics of the radical grafting reaction largely correspond to the normal kinetics of radical polymerization. At low rubber concentrations deviations occur because of cross-linking reactions. Grafting cannot be carried out with 2,2′-azobisisobutyronitrile as an initiator. The resonance stabilization of the $(CH_3)_2(CN)C\cdot$ radical prevents H-abstraction from the rubber backbone [96]. In the thermally initiated grafting of styrene onto polybutadiene the graft yield increases with increasing temperature and with the 1,2-vinyl group content of the graft base [97].

The degree of grafting can be varied within wide limits by factors such as the choice of polymerization process, the graft base : monomer ratio, the degree of conversion, the activating and regulating systems, and the use of redox initiators based on organic peroxides [98].

Cross-Linking of the Rubber Phase. The high hardness and toughness of ABS polymers requires controlled cross-linking of the rubber phase. If cross-linking is insufficient, the rubber particles dispersed in the SAN matrix (particle size ca. 100–1000 nm) are destroyed by the action of shear forces during processing. Rubber which is not cross-linked has no elasticity. The rubber may be cross-linked during the production of the graft base (emulsion polymerization), during the grafting reaction, or in the subsequent workup (bulk polymerization). The swelling index in a good solvent is usually used as a measure of the degree of cross-linking [99]. Quantitative relationships between the degree of swelling and the cross-linking density have also been established [100].

5.1.4. Properties of the Resin Matrix

The resin matrix of ABS polymers is mainly responsible for properties such as processibility and heat resistance of the molding compounds produced from it. Processibility depends predominantly on molecular mass and molecular mass distribution, whereas heat resistance is mainly determined by the chemical composition (i.e., the monomer units and their arrangement in the polymer chain) and the resulting glass transition temperature.

Table 7 summarizes the important properties of ABS matrix components.

Styrene–Acrylonitrile (SAN) Copolymers. See also Chapter 2. Styrene–acrylonitrile copolymer resins with an acrylonitrile content of ca. 20–35 wt % are usually used for ABS polymers. The weight-average molecular masses are in the range ca. 50 000 to 180 000; the molecular nonuniformities $U = (M_w/M_n) - 1$ are ≥ 2 (for emulsion polymers) and between 1 and 2 (for bulk and suspension polymers); the glass transition temperature is ca. 115 °C. SAN resins can be

Table 7. Properties of ABS matrix resins

Matrix component	Chemical construction	T_g, °C	Concentrations in the ABS blend, wt %	Heat resistance (Vicat B 120), °C	Other properties
SAN	random copolymer S : AN 80–65 : 35–20	115	95–50	104	decrease in thermostability at high acrylonitrile contents
AMS–AN–S copolymer	random copolymer AMS : S : AN 45 : 35 : 20		95–50	108 110	
AMS–AN copolymer	random copolymer AMS : AN ca. 70 : 30	128	95–50	117	depolymerization begins at 280 °C
AMS–AN sequence polymer	AMS : AN ca. 70 : 30 high proportion of AMS pairs	140	95–50	~ 130	toughness lower than with random copolymers
Styrene–AN–NPMI terpolymer	random terpolymer S : AN : NPMI ca. 67 : 28 : 5	140	95–80	~ 130	
Styrene–AN–MA terpolymer					high reactivity of the anhydride ring, heat resistance limited

AN = acrylonitrile; AMS = α-methylstyrene; MA = maleic anhydride; NPMI = *N*-phenylmaleimide; S = styrene

synthesized by separate copolymerization or during graft polymerization. All ABS polymers also contain ungrafted SAN resin formed during graft polymerization.

α-Methylstyrene–Acrylonitrile (AMS–AN) Copolymers. See also Section 4.1. Copolymers of α-methylstyrene and acrylonitrile are closely related to SAN polymers. Their high glass transition temperatures and their chemical behavior, which is similar to that of SAN resins, yield ABS systems with improved heat resistance. Their thermostability decreases with increasing α-methylstyrene content (back cleavage of triads of α-methylstyrene units).

Resin production is carried out by emulsion [101], solution, or bulk polymerization [102]. Products usually have acrylonitrile contents of ca. 20–35 wt % with weight-average molecular masses of ca. 50 000–150 000.

Special copolymers with a high proportion of α-methylstyrene-containing sequences can be produced by emulsion polymerization and yield ABS polymers with high heat resistance (Vicat B temperature) of up to ca. 130 °C [103].

Other Vinyl Polymers. Copolymers of styrene and methyl methacrylate are used in transparent ABS. 4-Methylstyrene–acrylonitrile copolymers [104], styrene–maleic anhydride copolymers (Section 4.3), polyglutarimides [105], and *N*-phenylmaleimide–styrene–acrylonitrile terpolymers [106] are used for the production of systems that are analogous to ABS but with high heat resistances.

5.2. Structure–Property Relationships

The individual components described in Sections 5.1.3 and 5.1.4 can be used to draw up structure–property relationships for ABS polymers which, in turn, can be employed to predict properties from a small amount of basic data. The physical behavior of ABS polymers is partially based on the properties of the matrix and the rubber component.

The room-temperature toughness of ABS polymers generally passes through a maximum as the proportion of the rubber phase increases (Fig. 14). In parallel to this the modulus of elasticity, heat resistance, and flow properties decrease [107]. The low-temperature toughness behaves analogously to the room-temperature toughness; its absolute value, however, is determined by the glass transition temperature of the rubber component. Polymer properties are related to the acrylonitrile content of the resin matrix in the range relevant to industry (i.e., ca. 20–35 wt % acrylonitrile). Increasing the acrylonitrile content slightly improves chemical resistance and toughness (maximum at 34 %) but flow properties deteriorate [108].

The most important structural parameters for a given matrix resin and rubber and a constant proportion of the rubber phase are the molecular

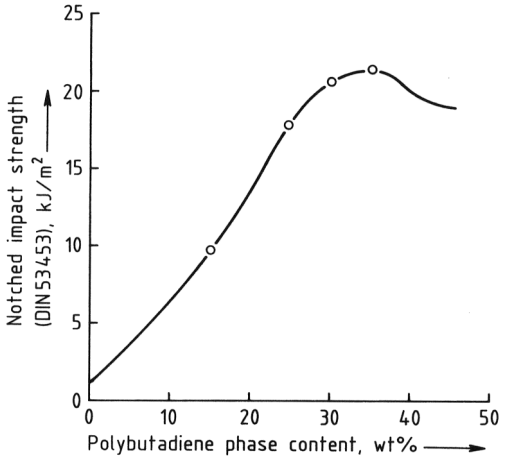


Figure 14. Variation of the toughness of ABS with content of the elastomer (polybutadiene) phase

mass and molecular mass distribution of the matrix resin and the structure of the grafted rubber, especially the particle size, particle size distribution, and degree of grafting and cross-linking.

An increase in the molecular mass of the matrix resin results in an increase in toughness and chemical resistance (environmental stress cracking) but simultaneous deterioration in the thermoplastic flow properties [109]. Broadening of the molecular mass distribution results in easier flow.

The use of cross-linked matrix resins in ABS polymers leads to embrittlement. Even a low degree of cross-linking is detectable because it lowers the surface gloss of molded products.

The properties of ABS polymers are most strongly influenced by the characteristics of the grafted rubber components. Toughness increases with particle diameter.

Grafted rubbers with average particle diameters below ca. 150 nm and a narrow particle size distribution lead to ABS systems which are brittle when subjected to high-velocity impact. In the particle size range of ca. 200–300 nm, the toughening effect of the grafted rubber is very strongly dependent on the degree of cross-linking and the cross-linking structure of the rubber base. A good toughening effect can also be achieved with relatively small particles if the rubber is weakly cross-linked. At particle sizes exceeding 300 nm, grafted rubbers with high toughness are generally obtained. However, with very large, compact particles (emulsion polymers with average particle sizes $\geq$ ca. 450 nm) toughness may decrease due to insufficient coupling to the matrix.

ABS molding compounds produced by bulk polymerization (particle size ca. 1–10 μm) generally have enhanced toughness because of their high proportion of grafting and matrix inclusion within the rubber phase (rubber phase volume).

Thermoplastic flow properties and the surface gloss of ABS polymers are also strongly dependent on the grafted rubber. Increasing particle size for a given rubber content (i.e., smaller number of particles) improves processibility [110], but leads to loss of surface gloss as a result of light scattering [111].

The degree of grafting, the graft density, and the length of the grafted chains of the grafted rubber also affect the properties of the ABS polymers [112]. An increasing degree of grafting improves coupling to the resin matrix resulting in a more uniform distribution within the matrix and a higher toughness. Grafted rubbers with a low degree of grafting tend to agglomerate so that the properties of the molded articles depend increasingly on processing conditions.

At a fixed degree of grafting, the length of the grafted chain and thus the graft density can be varied. Low graft density corresponds to a small number of very long grafted chains and a high graft density to very many short chains. A fine balance during the grafting reaction allows adjustment of the special requirements of ABS molding compounds (e.g., high toughness, improved flow properties).

5.3. Production of ABS Polymers

ABS can be produced by emulsion polymerization, bulk polymerization, or combined processes (Fig. 15).

There are two main types of *emulsion polymerization* which yield ABS graft rubbers with a rubber content of 5–85 wt %.

1. Separate production of the ABS graft rubber and SAN matrix with a subsequent mixing and compounding step
2. Total emulsion process, i.e., production of the molding compound containing both the grafted rubber and the SAN matrix by

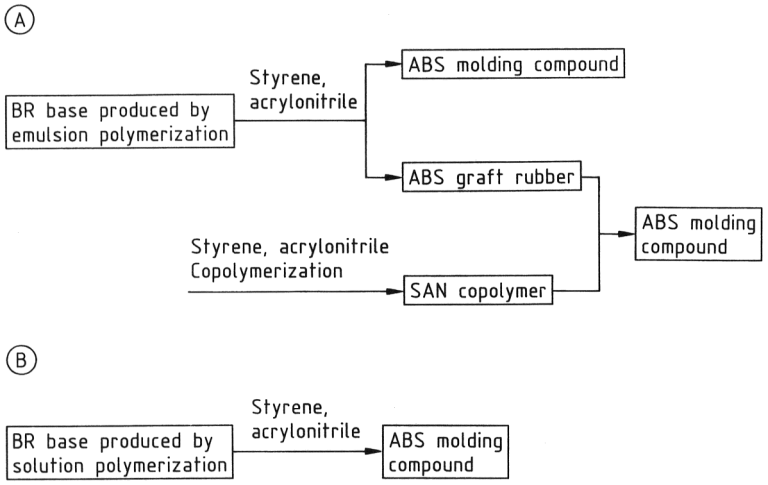


Figure 15. Overview of ABS production processes A) Emulsion polymerization; B) Bulk polymerization

emulsion polymerization (the synthesis of a polybutadiene base precedes the ABS grafted polymer production)

Bulk polymerization starts from a separately produced rubber base (BR or SB solution rubbers). The compound is produced in a bulk process run continuously over several stages. Rubber content is limited to $\leq$ 20 wt% for viscosity reasons.

The *combined processes* include, e.g., the addition of emulsion graft rubber to bulk ABS molding compounds

The separate production of the grafted rubber and the SAN matrix has the advantage that the properties of each component can be controlled independently and different production processes can be used for the grafted rubber phase and the SAN matrix. SAN matrix copolymers are produced almost exclusively by thermally or radically initiated bulk polymerization [113, 114]. The two-stage bulk suspension process is also still used.

Other styrene copolymers besides SAN can also be combined with the ABS graft rubber (see Section 5.1.4). α-Methylstyrene–acrylonitrile (AMS–AN) copolymers or styrene–acrylonitrile–*N*-phenylmaleimide terpolymers, for example, give products with a high heat resistance because of their high glass transition temperatures [115, 116]. Some copolymers are only accessible via the separate bulk polymerization route [117]. Bulk or emulsion polymerization is used for AMS–AN copolymers [118, 119]. The bulk process has the advantage of an inherent degassing stage, so that products with very low residual monomer contents and thus high heat resistance can be obtained. However, yields and molecular masses are limited. The advantages of the bulk process lie in the fact that completely continuous processing is possible and that the grafted rubber particles are formed in situ, i.e., at the same time as SAN polymerization. The proportion of internal grafting is thus higher [120, 121] and products have a more favorable notched impact strength–hardness relationship than those produced by emulsion polymerization. The bulk ABS process includes a degassing step which means that unreacted monomers can be directly recycled.

5.3.1. ABS Production by Emulsion Polymerization

The emulsion process is the standard ABS production process but the principle of this method has also been applied to other rubber-modified, two-phase styrene copolymer systems [122–124].

The production of grafted rubbers with high rubber contents and their mixing with a separately produced SAN matrix is used worldwide. The total emulsion process is of minor importance and is not described here.

The production of ABS grafted rubber consists of three stages:

1. Production of the graft base, i.e., a polybutadiene or butadiene copolymer latex with defined particle size, particle size distribution, and gel content
2. Grafting the styrene–acrylonitrile monomer mixture onto the graft base
3. Workup of the grafted rubber latex

The particle size, particle size distribution, and cross-linking density of the graft base; the degree of grafting; the proportion and morphology of the rubber-phase volume; and the molecular mass of the grafted SAN chains largely determine the properties of the resulting grafted rubber system. Bimodal ABS systems have optimal surface properties and toughness synergies. These systems are produced from a graft base with a bimodal particle size distribution, or from two grafted rubbers of differing particle size that are mixed at the latex stage and then worked up together. The particle size of ABS emulsion grafted rubbers lies in the range 50–600 nm, values of 100–400 nm being preferred. Figure 16 shows the production of uni- and bimodal ABS graft rubber systems.

Production of the Graft Base. The production of graft bases mostly takes place batchwise. The butadiene is polymerized at 5–75 °C and ≤12 bar. In the case of butadiene copolymers, the reactivities of the individual monomers must be taken into account. If compositions of the copolymers are chosen which lie outside the "azeotrope region" of the monomer mixture, then high chemical nonuniformity is avoided by using a continuous process and carrying out the polymerization until a given monomer conversion is reached. Unreacted butadiene is fed back into the first reactor of the reactor cascade.

Monomer–water weight ratios of 1 : 0.6 to 1 : 2 are used. Anionic emulsifiers are added in quantities of 1–5 parts per 100 parts of monomer to disperse the monomers and stabilize the polybutadiene latex particles. The alkali salts of disproportionated abietic acid or fatty acids, C_{12}–C_{18} *n*-alkyl- and *n*-alkylarylsulfonates are commonly used as emulsifiers. Emulsifiers are dosed such that the resulting latices have a surface tension of < 0.065 N/m and the particles are extensively coated with emulsifier. Emulsifier systems are preferred which are also used for the subsequent grafting reaction and which readily allow coagulation of the dispersed system on addition of acid or electrolytes to facilitate product isolation.

Polymerization is initiated with alkali peroxydisulfates or combinations of reducing agents with peroxydisulfates or organic (hydro) peroxides. The use of (hydro)peroxide systems allows a sufficiently high reaction rate at low temperature and modification of the polybutadiene microstructure [125].

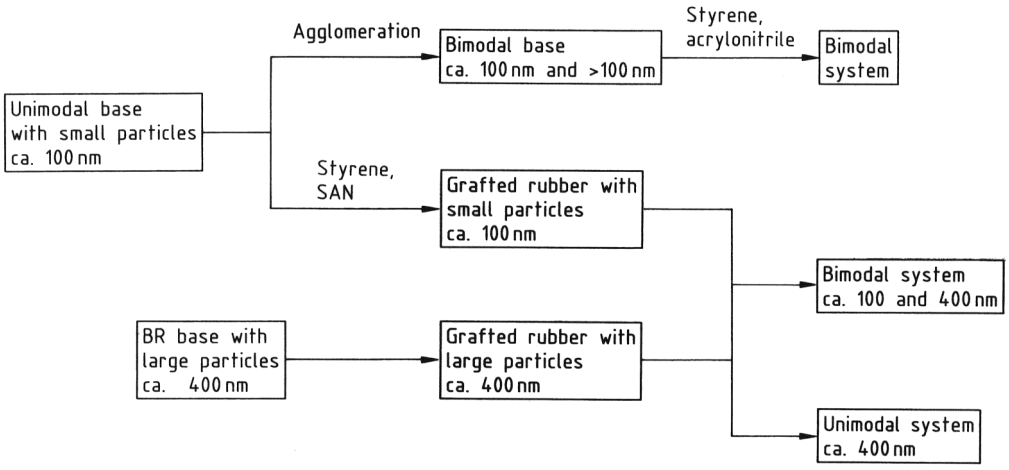


Figure 16. Composition of unimodal and bimodal ABS graft rubbers

Table 8. Production of bimodal ABS graft bases by agglomeration processes

Starting latex (particle size)	Emulsifier	Agglomeration process	Mean final particle size, nm	Reference
BR latex (100 nm)	alkylsulfonate	chemical agglomeration by addition of latices with hydrophilic groups	200 – 500	[127]
Butadiene – acrylonitrile copolymer latices (100 nm)	Na stearate	chemical agglomeration by addition of carboxylic acid anhydrides	200 – 400	[128]
BR latex (100 nm)	Na oleate, cannot be substituted	pressurized agglomeration using Manton – Gaulin homogenizer	200 – 800	[129]
Butadiene – styrene copolymer latex (50 nm)	alkali salts of abietic acid and fatty acids	chemical agglomeration	200	[130]
Butadiene – styrene copolymer latex, polybutadiene	alkali salts of fatty acids and abietic acid	agglomeration by freezing	200 – 400	[131]

The particle size can be controlled by varying the monomer–water ratio, by stepwise addition of emulsifier, and by adjusting the reaction temperature. A much more elegant method involves the use of seed latex technology, mostly in a semibatch process [126].

Polybutadiene bases with a bimodal particle-size distribution can also be produced by chemical or physical agglomeration of latex particles (Table 8). The advantage of this process lies in the fact that latices with a small particle size can be produced much faster than latices with a large particle size.

The molecular mass and cross-linking density of the polybutadiene bases are adjusted by means of modifiers (e.g., *n*-alkylthiols). Increasing quantities of modifier decrease the average polymer chain length.

Polymerization is usually terminated above 80 % conversion to ensure sufficient cross-linking of the rubber (gel contents > 60 %, preferably > 70 %). No shortstopping agents are used (apart from pure reducing agents) to prevent disruption of the subsequent grafting reaction.

The latex product is devolatilized to remove residual monomers by using vacuum and/or steam in a batch reaction, or continuously in a bubble column.

Grafted Rubber Production. A styrene–acrylonitrile monomer mixture is polymerized in the presence of the graft base. An increase in the ratio of monomers to polybutadiene is accompanied by increases in the net reaction rate, in the molecular masses of the grafted chains and of the "free" SAN copolymer, and in the degree of grafting. Since the reaction is exothermic ($\Delta H = -840$ kJ/kg), a monomer-feed process or a completely continuous process is used [132, 133]. If the copolymer compositions lie outside the azeotrope region of styrene and acrylonitrile, an increase in chemical nonuniformity is avoided by adding the more rapidly reacting monomer later (staggered dosing). The kinetics of the reaction are described by the Smith–Ewart theory, [134, 135]. Details of the grafting mechanism are given in [136–139].

The particle size, particle size distribution, and cross-linking density of the graft bases are directly related to the degree of grafting, graft density, rubber phase volume, and morphology of the grafted rubber [140]. The proportion of internal grafting generally increases with increasing particle size and decreasing cross-linking density of the rubber base. At constant particle size and rubber cross-linking density, the degree of grafting and the graft density become the factors determining the properties of the ABS product [77, 141]. The choice of initiator can influence the ratio of SAN copolymerization to graft reaction and the ratio of external to internal grafting. In comparison with monomer-soluble initiators, water-soluble peroxydisulfates lower the proportion of internal grafting and increase the proportion of free SAN copolymer [77].

The degree of grafting can also be affected by stepwise grafting whereby the formation of the graft shell determines the diffusion rate of the monomers [142].

If the weight ratio of monomers to graft base exceeds unity, molecular mass modifiers are

usually added to the monomer mixture. They affect the graft reaction and the styrene–acrylonitrile copolymerization, the molecular masses of the free and bound SAN chains, and the degree of grafting decrease.

The emulsifier systems used in the grafting reaction are usually the same as those used in the production of the graft base. High latex stability during the polymerization and ready coagulation during the product workup are also desired.

Stabilization and Workup of the Grafted Rubber. After completion of polymerization, excess (hydro)peroxide initiator is reduced with sodium hydroxymethanesulfinite. Stabilizers are added, generally in the form of a synergistically acting system, to protect the grafted rubber from oxidation during subsequent powder drying and compounding. The stabilizers usually comprise one or more phenolic antioxidants and a heat stabilizer. Long-chain alkyl thiodipropionates, long-chain alkyl phosphites, and low molecular SAN polymers with *S*-alkyl terminal groups are particularly effective [143–145]. The stabilizer systems should have a low volatility and must fulfil all ecological and toxicological legal requirements. To obtain a homogeneous distribution, the stabilizer system is added to the grafted rubber latex as an aqueous dispersion (0.2–1.5 parts by weight/100 parts of polymer) and coprecipitated with the grafted rubber after mixing.

To isolate the ABS graft rubber from the polymer latex, the emulsifier must be deactivated. Emulsifiers based on alkali carboxylates are coagulated and precipitated by adding dilute acid (acetic or mineral acid) to adjust the pH to below 3. Emulsifiers based on alkyl(aryl) sulfonates are coagulated by adding dilute aqueous solutions of inorganic electrolytes (e.g., $MgSO_4 \cdot 7\ H_2O$ or $CaCl_2$).

Strict control of the precipitation conditions is necessary to obtain a powder with a uniform particle structure and size distribution, from which all water-soluble polymerization and coagulation additives can be easily washed out. Coarse powder particles contain inclusions of precipitants which adversely effect drying and processing. Finely divided powders lead to filtration and wastewater problems. Powder structure, particle size, and particle size distribution can be affected by:

1. Consecutive or parallel addition of two or more grafted rubber latices and the precipitating agent [146]
2. The ratio of latex to precipitant solution
3. The temperature at which the precipitating agent and the grafted rubber latex are charged to the coagulation reactor or coagulation cascade
4. The type of stirring used to mix the process streams, the temperature control in the coagulation reactor cascade, and the average residence time

After coagulation the material is filtered with band, plane, or rotary filters and washed. The filter cake is then fed into a reslurry tank and mixed with fresh water. The slurry is processed in filter presses, extruders, or sieve centrifuges and the wastewater recycled to the process. The powder products have water contents of ca. 15–40 wt %. They are dried to moisture contents of < 1.0 wt % with two-stage paddle dryers, flow dryers, or vacuum tray dryers.

Alternatively, further processing of the moist grafted rubber can be performed in screw extrusion machines. In this case, dewatering leads to grafted rubber granulate [147] or, after mixing with a thermoplastic resin melt, to solid ABS products [148].

During the workup, measures are taken to lower the residual monomer content to comply with legal limits. Examples include latex degassing with a perforated plate column and countercurrent steam, the use of a precipitation–stripping process, and powder workup with a helical sieve followed by compacting and degassing in a twin-screw extruder [149, 150].

Production Process (Fig. 17). The first stage involves production of a polybutadiene latex with a defined particle size. An aqueous soap solution is formed in the polymerization reactor (a) at ca. 65 °C and the molecular mass modifier is added. After flushing with nitrogen, butadiene is pumped in and the polymerization is initiated with potassium peroxydisulfate solution. The reaction rate is determined by the heat removal capacity of the reactor. The maximum conversion rate is ca. 10 %/h. At conversions of ca. 80–90 % the reaction rate decreases; the monomer is then extensively consumed and cross-linking reactions begin. Polymerization is terminated

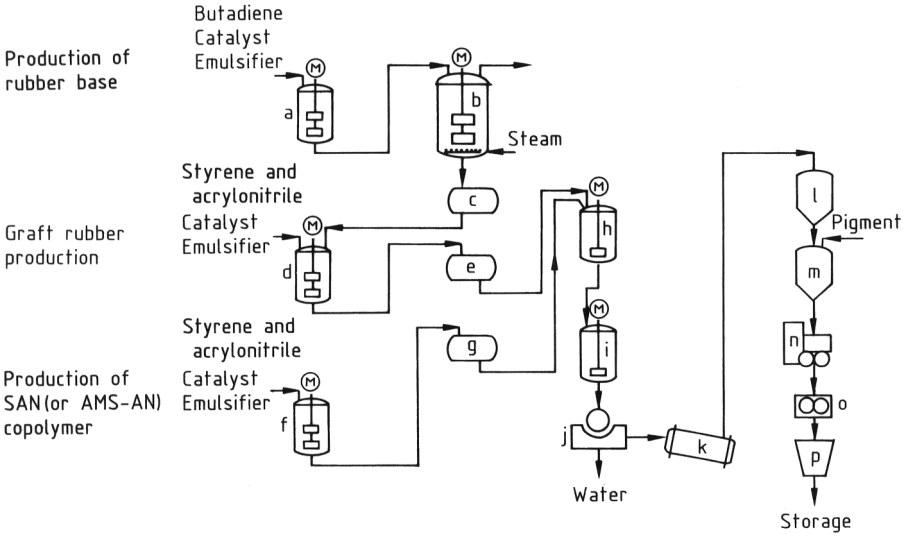


Figure 17. Production of ABS graft rubber and ABS by emulsion polymerization a) Polybutadiene reactor; b) Degassing reactor; c) Polybutadiene latex tank; d) Grafting reactor; e) Graft latex tank; f) SAN reactor; g) SAN latex tank; h) Latex mixing and stabilization tank; i) Coagulation reactor; j) Filter; k) Dryer; l) Powder silo; m) Premixer; n) Internal kneader; o) Rollers; p) Granulator

by lowering the temperature to below 50 °C. Unconverted butadiene is vented and stirred out under vacuum.

In the second stage (the ABS graft rubber production process), the polybutadiene latex, an aqueous potassium persulfate solution, and part of the emulsifier solution are charged to the grafting reactor (d). The temperature is increased to ca. 60 °C and a styrene–acrylonitrile monomer mixture and the remainder of the emulsifier solution are charged to the reactor at a constant rate over 5 h. The reaction temperature is then increased to ca. 65 °C to complete polymerization (conversion ≥96 %, cycle time ca. 8 h, average reactor size is ca. 40 m^3). After running through the stabilization tank (h), the latex is coagulated. Washing and drying yield a powder which is subjected to a compounding step. After the addition of lubricants, dyes, and other additives, the polymer is pelletized (p).

5.3.2. Production of the Matrix Copolymer

The properties of the matrix copolymers are summarized in Section 5.1.4.

SAN Copolymers. The main ABS matrix components are styrene–acrylonitrile (SAN) copolymers with an acrylonitrile content of 20–35 wt % and a molecular mass in the range 50 000–180 000.

The production of SAN copolymers can take place by bulk, bulk suspension, or emulsion polymerization. In bulk polymerization the "azeotrope composition" is about 75 wt % styrene and 25 wt % acrylonitrile. In emulsion polymerization the quasi-azeotrope composition is 71.5 wt % styrene and 28.5 wt % acrylonitrile due to monomer partitioning [151].

Chemically and physically uniform SAN copolymers are obtained by *continuous bulk polymerization* (see also Section 2.1) [114, 152]. This also applies to compositions that lie outside the azeotrope region. Compared with suspension and emulsion polymerization, bulk polymerization has environmental advantages: production of wastewater is avoided and virtually all volatile components are removed from the product during workup. A disadvantage is, however, the fact that it is not possible to produce very high molecular masses due to high viscosities. Most of the matrix material is produced by this process.

Uniform SAN copolymers can also be obtained by *bulk suspension polymerization*, within the styrene–acrylonitrile azeotrope range [151]. A SAN prepolymer is first produced which is dispersed in water after addition of

water-soluble dispersants and polymerized to give small beads [153]. Unreacted monomers are removed from the beads by means of steam or a degassing extruder before or after the separation of the polymer–water mixture.

In *emulsion polymerization* (Fig. 17, f) the monomers are dispersed in water using an emulsifier. After addition of an activator dispersion, polymerization occurs to give latex particles (diameter ca. 50–200 nm). SAN production by emulsion polymerization is analogous to the production of ABS graft rubbers (See Grafted Ruuber Production, Stablization and workup of the Grafted Rubber) except that polybutadiene latex is not present.

Semibatch or continuous emulsion polymerization can be used to obtain product compositions with extensive chemical uniformity outside the azeotrope region. The semibatch process leads to molecular nonuniformities of ca. 1.5–2. In the continuous process the molecular nonuniformities are in the range 1.5–5 depending on the number of reactors and the average residence time. The emulsion-polymerized SAN copolymers show better flow properties and better resistance to stress cracking in the ABS blend compared with bulk-polymerized SAN. The toughness properties of bulk-polymerized SAN copolymers are not, however, achieved. The emulsion process always offers advantages if high molecular masses are desired [154]. The SAN emulsion copolymers are not usually isolated as such, but are mixed with the ABS grafted rubber latex in the latex step (Fig. 17, h). The mixture is then subjected to workup and residual monomer degassing to give an ABS powder blend.

α-Methylstyrene–Acrylonitrile (AMS–AN) Copolymers. ABS grades with a high heat resistance (HT-ABS) are produced by partial or complete exchange of the SAN matrix with compatible (AMS–AN) copolymers or α-methylstyrene–styrene–acrylonitrile terpolymers [155]. AMS–AN copolymers have a higher glass transition temperature and a higher heat resistance in the ABS blend. This system has an azeotropic mixture (69 wt % α-methylstyrene, 31 wt % acrylonitrile) [156].

Like SAN copolymers, AMS–AN copolymers can be produced by bulk and emulsion polymerization. The AMS–AN system has a much lower reaction rate, however, because of the small AMS growth-rate constant. The reaction rate cannot be increased by raising the temperature because depolymerization occurs [157, 158]. Two alternative approaches are used industrially:

1. A drastic increase in the acrylonitrile concentration of the monomer mixture in the starting phase of the reaction
2. Addition of styrene as a third monomer to give terpolymers with glass transition temperatures between those of SAN and AMS–AN copolymers [159]

The equipment requirements for the production of AMS–AN copolymers are similar to those for SAN bulk polymerization. However, higher average residence times are needed and thermal initiation is not possible. Multistep degassing is used to remove residual monomers and to achieve maximum heat resistance.

The most common route for the production of AMS–AN copolymers is semibatch emulsion polymerization. A high monomer purity ($\geq$ 99.5 %) is necessary. Long incubation times can be overcome by using seed latex technology [101]. Process conditions are similar to those of ABS graft rubber production (Grafted Rubber Production, Stablization and workup of the Grafted Rubber). To achieve monomer conversions of > 95 %, a pH of $\leq$ 6 must be maintained and an appropriate emulsifier chosen. More details on chemical composition are given in [160].

The emulsion copolymer is usually subjected to workup after latex mixing with ABS graft rubbers. A degassing step must be included between polymer workup and product compounding.

The glass transition temperature of the binary AMS–AN copolymer (ca. 128 °C) can be raised to 140–150 °C if the α-methylstyrene concentration at the beginning of emulsion copolymerization is raised above the azeotrope ratio and the reaction is terminated at conversions of $\leq$ 90 %. This increase is due to formation of sequence polymers containing AMS–AMS–AN blocks [161, 162]. The reaction rate and latex stability can be improved by using low concentrations of other monomers [163]. In the ABS blend these AMS–AN sequence polymers produce heat resistance (Vicat B 120) of 130 °C. Toughness diminishes slightly, however, because of incompatibility between the grafted rubber and the matrix.

ABS molding compounds with an AMS–AN matrix have less favorable flow properties than those with a SAN matrix. Although styrene can be replaced by α-methylstyrene in the ABS graft rubber system, this has not been used industrially for processing reasons [164].

Styrene–Acrylonitrile–NPMI Terpolymers. Incorporation of imide comonomers into the SAN matrix yields heat-resistant ABS polymers [165, 166]. *N*-Phenylmaleimide (NPMI) has been used to produce styrene–NPMI–AN terpolymers [167]. Compare Section 5.3.3.

Other Styrene Copolymers. Attempts have been made to replace the SAN matrix by co- or terpolymers other than those described above. Although styrene can be copolymerized with almost all important vinyl monomers [168], none of the efforts made so far has been used industrially. Attempts to shift the heat distortion temperature of ABS polymers into the Vicat B region 120–130 °C by adding styrene–maleic anhydride co- and terpolymers failed because the anhydride ring opened under processing conditions [169, 170].

5.3.3. ABS Production by Bulk Polymerization

ABS production by bulk polymerization (Fig. 15 B) is based on the polymerization of styrene–acrylonitrile mixtures in the presence of a rubber substrate dissolved in this monomer phase. The process can be divided into three steps:

1. The rubber substrate is dissolved in the monomer mixture
2. The rubber–monomer mixture is prepolymerized with continuous mixing (conversion 15–30 wt %)
3. The polymer–monomer mixture is polymerized further by bulk suspension polymerization or by continuous bulk polymerization in a high-viscosity reactor cascade

Unlike the emulsion process (Section 5.3.1), no preformed rubber particles are present at the beginning of the grafting reaction. In emulsion polymerization the particle size distribution is determined by the particle size of the grafting base, in bulk polymerization it is mainly determined by the choice of the rubber base and the reaction conditions during prepolymerization and phase inversion. BR rubbers with a glass transition temperature of ≤ -80 °C are usually used as the grafting base. BR rubbers containing ca. 40 % of units with a 1,4-*cis* configuration are preferred because they do not crystallize and the resulting ABS blend has a good low-temperature toughness. The molecular mass and degree of branching are very important for adjusting the particle size and the rubber phase volume in the prepolymerization stage. Long-chain branched BR rubbers with an average molecular mass of 180 000–260 000 are commonly used [171]. High glass grades are made from star-branched BR rubbers with low solution viscosity. The rubber content is limited to ca. 20 wt % in ABS bulk processes for viscosity reasons.

The rubber is chopped to pieces and charged to a dissolving vessel. Dissolution in the monomer mixture and optionally a solvent (ethylbenzene, toluene and the like; usually 5–15 %) may take up to 10 h. Acrylonitrile acts as a precipitation agent for the butadiene rubber; with increasing acrylonitrile content of the solution less rubber can be dissolved and additional solvents are necessary. The rubber solution is transferred to a feed tank and continuously fed to the reactor cascade.

The prepolymerization stage is performed with continuous stirring. Phase separation and phase inversion begin during prepolymerization and largely determine the size, structure, and particle size distribution of the rubber phase in the resin matrix and thus the properties of the products. In the radical-initiated prepolymerization step, an oil-in-oil emulsion is formed at conversions of ca. 2 % [172–174]. Monomer-charged SAN droplets are emulsified in the rubber solution by graft SAN polymer chains which are simultaneously formed on the rubber. With increasing SAN formation the phase-volume ratio changes [175]. When the phase-volume ratio reaches unity, phase inversion begins and the rubber phase is then dispersed in the SAN phase [176], i.e., the SAN–styrene–acrylonitrile monomer phase becomes the continuous phase [177]. SAN is enclosed in the newly formed polybutadiene particles in the form of subinclusions. The phase inversion process, which is initially reversible, is terminated at conversions

of ca. 12–15 %, depending on the rubber content of the starting solution.

The rubber particle size is determined by three main parameters:

1. The shear forces applied during stirring [178]
2. The viscosity ratio of the two phases [179]
3. The interfacial surface tension between the two phases [180]

Phase inversion can be detected by viscosity measurements. After phase inversion polymerization is continued to a conversion of ca. 25–30 %. The viscosity of the polymerizing mass is then already so high that the phase inversion becomes irreversible.

Another important factor affecting ABS production by bulk polymerization is the degree of grafting [181]. Grafting occurs as a result of hydrogen abstraction in the allyl position, grafting by copolymerization has also been discussed (Section 5.1.3) [93]. A first attempt to calculate the maximum possible degree of grafting as a function of conversion is described in [182]. The degree of grafting depends on the nature of the initiators and modifiers, as well as the different solubilities of styrene and acrylonitrile in the rubber and matrix phases [183]. This difference in solubility lowers the degree of grafting and leads to differing acrylonitrile contents in the grafted rubber and the matrix resin.

The molecular mass and molecular mass distribution are principally determined by process parameters (temperature, initiator concentration, solvent, and chain-transfer agents). Thiols are especially effective as molecular mass modifiers in the initial phase of polymerization, chain-transfer agents (e.g., terpinols) are only effective at higher conversions because of their smaller transfer constants.

Another important parameter is the establishment of defined rubber cross-linking densities. The rubber must be highly cross-linked to avoid crack formation within the particles on continuing "hardening out" of the system. If the rubber phase volume is known, the cross-linking density achieved in ABS polymers can be described quantitatively by a modified Flory–Rehner equation [100]. Since the cross-linking density is thermally controlled, this parameter is mainly determined in the degassing stage of the continuous bulk ABS process by variation of the temperature and the residence time [99, 184].

In the continuous bulk solution process, polymerization is carried out in a cascade of two or more reactors [185, 186]. Solvents or mineral oils are often added to lower the viscosity and improve heat transfer.

Prepolymerization is performed in tower or stirred-tank reactors. Prepolymerization is followed by polymerization in a high-viscosity reactor or a tower reactor cascade [187]. Producers use specially constructed reactors for bulk solution polymerization (Fig. 18) mostly with laminar flow conditions [190]. The average residence times are ca. 10–15 h, and the reaction

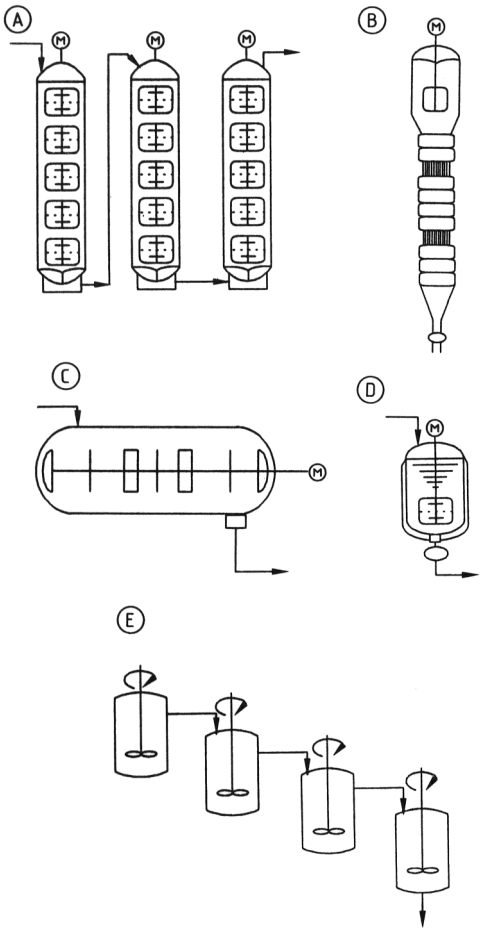


Figure 18. Continuous stirred-tank reactor types [189] A) Tower cascade; B) Stirred tank – tower combination; C) Ring disk; D) Continuous stirred-tank reactor; E) Stirred-tank cascade

temperatures 170–270 °C [191]. Final conversions of 80–85 % are established. Various processes are used to separate the polymer and residual monomer at the end of the bulk polymerization stage: strand degassers, degassing extruders, thin-film evaporators, and spray evaporators. Common are two-stage processes involving a flash tank and a second facility.

The SAN matrix of ABS polymers usually has molecular masses in the range 50 000–170 000, the molecular nonuniformity M_w/M_n is ca. 1.5–3.0. To achieve maximum toughening, an average rubber particle size of ca. 2.5 μm is aimed at. The particles generally have a cellular structure but other structures (e.g., capsules or lamellae) can be obtained by using polybutadiene or butadiene–styrene block copolymer bases or special phase and reaction conditions in the prepolymerization stage [192–194].

Bimodal or multimodal bulk ABS systems are being increasingly described [141, 195, 196]. There are two ways of producing them:

1. Two separately produced prepolymers with different particle sizes and graft structures are mixed with one another before charging to the bulk polymerization stage
2. Two polymers produced in separate prepolymerization and bulk polymerization stages are charged together to a workup zone

In 1990s, intensive research has been carried out on the production of bulk ABS products with a particle size of the rubber phase comparable to that of the emulsion rubber particles (≤ 0.6 μm) [197] with the aim of producing lustrous moldings.

Common to all bulk ABS processes is the fact that the polymers are formed directly as pellets and are also sold in this form for certain uses. More demanding areas of use with defined color requirements need a subsequent compounding stage.

The bulk polymerization process is considered to be more economical than the emulsion and bulk suspension processes because of lower investment costs.

5.3.4. ABS Production by Bulk Suspension Polymerization

After prepolymerization, subsequent polymerization in the suspension process is carried out batchwise in cycles in two or more reactors.

Prepolymerization is started as a batch process. After the end of the phase inversion (conversion 25–30 %), the prepolymer is discharged from this reactor and is subjected to further polymerization in a second reactor or reactor cascade. Depending on the initiator system, the polymerization temperature is 80–120 °C [188] and the average residence time 2–4 h.

In the suspension stage the prepolymer is dispersed in the form of droplets (diameter ca. 0.1–1 mm) in an aqueous medium by means of intensive stirring. The water–prepolymer ratio is in the range 3 : 1 to 1 : 1. The suspension is stabilized by adding water-soluble organic polymers, e.g., poly(vinyl alcohol), or colloidal, water-insoluble compounds, e.g., calcium phosphate. Each droplet may be considered as a well-cooled bulk reactor. The bead size depends on the viscosity of the prepolymer syrup, the stirring conditions, the density difference between the organic and the aqueous phase, and the surface tension between the prepolymer syrup and the aqueous medium. The temperature is raised stepwise to 80–170 °C. "Oil-soluble" initiators are used. Since the necessary rubber cross-linking is only achieved at conversions of ≥80 %, it is important to adopt a definite temperature–time program. The average residence time of the suspension polymerization stage is ca. 10 h. The polymer dispersion is freed from unreacted monomer by the introduction of steam and transferred to a buffer tank. The polymer is separated from the aqueous phase in centrifuges; the polymer beads have a moisture content of < 10 % and are dried with air in a rotating drier.

Production Process (Fig. 19). The BR or SBR rubber bales are cut into pellets (b) and charged to the dissolving vessel (c). The monomer–modifier mixture (a) is added.

The rubber–monomer mixture is transferred to the prepolymerization reactor (e), which is equipped for mixing highly viscous systems. After addition of the initiator, bulk solution polymerization is started by raising the temperature to ca. 90 °C. After ca. 8 h a conversion of ca. 20–30 % is reached. (The start of phase inversion is recognized by a sharp increase in the solution viscosity). After lowering the temperature to ca. 60 °C the peroxide initiators are added for the subsequent suspension stage. A ca. 20 % poly(vinyl alcohol) solution is often used as suspension agent (f).

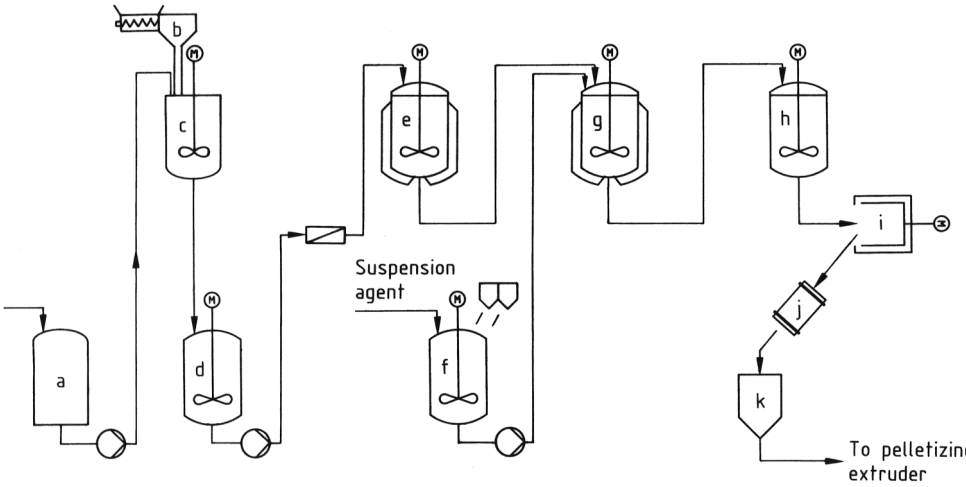


Figure 19. Production of ABS by bulk suspension polymerization [186] a) Monomer feed; b) Rubber chopper; c) Rubber dissolver; d) Solution storage; e) Prepolymerizer; f) Suspension makeup; g) Suspension polymerizer; h) Suspension buffer tank; i) Centrifuge; j) Dryer; k) Bead storage

The prepolymer syrup is heated to 120 °C and then pumped into the suspension polymerizer (g). The ratios of aqueous phase to prepolymer syrup are chosen to give a solids concentration of ca. 40 %. After 3–4 h the temperature is raised to ca. 140 °C and maintained at that level for 3–4 h. At strongly decreasing monomer concentrations the required rubber cross-linking is thus obtained.

The resulting polymer suspension is led via a suspension buffer tank (h) into a sieve centrifuge (i) and separated. The aqueous phase is filtered and transferred to a water treatment plant. The polymer beads are dried in the presence of atmospheric oxygen (k) and then compounded.

5.3.5. Process Combinations

Producers have gone over to combining individual processes or process steps to exploit their advantages. Two possibilities are available:

1. The individual components are produced separately and worked up or compounded together
2. Different polymerization processes follow one another and are used to produce one product

Examples of the first alternative are:

1. An ABS polymer produced by emulsion polymerization is mixed (e.g., in a twin-screw extruder, with a SAN copolymer produced by bulk polymerization [198]).
2. ABS graft rubber is added to the workup stage of a continuous bulk SAN process [199].
3. An ABS polymer produced by bulk suspension polymerization is mixed in the compounding stage with ABS graft rubbers obtained by emulsion polymerization [200, 201]. This process can be used to obtain bimodal bigraft ABS systems [77, 202].

Examples of the second alternative include a latex suspension process (which is also used for high-impact polystyrene [203]) and a bulk dispersion process. Latex suspension polymerization can be performed batchwise or continuously, whereas the bulk dispersion process must be run continuously. Neither variant has achieved industrial importance so far. The bulk dispersion process combines the advantages of emulsion polymerization of a rubber base that has a defined particle size and particle size distribution with a bulk grafting step and a bulk SAN polymerization running parallel to it [204].

Like the bulk dispersion process, the latex suspension process starts from a rubber latex produced by emulsion polymerization. The latex is added to a styrene–acrylonitrile monomer mixture and the swollen mixture then converted into a monomer–polymer–water suspension by addition of dispersing and precipitating agents. Conventional bulk suspension polymerization then follows [205].

The main advantages of these two methods over the emulsion process are: there is no precipitation stage, wastewater contamination is reduced, larger particle sizes can be achieved more easily, and less polymerization auxiliaries are required. Advantages over the conventional bulk process are that the rubber chopping step and the production of a rubber solution are omitted. Because of the defined structure of the rubber particles, higher rubber contents can be used without incurring viscosity and heat removal problems. The critical phase inversion stage is circumvented and the process is reduced to a bulk process.

5.3.6. Additives [137]

See also, → Plastics, AdditivesPlastics, Additives.

Antioxidants. The rubber phase of ABS polymers is degraded by thermooxidation and light in the presence of atmospheric oxygen. Degradation is thought to proceed via a free-radical mechanism [206], resulting in yellowing, deterioration of mechanical properties, and embrittlement. Stabilizers or stabilizer systems are added at concentrations of 0.1–1 wt % to prevent degradation [207, 208] by scavenging radical intermediates or destroying hydroperoxides. They can be divided into sterically hindered phenols, organic compounds with divalent sulfur (thioethers) [143, 209], and organic compounds of trivalent phosphorus (phosphites) [207–210].

Light Stabilizers. ABS polymers undergo degradation reactions when exposed to UV light in the wavelength region 250–320 nm. They can be protected by UV absorbers, mainly derivatives of 2-hydroxyphenylbenzotriazole, 2-hydroxybenzophenone, and cinnamate esters. Hindered amine light stabilizers (HALS) [211] act by scavenging radicals produced during photooxidation [212].

Optimal protection can be attained by combining UV stabilizers and HALS compounds, generally at levels of ca. 0.2–1.5 %.

Lubricants. Long-chain alkyl compounds are often added to ABS polymers as lubricants to improve thermoplastic flow properties and facilitate removal of parts made by injection molding. Fatty acid esters, fatty acid amides, metal stearates (e.g., calcium stearate), or combinations of these substances are used at levels of ca. 0.5–2 %.

Antistatic Agents. Like all plastics of low polarity, ABS polymers tend to build up electrostatic charge on their surfaces which causes adverse effects such as static discharge or dust attraction. Polar antistatic agents are added at levels of 0.5–3 % to prevent this. They can be divided into cationic, anionic, or nonionic compounds [213, 214].

5.4. Quality Assurance and Standardization

Assurance of uniform quality is important both for the raw materials and the final products. A quality assurance scheme is shown in Figure 20. General guidelines on quality assurance, quality assurance programs, and quality audits are laid down in the EC standard EN 29 001 [215]. The test procedures include:

1. Chemical and physical analysis and methods of determination [216, 217]
2. Product-specific approval tests

Analytical procedures are based on appropriate DIN, ISO, and internal company or client-specific standards. They relate to monitoring of the production process and the final products.

Approval tests are based on the properties of the end product. They include mechanical properties (e.g., notched impact strength, hardness), thermal properties (e.g., heat distortion temperature), processing behavior (e.g., flow properties, dispersing), and fire behavior. They are carried out according to relevant national or international standards.

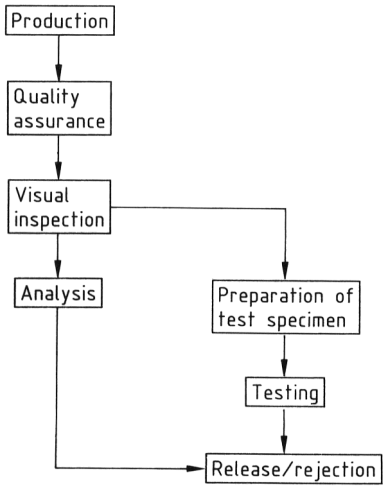


Figure 20. Quality assurance scheme
Visual inspection: Testing the pellets for impurities, pellet shape, and foreign bodies
Analysis: Chemical and physical analysis
Preparation of test specimen: Preparation under standardized conditions and processing parameters
Testing: Product-specific properties
Release/rejection: Authorized by quality assurance department according to prescribed specifications and guidelines

ABS plastics with an elastomer phase based on butadiene and that do not contain fibrous fillers are standardized according to ASTM D 1788–81, DIN 16 772 part 1, and ISO/DIS 2580–1. The large number of ABS types are classified in a grid system (cells), based on three or four properties, each with several ranges of values.

ASTM D 1788–81	
Izod impact strength at 23 °C (D 256)	6
Deflection temperature under load 264 psi (D 648)	6
Tensile stress at yield point (D 638)	6
Density (D 792)	1.0–1.2
Acrylonitrile content, %	min. 13 %
DIN 16 772 Parts 1 and 2 (Sept. 87, Dec. 88)	
Acrylonitrile content of the continuous phase	2
Vicat softening temperature VST B/50	4
Melt flow index, 220/10	4
Notched impact strength at 23 °C	5
ISO 2580–1 (1990)	
Acrylonitrile content of the continuous phase	2
Vicat softening temperature	4
Melt flow index, MFI 220/10	4
Notched impact strength at 23 °C	5
Modulus of elasticity from the bending test (ISO 178)	4

5.5. Properties

ABS polymers have a high toughness (even in the cold), satisfactory rigidity, and good resistance to heat, chemicals, and environmental stress cracking. Molded articles with high dimensional stability and good surface quality can be produced by simple processing techniques. Although each of these properties can be bettered by other thermoplastics, no other system displays such a good combination of technically important properties.

A deeper knowledge of structure–property relationships [77, 218, 219] allows producers to supply a range of commercial products with user-oriented property profiles. Table 9 gives an overview of some commercial grades [220].

The properties of ABS polymers are determined by molecular and morphological parameters. The matrix composition and molecular mass, the type of rubber, the volume ratio of the rubber to the continuous phase, the rubber particle size, the grafted rubber structure, and the additive content are also important.

Standard ABS systems are opaque because their two phases have different refractive indices. Opacity depends on the particle size of the grafted rubber phase and the difference between the refractive indices of the two phases (Mie's theory) [221]. If the particle diameter is small enough compared with the wavelength of visible light, the two phases can be considered as optically homogeneous, and they appear translucent. Completely transparent systems are obtained if the refractive indices are equal. This is achieved, for example, by using a MABS resin matrix [222] or by completely substituting methyl methacrylate for acrylonitrile [223] (see also Section 5.12.2). In bimodal graft rubber systems, depending on ratio of the graft base to the grafted polymer, opacity may be observed despite equal refractive indices. The same applies if grafted rubber particles accumulate to form clusters during processing or tempering because of an incompletely closed graft shell.

In all ABS polymers the continuous phase (SAN and/or AMS–AN copolymer) is responsible for most of the chemical properties. Since only C–C bonds are present in the polymer chains, hydrolysis reactions are unimportant. ABS polymers are therefore generally resistant

Table 9. Physical properties of various ABS types

Modulus of elasticity, N/mm^2	Yield stress, N/mm^2	Izod notched impact strength, kJ/m^2 (ISO 180, 80 × 10 × 4 mm)		Ball indentation hardness, N/mm^2	Vicat softening temperature, °C	Melt flow rate cm^3/10 min
(ISO 178)	(ISO R 527)	23 °C	– 30 °C	(ISO 2039)	(ISO 306)	(ISO 1133)
Injection molding and standard grades						
2500	45	10	4	120	95	45
2400	45	15	7	115	96	31
2200	40	22	8	100	98	17
2100	40	29	12	90	97	5
1700	34	38	25	70	96	3
2400	44	16	5	115	93	37
Heat-resistant grades						
2500	47	18	8	105	103	8
2500	53	15	6	110	108	3
2700	53	15	5	115	113	2
Galvanizable grades						
2100	40	24	10	90	95	25
2800	55	12	5	115	111	4
Flameproofed grades						
2400	45	8	5	110	87	45
2300	43	17	6	105	88	19
Extrusion grades						
2400	44	19	10	105	98	7
1900	38	31	19	80	96	4
Special grades						
2300	49	30	10	105	105	5
2900	50	5	4	130	98	50
1900	39	35	22	78	98	12
2000	38	12	6	90	94	10

to aqueous solutions of salts, acids, or bases. They can absorb up to 1.5 wt % water on storage in aqueous media due to residual emulsifier and the polarity of the nitrile side groups. Under normal conditions, dimensional or property changes are negligible.

Paraffinic hydrocarbons do not dissolve ABS polymers. A certain weight gain can be detected on storage in such media, and depends on the nature and quantity of the rubber phase. ABS polymers show equally good resistance to animal and vegetable fats and to a range of cosmetic creams.

Other organic liquids, such as halogenated hydrocarbons, aromatics, esters, and ketones dissolve the SAN phase. Oxidizing agents, especially inorganic acids, break up the chains and thus degrade the polymer. The resistance tables published by ABS producers only have limited meaning for practical applications. In order to answer specific questions, the running of a creep test under constant deformation, or, better, under constant tension is recommended. States of stress exist in each molded article as a result of its production. Additional stress is often produced by binding elements (e.g., rivets, screws, molded-in or enclosed metal parts) or on use of the article. Environmental stress cracking is low compared with polystyrene, but cannot always be excluded. Sensitivity towards stress cracking can be further lowered by increasing the acrylonitrile content and the molecular mass of the SAN phase, as well as by relaxation processes that are favored by the disperse rubber phase.

The double bonds in the elastic rubber phase (BR rubber) are responsible for the relatively high sensitivity of ABS polymers towards the long-term effects of heat, light, and weathering which result in yellowing and graying of the surface and a decrease in toughness [224]. Although satisfactory protection can be provided by using stabilizer combinations (phenolic antioxidant, a thiodipropionate ester, and/or a

phosphite ester) during production and processing at 220–260 °C, long-term stabilization, particularly during simultaneous exposure to UV light and weathering, is difficult. Use of established stabilizer systems allows, however, repeated processing (e.g., recycling) without a serious decrease in toughness. For all indoor applications, ABS is aging-resistant. For outdoor use, adequate resistance to weathering is necessary. Three routes are currently used for this:

1. "Pigmenting" with soot (dark grey shades and black) to absorb UV radiation.
2. Coating semifinished or finished articles with barrier layers having a low oxygen permeability, with less sensitive materials, or with UV-protective paints.
3. Using grafted rubber systems with few or no double bonds. Although these systems do not contain the butadiene monomer unit they are nevertheless members of the ABS family because they have the same basic structure and morphology. They are SAN copolymers that are rendered impact-resistant by a dispersed elastomer phase.

At processing temperatures above 280 °C, ABS polymers lose their toughness because of damage of the rubber phase. Depolymerization begins above 300 °C. In the presence of atmospheric oxygen, decomposition can begin at ca. 280 °C.

5.6. Special Product Modifications

Heat-Resistant ABS Polymers. To increase heat resistance the SAN matrix is generally replaced totally or partially by an AMS–AN copolymer matrix. This is associated with small reductions in toughness, flow properties, and surface quality [225, 226]. To counteract these disadvantages, several methods are available to the producer:

1. Use of an AMS–AN sequence polymer matrix with an increased proportion of AMS–AMS–AN structural units (Vicat B values of ca. 130 °C can be reached) [161, 162]
2. Use of a matrix consisting of a styrene–acrylonitrile–*N*-phenylmaleimide terpolymer (Vicat B values of 130 °C)
3. Use of blends with polymers having higher heat resistance, e.g., polycarbonates or poly(butylene terephthalate) [227–229]

Commercial high-temperature ABS (HT-ABS) grades may either have good toughness with only a limited increase in the Vicat values or a limited toughness and Vicat values in the range 115–130 °C.

Glass-Fiber-Reinforced ABS Polymers. Reinforcement of ABS with 15–20 wt % glass fiber increases the modulus of elasticity by a factor of 2–2.5 [230]. The reinforced material has a lower thermal expansion coefficient (and thus high dimensional stability) as well as high rigidity, hardness, and heat resistance. Finished articles with smooth surfaces can then be obtained by appropriate coordination of the flow properties, glass fiber length, and glass fiber sizing material.

Flameproofed ABS Polymers. Standard ABS plastics are classified as flammable according to ASTM D 635 (rate of combustion 5–7 cm/min) and as class HB according to the UL 94 test. They also pass the Motor Vehicle Safety Standards (MVSS) test 302 and the so-called Kleinbrenner-Test (limited burning test) DIN 4102 B 2 (see also → Flame RetardantsFlame Retardants, Chap. 2.). For certain applications addition of flame retardants is necessary (mostly halogen compounds in combination with antimony trioxide) to obtain UL 94 V-0 grades.

The brominated diphenyl ethers used in the past as flame retardants have been replaced by other compounds (e.g., brominated oligostyrenes and polycarbonates).

5.7. Legal Aspects

ABS polymers are subject to a large number of legal regulations during production, processing, use, and disposal. A few examples are given here and they relate to the situation in Germany. Similar regulations apply in other countries.

The monomer building blocks A, B, S, and AMS are classified as hazardous substances [231]. Contact with these monomers requires observance of maximum workplace concentrations. See also, → AcrylonitrileAcrylonitrile, Chap. 9.; → ButadieneButadiene, Section

8.3.; → NitrilesNitriles, Section 2.5.; → StyreneStyrene.

Emissions of ABS production plants are controlled by clean air regulations (TA-Luft) and the law governing wastewater discharge (Abwasserabgabengesetz). Waste materials are subject to the waste disposal law (Abfallbeseitigungsgesetz).

In the processing of ABS pellets, traces of volatile components are formed, which may include residual monomers. As in ABS production, the maximum workplace concentrations must be observed.

Finished articles based on ABS polymers can be used in industry without limitation. EC guidelines govern toys and contact with foods [232]. Similar guidelines apply in other countries. These stipulate the monomers permitted for plastics production, polymerization auxiliaries, and additives. They also prescribe limiting values for the use of individual components and for their maximum transfer from the plastic into foods and food substitutes. The maximum proportion of heavy metals in pigments is an important criterion for toys [233].

In the area of disposal, restrictive legal measures are being prepared that prescribe recycling of used components (e.g., in the automotive and electrical sectors).

5.8. Storage and Transportation

ABS pellets can be stored and transported in polyethylene sacks stacked on pellets, in octatainers with polyethylene liners, in big bags, and also in silo containers. Labeling according to GefStoffV and EC guidelines is not necessary. Safety data sheets must be enclosed with the goods for road, rail, or marine transport. The surfaces of the pellets absorb water, which must be removed by predrying (e.g., 2 h at 70 °C) before processing.

ABS powders which are used as additives (e. g., for PVC) must be stored and transported in explosion-proof systems because of their ready oxidizability and large specific surface area. Measures should also be taken against buildup of electrostatic charge. The powders are stored and transported in polyethylene sacks or silo containers. If there is a danger of dust formation, dust masks must be worn.

5.9. Uses

ABS polymers are widely used as engineering materials [234–236]. The main consumers are the automotive industry, the domestic appliances industry, the data technology and telecommunications area, and producers of refrigeration equipment, toys, sports articles, and semifinished articles. ABS polymers have a very favorable price–performance ratio. In the automotive industry ABS often competes with modified polypropylenes, but in other applications it also replaces industrial thermoplastics and thermoplastic blends.

Trade names and producers of ABS polymers follow:

BASF	Terluran
Chi Mei	Polylac
Cheil	Starex
Dow Chemical	Magnum
Formosa Plastics	-
GE Plastics	Cycolac
Lanxess	Novodur
LG Chemicals	-
Techno Polymer	-
Toray Industries	Toyolac

5.10. Economic Aspects of Acrylonitrile-Based Styrene Copolymers

The different polymer production and sales options only permit the joint evaluation of data for all acrylonitrile-based styrene copolymers (ABS, SAN, ASA, AES, and ACS). The major part (> 75 %) is assignable to ABS.

Consumption of acrylonitrile-based styrene copolymers has grown considerably during the last years (Table 10) reflecting their wide use as engineering materials and blend components for other industrial thermoplastics. Nominal

Table 10. Product development of acrylonitrile based styrene copolymers (ABS, SAN, ASA, etc.) (10^3 t)

Region	1995	2000	2005
EU	650	800	800
NAFTA	700	800	800
Asia	2300	3400	4700
Others	200	250	300
Total	3850	5250	6600

Table 11. Worldwide production capacities for acrylonitrile-based styrene copolymers in 2006 (10^6 t)

Company	Region	Capacity
Chi Mei	Asia	1.2
BASF	Asia, EU, NAFTA	0.9
LG Chem	Asia	0.75
Lanxess	Asia, EU, NAFTA	0.7
GE Plastics	Asia, EU, NAFTA	0.6
Formosa Chemicals	Asia	0.45
Cheil Industries	Asia	0.4
Dow Chemical	Asia, EU, NAFTA	0.4
Techno Polymer	Asia	0.3
Grand Pacific	Asia	0.25
Kumho	Asia	0.2
Jilin Chemical	Asia	0.2
others		1.2

production capacities and producers are listed in Table 11. Consumption is estimated to grow by 5–6 % over the next years.

5.11. Recycling

ABS articles can be recycled in two ways:

1. The used articles are returned and used directly in the production process (direct recycling)
2. They are degraded chemically into their individual components (i.e., acrylonitrile, butadiene, styrene) or other organic compounds which are then recycled (chemical recycling) [237]

The interest of ABS producers and consumers is concentrated on the first method. Investigations carried out by raw materials producers and the automotive industry show that sorted ABS polymers are well suited to direct recycling (i.e., defined quantities of recycled material are added to the primary material) [238, 239]. Tests have shown that incorporation of 20 % and 50 % recycled ABS derived from articles sorted into pure grades has very little effect on (notched) impact strength, heat resistance (Vicat B 120), and the melt flow index [240]. The basic operations involved in ABS recycling are summarized in Figure 21.

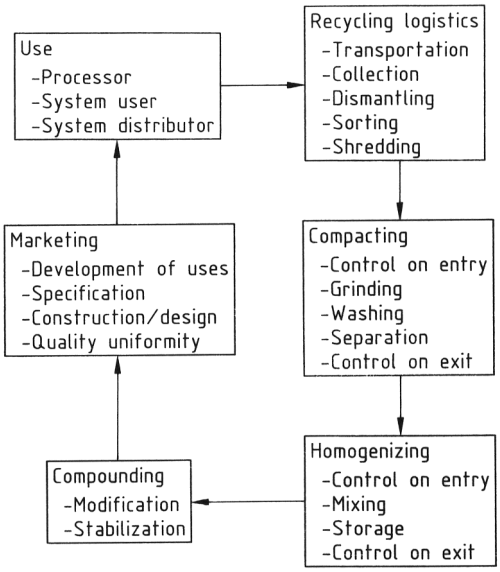


Figure 21. ABS recycling operations
Impact strength of ASA, AES, and ABS

5.12. ABS-Analogous Systems

ABS-analogous systems are elastomer-modified, two-phase thermoplastic systems with the same basic structure as ABS (i.e., a SAN-grafted rubber phase embedded in a SAN matrix). Production methods and principles are the same as those used as for ABS.

5.12.1. ASA, AES, and ACS Polymers

ASA, AES, and ACS polymers consist of acrylonitrile and styrene grafted onto acrylate, EPDM, or chlorinated polyethylene rubbers, respectively. In these polymers, aging resistance is increased by substituting the polybutadiene rubber of ABS by a rubber base which is only slightly or not at all susceptible to oxidation. Other features of ABS (e.g., toughness–hardness and toughness–heat resistance behavior or the coupling behavior of the grafted rubber) should be retained. These conditions can, however, only be partly satisfied because appropriate "saturated" elastomer candidates behave less favorably than butadiene polymers; they have a higher glass transition temperature and are less prone to grafting reactions. The SAN matrix itself does not have unlimited aging and weather resistance; SAN copolymers undergo oxidative degradation in the presence of air and this is independent of the degradation behavior of the

Table 12. Producers and trade names of two-phase ASA, AES, and ACS plastics

Abbreviation	Matrix	Elastomer base	T_g of the elastomer base, °C	Producer	Trade name
ASA	SAN	acrylate rubber	ca. −48	BASF	Luran S
				Lanxess	Centrex
				GE Plastics	Geloy
				Hitachi Chemicals	Vitax
				UMG ABS Ltd.	Dialac
AES	SAN	EPDM rubber	−50 to −60	Dow Chemical	Rovel
				Polimeri	Koblend
				Techno Polymer	AES
				Nippon A&L	Unibrite
ACS	SAN	chlorinated polyethylene	−20 to −30	Asahi Kasei	Stylac ACS

grafted rubber system [241]. Addition of light stabilizers can delay, but not prevent degradation. To obtain rubber-modified, two-phase plastics that are completely aging- and weather-resistant, another matrix system such as poly(methyl methacrylate) must be used.

Acrylate rubbers (ACM), ethylene–propene rubbers (EPM or EPDM) (→Rubber, 3. SyntheticRubber, 3. Synthetic), chlorinated polyethylene, and other oxidation-resistant rubbers (e.g., silicone rubbers) have been suggested for the production of elastomer-modified, two-phase plastic systems [242, 243]. However, only the first three of these elastomers have been used in aging-resistant ABS polymers. Only ASA [244], AES [245], and ACS polymers are of industrial importance.

ASA production starts from a poly(butyl acrylate) rubber produced by emulsion polymerization and with a uni- or bimodal particle size distribution. To achieve a sufficiently high degree of grafting in the subsequent grafting stage, one of the following grafting bases is used:

1. A terpolymer from *n*-butyl acrylate, vinyl methyl ether, and butadiene [246]
2. An *n*-butyl acrylate–butadiene copolymer [247]
3. A copolymer consisting of butyl acrylate and a monomer acting as a cross-linking or grafting center [248]

Production and workup of ASA graft rubber obtained by emulsion polymerization require the same process parameters and reaction conditions as those described for ABS in Section 5.3.1.

Seed latex technology offers a further possibility, starting from a finely divided polybutadiene seed latex [249].

ASA products are obtained by compounding the grafted polymers and separately produced SAN copolymers with additives and colorants.

AES production usually starts with an EPDM rubber system with 7–12 double bonds for every 1000 carbon atoms [250]. At a rubber content of 10–50 % the AES and grafted rubber are produced by continuous bulk solution polymerization as described for ABS in Section 5.3.3 [251]. The rubber is dissolved in a monomer–solvent mixture and then charged to the first reactor of a bulk solution polymerization plant. The final product can be isolated analogously to ABS but a precipitation stripping process can also be used for grafted rubber systems with high EPDM contents.

ACS production is analogous to AES production, but is declining in importance.

Table 12 lists producers and trade names of ASA, AES, and ACS polymers.

ASA and AES polymers exhibit better aging behavior than ABS polymers (Fig. 22). The

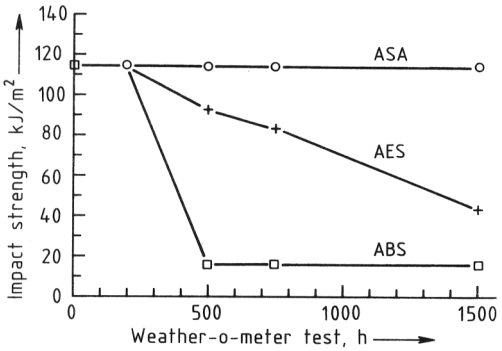


Figure 22. Graft rubber systems after exposure to light (weatherometer test)

principal disadvantages of AES and ASA polymers compared with ABS polymers are their lower low-temperature toughness and lower heat resistance. Deeply colored modifications are difficult to produce (increased opacity due to the different refractive indices of the rubber base and the matrix).

5.12.2. MBS and MABS Polymers

MBS polymers contain a methyl methacrylate (M)–styrene (S) copolymer matrix. The grafted rubber system embedded in the matrix consists of a methyl methacrylate–styrene copolymer shell grafted onto a polybutadiene or butadiene–styrene copolymer core. MABS polymers denote systems in which acrylonitrile is incorporated into the polymer matrix or the grafted rubber shell as an additional monomer. Table 13 lists producers and trade names of MBS and MABS polymers.

The composition of MBS and MABS polymers is usually chosen to ensure good transparency: the refractive indices of the matrix, the grafted rubber shell, and the rubber core should be the same; the grafted rubber particle diameter should be less than half the wavelength of visible light (i.e., <200 nm).

MBS and MABS polymers are seldom used in the pure form; they are generally employed to modify other thermoplastics. They improve processing behavior, notched impact strength, and heat resistance of rigid poly(vinyl chloride) (PVC). The modifiers must be in powder form because rigid PVC is mostly processed as a powder. MBS and MABS polymers are therefore produced by emulsion polymerization or latex suspension polymerization.

MABS polymers used to modify PVC have the following requirements [252]:

1. The particle diameter of the grafted rubber must be < 200 nm to ensure high transparency [253]
2. To obtain transparent, colorless polymer blends, the composition of the modifier must be chosen such that its refractive index is the same as that of PVC ($n_D^{20} = 1.54$) [254, 255]
3. The modifier should have high activity at low dosage to minimize loss in modulus and heat resistance

A butadiene–styrene copolymer (weight ratio 75 : 25) is usually used as the rubber base to achieve a refractive index n_D^{20} of 1.54. Since methyl methacrylate is hydrolyzed relatively rapidly at alkaline pH [256], the grafting reaction is carried out at neutral or weakly acidic pH. Long-chain alkyl or arylsulfonates are used as emulsifiers and yield stable dispersions even below pH 7. Inorganic peroxides (e.g., potassium peroxydisulfate) and redox systems (e.g., cumene hydroperoxide and sodium hydroxymethane-sulfinite) are generally used as initiators [257]. The degree of grafting is controlled by adjusting the ratio of the grafted monomers to the rubber base and by the addition of molecular mass modifiers. The particle size of the grafted rubber is determined by that of the rubber base [120]. This, in turn, is controlled by the water–monomer ratio used in the polymerization, by the emulsifier concentration, or, in seed latex polymerization, by the particle size of the seed latex.

It is advantageous to carry out the grafting reaction in several stages [257, 258], or to use blends of grafted polymers which have a synergistic effect on the toughness of the PVC blend.

The grafted rubber and resin matrix can be synthesized separately and mixed in a workup [259] or compounding stage. Further workup

Table 13. Examples of producers and trade names of ABS, MBS, MABS, and MACR modifiers

Producer	Country	Product	Modifier for *	Trade name
BASF	Germany	ABS, MBS, MACR	PVC	Vinuran
Lanxess	Germany	ABS, MBS, MABS, MACR	PVC	Baymod
GE Plastics	United States	ABS, MABS	PVC, PC/PBT	Blendex
Rohm & Haas	United States	MBS, MABS	PVC, PC/PBT	Acryloid/Paraloid
Kaneka	Japan	MBS, MABS	PVC	Kane ACE
Mitsubishi Rayon	Japan	MBS, MABS	PVC, PBT	Metablen
Nippon A & L	Japan	ABS, MBS, MABS	PVC	Kralastic

* PBT = poly(butylene terephthalate); PC = polycarbonate; PETP = poly(ethylene terephthalate); PVC = poly(vinyl chloride).

and powder isolation are similar to those of ABS emulsion polymers. Like ABS polymers, MBS and MABS polymers must be protected from attack by atmospheric oxygen by the addition of stabilizers. MBS polymers are being increasingly used for modifying aromatic polyesters and polyester–polycarbonate blends [260, 261]. Since the processing temperature exceeds 280 °C, MACR polymer modifiers are used in which the SBR base is replaced by an acrylate rubber base (see also Table 13). Production requirements for MACR polymers are the same as for ASA and MBS graft rubber systems [262].

5.13. ABS Blends

Polymeric materials with novel properties can be obtained by the combination of known polymers in blends (alloys). Table 14 summarizes ABS-containing polymer blends. See also → Polymer BlendsPolymer Blends, Section 4.3.

Mixtures of ABS with polycarbonate (PC), poly(butylene terephthalate) (PBT), PBT–polycarbonate (PC), PVC, polyamide and thermoplastic polyurethane (TPU) are industrially important, both with regard to quantity and properties [263–265]. Other blends not mentioned in Table 14, (e.g., ABS–PETP and ABS–polysulfone blends) have not yet become important [266]. Blending of polycarbonate with ABS improves heat resistance, processing behavior, low-temperature toughness, and leads to synergistic effects [267, 268].

The combination of ABS–polycarbonate blends with triphenyl phosphate as a flame retardant and polytetrafluoroethylene as an antidripping agent yields molding compounds with a low flammability (UL 94 V-0) that are highly suited as housing materials.

ABS–polycarbonate and ASA–polycarbonate blends are predicted to have growth rates of 7–8 % in the next years.

The use of plastics for external automotive parts makes certain demands concerning heat resistance, low-temperature toughness (no spall fracturing), resistance to gasoline, and rigidity. Rubber-modified polymer blends have been developed as a solution to these problems. ABS, PBT, and ABS–PBT–PC blends are widely used. The addition of ABS graft rubbers to PBT improves impact properties [269].

Table 14. Overview of ABS blends

Grafted rubber	Matrix component I	Matrix component II	Phase ratio grafted rubber to matrix I/matrix II	Advantages	Uses
ABS	SAN [a] AMS–AN [c]	BPA–PC [b]	0.05–0.8/0.95–0.2	higher heat resistance, higher toughness than ABS, better processibility and environmental stress cracking behavior than PC	interior car fittings, housings for electronic instruments
ABS	SAN	PBT or PBT–PC [d]	0.25–0.45/0.75–0.55	higher toughness, higher low-temperature toughness than PBT or PC–PBT	car bumpers, housings
ABS		PVC [e]	0.05–0.5/0.95–0.55	higher toughness, higher heat resistance, better processibility than PVC, better flame resistance than ABS	containers, housings
ABS	AMS–AN	PVC			
ABS	SAN	PVC			
ABS	SAN	PUR [f]	0.05–0.25	higher low-temperature toughness, higher rigidity than PUR	ski boots, other injection-molded articles
ABS (modif.) [g]	SAN	PA 6, PA 66	0.05–0.4 0.95–0.6	higher toughness, better dimensional stability than PA, or PA 66	car parts

[a] SAN: Styrene–acrylonitrile copolymer, weight ratio S : AN 0.9–0.6/0.1–0.4;
[b] BPA–PC: Polycarbonate based on bisphenol A (BPA);
[c] AMS–AN: α-Methylstyrene–acrylonitrile copolymer in weight ratio AMS : AN 0.90–0.65/0.10–0.35;
[d] PBT–PC: Blend of poly(butylene terephthalate) and BPA polycarbonate in weight ratio 0.9–0.3/0.1–0.7;
[e] PVC: Rigid PVC, i.e., without addition of plasticizer;
[f] TPU: Thermoplastic polyurethane elastomer, preferably based on methylene diphenylene diisocyanate;
[g] ABS modif.: Incorporation of functional groups into the graft shell to achieve coupling to the amide group.

The addition of 5–20 wt % of ABS graft rubbers to PVC increases its toughness and thus its possible uses. Opaque and transparent blends can be made depending on the size of the grafted rubber particles. The ABS modifier also improves processing behavior, particularly in the production of calendered films [270].

Addition of heat-resistant ABS polymers to rigid PVC (exchange of the SAN matrix for an AMS–AN or styrene–acrylonitrile–NPMI copolymer) increases the Vicat softening temperature and improves toughness. The addition of PVC to ABS polymers improves their flammability behavior and, in combination with antimony trioxide, gives UL 94 V-0 materials. These blends are used on a large scale in the United States, Japan, and the Pacific Rim.

Crashpad sheets are used for covering car dashboards. They contain an ABS–PVC blend as the main component and their flexibility can be altered by extending the blend system with NBR (butadiene–acrylonitrile copolymer) or other polymer plasticizers.

The addition of ABS graft rubbers to thermoplastic polyurethanes in an in-situ reaction [271] can improve their rigidity and low-temperature toughness. Blends of this type (trade name Cycoloy, GE Plastics or Desmopan, Bayer) are widely used in ski boots. Addition of soft TPU types to ABS polymers allows wide variation of low-temperature toughness and processing behavior [272].

Polyamide 6 and polyamide 66 do not exhibit sufficient compatibility with standard ABS grades. This can be overcome by incorporating functional groups (preferably –COOH groups) into the shell of the ABS graft rubber system or using compatibilizing agents [e.g., imidized poly(methyl methacrylate) [273], or maleic anhydride copolymers [274].

ABS polymers and all other thermoplastics mentioned in Table 14 are produced as powders or pellets. Compounding can be carried out in two ways, usually in internal kneaders or twin-screw extruders [275]:

1. Powder mixing with subsequent melt compounding
2. Direct melt compounding in which the individual components are charged simultaneously or consecutively into the compounding equipment

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Polyureas

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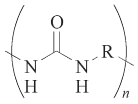
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1. Introduction

Polyureas are defined as polymers which contain ureylene groups –NHCONH– in the polymer chain. Urea, regarded as the diamide of carbonic acid, was first synthesized by Wöhler in 1892, but the chemistry and technology of polyureas have a more recent origin.

Linear polyureas are thermoplastic polycondensation products with aromatic (R = arylene) or aliphatic (R = alkylene) structures:



Polyureas or copolyureas with aliphatic structures exhibit a difference of 50 – 100 °C between the softening point and the onset of decomposition. They can be used as moldings. Polyureas and copolyureas with aromatic structures have softening points near their decomposition temperatures and are soluble in organic solvents, particularly in aprotic dipolar solvents such as DMF, *N*-methylpyrrolidinone (NMP), and DMSO. They are used for the preparation of lacquers, varnishes, and coatings [1]. The relationship between the softening points and structure is shown in Table 1.

Polyureas were first produced on a commercial scale at I.G. Farben by employing the reaction between diisocyanates and diamines. Mitsui Toatsu Chemical produces synthetic fibers from nonamethylenediamine and urea. Polyureas and copolyureas, particularly poly(urethaneurea)s, have many practical applications as foams, elastomers, fibers, etc.

Worldwide consumption was below 4.8×10^6 t in 1984 (in Europe, 2×10^6 t) and 5.9×10^6 t in 1995 [4]. More than 75 % of consumption was for foams [5]. Growth is estimated at 3 – 5 % per annum in the period 1995 to 2000. The number of products and producers continues to increase, and new processing technologies for thermosets, such as reaction injection molding (RIM), liquid injection molding (LIM), and others, are being developed.

2. Synthesis

The synthesis of polyureas is based on reactions between polyamines, especially diamines, with

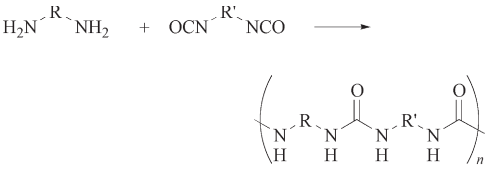
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Table 1. Alternating copolyureas derived from diamines and diisocyanates

Diamine	Diisocyanate	Intrinsic viscosity, dL/g	Softening point, °C	Ref.
Piperazine	1,4-cyclohexylene diisocyanate	0.60	324	[2]
2,5-Dimethylpiperazine	1,4-cyclohexylene diisocyanate	0.48	390	[2]
2,5-Dimethylpiperazine	1,2-bis(4-isocyanatophenyl)ethene	0.33	362 (decomp.)	[2]
2,5-Dimethylpiperazine	bis(4-isocyanatophenyl)methane	1.30	350 (decomp.)	[2]
1,4-Phenylenediamine	bis(4-isocyanatophenyl)methane	0.36	400 (decomp.)	[2]
Hexamethylenediamine	4-methyl-1,3-phenylene diisocyanate	0.47	225 – 230	[3]

aliphatic, aromatic, or heterocyclic structures and carbon dioxide, carbonyl sulfide, carbonic esters, phosgene, urea, urethane, and isocyanates.

From Diisocyanates and Diamines. Polyureas are readily prepared by a polyaddition reaction between diisocyanates and diamines.

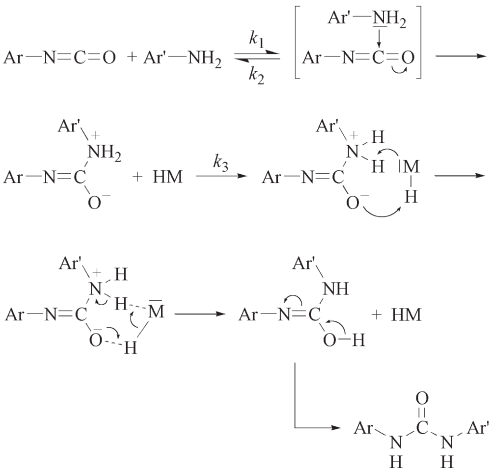


Isocyanates are reactive products, and the reactivity toward compounds containing active hydrogen is as follows: RNH_2 > $ArNH_2$ > primary OH > water > secondary OH > tertiary OH > phenolic OH > COOH > RNHCONHR′ > RCONHR′ > RNHCOOR′ [6]. An isocyanate group bonded to an aromatic ring is more reactive than one bonded to an aliphatic chain. Many aliphatic amines are extremely reactive with isocyanates, even at low temperatures. Relative reactivities of amines with phenyl isocyanate in diethyl ether at 0°C [7] follow:

NH_3	1.00
Ethylamine	9.72
n-Propylamine	8.22
n-Butylamine	9.17
n-Amylamine	9.17
Aniline	0.53

Secondary aliphatic and primary aromatic amines react similarly. Secondary aromatic amines are less reactive [7].

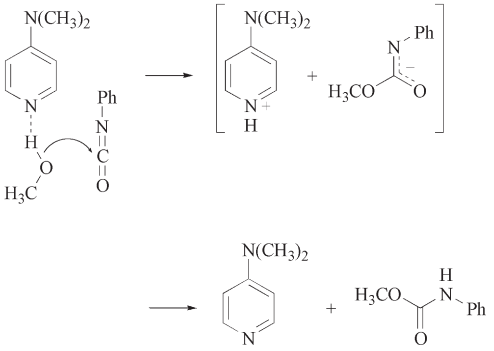
For the amine – isocyanates reaction, the following mechanism has been proposed [8]:



In this mechanism, HM is a proton acceptor/donor, for example, an amine, urea, or carboxylic acid, which acts as catalyst [9]. The reactions between isocyanates and amines are usually autocatalytic, but they can be catalyzed by many other catalysts, amines, or acids [10], [11].

Weak aromatic carboxylic acids show a high catalytic activity [12]. In benzoic acid derivatives, electron-acceptor substituents such as NO_2, Cl, or OH reduce catalytic activity, whereas electron-donor substituents such as alkyl groups increase it; 2-methylbenzoic acid is the most active catalyst.

Lewis bases such as 1,4-diazabicyclo-[2.2.2.]-octane (DABCO), triethylamine, dimethylbenzylamine, and pyridine also exhibit catalytic activity. 4-(Dimethylamino)pyridine is an exceptional catalyst, not only in reactions with amines (strongly nucleophilic reagents), but even with alcohols (weakly nucleophilic reagents) [13]. For reactions with alcohols, the following mechanism has been proposed [14]:



Insertion catalysts such as dibutyltin dilaurate, tin(II) octanoate, and cobalt naphthenate have also been used in this field [15].

The effect of substituents on the reaction between aromatic isocyanates and aromatic amines has been studied [10]. The reaction rates were determined by refluxing 0.005 mol substituted phenyl isocyanate and 0.005 mol substituted aniline for 1 h in a mixture of toluene and benzene. The urea yields are shown in Table 2.

The effect of substituents on the reactivity of the isocyanate decreases in the order: 2,4-$(NO_2)_2$ > 3,5-$(NO_2)_2$ > 4-NO_2 > 3-NO_2 > 2-NO_2 ≫ H, 4-CH_3, 3-OCH_3, 4-OCH_3. Electron-acceptor substituents in aromatic isocyanates increase the reaction rate. The same substituents in aromatic amines reduce the reaction rate. Steric hindrance is also influential. *Ortho* substitution in aromatic isocyanates or amines reduces the reaction rate.

The reaction between diamines and diisocyanates is usually carried out by interfacial polyaddition [16] or in solution [17]. In the bulk, infusible, insoluble cross-linked polymers can be obtained instead of the desired linear polyureas. Cross-linking occurs by the interaction of the highly reactive free isocyanate groups with active hydrogen atoms from the urea groups [18]. The most important application of this reaction is the synthesis of poly(urethaneurea) s, also called copolyureas.

Another interesting application for polyureas is in nonlinear optics (NLO); the NLO response of polyureas is extremely rapid, because effects occur primarily through electronic polarization [19]. It is now well-known that molecules containing electron-donor and electron-acceptor groups separated by a large conjugated π framework possess large values of second-order molecular hyperpolarizability [19]. For the synthesis of polyureas with these properties, 4-(dialkylamino)-4′-(alkylsulfonyl)azobenzene NLO chromophores have been used, which contain methylsulfonyl groups as electron-acceptor groups, 4-dialkylamino groups as electron-donor groups, and between them azo groups [20–22].

Another interesting application is the synthesis of hyperbranched polyureas (Fig. 1) [23], which have unusual properties [24].

In these syntheses, the most important monomer is 3,5-diaminobenzoyl azide (), which on heating in NMP at 110 °C under argon for 16 h gives unstable 3,5-diaminophenylisocyanate (**5**) and finaly hyperbranched polyureas. Curiously, these hyperbranched polyureas are soluble in aprotic dipolar solvents such as DMSO, NMP, and DMF.

From Diisocyanates and Water. Polyureas can be prepared from diisocyanates and water:

Table 2. Urea yields from aromatic isocyanates and aromatic amines

Isocyanate substituent	Amine substituent								
	2,4-$(NO_2)_2$	2-NO_2	3,5-$(NO_2)_2$	4-NO_2	3-NO_2	3-OCH_3	H	4-CH_3	4-OCH_3
4-OCH_3	–	–	–	–	15	91	90	95	98
4-CH_3	–	–	–	3	14	90	95	98	–
H	0	0	0	0	26	92	92	100	–
3-OCH_3	–	–	–	0	46	95	–	–	–
3-NO_2	0	0.5	4	13	52	96	100	–	–
4-NO_2	0	4	8	14	61	97	100	–	–
3,5-$(NO_2)_2$	0	8	16	54	76	95	100	–	–
2-NO_2	0	0	1	8	60	98	100	–	–
2,4-$(NO_2)_2$	0	45	51	76	84	87	100	–	–

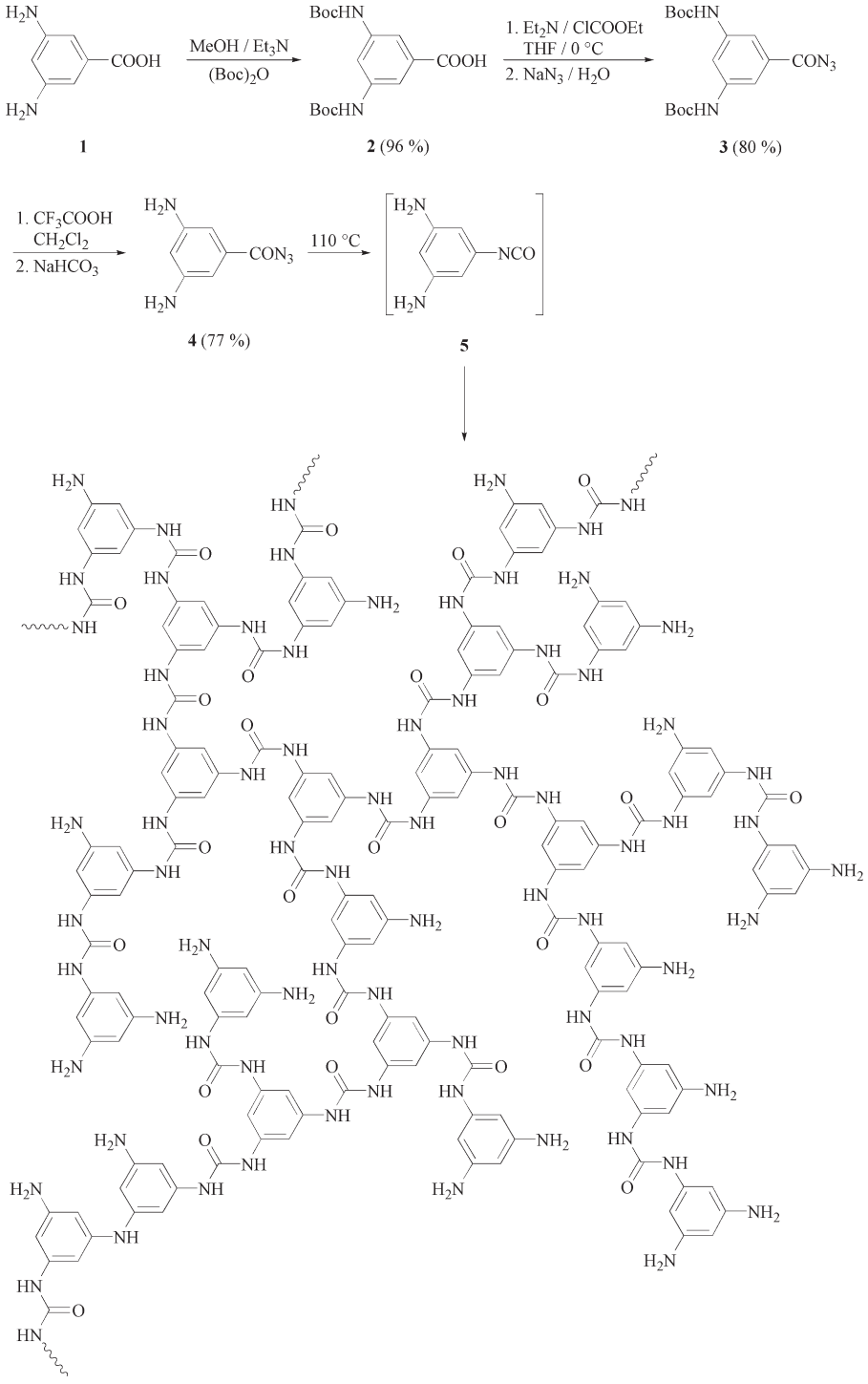
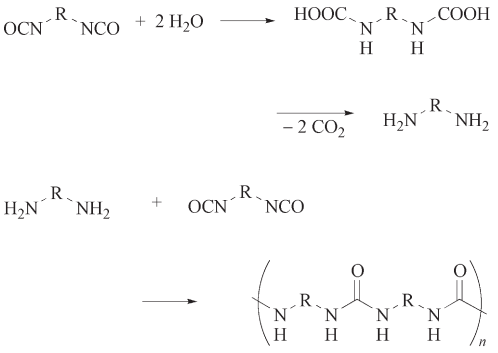
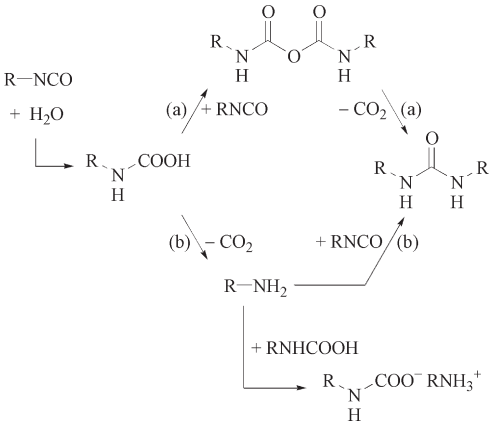


Figure 1. Synthesis of hyperbranched polyureas

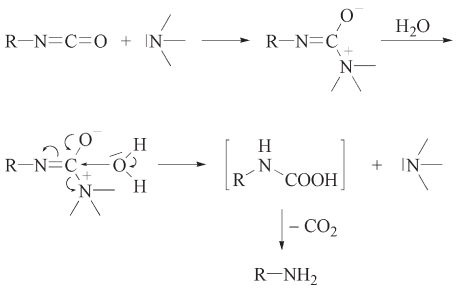


The diamine resulting from reaction of water with the diisocyanate reacts with unconverted diisocyanate more rapidly than water, and polyureas are obtained in high yields. The reactivity of water with diisocyanates is similar to that of secondary alcohols [10]. This apparently simple reaction is, in fact, quite complicated:

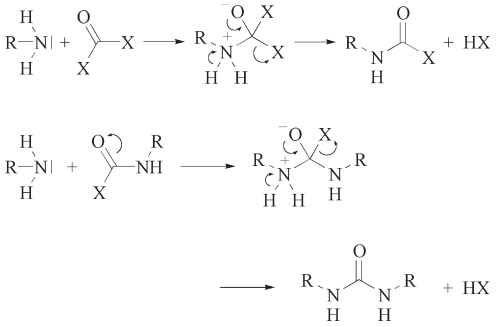


Route (a) is favored when the carbamic acid is stable and reactive toward the isocyanate [25]. Route (b) is favored when the carbamic acid is unstable and decomposes to an amine, which reacts quickly with the isocyanate. Route (c) is favored when the reaction between the carbamic acid and amine is faster than the reaction between the amine and isocyanate. The effect of substituents on the reaction of aromatic isocyanates with water is similar to that observed in the reaction of aromatic isocyanates and amines.

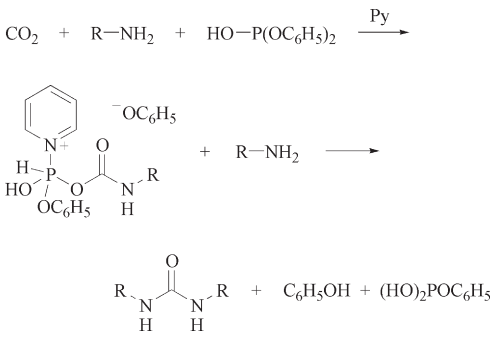
This simple reaction is employed in the manufacture of foams, in which the resulting carbon dioxide acts as a foaming agent. Different amines or amine complexes of metal salts are suitable catalysts for this reaction [26]. With tertiary amines, the following mechanism is proposed [27]:



From Diamines and Carbon Dioxide or Its Derivatives. The polycondensation of diamines and carbon dioxide or its derivatives gives polyureas in high yields (X = halogen, OR, NH_2, etc):

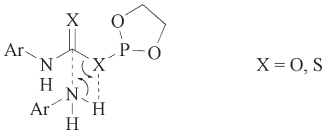


Polyureas are obtained by the polycondensation reaction of *carbon dioxide* and diamines in the presence of diphenyl phosphite in pyridine at 40 °C and 2 MPa. This reaction involves a carbamoyloxy-*N*-phosphonium salt of pyridine as intermediate [28]:



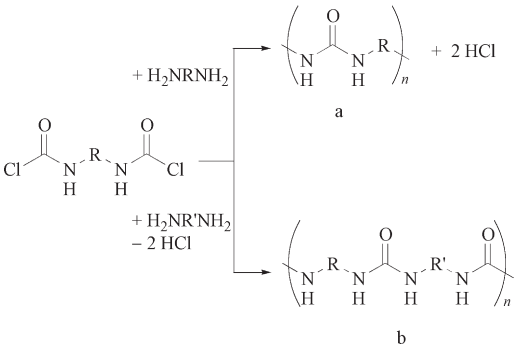
Ethylene chlorophosphites with aliphatic structures are also suitable reagents for this

reaction under mild conditions, the mechanism of which involves a four-center transition state [29]:



Without catalysts, the reaction of carbon dioxide with diamines requires high temperatures and high pressures [30].

Polycondensation of *phosgene* (carbonic acid dichloride) with diamines gives polyureas [31]. Similarly, *bis(carbamyl chloride)s* prepared from diamines and phosgene, can react with diamines of similar or different structures to afford polyureas (a) or alternating copolyureas (b), respectively:



From aliphatic or aromatic diamines and *urea* at high temperatures, polyureas result with the evolution of ammonia. This reaction can be carried out in the melt [32] or in solution [33].

Diphenyl carbonate does not react with aromatic amines in boiling toluene, but the addition of $MgCl_2$ as catalyst in pyridine makes this reaction possible at 120 °C [34]. The same reaction is also possible in phenol or cresol, but at 210 – 230 °C [35]. Activated *carbonic esters*, such as bis(*p*-nitrophenyl)carbonate or bis(2,4-dinitrophenyl)carbonate, can react with diamines at low temperatures to afford polyureas with high viscosities [36]. The rate of reaction is higher for aliphatic diamines than for aromatic diamines [37].

By Other Methods. Diamines can react with *N*, *N*′-carbonyldiimidazole in THF under reflux to give polyureas [38]. Polyureas with moderate molecular masses were prepared by the condensation reaction of lithium carbonate with aromatic diamines in presence of triphenyl phosphite and hexachloroethane in pyridine under reflux [39]. By using the same reaction, polyureas with high thermostability result from 2,8-diaminobenzothiophene or 2,8-diaminophenoxanthine and lithium carbonate [40].

A simple and ingenious method involves a controlled decomposition reaction of sebacoyl diazide in water to form poly(*n*-octylurea) [41].

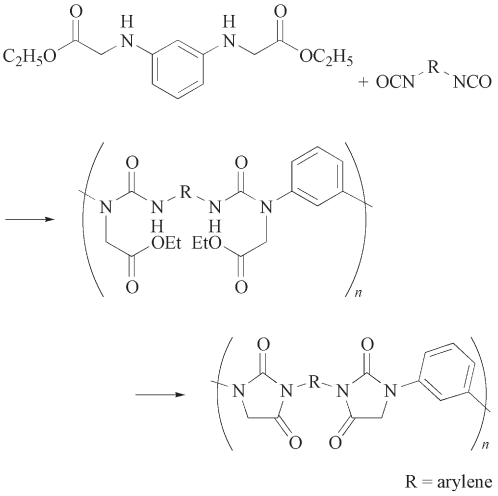
In an interesting reaction, palladium diacetate catalyzes oxidative polymerization reactions of aliphatic diamines $H_2N(CH_2)_nNH_2$ (n = 4, 6, 8, 10, 12) with carbon monoxide in presence of potassium carbonate, triphenyl phosphite, and iodine to afford polyureas [42].

Poly(*N*,*N*′-diacylurea)s have been obtained by polyaddition reactions of diamides to bis(*N*-acylisocyanate)s [43].

3. Polyureas as Starting Materials for Other Polymers

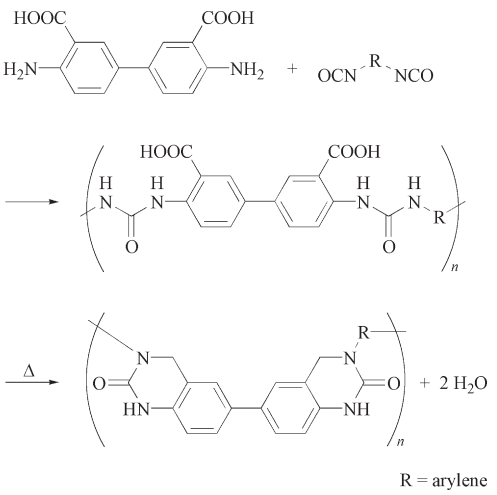
Polytriketoimidazolidines. Polymers with this structure in the macromolecular chains were prepared by reactions between various polyureas and oxalyl chloride in the presence of pyridine [44]; they decompose 70 – 100 °C higher than the corresponding polyureas.

Polyhydantoins. Aromatic polyhydantoins of high molecular mass have been prepared by a polyaddition/cyclocondensation reaction of diethyl *m*-phenylenebisiminoacetate and aromatic diisocyanates in cresol under reflux [45]:

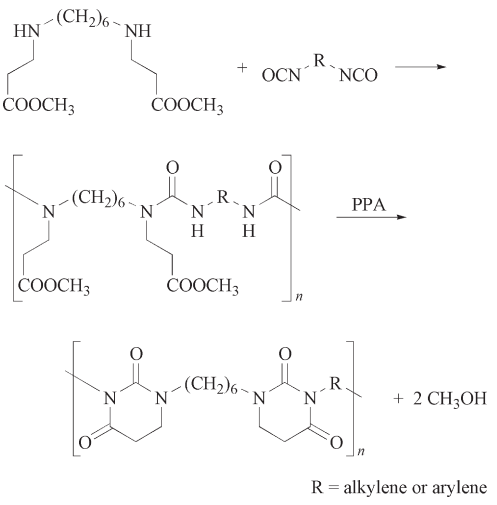


The polyhydantoin obtained from methylenebis(4-phenylisocyanate) is stable in air up to 400 °C. Aspartate polyhydantoin prepolymers can react with blocked polyisocyanates to give products that are useful for coatings, adhesives, and elastomers [46].

Polyquinazolinediones. The reaction of 3,3′-benzidinedicarboxylic acid and diisocyanates with triethylamine as catalyst and NMP as solvent results in polyureas, which are cyclized by heating at 220 °C to polyquinazolinediones [47]:



Polyhydrouracils can be obtained by the cyclization of 2-carbomethoxyethyl-substituted polyureas with polyphosphoric acid (PPA) [48]:



Polyhydrouracils decompose at 400 °C; analogous unsubstituted polyureas decompose at 300 °C.

Other Polymers. Poly(imideurea) elastomers with high elasticity and improved thermostability can be obtained by reaction of polyureas $(R^1NHCONHR^2NHCONH)_n$ with aromatic tetracarboxylic dianhydrides (R^1 = aromatic or aliphatic diisocyanate residue; R^2 = oligomer residue containing amino group-terminated elastomer segment; $n = 2 - 500$) [49].

Heat-resistant polycarbodiimide copolymers for electric cable insulation can be prepared from urea copolymers and 3-methyl-1-phospha-3-cyclopentane-1-oxide as dehydrating agent [50]. The resulting copolymers have high thermostability (at 331 °C, losses are 5 %). Soft Cu conductors were coated with these polycarbodiimides with excellent results.

The end groups of aliphatic polyamides can react with polyureas at high temperatures (200 °C) to give copolymers that exhibit improved fiber dyeability [51].

4. Homopolyureas

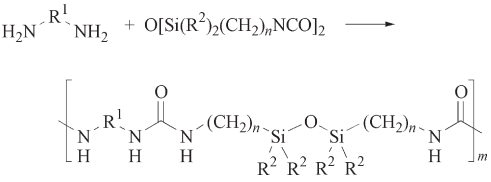
Homopolyureas, $[NHCOHN(R)]_n$ have polar structures and high softening points. Homopolyureas with aromatic or heterocyclic structures have softening points higher than those with aliphatic backbones. The introduction of a symmetrical 1,4-phenylene ring into the polymer chain raises the softening point. *N*-Alkylation lowers softening points. Aliphatic homopolyureas have softening points of about 200 °C and they can be injection-molded, extruded, and processed like other thermoplastics.

5. Copolyureas

Copolyureas have the general formula $[NH(R)NHCONH(R^1)NHCO]_n$, where R and R^1 can be aliphatic, aromatic, or heterocyclic and contain phosphorus, sulfur, silicon, or halogens (simple copolyureas). Copolyureas may contain other functional groups, such as urethane, amide, imide, carbonate, etc.

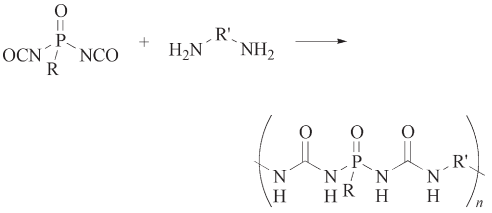
5.1. Simple Copolyureas

Copolyureas Containing Silicon. Thermostable polysilylureas with good flexibility have been obtained from diamines $H_2N–R^1–NH_2$ and $O[SiR^2(CH_2)_nHCO]_2$ (where $n = 1 – 3$, R^1 = alkyl or aryl, and $R^2 = CH_3$ or C_6H_5) [52]:



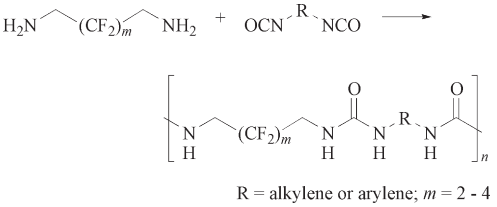
Also, from 1,3-bis(chloromethyldimethyl) siloxane and KOCN the corresponding Si-containing diisocyanate results, which reacts with diamines [53].

Copolyureas Containing Phosphorus. Polyphosphorylureas are prepared from aryl or alkyl phosphoric diisocyanates and diamines by interfacial polyaddition [54]:



Polyphosphorylureas in which R is C_6H_5 and R′ is *m*-C_6H_4 have a 10 % weight loss at 400 °C and a 40 % weight loss at 600 °C. Flame-retardant copolyureas useful for foams or films are prepared from 1-[(dialkoxyphosphinyl)methyl]-2,4-diaminobenzenes and diisocyanates in NMP at low temperature [55]. By similar methods, phosphorus-containing copolyureas have been prepared from phenyl bis(piperazidophosphate) and diisocyanates [56].

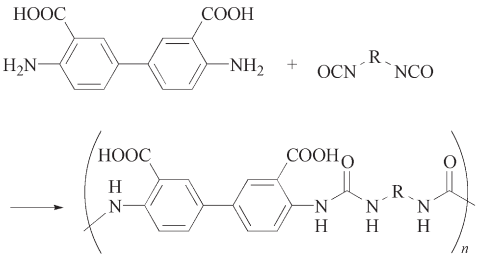
Copolyureas Containing Halogens. Heat-resistant, flame-retardant copolyureas are prepared from fluorinated primary diamines and diisocyanates [57]:



R = alkylene or arylene; *m* = 2 - 4

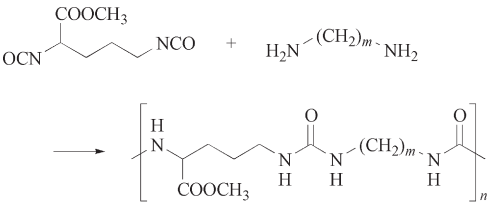
These copolyureas are useful for oil-resistant coatings and as curing agents for epoxides. Other halogen-containing diamines, such as 1,1,1-trichloro-2,2-bis(4′-chloro-3′-aminophenyl)ethane [58] or 1-(tetrafluoroethoxy)-2,4-phenylenediamine [59] can be used in reaction with diisocyanates, to afford flame-retardant copolyureas.

Copolyureas with Acid or Ester Groups. Polyurea electrolytes are prepared from sodium 3,3′-benzidinedicarboxylate and diisocyanates in the presence of sodium laurate as catalyst [60]:



R = alkylene or arylene

From L-lysine diisocyanate methyl ester and optically inactive diamines, optically active copolyureas have been prepared [61]:



m = 2 - 6

Optical studies on these copolyureas revealed that they contain macromolecules with different conformations, ranging from disordered to helical [62]. Treating the polyureas with trifluoroacetic acid causes rupture of hydrogen bonds and reduces the ordering. These

polymers can be degraded by chymotripsin or subtilisin [63]. An interesting method for the preparation of these copolyureas involves the polycondensation of L-lysine with 4,4′-dinitrophenylcarbonate [64].

Other Simple Copolyureas. Polycyanoureas with high molecular masses are prepared by a polyaddition of 3,3′-dicyano-4,4′-oxydianiline and diisocyanates in NMP with triethylamine as catalyst [65].

Thermostable copolyureas with oxadiazole rings in the main chain are prepared from bis[5-(3-aminophenyl)-1,3,4-oxadiazol-2-yl]alkanes and diisocyanates in DMF at 60 °C [66].

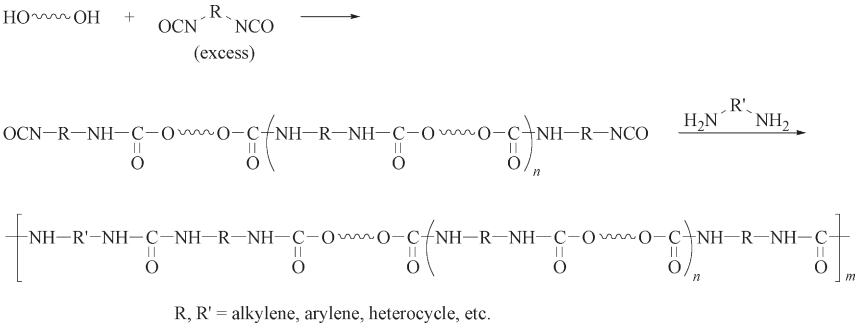
Polyverdazyl – polyureas are prepared from 1,4-bis[(1,5-diphenyl)-3-(4-aminophenyl)verdazyl-6-yl]butane and diisocyanates [67].

Triazine [68], carborane [69], and ferrocene [70] copolyureas also have high thermostability.

Copolyureas containing crown ethers (cryptates) are used as phase-transfer catalysts for alkylation, esterification, and oxidation. The copolyurea prepared from *trans*-Ar,Ar′-diaminodibenzo-18-crown-6 and TDI has a potassium ion absorption of 45 mg KOH per 100 g polymer, compared to 0.02 mg for the diamine monomer [71].

5.2. Copolyureas Containing Other Functional Groups

Poly(urethaneurea)s are the most important class of copolyureas. They can be prepared from a macrodiol (polyester diols, polyether diols, etc.) and an excess of a diisocyanate; this results in prepolymers with NCO end groups, which react with diamines (chain extenders). At the end of the reaction, a chain terminator (ROH, $RHNH_2$) is added [72], [73]:



R, R′ = alkylene, arylene, heterocycle, etc.

In the scheme presented above, the NCO – NH_2 polyaddition reaction is much more rapid than the NCO – OH polyaddition reaction and requires no catalysts. This rapid curing results in short production cycles.

Prepolymers with NCO end groups can also react with water, whereby the resulting carbon dioxide byproduct is used as a foaming agent in the production of poly(urethaneurea) foams. Poly(urethaneurea) copolymers have many practical applications as foams, cellular elastomers, fibers, aqueous dispersions, etc.

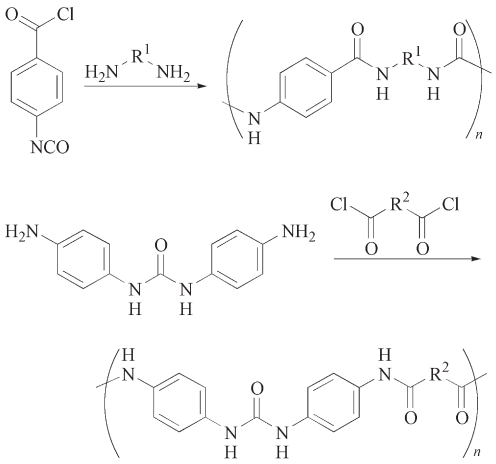
Optically active poly(urethaneurea)s were synthesized by solution polyaddition of (1*S*,2*S*)-(+)-2-amino-3-methoxy-1-phenyl-1-propanol with diisocyanates [74].

Poly(urethaneurea)s obtained from D-glucosamine and diisocyanates also have optical activity [75]. These polymers absorb 10 – 24 % water, whereas the poly(urethaneurea)s prepared from $HO(CH_2)_5NH_2$ and diisocyanates are almost non-hygroscopic; acetylation reduces the hygroscopicity.

Light-resistant poly(urethaneurea)s are prepared from 1,3-bis(isocyanatomethyl)adamantane and polyester diols with diamines as chain extenders [76].

Poly(urethaneurea)s with ionic links in the main chain were synthesized from MDI or 2,4-TDI and 4-hydroxybutyl phthalate as salts with divalent metal ions such as Ca^{2+}, Mn^{2+}, and Pb^{2+} [77].

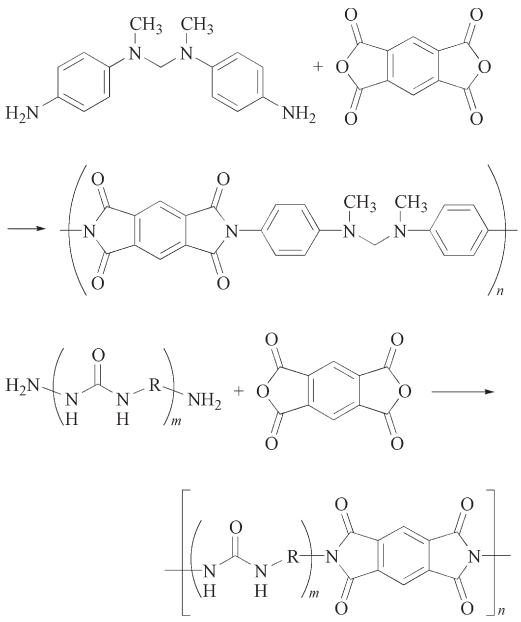
Poly(AmideUrea)s. Aromatic poly(amideurea)s are prepared from 4-isocyanatobenzoyl chloride and diamines [78] and from 4,4′-diaminocarbanilide and $R(COCl)_2$ [79]:

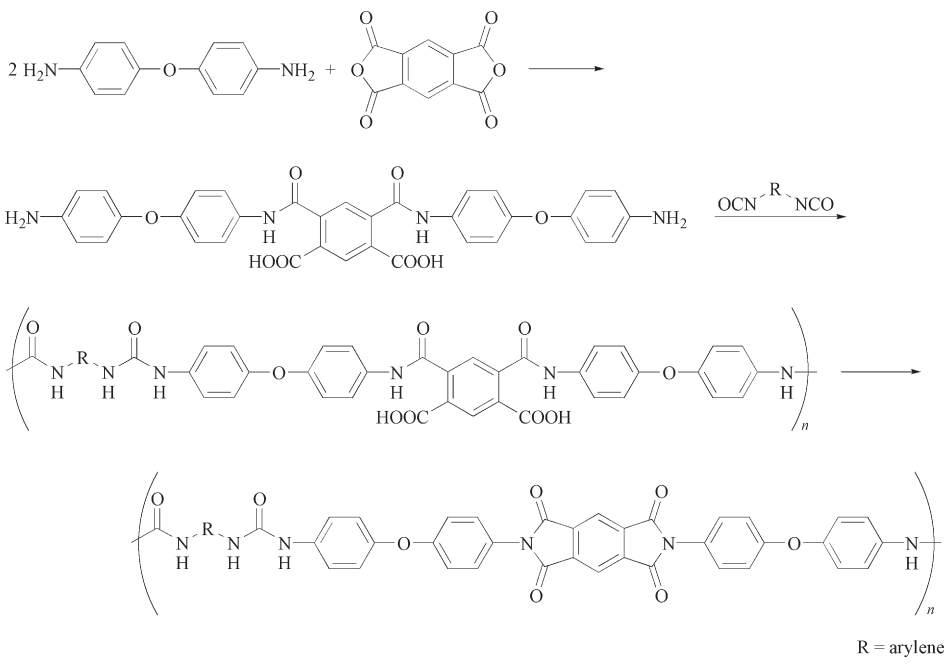


These poly(amideurea)s have excellent thermal stability and good solubility in aprotic dipolar solvents.

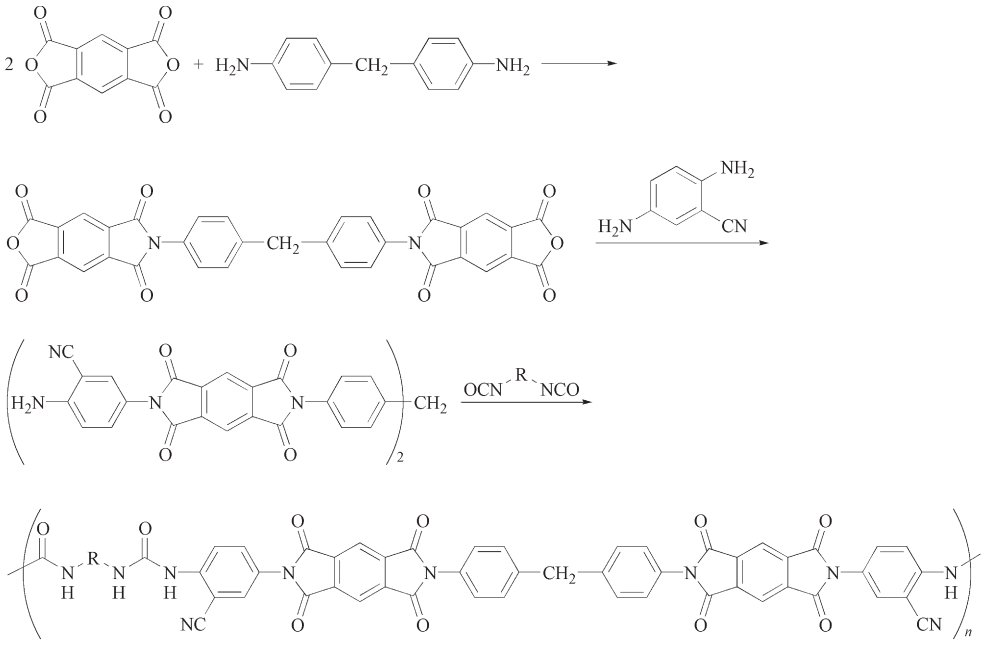
Thermostable poly(amideurea) acids can be prepared from 4,4′-diaminodiphenyl ether, pyromellitic dianhydride, and diisocyanates, which can be used as intermediates in the syntheses of poly(imideurea)s [80]:

Poly(imideurea)s with improved thermal stability are obtained from pyromellitic dianhydride and *N*,*N*′-dimethyl-*N*,*N*′-bis(4-aminophenyl) urea [81], or from the same dianhydride and $H_2N(NHCONHR)_mNH_2$, where R is $-(CH_2)_{12}-$; $-C_6H_4OC_6H_4-$, $-C_6H_4CH_2C_6H_4-$, or $-C_6H_4SO_2C_6H_4-$ [82]:



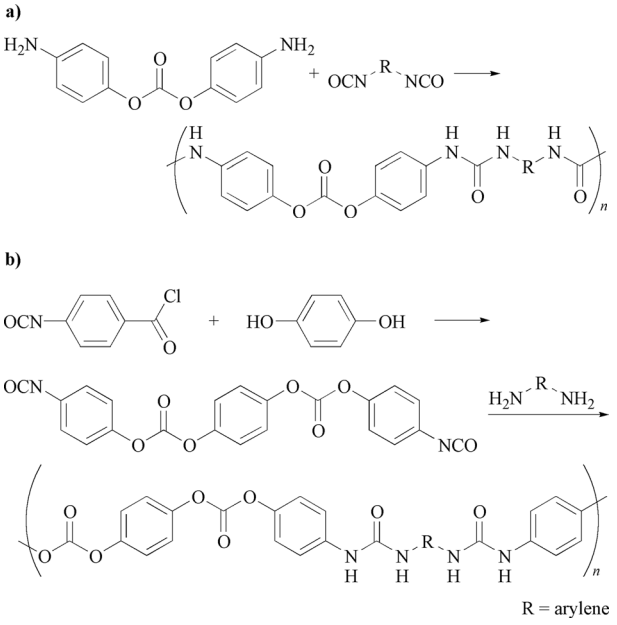


Sequential condensation can result in poly (imideurea)s with thermal stability up to 380 °C:



These poly(imideurea)s can be cyclized to polyiminoquinazolinediones.

Poly(carbonateurea)s can be prepared from bis-(4-aminophenyl) carbonate and diisocyanates (a) [83], or from *p*-isocyanatobenzoyl chloride and hydroquinone, which give a monomer with NCO end groups (b) that reacts with diamines [84].



These poly(carbonateurea)s have properties similar to these of aromatic polyureas, but exhibit higher solubility.

6. Structure

The structure of polyureas and copolyureas controls their chemical and mechanical properties.

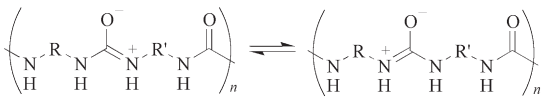
Poly(urethaneurea)s contain hard and soft segments. Usually, the hard segments have an aromatic structure and the soft segments an aliphatic structure. During solidification from solution or melt, the hard and soft segments undergo phase separation, which results in elastomeric properties. The properties of poly(urethaneurea)s depend largely on the extent of phase separation, which is due to thermodynamic incompatibility [85]. Compositional variables, such as symmetry in the diisocyanate structure [86], chain extenders, aromatic or aliphatic diamines [87], molecular mass distribution of the soft and hard segments [88], crosslinking [89], and hydrogen bonding [90], have a strong influence on the extent of phase separation.

In each urethane or urea linkage, the NH and CO groups act as proton donor and proton acceptor, respectively. Since the urea group is more polar than the urethane group, the separation of hard and soft segments is more marked, the melting range of the hard segment domains is higher, and the intermolecular (interchain) interactions are stronger. The urea carbonyl groups are considered to be completely hydrogen-bonded [91]; this feature is probably responsible for the increased phase separation in poly(urethaneurea)s.

The presence of hard segments is responsible for the high tensile strength and modulus exhibited by the materials derived from these copolyureas. The soft segments determine the thermoplastic behavior.

Phase separation has been proved by electron microscopy [92], small angle X-ray scattering [93], differential scanning calorimetry [94], and other methods [95]. The same phenomenon was studied by advanced solid-state NMR spectroscopy; the sizes of various domains and the interfaces between them were quantified by spin measurements. Also, the impact of annealing, method of polymerization, and hard segment content on the properties of poly(urethaneurea)s were studied. Major tranformations have been observed after annealing at 190 °C, when the system behavior changes from "soft in hard" to "hard in soft". The highest microphase separation is observed in solution-polymerized samples. These NMR experiments reveal the nonequilibrium nature of RIM systems for poly (urethaneurea)s [96]. For the same system of RIM poly(urethaneurea)s, FT-IR spectrophotometric data suggested that an increase in degree of phase separation and a decrease in the size of hard-segment domains take place with increasing catalyst concentration [97].

Problems of structure arise in the field of polyureas and poly(urethaneurea)s expanded by water for foams. The reaction of isocyanate groups with water to give urea groups can be monitored by IR spectroscopy at 1646 cm^{-1} for carbonyl groups and 3300 – 3320 cm^{-1} for NH groups [98]. The absorption of the carbonyl group from polyureas is not restricted to the region around 1640 cm^{-1} and varies within wide limits according to the degree of association [99]. A band at 1695 cm^{-1} has been attributed to an unassociated urea group in polyureas [100]. The NH absorption at 3320 cm^{-1} indicates that most of the NH groups are hydrogen-bonded, because the free-NH absorption at 3445 cm^{-1} is negligible [91]. This polar structure can be represented by the following structures:



R, R' = arylene, alkylene, etc.

The high melting points, thermostability, and crystallinity of polyureas may be due to the partial polar structure.

The capacity for hydrogen bonding between urea groups and solvents is as follows: alcohols $\gg$ THF > $CHCl_3$ > toluene [101].

7. Properties

7.1. Physical Properties

Melting Temperature. The polar structure of polyureas results in high melting points that are higher than those of the corresponding

Table 3. Melting points of homopolyureas

Main chain	*mp*, °C	Prepared from	Ref.
Aliphatic	180 – 230	diamines and urea	[104]
Aromatic	260 – 320	diamines and carbon dioxide	[105]
Aliphatic/aromatic	200 – 240	aromatic/aliphatic dihalide and alkali metal cyanate	[106]
Naphthalenediyl	350 – 380	diamines and urea	[107]
Heterocyclic	330 – 350	diamines and diisocyanates	[108]

polyimides. Aliphatic polyureas melt at lower temperatures than aromatic polyureas. The melting temperature of aliphatic polyureas decreases with increasing number of methylene groups. Thus, nonamethylenediamine gives polyureas with melting temperatures of about 200 – 210 °C that can be injection-molded and extruded [102]. Alkylation or acylation of the nitrogen atoms lowers the melting points [103]. The copolyureas also melt at lower temperatures. For homopolyureas, melting point variations can be seen in Table 3.

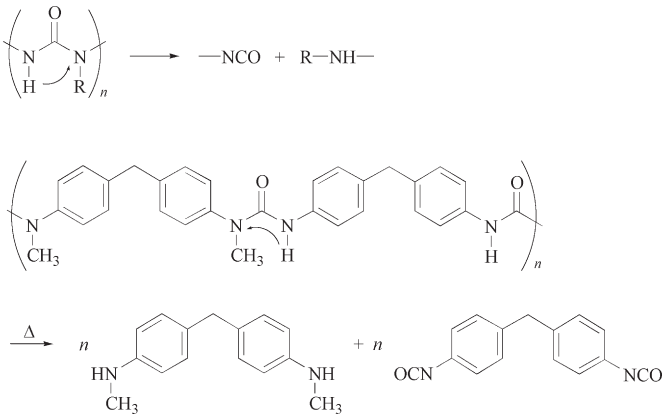
The glass transition temperature T_g also depends on structure. Aliphatic polyureas usually have a T_g below 100 °C, whereas the T_g of aromatic polyureas is above 100 °C.

Solubility. Polyureas having polar structures, are difficult to dissolve in organic solvents. Aliphatic polyureas are soluble in phenol, cresols, acetic acid, and similar solvents. Aromatic polyureas are usually soluble only in aprotic dipolar solvents such as DMF, DMA, and NMP [109]. The symmetry or asymmetry of the aromatic monomers influences the solubility of the polyureas. Copolyureas, particularly aliphatic ones, are usually more soluble than polyureas. The solubility of poly(urethaneurea)s can be improved by reaction with trifluoroacetic anhydride to give polymers with $=N–COCF_3$ groups.

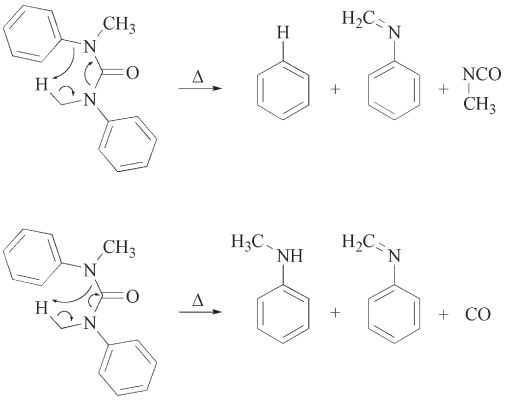
Water Absorption and Permeability. The water absorption of polyureas is low and depends on structure. Water absorption is increased by incorporation of heteroatoms, such as oxygen, sulfur, –COOH, or $–SO_3H$, whereas it decreases with increasing number of carbon atoms. Poly(urethaneurea)s derived from D-glucosamine and diisocyanates have a water absorption of 10 – 24 % [110]. The water permeability of polyurea films is higher than that of polyamide films.

7.2. Chemical Properties

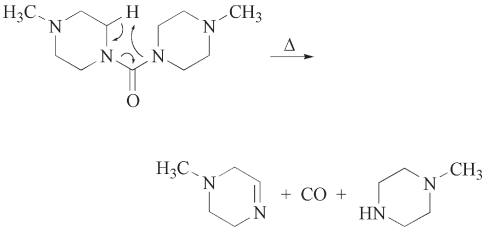
Thermal Stability. Polyureas have a thermal stability higher than that of polyurethanes but lower than that of polyamides [111]. The thermal stability of the urea group is a complex issue. Thus, polyhexamethyleneurea (*mp* = 300 °C) can be heated to 260 °C without decomposition, whereas polydecamethyleneurea (*mp* = 230 °C) decomposes rapidly at 260 °C in the molten state. The mechanism of this thermal decomposition has been studied by mass spectrometry and involves a hydrogen transfer to give isocyanates and amines [112]:



N,*N*′-Disubstituted polyureas decompose at higher temperatures than unsubstituted polyureas because of the higher energy required for the C–H hydrogen transfer, which involves two competing decompositions [112]:



This six-centered transition state is indicated by a peak in the MS (mass spectrometry) spectrum that corresponds to methyl isocyanate [112]. The thermal decomposition of polymers containing a carbonyl group flanked by 1,4-piperazinediyl units involves hydrogen transfer from a methylene group to nitrogen [113]:



A method has been reported for the synthesis of isocyanates by thermal decomposition of polyureas that involves this interesting reaction [114].

Thermal stability of polyureas can be improved by copolymerization to give poly(phosphorylurea)s, poly(silylurea)s, poly(amideurea)s, poly(imideurea)s, etc. Thermal stabilities of *N*-substituted polyureas are higher than those of the corresponding unsubstituted polymers.

Hydrolytic Stability. Polyureas have excellent stability to hydrolysis under acidic and alkaline conditions. For example, polynonamethyleneurea fibers are more resistant to acid than nylon 6 or nylon 6,6; resistance to alkalis is higher than that of poly(ethylene terephthalate). In 40 % sulfuric acid or 40 % caustic soda solution at room temperature, these fibers lose less than 10 % of their strength after 10 h [115].

Improved resistance toward acids and bases has been reported for *N*-substituted polyureas prepared from *N*,*N*′-dialkylhexamethylenediamines and phosgene [116].

Biodegradation. Copolyureas containing amino acids or peptides in their chains are degraded by living organisms. Copolyureas containing dipeptides are degraded twice as fast as than those containing amino acids [117]. Similar polyureas are also degraded by chymotrypsin or subtilisin [118].

8. Uses

The urea linkages in poly(urethaneurea)s or polyureas extended with diamines cause an increase in phase separation compared to polyurethanes extended with diols. This phase separation improves various mechanical properties, such as elongation at break, hysteresis, and stress elongation [119].

8.1. Foams

Polyurethane and poly(urethaneurea) foams are generally divided into flexible, semiflexible, and rigid products, which can be produced by one-shot or by prepolymer methods.

In the one-shot method, the components are mixed directly, generally with simultaneous addition of auxiliaries such as catalysts, reinforcing agents, fillers, foam stabilizers, and flame retardants. These systems are exothermic.

In the prepolymer method, NCO prepolymers can be obtained from di- or polyhydroxy compounds, usually hydroxy-terminated polyethers or polyesters, which react with di- or polyisocyanates in excess. These NCO prepolymers are important compounds, because they can be cured with active hydrogen atoms from diamines, diols, water, etc. Many polyurethane and poly(urethaneurea) elastomers are produced via NCO prepolymer intermediates.

The curing of NCO prepolymers with diols is used in the production of polyurethane elastomers.

The same reaction, but with diamines, gives poly(urethaneurea) elastomers. With aliphatic amines (strong nucleophiles), this reaction is too fast to allow satisfactory mixing and a sufficiently long pot life. For this reason, less reactive aromatic diamines are used as chain extenders, in particular sterically hindered diamines or diamines whose nucleophilicity is weakened by electron-withdrawing groups.

Chain extension with diamines has advantages. For example, this curing process occurs rapidly and without additional heating; short production cycles are therefore possible. Usually, the NCO/NH_2 reaction ratio is about 1 : 1. Symmetrical diamines with deactivating substituents are used for elastomer synthesis, and alkyl-substituted toluenediamines, such as diethyltoluenediamine, are usually employed for reactions with NCO prepolymers in the RIM process.

If this reaction is carried out in polar organic solvents, practically any diamine can be used, even especially reactive aliphatic ones such as ethylenediamine.

The NCO/H_2O reaction (chemical blowing process) is a very important process for the production of foams. This chemical blowing process can be supplemented by physical blowing with low-boiling liquids as blowing agents, such as trichlorofluoromethane, which can be used to reduce the foam density further.

Organometallic compounds such as organotin compounds, in combination with tertiary amines, have a synergistic effect in the catalysis of the isocyanate – water reaction (Table 4) [120].

Linear or slightly branched polyols with a relatively high molecular mass (2000 – 8000) yield flexible foams. Combinations of these polyols with low molecular mass glycols or amines as chain extenders afford semiflexible foams. Highly branched polyols with a relatively low molecular mass (< 1000) yield rigid foams.

Table 4. Effects of catalysts on relative reactivities of phenyl isocyanate with active hydrogen compounds in dioxane at 70 °C

Catalyst,	Relative reactivity with		
10 mol %	*n*-Butanol	Water	Diphenylurea
None	1.0	1.1	2.2
N-Methylmorpholine	40	25	10
Triethylamine	80	47	4
Tetramethyl-1,3-butanediamine	260	100	12
Triethylenediamine	1.20	380	90
Tributyltin acetate	80	14	8
Dibutyltin diacetate	600	100	12

Polyurea foam materials are also prepared from diisocyanates with different structures by reaction with water. For flexible foams, linear or slightly branched prepolymers are used; more highly branched prepolymers produce rigid polyurea foams.

Flexible foams are prepared from diisocyanates, polyfunctional polyols, blowing agents, catalysts, and surfactants. Although various diisocyanates have been used for flexible foams, toluene-2,4-diisocyanate (TDI) is preferred. Modifiers, fillers, and plasticizers are used to confer special properties. The flexibility of these foams depends on the molecular mass of the polyesters and polyethers used. The ether group imparts flexibility, which, in turn, promotes softness, low melting point, low glass transition temperature, and elasticity. Surfactants promote intimate mixing of the components, regulate and control cell size, and impart stability. Many types are used, such as organic nonionic or ionic surfactants and silicones.

The properties of flexible foams also depend on the processing conditions (mixer speed, air-injection rate, etc.). Polyester-based flexible foams have higher tensile strength and elongation-at-break than polyether foams.

Flexible foams are characterized by reversible deformability and open-cell structure that is associated with air permeability. They have many applications, for example, mattress manufacture, automobiles, and aircraft construction.

Semiflexible foams are used almost exclusively as moldings and are 90 % open-celled. They have lower elasticity and good damping properties. In consequence, they are used as protective cushioning for control panels and consoles and for door and pillar paneling.

Rigid foams are prepared similarly to flexible foams but with different starting materials. In rigid foams, groups that restrict chain rotation, particularly aromatic rings, confer stiffness, which increases the melting point and hardness, and reduces elasticity.

Polyether resins used for rigid foams have lower molecular mass (300 – 1000) than those for flexible foams (3000 – 5000). Polyethers

with aliphatic/aromatic structure, prepared from aromatic diamines and propylene oxide, contribute to the stiffness of rigid poly(urethaneurea) foams.

The production of rigid poly(urethaneurea) foams from hydroxy-terminated resins and isocyanates requires auxiliaries such as blowing agents, catalysts, cell-size regulators, flame retardants, surfactants, and cross-linking agents. As with flexible foams, the reaction between diisocyanates and water generates CO_2, which serves as blowing agent. A halogenated hydrocarbon, such as trichlorofluoromethane, may also be employed, because this inert liquid with *bp* 23.8 °C is quickly volatilized by heating. The gas bubbles expand the foam and remain in the closed cells of the final product. In addition, CCl_3F has a low thermal conductivity and is nonflammable.

The density of rigid foams depends on the amount of gas trapped in the cells. A commercial rigid foam that contains 3 % solid polymer and 97 % gas has a density of about 16 kg/m^3. These foams are manufactured in such a way as to minimize convection currents [121]. Rigid foams are predominantly of the closed-cell type. For special uses, open-cell types are also produced.

Mechanical properties depend on the composition used in the formulation and the plastic nature of the foam at high temperature. Rigid poly(urethaneurea) foams provide excellent thermal insulation, especially when blown with fluorocarbons; high strength combined with light weight; heat resistance; and adhesion to wood, glass, ceramics, and fibers. The rigid foams can be used between − 200 and + 130 °C, and for short periods they can tolerate + 250 °C. As cross-linked plastics, the rigid foams are largely stable to chemicals, such as dilute acids and alkalis. The chief uses of rigid foams are in the heat and cold insulation field. They are used for insulation of refrigerators, including industrial refrigerators, freezers, and hot water accumulators, and as insulation for industrial tanks, containers, etc.

Polyurea foams are prepared by the reaction of diisocyanates and water; the mechanism is similar to that involved in the preparation of poly (urethaneurea) foams. In this reaction, tertiary amines are used as catalysts. Cu(II) and Zn(II) salts and tertiary amines exhibit a synergistic effect in the catalysis of the MDI – water reaction, which gives polyurea foams with satisfactory properties [122]. In these formulations, when *N*,*N*′-dimethylaminoethanol is used as catalyst, better results are obtained with copper nitrate as cocatalyst than with zinc nitrate. Flexible polyurea foams are used for cushions and in the automotive industry, where they provide light weight, high strength, and ease of fabrication. Rigid polyurea foams are used for refrigerators and in constructions.

8.2. Moldings

The production of polyurethanes, poly(urethaneurea)s, and polyureas by reaction injection molding (RIM) is now a well-established process. It offers several advantages for high-volume production of large parts: low pressure (< 343 kPa), low temperatures (54 – 60 °C) and use of reactive liquid intermediates [123]. Since the urethane polymerization process is highly exothermic, minimal heat input is required to maintain tooling temperature during production. With polyols, isocyanates, and extenders, different polymers can be formulated with a wide range of properties, from a flexible elastomer to a rigid plastic. The final product can be solid, microcellular, or foam-modified with a variety of fillers. Glass fiber reinforced RIM (RRIM) provides dimensional stability and high impact strength [124].

Poly(urethaneurea) and polyurea elastomers represent new classes of commercial RIM elastomers. They are obtained from diisocyanates and macrodiols or macrodiamines with hindered aromatic diamines as extenders. Diethyltoluenediamine (DETDA) is used in large quantities as an extender for these elastomers which have high thermostability [125]. Because of the high rate of urea formation, aliphatic diamine extenders have found limited application in RIM.

Poly(urethaneurea) and polyurea elastomers have many practical applications; the most important is in the automotive industry. To reduce the weight of automobiles, high-modulus RIM and RRIM materials suitable for external body panels have been developed from these elastomers. In addition, these elastomers are corrosion- and impact-resistant.

Because of their mechanical and thermal properties, these rigid foams are especially suitable for structural applications and can compete with wood, glass fiber reinforced plastics, and other materials.

High-modulus poly(urethaneurea) RIM elastomers are prepared from a prepolymer of MDI and diamine, using a system termed Bayflex 110 [126]. Some properties of Bayflex 110 follow:

Density	1042 kg/m^3
Flexural modulus	
at – 30 °C	829 MPa
at 20 °C	359 MPa
at 65 °C	241 MPa
Tear strength	105 kN/m
Tensile strength	26.2 MPa
Elongation	275 %

These RIM elastomers, manufactured by Mobay Chemicals, have superior physical properties and can be released from the mold after 15 s with excellent green strength.

Polyurea RIM elastomers with high modulus can be prepared from a polyamine (Jeffamine D-2000), polyisocyanate, and an amine-terminated chain extender in an Accuratio V-R100 RIM machine, and released after 1 min. The resulting elastomer is cured at 121 °C for 1 h; properties are given below:

Tensile strength	23 – 28 MPa
Elongation	280 – 360 %
Tear strength	65 – 68 kN/m
Flexural modulus	
at 25 °C	148.2 – 148.9 MPa
at – 29 °C	526 – 599 MPa
Heat sag	6.8 – 11.5 mm

The molding behavior of the RIM polyurethane depends on the catalyst [127]. The catalyst used for the isocyanate – water reaction can affect the physical properties of the final product. Because of yellowing under the influence of UV light, the moldings must be coated with a paint of high opacity, unless they are colored black or dark brown in the solid. In the photodegradation of MDI-based poly(urethaneurea) elastomers, photo-Fries products have been observed by UV and IR spectroscopy [128].

Polyols in polyurethane and poly(urethaneurea) elastomers increase the hygroscopicity and affect the physical properties. These elastomers are less stable at elevated temperature than polyurea elastomers. Polyisocyanates react slowly with polyols, which prevents automation of the process.

Advances in RIM technology include the development of new polyurea systems for the production of automobile body panels. These catalyst-free systems are based on amine-terminated polyesters. In automobile body panels, polyurea RIM materials offer greater impact resistance at equivalent glass-flake reinforcement; improvement in thermal stability for less distortion during paint cure cycles; and lower water absorption for better environmental resistance. These polyureas are usually prepared by the reaction of an amine – MDI-based isocyanate with an amine-terminated polyether (instead of the standard hydroxy-terminated polyether) and an aromatic diamine as chain extender.

Polyurea RIM elastomers present the following advantages:

- The autocatalytic reaction of isocyanate with amine is faster than the isocyanate – water reaction and results in high modulus polymers for automotive applications
- Catalysts are not necessary, and the process can be automated
- Decomposition and yellowing of the final product do not occur
- The higher thermostability extends their practical utility

Table 5 shows the development of RIM technology for polyurethane, poly(urethaneurea), and polyurea [129]. Texaco produces a polyether with amino end groups and a molecular mass of ca. 4000 (Jeffamine), which can be used to replace the polyols in polyurethanes and poly(urethaneurea)s. Mobay Chemicals investigated and established the optimum conditions for poly(urethaneurea) systems (Bayflex 110) and polyurea systems (Bayflex 150). Dow Chemicals investigated Spectrim HT systems; ICI developed the polyurethane Rubicon; and Admiral Equipment investigated machines with a high degree of automation adapted for a very fast RIM process.

The PHD (Polyharnstoff Dispersion) polyols constitute an important class of poly

Table 5. Development of polyurethane, poly(urethaneurea) and polyurea RIM elastomers

Parameter	Polyurethanes (1974 – 1975)	Poly(urethaneurea)s (1980 – 1984)	Polyureas (1985)	
			at 20 °C	at 70 – 75 °C
Productivity, kg/s	2.3 – 3.2	3.2 – 4.5	5.4 – 6.8	10.9 – 13.6
Cream time, s	4 – 8	2.5 – 3	2 – 2.5	1 – 1.5
Total production cycle*, s	180 – 420	180	60 – 70	60

* Rise time.

(urethaneurea)s with applications such as RIM elastomers, which were first prepared at Bayer by a polyaddition reaction in situ from diisocyanates and diamines in a polyol medium [130].

8.3. Fibers

Polyureas can be used for fibers because they have good physical and mechanical properties, melting points over 200 °C, low specific gravity, high stability toward acids and alkalis, and excellent dyeability. For example, polynonamethyleneurea has a melting point of 237 °C and a softening point of about 205 – 210 °C, which are suitable properties for fibers.

Polyureas with fiber-forming properties are also obtained by the reaction of $H_2N(CH_2)_nNH_2$ and $O[(CH_2)_4NCO]_2$. For $n = 4$, the resulting polyurea melts at 223 – 225 °C and is suitable for fibers [131].

A copolymer polyester – polycarbonate – polyurea is suitable for spandex fibers with good resistance to environmental degradation [132].

In an interesting continous solventless process, elastomeric filaments and fibers with a poly(urethaneurea) structure have been prepared by spinning in the gas phase from the corresponding monomers [133].

The addition of a polyurea to polyoxymethylene gives heat-stable transparent fibers with good dye affinity [134].

A polyester – cotton blend with improved luster and washfastness was prepared by impregnating the fabric with a diamine and then with a diisocyanate; calendering the fabric formed the polyurea in situ [135].

8.4. Films and Membranes

An interesting application of polyureas is for new nonlinear optical materials prepared as thin films from aromatic polyureas. For example, such thin films were prepared by simultaneous deposition of 4,4′-diaminodiphenylmethane and MDI. Investigations suggest that the poling process of polymerization of oligomers takes place at about 116 °C under a high electric field to give polar urea bonds with a large residual polarization. This polarization determines the pyroelectric and piezoelectric activities after poling treatment [136].

Similar results have been obtained for polyureas prepared from α,α'-dianilino-*p*-xylene and MDI, whose large second-order optical nonlinearity coupled with their unique optical transparency in the UV region make them potentially useful materials for nonlinear optics [137].

Microporous films for artificial leather can be obtained from poly(urethaneurea)s, provided these materials have adequate mechanical properties and good permeability to water [138]. Large quantities of these polymers are used for artificial leather.

Poly(urethaneurea) membranes with high H_2S/CH_4 selectivity have been obtained [139].

Ultrathin polyurea membranes are employed for water desalination by reverse osmosis. The urea group in polyureas is hydrophilic and resistant to chemicals and organic solvents; thus, these polymers are suitable for ultrafiltration applications [140].

Polyurea films are useful as flexible materials impermeable to air and other gases and for construction of inflatable boats, balloons, and similar applications [141].

Polyisocyanates with the general formula $R(CH_2)_y(NCO)_x$, in which R = alkyl, $y = 0$ or 1, and $x = 2 - 4$, react with polyamines; the resulting polyurea films have good adhesion to steel and aluminum and high resistance to chemicals and solvents [142].

Semipermeable membranes with high salt rejection have been prepared from polyureas [143].

The polyurea films produced by an interfacial polymerization reaction between water and a triisocyanate facilitate the formation of stable emulsions [144].

8.5. Coatings

Coating materials can be made from polyureas or poly(urethaneurea)s in solution or emulsion. A new spraying technology has many practical applications; polymers thus applied show excellent adhesion to a variety of substrates, including sand-blasted or primed steel, aluminum, and concrete. The products include two-component sprayed polyurea elastomers, prepared from amine-terminated polyether resins and polyisocyanates. The polyurea spray elastomers systems require no catalyst and have extremely high reactivity and cure [145]. In other applications, aqueous polyurea dispersions can be used for coatings with improved hardness and solvent resistance [146].

8.6. Biomedical Applications

Several polyurea and poly(urethaneurea) materials exhibit blood compatibility and have found applications in medical equipment and artificial organs [147]. The polymer membranes in pneumatic blood pumps [148] should have high tensile strength, low permanent deformation, low hydrolyzability, and high purity.

The hydrolytic stability of poly(urethaneurea)s in extracellular solutions was studied. After 50 d, failure was observed. After 120 d, resistance decreased by 15 – 20 % due to hydrolytic degradation of the polymers. The rate of hydrolysis was higher in extracellular solutions than in water [149]. Poly(esterurethaneurea)s are not suitable for medical applications because of their hydrolytic instability caused by the ester group.

Cross-linkable polyureas have been prepared for contact lenses [150].

8.7. Other Applications

Polyureas are used as thickeners for lubricating oils; the resulting lubricating greases have long lifetime at high temperatures, high oxidation resistance, good corrosion protection, high structural stability, and good low-temperature properties [151].

Polyureas and poly(urethaneurea)s can be used for the microcapsulation of herbicides, inks, colorants, medicines, and other products [153], [153].

Polyureas with carboxylic or sulfonic groups are good ion exchangers [154].

Polyureas are used for the removal of oils and bitumen from wastewater by filtration [155].

Petroleum production from oil wells is increased by injection into the borehole of a polyamine followed by a polyisocyanate. These react in situ and form polyureas that contribute to the consolidation of the oil sand and prevent clay swelling [156].

Trimellitic anhydride, polyisocyanates, and polyamines give electric insulator compositions for Cu wire with excellent flexibility and resistance to heat, abrasion, solvents, and thermal shock [157].

9. Safety and Environmental Aspects

Due to the wide range of applications of polyureas, copolyureas, and especially poly(urethaneurea)s, millions of people come into contact with them.

Many years' experience in handling the raw and auxiliary materials for these polymers has shown that these products can be handled safely. Air extraction systems must be present at all workplaces where TDI is processed at room temperature or MDI at temperatures above 40 °C. Aminopolyethers are moderately irritating to the eyes and skin; hence, contact with them should be avoided. The same applies to tertiary amines used as catalysts.

Since the carbon dioxide formed in the reaction of water with isocyanates is a natural constituent of air, it presents no problem. The other blowing agents are discharged into the outside air.

Wastes for which no utilization is possible can be disposed of in incineration plants. Granulated RIM wastes can be molded by the flow molding process at high pressure and high temperature to give new moldings. Fine-ground wastes can be used as fillers in production.

The glycolysis of reinforced reaction injection moldings (RRIM) of these polymers with diethylene glycol or dipropylene glycol at high temperatures can be used for the recovery of polyols and aromatic polyamines as suitable products for new RIM [158].

Organic isocyanates can be prepared by thermal decomposition of polyureas at 220 °C [114]. Another route is to utilize the energy by incineration of these polymers, but the calorific yield is small in comparison with other polymers, for example, polyethylene.

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Polyurethanes

ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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1. Introduction

Polyurethane (PUR) is the collective name for an extensive group of polymers with very different compositions and correspondingly varied property profiles. All PURs are built on a common principle: they are produced by the polyaddition process [1, 2] of (poly)isocyanates typically with (poly)alcohols. The characteristic chain link is the urethane group. In most cases two or more closely positioned urethane groups link poly(alkylene ether) and/or polyester sequences with molecular masses between ca. 200 and 6000 g/mol. Thus, the urethane group usually is only present to a minor extent.

PURs also include polymers produced from polyisocyanates that have urea, isocyanurate, or carbodiimide groups as their characteristic structural unit. As a result of the increasing importance of di- and polyamines and water as reactants, most of the industrially produced PURs contain urea groups (including the isocyanurates as cyclic ureas) as their main property-determining structural units.

A PUR is usually understood to be the fully reacted finished product (e.g., foams and coatings). These products are free from monomeric isocyanates, and unconsumed isocyanate groups, which may be present in small amounts, are bound to the PUR matrix. In adhesives and paints, the isocyanate-containing precursors are often called "PUR adhesive," "PUR hardener," or "PUR paint" to indicate the field of application of the end product produced from them.

The diisocyanate polyaddition process for synthesizing PURs is characterized by the following statements:

1. A large number of different reactants (monomers and oligomers) are available.
2. It is an exothermic reaction that can even take place at room temperature. No byproducts need be separated.
3. The reaction rate can be controlled over a wide range by catalysts, and in some cases a specific reaction can be accelerated by careful choice of the catalyst (e.g., tin compounds catalyze the urethane reaction, tertiary amines catalyze the isocyanate-water reaction; see Section 7.1.1).
4. Intermediates (prepolymers) with reactive end groups can be produced.

5. The stoichiometry influences the molecular mass (see Section 5.2.2).
6. Production and composition can be adapted to various process techniques and extremely diverse product requirements.
7. A large number of end products can be made.

Besides their unique properties, one of the main advantages of PURs is that all types of articles (foams, elastomers, thermosets) can be produced starting from liquid reactive components. This has led to their great industrial importance (see Section 5.2.1 and Chap. 15).

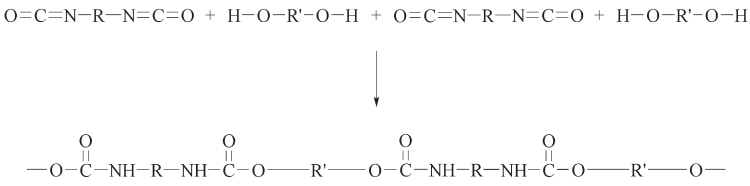
PUR products include highly elastic foams (mattresses, cushions, car seats), rigid foams (insulation materials); rigid and flexible moldings with compact skins (window frames, housings, skis, damping units such as car shock absorbers, front- and rear-end body parts, steering wheels, and shoe soles); engineering moldings with a high hardness and elasticity, ski boots, films, hoses, blow-molded parts, noise shields for trucks, seals for stoneware pipes, roller coatings, sealants, grouting compounds, surfacings for sport and play areas, off-road tires, windsurfing equipment, hydrocyclones, fenders, printing rollers, cable sheathing, catheters, high-quality paints, corrosion protection for steel-reinforced concrete, adhesives, textile coatings, high-gloss paper coatings, leather finishes, poromerics, glass fiber sizes, and wool finishing agents. The number and range of applications are constantly growing. The production, properties, technology, and use of PURs are reviewed in [3–13].

2. Basic Reactions [3, 4, 8]

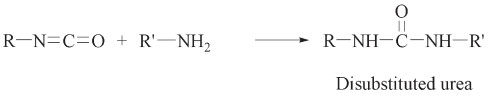
The addition reaction of an alcohol to an isocyanate to give an urethane (carbamate) has been known since 1849 (WURTZ):



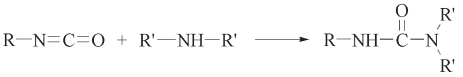
The extension of this reaction to di- and polyfunctional isocyanates and hydroxy compounds by OTTO BAYER in 1937 led to the principle of the polyaddition reaction resulting in the formation of linear, branched, or cross-linked polymers:



In addition to alcohols, the most important group of NCO-reactive compounds are the amines, which lead to the formation of ureas:

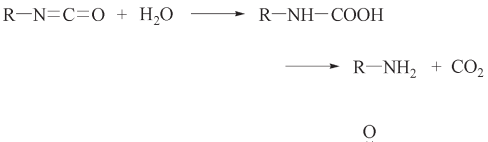


Disubstituted urea



Trisubstituted urea

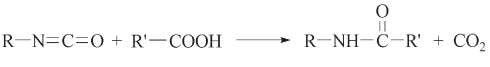
Ureas are also formed by the reaction of water with isocyanates, in which the carbamic acid formed in the first step of the reaction spontaneously decomposes to an amine with elimination of carbon dioxide. This amine then reacts with excess isocyanate to yield symmetrically substituted ureas:



Disubstituted urea

This reaction is the basic reaction leading to PUR foams, especially flexible foams.

Another process which leads to the formation of carbon dioxide is the reaction of isocyanates with organic acids. The reaction product formed in this way is an amide:

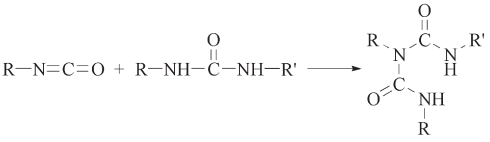


Amide

As the urethanes and ureas formed in the reaction mentioned above still contain reactive hydrogen atoms they can react with excess isocyanate to form allophanates and biurets, respectively.



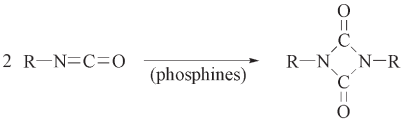
Allophanate



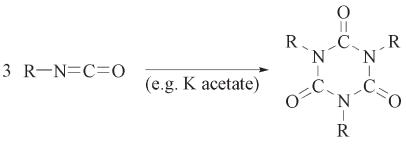
Biuret

These cross-linking reactions are important in the production of PURs and play a key role in the development of polymeric materials with tailor-made properties.

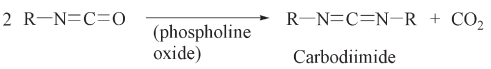
Apart from these polyaddition reactions, the following reactions involving two or more isocyanate groups are also important in PUR chemistry (catalyst in parentheses):



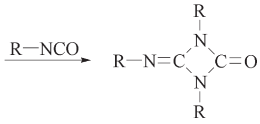
Uretdione



Isocyanurate

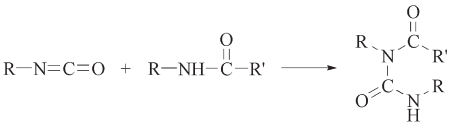


Carbodiimide

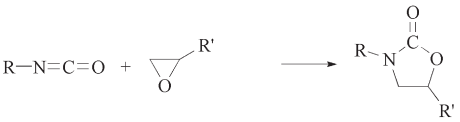


Uretonimine

Due to the high reactivity of the isocyanate group some further reactions are well known but only of minor importance in the production of PURs. Examples are the reactions of amides and epoxides with isocyanates:



Acylurea



Oxazolidone

The tremendous number of different possible reactions not only play a role in the production of the final PUR polymers but also in the production of modified polyisocyanates (see Section 3.1) used as raw materials for PURs.

Usually the reactions described above proceed in parallel. For example, the production of foams is based on the combination of the NCO/ROH reaction leading to urethanes and the NCO/H_2O reaction leading to ureas and causing foaming of the reaction mixture by the evolution of carbon dioxide.

Other methods for preparing PURs which are usually not used in industrial applications are the polycondensation of bis-chloroformate esters and diamines, and the reaction of polyamines with carbonylbiscaprolactam (CBC) or polycyclocarbonates.

Thermally stable *N*-alkyl PURs are formed by the reaction of isocyanates with secondary diamines (e.g., piperazine). Since these products are unable to form hydrogen bonds, their properties are different from those of conventional PURs.

3. Starting Materials [3]

The range of PUR starting materials developed since the early 1950s is based on light petroleum fractions (ethylene, propene, naphtha). To a minor part renewable raw materials (natural products such as sugar, castor oil, etc.) are used [14–16]. The suitability of natural fatty acid esters [17, 18], lignin [19, 20], polysaccharides [19, 21, 22], and chitin as raw materials has been examined for special applications.

3.1. Polyisocyanates

See also → Isocyanates, Organic

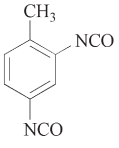
More than 90 % of PURs are produced from aromatic polyisocyanates. Compared to aliphatic and cycloaliphatic polyisocyanates, the aromatic polyisocyanates show higher reactivities towards hydroxyl compounds and give PURs with better mechanical properties.

The aliphatic and cycloaliphatic polyisocyanates are used to obtain PURs that do not become discolored on exposure to light or heat. This is particularly important for coating materials (paints, varnishes, textile coatings, and glass-fiber sizes). The stability of aliphatic or cycloaliphatic polyisocyanates PURs can be improved by incorporating urea, biuret, or hydrazide groups into the polymer [23–25].

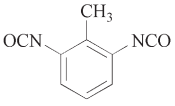
3.1.1. Aromatic Polyisocyanates

Aromatic polyisocyanates are primarily used for a wide variety of PUR foamed plastics, elastomers, thermosets, and adhesives.

2,4-Toluenediisocyanate [584-84-9] (TDI), 2,4-diisocyanatotoluene (**1a**), *bp* 121 °C (1.33 kPa), *mp* 21.8 °C.



1a



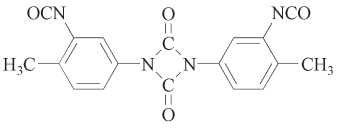
1b

Usually the pure 2,4 isomer or mixtures of 2,4-TDI (**1a**) with 2,6-TDI (**2b**) are used for industrial applications:

TDI 80 (80 % 2,4-TDI, 20 % 2,6-TDI), *bp* 121 °C (1.33 kPa) *mp* 13.5 °C, vapor pressure (25 °C) 3 Pa, equilibrium vapor concentration 30 ppm, MAK value 0.005 ppm (according to TRGS 900).

TDI 65 (65 % 2,4-, 35 % 2,6-), *bp* 121 °C (1.33 kPa), *mp* 5 °C.

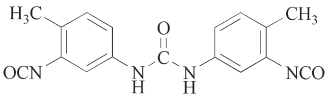
1,3-Bis(3-isocyanato-4-methylphenyl)-2,4-dioxo-1,3-diazetidine [26747-90-0] (**2**) (uretdione of 2,4-TDI, TDI-dimer; Desmodur TT, Bayer MaterialScience), *mp* 153 °C.



2

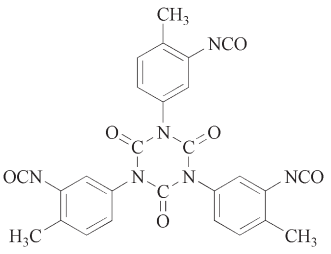
Uretdiones react as blocked isocyanates: the four-membered ring opens at elevated temperature to release the NCO groups.

"TDI-urea" [5206-52-0] (**3**) (TDIH, Bayer MaterialScience) *mp* 180–184 °C [26, 27]



3

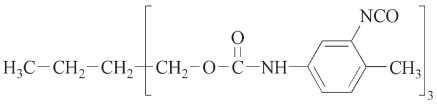
1,3,5-Tris(3-isocyanato-4-methylphenyl)-2,4,6-trioxohexahydro-1,3,5-triazine [20649-21-6] (**4**) (TDI-trimer), ca. 51 % in butyl acetate (Desmodur IL, Bayer MaterialScience): NCO content ca. 8 %, viscosity (20 °C) 2000 ± 500 mPa · s.



4 (idealized)

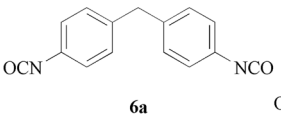
Adduct of TDI and trimethylolpropane [21092-47-7] (**5**), 75 % solution in ethyl

acetate (Desmodur L, Bayer MaterialScience): NCO content 13 ± 0.5 %, viscosity (20 °C) 2000 ± 500 mPa · s.

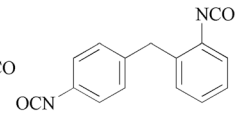


5

Monomeric MDI, 4,4′-Methylene diphenyl diisocyanate [101-68-8], 4,4′-methylene-bis (phenyl isocyanate), bis(4-isocyanatophenyl) methane, 4,4′-diisocyanatodiphenylmethane (**6a**), Monomer-MDI, *bp* 208 °C (1 kPa), *mp* 39.5 °C, vapor pressure (25 °C) <1 mPa, equilibrium vapor concentration 0.009 ppm, MAK value 0.005 ppm (according to TRGS 900)



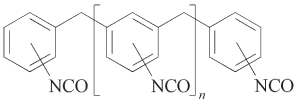
6a



6b

60 % 2,4′-MDI (**6a**), 40 % 4,4′-MDI (**6b**) (Desmodur 1806, Bayer MaterialScience), *mp* 16–17 °C.

Polymeric MDIs (PMDIs) [9016-87-9] (**7**) typically contain 30–70 % dinuclear components (n = 0), 14–40 % trinuclear components (n = 1), and 15–30 % higher nuclear components (n > 1), viscosity 50–20000 mPa · s, NCO content 25–33 %.

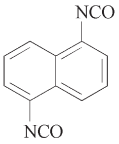


7

Urethanized 4,4′-MDI [60440-22-4] (Desmodur PF, Bayer MaterialScience) *mp* 10–15 °C.

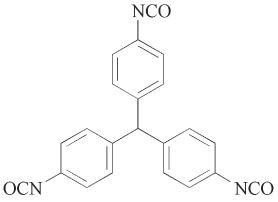
Carbodiimidized 4,4′-MDI [37353-55-2], *mp* 10–15 °C (Desmodur CD, Bayer Material Science; for carbodiimidization, see Chap. 2).

1,5-Naphthalene diisocyanate (NDI) [3173-72-6], 1,5-diisocyanatonaphthalene (**8**), *mp* 127 °C (Desmodur 15, Bayer MaterialScience).



8

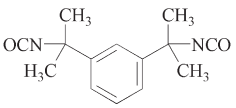
Tris(4-isocyanatophenyl)methane [2422-91-5] (**9**), 20 % solution in ethyl acetate, NCO content 7 ± 0.1 %, viscosity (20 °C) ca. 1 mPa · s.



9

Aromatic isocyanates with the NCO group in the benzylic position behave similarly to the (cyclo-)aliphatic isocyanates with regard to reactivity and light stability:

1,3-Bis(1-isocyanato-1-methylethyl)benzene [2778-42-9] (**10**), m-tetramethylxylylene diisocyanate (TMXDI, American Cyanamid) [28, 29], *mp*–10 °C, *bp* 150 °C (49.5 kPa).

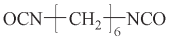


10

3.1.2. Aliphatic Polyisocyanates

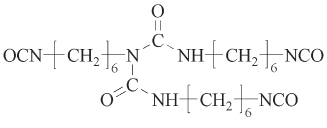
Aliphatic and cycloaliphatic polyisocyanates are used to obtain light-stable PURs. This is particularly important for coating materials (paints, varnishes, textile coatings, and glass-fiber sizes).

Hexamethylene diisocyanate (HDI) [822-06-0], 1,6-diisocyanatohexane (**11**) (Desmodur H, Bayer MaterialScience), *bp* 127 °C (1.33 kPa).



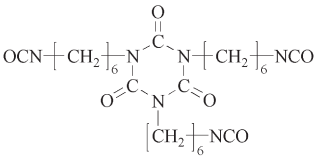
11

Biuret based on HDI, *N*-isocyanatohexylaminocarbonyl-*N*, *N*′-bis-(isocyanatohexyl) urea [28182-81-2] (**12**), biuret triisocyanate (technical mixture), ca. 75 % solution in methoxypropyl acetate/xylene (1/1) (Desmodur N75, Bayer MaterialScience), NCO content 16–17 %, viscosity (20 °C) 250 ± 100 mPa · s.



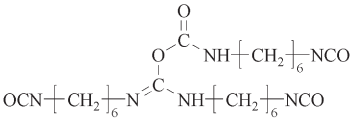
12 (idealized)

Trimer based on HDI, 2,4,6-trioxo-1,3,5-tris (6-isocyanatohexyl)hexahydro-1,3,5-triazine [28182-81-2] (**13**), trimeric hexane diisocyanate, ca. 90 % solution in butyl acetate (Desmodur N3390, Bayer MaterialScience), viscosity (25 °C) 2500 ± 500 mPa · s, NCO content 21.5 %, monomer content < 0.5 %.



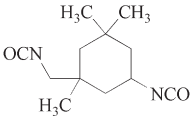
13 (idealized)

Unsymmetrical trimer based on HDI, 2,4-dioxo-3,5-bis(6-isocyanatohexyl)-6-(6-isocyanatohexyl)hexahydro-1-oxa-3,5-diazine [28182-81-2] (**14**), unsymmetrical trimeric hexane diisocyanate [30] (Desmodur XP2410, Bayer MaterialScience), viscosity (23 °C) ca. 700 mPa · s, NCO content ca. 24 %, monomer content <0.3 %.



14 (idealized)

Isophorone diisocyanate (IPDI) [4098-71-9], 3,5,5,-trimethyl-1-isocyanato-3-isocyanatomethylcyclohexane (**15**) (IPDI, VEBA), *bp* 158 °C (1.33 kPa), 70 % cis, 30 % trans [31, 32]. For reactivity, see [33].

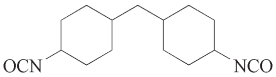


15

Uretdione of IPDI (Crelan TP.LS 2147) [34], *mp* 105–115 °C, ca. 15.4 % NCO.

Trimer based on IPDI, 2,4,6-trioxo-1,3,5-tris (5-isocyanato-1,3,3-trimethylcyclohexylmethyl) hexahydro-1,3,5-triazine [53880-05-0], ca. 70 % solution in xylene/methoxypropyl acetate (1/1) (Desmodur Z4470, Bayer MaterialScience), softening range 90–110 °C, NCO content 17 %, monomer content < 0.5 %.

1,1-Methylenebis(4-isocyanatocyclohexane), H12-MDI [5124-30-1], 4,4′-diisocyanatodicyclohexylmethane (**16**), trans,trans-4,4′-diisocyanatodicyclohexylmethane, *mp* 83 °C [35]. Technical isomer mixture (24 % *cis*, *cis*, 43 % *cis*, *trans*, 20 % *trans*, *trans*, 13 % 2,4 and 2,2′ isomers): *mp* 15 °C (Desmodur W, Bayer MaterialScience)



16

3.1.3. Blocked Isocyanates [36–39]

Polyisocyanates or prepolymers containing NCO groups are not stable on storage in the presence of atmospheric humidity or compounds that contain reactive hydrogen atoms.

Reaction of the NCO groups with certain organic compounds that have acidic hydrogen atoms such as phenol, cresol, nonylphenol, caprolactam, and methyl ethyl ketoxime leads to “blocked isocyanates,” which are stable (storable) at room temperature and labile at elevated

temperatures. These adducts are inert to polyols at room temperature and can be mixed with them in one-pack systems. At higher temperatures, usually at 140–180 °C the blocking agent is released, and the free isocyanate reacts as usual with the NCO-reactive components. Due to their thermal lability, uretdiones and uretonimines also behave like blocked isocyanates.

For the physical blocking of solid polyisocyanates by a diffusion barrier layer, see Section 5.4.

3.2. Polyols

Polyols are the largest group of PUR starting materials. The wide range of properties of the resulting PURs is largely determined by the chemical composition and molecular mass of the polyols. The largest group of polyols used for PURs is the group of polyethers. The volume of polyesters is much smaller, but they nevertheless have become more important, especially for flame-retarded rigid foams (see Section 7.3.4).

3.2.1. Polyether Polyols

See also → Polyoxyalkylenes

Polyethers (polyether polyols) with terminal hydroxyl groups are produced by addition of cyclic ethers, especially propylene oxide (PO, $R'=CH_3$) and ethylene oxide (EO, $R'=H$), to polyfunctional "starter" molecules.



Usually, the EO and PO units can be structured as homo blocks, produced by batchwise addition of EO and PO to the starter molecule, or as mixed blocks by feeding an EO/PO mixture to the starter. The combination PO block-mixed block-EO block is common.

The structure determines the reactivity, the hydrophobic-hydrophilic properties, the surface activity, and consequently the foaming behavior of the polyethers. Polyols with terminal EO units contain primary hydroxyl groups and consequently have a higher reactivity than polyols with the secondary hydroxyl groups of terminating PO units.

The following starters are typically used industrially: ethylene glycol (EG), 1,2-propanediol (PG), bisphenol A (BPA), trimethylolpropane (TMP), glycerol (GLY), pentaerythritol, sorbitol, sucrose, water, ethylenediamine (EDA), and diaminotoluene (TDA). Monofunctional polyethers are usually started with 1-butanol.

Depending on their structure, two groups of polyethers can be distinguished: long-chain polyols, mainly used for flexible foams, and short-chain polyols, mainly used for rigid foams.

The long-chain polyols typically have hydroxyl numbers below 100 mg KOH/g and functionalities of 2 to 3, which corresponds to molecular weights of 2000 g/mol or more. The properties of some long-chain polyols are given in Table 1.

The short chain polyols usually have OH numbers of 200 mg KOH/g or more, functionalities of up to 6, and molecular weights of 1000 g/mol or less (Table 2).

Polyethers produced from trifunctional starters and bifunctional cyclic ethers (e.g., epoxy resins) are highly branched and, to some extent, intramolecularly cross-linked [40]. Special polyethers contain, for example, quaternary ammonium or sulfonate groups [41, 42].

An important special polyether is polytetrahydrofuran [43], which is described in detail elsewhere (→ Polyoxyalkylenes). It is used mainly for the production of high-grade elastomers for the engineering field and is liquid above 40 °C [44, 45].

A newer process, known as the IMPACT process, uses double metal cyanides (DMC) as catalysts for the production of especially long chain polyether polyols [46–48] that show improved properties compared to polyols

Table 1. Properties of long-chain polyether polyols

Starter	Alkylene oxide	Functionality	M_r, g/mol	OH no., mg KOH/g	Viscosity (25°C), mPas
PG	PO/EO	2	4000	28	870
PG	PO	2	2000	56	310
TMP/PG	PO	2.8	3750	42	630
GLY	PO/EO	3	4800	35	860

Table 2. Properties of short-chain polyether polyols

Starter	Alkylene oxide	Functionality	M_r	OH no., mg KOH/g	Viscosity (25°C), mPa s
TMP	PO	3	435	385	600
TMP	PO	3	305	550	1800
EDA	PO	4	350	620	19200
TDA	PO/EO	4	475	470	8000
Sucrose/PG	PO	3,1	385	450	15000

produced by the classical KOH process. During the addition of propylene oxide to the starter molecule, base-catalyzed isomerization of propylene oxide to allylic alcohol, which itself can act as starter molecule, leads to a mono-ol containing a double bond. These side products lower the average functionality of the polyols and reduce, for example, their stability against oxidation. The IMPACT process leads to polyols with extremely low mono-ol contents and therefore a low level of unsaturation and results in polyols with functionalities very close to the theoretical number. The IMPACT polyols have become more and more important, especially in the production of flexible foams.

Products based on polyethers have good low-temperature behavior and usually high hydrolytic stability. The viscosity of the liquid polyethers is relatively low (40–15000 mPa · s). A disadvantage of polyether polyols is that they undergo thermooxidative degradation on exposure to heat and atmospheric oxygen; UV radiation is mainly responsible for light-induced degradation changes. Both antioxidants and UV stabilizers counteract this degradation. In some special applications polyether polyols containing hydrazide or urea groups, both of which have a stabilizing effect, are used to avoid thermooxidative degradation.

Polyether dispersions (two-phase systems with a solid polymer as the disperse phase) are a further group of polyethers. Mainly styrene-acrylonitrile polymers (SAN polyols), polyurea, or poly(hydrazodicarbonamide) polymers (PHD polyols) are used as fillers. The dispersions are milky white, of higher viscosity than the corresponding base polyols, and completely stable to sedimentation. The average particle diameter is ca. 1 μm.

3.2.2. Polyester Polyols

Compared with polyethers, polyesters with terminal hydroxyl groups show outstanding resistance to light and thermal aging. PURs produced from them are therefore primarily used for paints, coating materials, and, due to their thermal stability, for flame-retarded rigid foams. Special types are suitable for high-grade PUR elastomers [49, 50].

Polyesters are produced by polycondensation of di- and trifunctional polyols with dicarboxylic acids or their anhydrides. Polyols commonly used are ethylene glycol, 1,2-propanediol, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol, diethylene glycol, glycerol, and trimethylolpropane. Common dicarboxylic acids or anhydrides are succinic acid, glutaric acid, adipic acid, phthalic anhydride, isophthalic acid, and terephthalic acid.

The hydrolytic stability of a polyester urethane is determined by the constitution of the polyester. Polyesters synthesized from glycols and dicarboxylic acids that each contain at least five carbon atoms have good hydrolytic stability. This is because the increase in hydrophobicity of the polyester segments repels moisture [49, 50]. The best results have been obtained with polyesters derived from 1,6-hexanediol and adipic acid.

Common polyesters based on adipic acid and ethylene glycol or ethylene glycol/1,4-butanediol provide inexpensive PUR elastomers of excellent quality. Their hydrolytic stability is lower than that of the polyesters mentioned above and can be considerably improved by appropriate stabilizers (see Section 3.5).

Polyesters have a wide molecular mass distribution and, compared with polyethers, a high viscosity; many are glassy solids (polyphthalates) or crystalline (polyadipates). Polyesters containing diethylene glycol are ether esters; their viscosities are relatively low and their stability to hydrolysis and UV radiation is moderate. The average molecular mass of polyesters is 500–4000 g/mol. For properties, see Table 3.

The polyesters always contain significant proportions of the monomeric glycol used in

Table 3. Properties of polyester polyols

Acid	Glycol	Functionality	M_r	OH no., mg KOH/g	Viscosity, mPas
Adipic acid	ethylene glycol	2	2000	56	500 – 600 (75°C)
Adipic acid	diethylene glycol/TMP	2.5	2300	60	900 – 1100 (75°C)
Phthalic anhydrid/adipic acid	ethylene glycol	2	1750	64	2200 – 3200 (75°C)
Phthalic anhydrid/adipic acid	diethylene glycol	2	560	200	6300 – 7600 (25°C)
Terephthalic acid	diethylene glycol	2	450	250	2700 – 7700 (25°C)

their synthesis, as well as short-chain oligomers and often nonfunctional cyclic esters. These substances can be removed for a limited time by thin-film distillation, but they are gradually reformed by transesterification.

3.2.3. Polycarbonate Polyols

Aliphatic carbonate esters (→ Polycarbonates) are produced by transesterification of dimethyl carbonate (DMC) or diphenyl carbonate (DPC) with glycols (e.g., 1,6-hexanediol).

Many investigations have been carried out on the production of polycarbonate by copolymerization of alkylene oxides with carbon dioxide [51–55], but this reaction is not used on an industrial scale as yet.

Polyaddition of caprolactone or pivalolactone to low molecular mass diols yields hydroxy-functional polylactones.

As the susceptibility of polyesters to hydrolysis increases with increasing dissociation constant of the acid on which they are based, the polycarbonates are highly stable against hydrolysis. In particular, polyester urethanes based on 1,6-hexanediol polycarbonate show an unmatched resistance to hydrolysis.

3.2.4. Other Polyols

Other oligomers and polymers with functional groups (OH, SH, COOH, NHR) can also be used for PUR synthesis (e.g., polythioethers, polyacetals, polyester amides, alkyd resins, and polysiloxanes).

Hydroxy-functional poly(1,3-butadienes) contain the hydroxyl function mainly in the terminal position as a result of polymerization with hydrogen peroxide. These compounds yield PURs with moderate mechanical properties but extremely high hydrolytic stability and good low-temperature behavior. Bifunctional poly(1,3-butadienes) can also be obtained by anionic polymerization.

Hydroxyl-bearing polyacrylates based on 2-hydroxyethyl acrylate or methacrylate monomers are used in the production of high-quality, two-component paints [56] (see also → Paints and Coatings, 2. Chap. 9.).

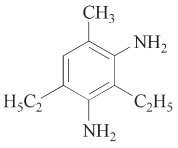
Low molecular mass polyols, in contrast to the higher molecular mass polyols mentioned above (Section 3.2.1), are used as chain extenders. In the production of PUR elastomers they are generally used in the synthesis of the "hard" segment (see Section 4.2). Important representatives are ethylene glycol, 1,4-butanediol, 1,6-hexanediol, and 1,4-bis(hydroxyethoxy)benzene.

Trimethylolpropane or glycerol is added to introduce a defined small degree of branching.

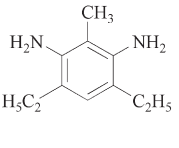
3.3. Diamines and Amino-Terminated Polyethers

Diamines are used as building blocks for PURs that contain urea groups. Due to their high reactivity the polyaddition is very fast even without a catalyst, leading to polymers with considerably improved properties compared with "standard" PURs.

For polyaddition in bulk, sterically hindered diamines (e.g., isomeric diaminodiethylmethylbenzenes **17** [57]) or other aromatic diamines with mono- or dialkyl ring substituents [58–61] are preferred.



17a



17b

These amines are liquid at room temperature and therefore suitable for processing in two-component devices (see Section 6.2).

Less reactive diamines with electron-withdrawing substituents are used for producing elastomers by the prepolymer process (see Section 5.2.2); examples include bis(4-amino-3-chlorophenyl)methane [101-14-4] (MBOCA) and 2-methylpropyl-4-chloro-3,5-diaminobenzoate [32961-44-7] [62–64]. For the toxicological and adverse health effects of MBOCA, see [65].

Amino-terminated polyethers (ATPE) are obtained primarily from the appropriate polyether polyols (see Section 3.2.1) by exchanging the hydroxyl groups with ammonia [66–68] or primary amines [69]. Aminopropoxy end groups are obtained by cyanoethylation of polyols followed by hydrogenation. The high reactivity of the amino groups can be reduced by using their adducts with carbon dioxide (carbonates, carbamates). During the polyaddition reaction the carbon dioxide is released and acts as a blowing agent.

Various processes have been proposed for producing ATPEs with aromatic amine end groups [70]. For example, NCO prepolymers can be hydrolyzed to give the corresponding amino-terminated prepolymers [71]. Other methods include the preparation of N-substituted crotonic acid esters by acetoacetylation of polyols followed by amination [72, 73] and nitrophenylation followed by hydrogenation [74–76].

The adducts of (cyclo-)aliphatic di- and polyamines with ketones are bis- and polyketimines, respectively. They function as capped amines, with which they are in equilibrium in the presence of water (see Section 3.1.3). In the tautomeric enamine form, they also react with NCO groups to form urea and amides. Combinations of ketimines and isocyanates are thus both moisture- and heat-curing [77–79].

Polyether ketimines based on aliphatic polyether amines have a rather low reactivity and therefore a very good processability [80–83].

3.4. Special Building Blocks

Aqueous PUR-ionomer dispersions are synthesized from diols or diamines that contain ionic groups or groups that can be converted to ionic groups by alkylation or neutralization with compounds such as *N*-methyldiethanolamine, 2-(*N*, *N*-diethylaminomethyl)-2-ethyl-1,3-propanediol, and dimethylolpropionic acid, as well as salts of 2-sulfo-1,4-butanediol, *N*-sulfoethylethylenediamine, *N*-carboxyethylethylenediamine, lysine, and glycerol 2-phosphate [84, 85].

Hydroxy-functional polyisobutylene [86, 87], siliconediamines [88–90], and chlorosulfonated polyolefins [91] can be used as oligomer building blocks leading to segmented PUR polymers.

Other special polyols can be obtained by glycolytic degradation of polymer waste [92–94] (see Section 14.3).

3.5. Catalysts and Additives

Catalysts. In order to balance the two main reactions, the isocyanate-water reaction (blowing reaction) and the isocyanate-polyol reaction (gel reaction), various catalysts are used. The reactions of the isocyanate group are extraordinarily sensitive to many different kinds of catalysts:

1. Lewis bases: 1,4-diazabicyclo[2.2.2]octane [280-57-9] (DABCO), triethylamine [121-44-8], dimethylbenzylamine [103-83-3], bis[2-(dimethylamino)ethyl] ether [3033-62-3], 1,1,3,3-tetramethylguanidine [80-70-6], 1,8-diazabicyclo[5.4.0]undec-7-ene [6674-22-2] (DBU), 2,4-bis(dimethylaminomethyl)phenol [5424-54-4]
2. Lewis acids: bis(ethylhexanoyloxy)tin [301-10-0] (tin dioctanoate), bis(dodecanoyloxy) dibutyltin [77-58-7] (dibutyltin dilaurate), dichlorodimethyltin [753-73-1]
3. Insertion catalysts: bis(dodecylthio)dibutyltin, organotin alkoxides, organotin oxides, organotin thiolates, organotin sulfides, 1,3-dicarbonyl compounds

Almost every catalyst has a specific "activity profile" [13, 95–99]. The situation is extraordinarily complex, especially since the urethane group itself exerts a catalytic effect. As hydrogen bonds and the nature of solvents used in the reaction influence the reaction rates, most kinetic studies in solvents are not applicable to solvent-free PUR production [100]. Due to the desire to reduce emanations from PUR foams less volatile or reactive catalysts have been developed [101, 102].

Metal catalysts activate the isocyanate groups by making them more electrophilic,

while bases make the hydroxyl groups more nucleophilic [103].

Alkali metal salts of organic acids and phenols, as well as phenol Mannich bases catalyze not only the urethane reaction but also the trimerization of the isocyanate group. NCO prepolymers trimerize more rapidly than the corresponding diisocyanates because of the presence of urethane groups which act as cocatalysts (see Section 4.4).

Phosphines are special catalysts which dimerize the NCO group; phospholine oxides cause carbodiimidization.

Additives (see also → Plastics, Additives).

Foam Stabilizers. Besides the chemical structure and molecular weight of the polyols and isocyanates, cell size and fraction of open cells can be controlled to a certain extent by surfactants or foam stabilizers [104]. In some cases, foam formation is virtually impossible without these surface-active compounds. The majority of foam stabilizers are polysiloxane-polyether block copolymers [105–108]. Specific types, e.g., for liquid CO_2 as blowing agent [109], for flame-retarded foams [110], or for other specific foam types are available as well [111, 112].

Hydrolysis Stabilizers [113–116]. Monocarbo-Monocarbodiimides, polycarbodiimides, epoxides, cyanates, phenyliminooxazolidines.

Oxidation Stabilizers [113–115], [117–119]. These additives are used in foamed materials, especially in flexible foams, to prevent core scorching. They include sterically hindered phenols, alkylated anilines, phosphites, hydrazides, sulfides, and thioethers.

UV Stabilizers [113–115, 117–119]. Piperi-Piperidines with bulky substituents in the 2,6-positions, benzophenones, benzotriazoles, cyanoacetate ester derivatives, quenchers, Tinuvins (Ciba-Geigy).

Blowing Agents (see also → Foamed Plastics, Section 2.2.). According to the implementation of the Montreal Protocol (and the consecutive amendments) blowing agents with an ozone-depleting potential are no longer used as blowing agents for flexible foam by the member states since 1992. Several alternatives have been developed [120–127].

For flexible foams the predominant technology meanwhile is the addition of liquid or supercritical carbon dioxide (e.g., Novaflex by Hennecke, Cardio by Cannon). Another method is the application of varied ambient pressure, e.g., MegaFoam by Hennecke or VPF by Beamech (see Section 7.1.1.2) and depending on regulations of the local authorities, blowing agents like dichloromethane or acetone may be applied as well.

For rigid foams nowadays usually alkanes, namely, n-pentane, isopentane, and cyclopentane are used (see Section 7.3.1).

Flame Retardants (see also → Plastics, Additives, Chap. 6.). Various classes of chemicals are used to modify the combustion behavior of PUR flexible foams [128]. The selection of the appropriate flame retardant depends on the test that must be passed, as well as the chemistry of the foam (e.g., polyester vs polyether, HR vs. conventional foam). Most common are phosphorus- and/or nitrogen-containing compounds and halogenated phosphates such as tris(2-chloropropyl) phosphate (TCPP). As in the case of catalysts, less volatile or reactive flame-retardants have been developed in order to reduce the emissions of volatile organic compounds (VOCs) from the finished foam. The liquid flame retardants may be combined with solid ones such as melamine and ammonium polyphosphate. Brominated diphenyl ethers, which have been used for some special foam grades or in some regional markets, will be phased out due to concerns regarding their potential for bioaccumulation.

For rigid foams halogenated compounds such as TCPP, polyesters based on tetrabromophthalic acid, and special bromopolyethers are usually used. The use of polyisocyanurate rigid foams (see Section 7.3.4), which exhibit a superior flame behavior compared to PUR rigid foams, has increased. This has led to a reduction in flame retardant consumption.

Aluminum oxide trihydrate, magnesium hydroxide, and expandable graphite are also used as flame-retardants. The first two act by splitting off water vapor and the latter acts by forming protective layers.

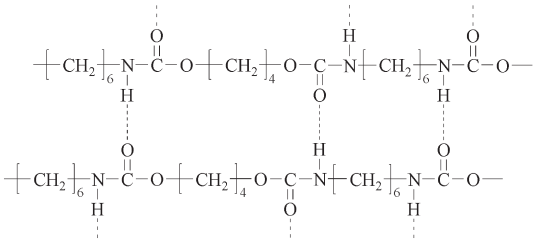


Figure 1. Hydrogen bond interactions between polymer chains of a PUR based on HDI and 1,4-butanediol

4. Structure and Morphology

Depending on their structure, PURs cover a broad range of properties. Besides the chemical composition, the chain length, and cross-linking, the properties are significantly affected by the interactions between the polymer chains (see Fig. 1), that is to say by the supramolecular structure and morphology.

4.1. Polyurethanes Without Segmented Structure

The properties of linear PURs, which are produced by polyaddition of monomeric diisocyanates and short- or long-chain diols, are similar to those of polyamides.

Short-Chain Polyols. The polyaddition of hexamethylene diisocyanate (HDI) and 1,4-butanediol leads to a very tough, crystalline material (mp 180–185 °C), which is used for manufacturing of fibers and bristles. The polyaddition of toluene diisocyanate (TDI) and butanediol or diethylene glycol yields very hard, transparent products with low heat resistance.

Long-Chain Polyols. Linear PURs based on diisocyanates (preferably MDI) and long-chain polyester or polyether diols are soft, rubbery, high molecular mass polymers with only a small proportion of urethane groups. Therefore, these materials are homogeneous (single phase), and the intermolecular physical interactions are mainly determined by the polyester and polyether segments (van der Waals forces [129]).

With increasing stiffness of the polyol chain (e.g., highly crystalline polyesters), and decreasing chain length, the resulting PUR becomes harder and less elastic.

4.2. Polyurethanes with Segmented Structure

To obtain PUR elastomers with superior properties, the polyaddition reaction mixture usually contains three components, namely, a diisocyanate, a long-chain polyether or polyester polyol, and a short-chain diol (chain extender). The resulting block copolymer type PURs are characterized by a segmented structure.

The secondary and tertiary structures, and as a consequence, the morphology of these PURs, depend on the chemical structure and the block length of the different segments. Due to the two- or multi-phase morphology, segmented PURs can exhibit extraordinary high-grade properties.

4.2.1. Hard and Soft Segments [12, 130–135]

The reaction of one equivalent of long-chain diol, one equivalent of short-chain diol, and two equivalents of diisocyanate leads to the idealized structure shown in Figure 2.

The long-chain polyols, which are flexible and are usually tangled (soft segments), alternate along the polymer chain with oligomeric rigid urethane units (hard segments).

Usually the structure of the PUR as well as the structure of the soft segment itself is determined by a Flory distribution [136, 137]. This results in a smaller number of larger hard segments than expected in theory. If polyester polyols are used, the low molecular glycols, which are usually present in considerable amounts, even enhance this effect. Further effects leading to deviations from theory include kinetic effects (if end groups with different reactivity are used) and phase transitions due

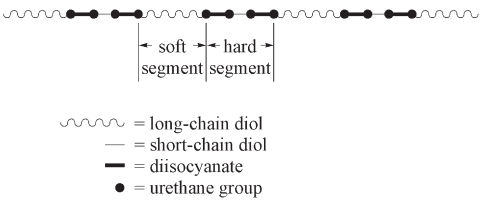


Figure 2. Schematic primary structure of a segmented PUR (idealized)

to temperature changes during the polyaddition reaction.

4.2.2. Segregation and Morphology

On cooling, the initially homogeneous PUR melt converts to a two-phase system. This is due to the incompatibility of the polar low-molecular glycols with the low-polarity polyether or polyester polyols and polyisocyanates. As the reaction progresses, the formation of polar urethane groups at the ends of the long-chain polyols leads to a certain degree of compatibilization. Nevertheless, the low miscibility of the hard and soft segments leads to segregation, which results in covalently bonded microphases in which paracrystalline oligourethane domains appear (tertiary structure, Fig. 3). On further cooling, these can aggregate and grow to form spherulitic microcrystallites (quaternary structure).

The hard segment domains form three-dimensional cross-linking centers of a noncovalent type (physical cross-linking). The formation of a large number of weak hydrogen bonds results in a high bonding strength, but allows shifts and rearrangements under load, where a covalent bond would rupture. As the hard segments are covalently bonded to the soft segments, flowability of the chains is restricted. This gives the segmented PURs their high elasticity. The hard segments are responsible for tensile strength, tear resistance, hardness, permanent elongation, and compression set, while the soft segments determine the elastic expansion and the glass transition temperature.

The interaction between different hard segment domains is mainly determined by the symmetry of the isocyanates and the nature of the chain extenders, which influence the possibility to form highly organized structures.

Most commercially produced PURs contain urea groups, which often determine the property profile more strongly than the comparatively small content of urethane groups. Since the urea group is more polar than the urethane group, the segregation of hard and soft segments is strengthened, the melting range of the hard-segment domains is higher, and the intermolecular (interchain) interaction stronger [138]. Due to these strong interactions, a single urea group

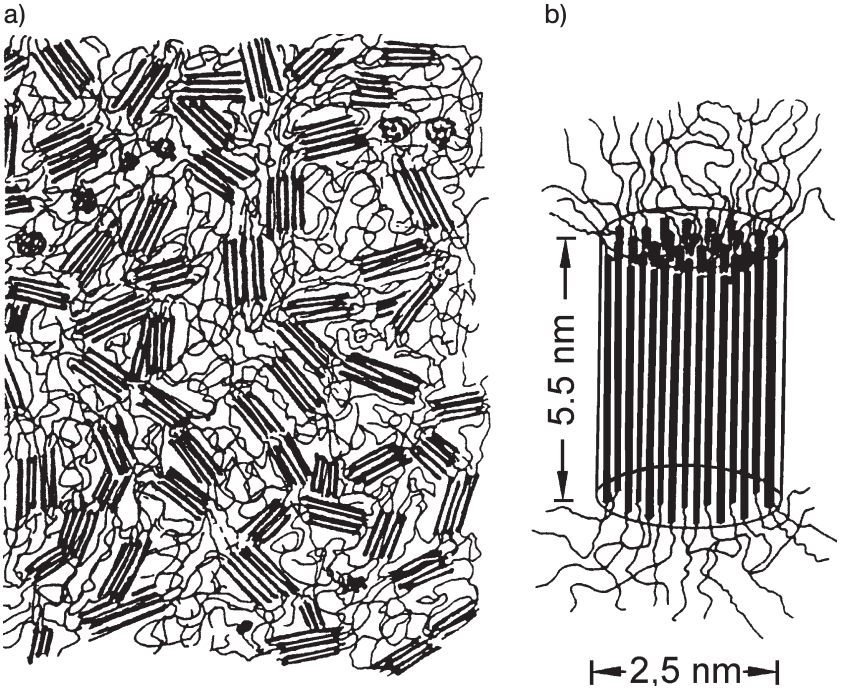


Figure 3. A) Tertiary structure of a linear segmented PUR with polydisperse soft segments and uniform (monodisperse) hard segments; B) Cylindrical model of a hard domain

shows hard-segment character. These interactions also explain the superior mechanical properties of polyureas and their low thermoplasticity.

The balance between these hard segment/hard segment interactions and the interactions between hard segments and soft segments determine the degree of segregation. Due to decreasing polarity, segregation increases from polyesters to polyethers to polybutadiene polyethers.

In the soft segments, strain-induced crystallization can be initiated by stretching or disentanglement. This strain-induced crystallization explains the high hysteresis of typical PUR elastomers [139, 140]. The mechanical properties of segmented PUR depend on the melting temperature of the crystalline domains.

Products based on 1,5-naphthalene diisocyanate (NDI) are no longer thermoplastic because the melting temperature of the hard segments is too high. They are usually produced with a small excess of isocyanate as casting elastomers (see Section 8.1). These products have extremely good mechanical properties: high tear strength, high abrasion resistance, high elasticity at high hardness, low damping, high load-bearing capacity, and excellent long-term dynamic endurance (load-bearing property) [135].

High-quality PUR thermoplastic elastomers are produced primarily from MDI. The melting temperature and the solubility of these segmented thermoplastic PURs can be influenced by modifying the chemical composition, especially of the hard segments. Use of a second short-chain diol lowers and widens the melting temperature range, and solubility is also improved.

As the properties of segmented PUR are highly determined by the phase segregation and the crystallinity of the domains, numerous production parameters [130, 131, 141–143] have tremendous influence on the behavior of thermoplastic PUR materials. Even thermoplastic PUR with monodisperse (uniform-length) N-alkylurethane hard segments, which are incapable of hydrogen bond formation show differing morphology and properties depending on their thermal pretreatment [144].

4.3. Cross-linking of Polyurethane

PUR flexible and rigid foams, cast elastomers, and most reactive systems are usually cross-linked. Even if these cross-linked PURs are not thermoplastic, the melting of the hard-segment domains is still observable, e.g., by softening (decrease in shear modulus) at elevated temperatures. With increasing cross-linking, the glass transition temperature increases, whereas the tendency to crystallize decreases.

If the cross-linking is not caused by subsequent reactions (formation of allophanate or biuret), but introduced by the use of highly functional raw materials, then the formation of segregated domains can be disturbed due to the rapid formation of a highly cross-linked PUR network, fixing the polymer chains or at least reducing their flexibility. In this case, even heating to elevated temperatures does not improve the material properties, as domain formation is not possible (e.g., in flexible foams).

4.4. Polyisocyanurates [145]

The general term PURs also covers products that contain cyclic urea structures (isocyanurates), which are formed by cyclotrimerization of isocyanate groups. The mechanism of isocyanurate formation is not completely understood. The most probable mechanism of base catalyzed trimerization [146] is shown in Figure 4.

Addition of the catalyst II to the carbon-nitrogen double bond leads to an urethane anion III, which by subsequent addition of two more isocyanate molecules I is transformed via IV to the adduct V. This adduct collapses into the stable isocyanurate VI and regenerates the catalyst II.

The isocyanurates exhibit improved mechanical properties such as compression strength and dimensional stability and generally show superior fire retardancy [147]. These advantages have led to the increasing importance of isocyanurates, especially since the blowing agent for rigid foams was switched from CFC to pentane (see Section 7.3.4).

5. Production of Polyurethanes

5.1. Stoichiometry

Isocyanates (RNCO) are specified by their percentage NCO content and in some cases also by their equivalent mass (molecular mass of NCO

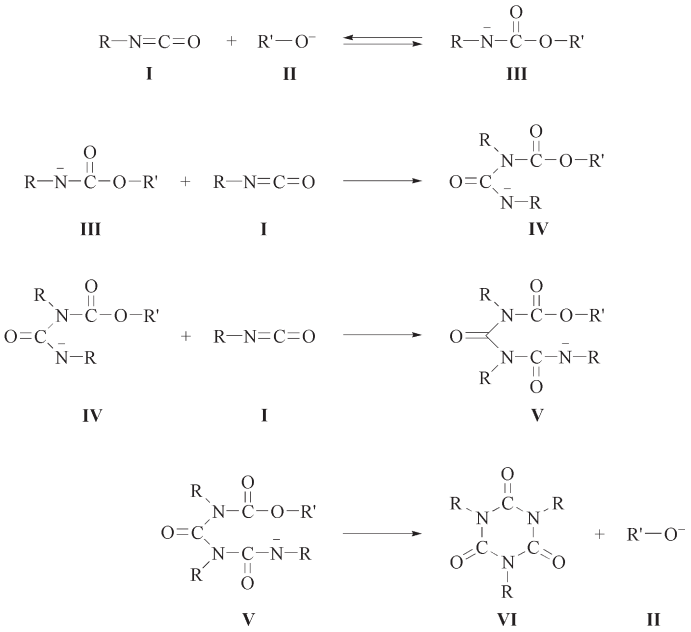


Figure 4. Mechanism of base-catalyzed isocyanate trimerization

moiety/functionality). Functionality means the number of isocyanate groups per molecule.

$$\text{Equivalent mass} = \frac{\text{molecular mass of RNCO}}{\text{functionality}} = \frac{42}{\%\text{NCO}} \cdot 100 \quad (1)$$

Polyols are specified by their hydroxyl number (OH no.) and sometimes also by their percentage OH content or their equivalent mass. The OH no. is given in mg KOH/g, owing to the method used for analyzing the OH groups: they are usually treated with acetic anhydride and, after hydrolysis with water, the excess acetic anhydride is titrated with potassium hydroxide. This means that a polyol containing 1 mmol OH groups per gram has an OH no. of 56 mg KOH/g.

$$\text{OH no.} = \%\text{OH} \cdot \frac{56 \cdot 1000}{17 \cdot 100} = \%\text{OH} \cdot 33 \quad (2)$$

$$\text{Equivalent mass} = \frac{56 \cdot 1000}{\text{OH no.}} \quad (3)$$

Water, *acids* (acid number AN), and secondary and tertiary amines are also most simply characterized by their equivalent mass. For mixed amines, a mean functionality must be used where necessary. For calculating quantities, 1 gram equivalent isocyanate corresponds to 1 gram equivalent Zerewitinoff-active hydrogen compound (e.g., polyol). In practice, the quantity of isocyanate is calculated almost exclusively for 100 parts by weight of the active-hydrogen compound(s). If the raw materials also contain water, then an additional quantity of isocyanate is required, since the latter reacts with water to form carbon dioxide and substituted urea.

The index (or isocyanate index) is equal to 100 (isocyanate index = 1) if the quantity of isocyanate added equals the amount necessary for reaction with all Zerewitinoff-active hydrogen atoms.

$$\text{Index} = \frac{\text{Used isocyanate quantity}}{\text{Necessary isocyanate quantity}} \cdot 100 \quad (4)$$

In practice, the index can be used to influence the properties of the PUR decisively, e.g., by "under-" or "over-cross-linking." Under-cross-linking means that free hydroxyl groups remain in the PUR; over-cross-linking means that the urethane moieties undergo consecutive reactions, i.e., the formation of allophanates. High indices of 300 or more are used to produce polyisocyanurates (PIR), in which the isocyanate groups undergo trimerization by reaction with each other (see Section 4.4).

5.2. Reaction without Solvents

The possibility of manufacturing PURs from liquid raw materials without the use of any solvent is one of the biggest advantages of PUR chemistry. As a result, most PURs are manufactured by a mass polyaddition process. This process can be a single-step reaction (one-shot process) or a two- or multiple-step reaction (prepolymer process). The reactivity is controlled by temperature or by the addition of catalysts. Due to the high exothermicity, reaction temperatures of about 100 to 180 °C are not unusual. These high temperatures guarantee good end curing of the molded PUR parts.

5.2.1. One-Shot Process

Bulk reactions without solvents are usually very fast, especially when catalysts are added. Therefore, the production of PUR foams is usually carried out by the one-shot process, in which all components are mixed directly, generally with simultaneous addition of auxiliaries such as catalysts, foam stabilizers, reinforcing agents, fillers, and fire retardants. The reaction is highly exothermic and largely completed in 0.5–30 min, depending upon the catalyst. The final properties, however, are frequently reached only after 24–48 h (post-curing).

The one-shot process requires that the reactivity of all isocyanate species is quite similar. Amines usually lead to excellent PUR properties but react much more rapidly than polyols. If diamines or polyamines are to be used it must be ensured that the urea formed at the beginning of the reaction does not precipitate and is no longer available for incorporation into the hard segments. This means that the use of polyamines is limited to amines which cannot undergo crosslinking (secondary amines), are sterically hindered [57–61, 148], or are deactivated by electron-withdrawing substituents [62–64, 149].

For easy processability all components should be liquid, of low viscosity, and miscible or at least be able to form a homogeneous reaction mixture for the very first moments of the reaction. Usually all the nucleophilic components, that is, polyols and/or polyamines, are premixed and homogenized. If these mixtures are incompatible with the short-chain diols (chain extenders), the miscibility must be enhanced by raising the temperature or adding emulsifiers.

In general, the polyaddition reaction of a multicomponent system by the one-shot process leads to a predominantly statistical structure of the polymer chains.

The term reaction injection molding (RIM) technology usually is used when highly reactive components are mixed and injected into a mold on a very short timescale (see Section 7.4). This technique allows for the handling of reactive systems with pot lives (i.e., the period in which no significant increase in viscosity is observed) of less than 1 s and reaction times of about 10–60 s.

RIM technology has initialized a development, which started with catalyzed highly reactive PUR systems [150], and, by the use of polyurethane-polyurea systems, chain extended by diamines [151–153], led to pure polyurea systems, in which the only isocyanate-reactive components are diamines [154–163].

5.2.2. Prepolymer Processes

In PUR chemistry, prepolymers are defined as intermediate reaction products of the polyaddition reaction which still contain free isocyanate or isocyanate-reactive groups. In contrast to the one-shot process, the prepolymer process allows for a highly controlled polyaddition reaction, e.g., to construct tailor-made segment structures.

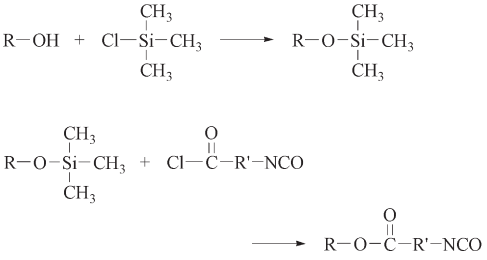
In the first step of the process, polyether or polyester polyols are usually treated with excess diisocyanate to yield homogeneous reaction mixtures, which may contain considerable amounts of unconverted isocyanate groups. If diisocyanates with NCO groups of different reactivity are used (2,4-diisocyanatotoluene, isophorone diisocyanate), the resulting NCO prepolymers exhibit narrow molecular weight distribution with only minor amounts of unconverted monomeric diisocyanate.

If prepolymers free of monomeric diisocyanate are required, the latter must be removed, e. g., by thin-film distillation or extraction with a hydrocarbon solvent which does not dissolve the prepolymer. The monomer content is then lowered to below 0.1 % [164, 165].

The production of storage-stable NCO prepolymers from aromatic diisocyanates is difficult and requires special precautions (e.g., the

exclusion of all traces of water and catalysts) to avoid side and consecutive reactions [166].

Low-viscosity, monomer-free NCO prepolymers can be obtained from silylated hydroxy compounds and isocyanates with a carboxylic acid chloride group [167, 168].



5.3. Reaction in Solvents

5.3.1. One-Component Systems

Linear or slightly branched PURs or polyurethane polyureas with molecular weights of 50 000 to 150 000 g/mol can be obtained by polyaddition reaction in solution. The PURs are usually isolated by evaporation of the solvents or by precipitation, e.g., by pouring the solution into a nonsolvent liquid.

The choice of solvent for the polyaddition is crucial, as the solvent must be able to dissolve both the soft and hard segments of the segmented PUR structure. Polar organic solvents (dimethylformamide, dimethylacetamide, 1-methyl-2-pyrrolidone, sulfolane, etc.) usually fulfill this requirement. In some cases, ketones like acetone or methyl ethyl ketone are also suitable. The ketones are especially suitable for chain extension of NCO prepolymers with aliphatic diamines as they reduce their activity by reversibly forming an adduct.

In industrial processes, linear PURs containing only urethane groups are usually produced without using solvents, but can be dissolved in a solvent if necessary for the application.

PURs containing urethane and urea groups are mainly produced by a two-step process. In the first step a prepolymer is made without the use of any solvents. In the second step this prepolymer is then treated with chain extenders such as diols or diamines. In the second reaction step, the solvent is usually added stepwise to avoid a too rapid increase in the viscosity of the solution. The obtained PUR solutions have PUR contents of ca. 20 to 30 %.

With increasing viscosity it is very difficult to achieve complete conversion of the functional groups. This problem is overcome by using NCO/OH ratios (indexes) slightly above 100 and running the reaction till the viscosity reaches a specified value, which must be determined empirically for each product. Then the reaction is stopped by adding a monofunctional stopper, e.g., dibutylamine.

If the reaction is carried out in highly polar solvents, especially in mixtures of water and acetone, methyl ethyl ketone, or DMF, even highly reactive aliphatic diamines such as ethylenediamine can be used. With increasing molecular mass the products may tend to gelation or precipitation. The solubility of the PUR can be improved by adding small portions of a second chain extender such as 1,2-diaminopropane, piperazine, or water to disturb the formation of the hard-segment domains.

5.3.2. Two-Component Systems [169]

Two-component systems are of tremendous importance for coatings and for leather and paper finishing. They usually consist of a polyhydroxy compound and an isocyanate cross-linker.

The polyhydroxy compounds are usually obtained by chain extension of common polyether or polyester polyols with diisocyanates; the isocyanate cross-linkers, which for ecological reasons must be free of isocyanate monomers, may be NCO prepolymers made by the reaction of diisocyanates with diols, diamines, or water; or they may be modified isocyanates, e.g., trimerization products of HDI (see Section 3.1.2).

To increase the amount of reactive components in the solvent-containing two-component systems, numerous improvements have been introduced to industrial processes: part of the solvent can be substituted by reactive thinners [170], which are incorporated into the cross-linked PUR. By using new catalysts an unsymmetrical trimerization product of HDI [30], with particularly low viscosity, has been developed, allowing for higher concentrations (high-solids systems) without deterioration in the processability.

5.4. Reactive One-Pack Systems

The term "one-pack system" denotes the storage-stable, ready-to-use formulation of a polymer precursor which cures without addition of further components, e.g., curing agents. Curing generally is caused by humidity, atmospheric oxygen (mainly used in paints), or by the thermal elimination of a blocking agent (see Section 3.1.3), which either vaporizes or remains in the cured polymer.

Other curing systems involve encapsulated materials with a diffusion barrier layer, which is broken, e.g., on heating. They cure without uptake or release of a substance.

Moisture Curing. Relatively low molecular mass NCO prepolymers can be dissolved in small amounts of low-polarity solvents (e.g., 75 % solution in ethyl acetate) and cured by the action of atmospheric moisture. The curing rate depends on the atmospheric humidity and temperature. Usually these solutions are used as paints or coatings, and the carbon dioxide formed as a byproduct escapes from the thin film without bubble formation.

Eliminating Blocking Agents. Mixtures of blocked NCO prepolymers with polyols are stable at storage temperatures (20–50 °C) and are cured by heating (> 120 °C) to eliminate the blocking agent (see Section 3.1.3). The reaction can be conducted in such a way that an isocyanate intermediate does not appear [39]. Appropriate hydrophilic modification can be used to produce such combinations as low-viscosity aqueous emulsions or dispersions, in which one of the components usually has a high molecular mass [38].

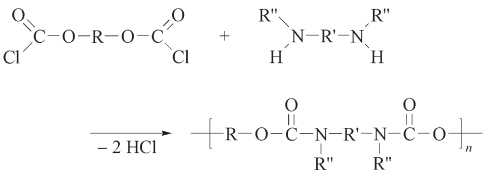
Removal of a Diffusion Barrier Layer. Some solid diisocyanates such as NDI, TDI-urea, and TDI-uretdione (TDI-dimer) can be stabilized by encapsulation with a diffusion barrier layer. The barrier layer is produced by dispersing the solid isocyanate in a solvent and reacting the NCO groups at the particle surface with (cyclo-)aliphatic diamines. After removal of the solvent the encapsulated isocyanates are dispersed in polyols or polyamines.

Liquid, pasty, or granular one-pack systems are produced in this way. They can be stored for several months and are made to react by heat shock, e.g., 1 min at 120 °C. Heat-curable reactive powders can also be produced on this basis [171].

5.5. Other Processes

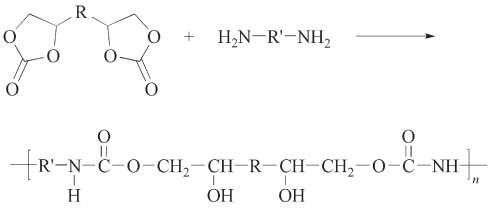
In addition to the industrial isocyanate polyaddition processes described previously and in subsequent sections, several other synthetic methods for PURs or polyureas are of scientific interest [172].

PURs can also be obtained by the polycondensation reaction of bis-chloroformate esters and diamines. This method has the advantage over the polyaddition method that it can be carried out under very mild conditions (at ⩽20 °C).



If secondary diamines such as piperazine are used in the polycondensation reaction, thermostable poly(N-alkylurethanes) are obtained. This principle has been used to produce, e.g., high-melting PURs [173] for fibers or PURs with liquid-crystalline character [174]. Liquid-crystalline PURs have also been produced from *N*-alkylcarbamic acid chlorides and diols.

Another method for preparing PURs is the ring-opening polyaddition of oligomers with cyclic ethylene carbonate groups and di- or polyamines, which leads to segmented PURs with free hydroxyl groups [175, 176]:



Functionalized PURs can be obtained if carbonylbiscaprolactone (CBC) is used as carbonyl source [177]. Due to its high selectivity, reactions

with diamines can be carried out even in the presence of additional hydroxyl groups.

High-molecular mass α,ω-bis(amino) prepolymers for use in RIM technology (see Section 7.4) have been produced by the reaction of α,ω-bis(amino)polyethers with urea [178].

6. Processing of Polyurethanes

6.1. Supply, Storage, and Preparation of Raw Materials

The raw materials are transported in small (< 100 kg) and normal-sized drums (200–250 kg), and (road) tank trucks and trailers (ca. 23 t). The regulations applicable to the transportation of chemicals (including labeling) must be observed, as well as the transportation conditions prescribed by the manufacturer for preserving the quality of the raw materials. If raw materials are delivered by tank truck, storage tanks for polyol and isocyanate should be installed in pairs at the processing site (Fig. 5). The size of the storage tanks should be adapted to the delivery volume (frequently 15 or 30 m^3). Since the raw materials in the tank truck are usually delivered at elevated temperature, they must be cooled to the processing temperature (22–25 °C) in the storage tank. Ordinary thick plate can be used as the tank material.

6.2. Metering and Mixing Technology

In contrast to the machines used for processing thermoplastics, which consist of devices for melting, molding, and solidifying, the machines used for producing PUR moldings or semifinished parts contain all the elements of a chemical reactor.

The raw materials are conveyed from the storage tank, optionally via premixing stations for adding auxiliary materials, to the processing machine. Often the metering and mixing machine is called the wet part of the processing plant. Figure 6 schematically depicts a two-component metering and mixing machine with an impingement mixer as the mixing unit. In practice, machines using the impingement mixing principle are available for mixing up to six components. In the working tanks (a), the raw materials are prepared for processing, i. e., primarily their temperatures are adjusted precisely. Any temperature change, especially of the polyols, results in a viscosity change, which can impair later processing. The working tanks (volume 20–500 L according to the machine size) are therefore usually provided with heating and cooling jackets. Separate temperature-control circuits via heat exchangers are also common. The working tank is also equipped with an agitator for homogenization as well as an automatic refilling system and indicators for level, pressure and temperature. The conditioned raw materials are conveyed via

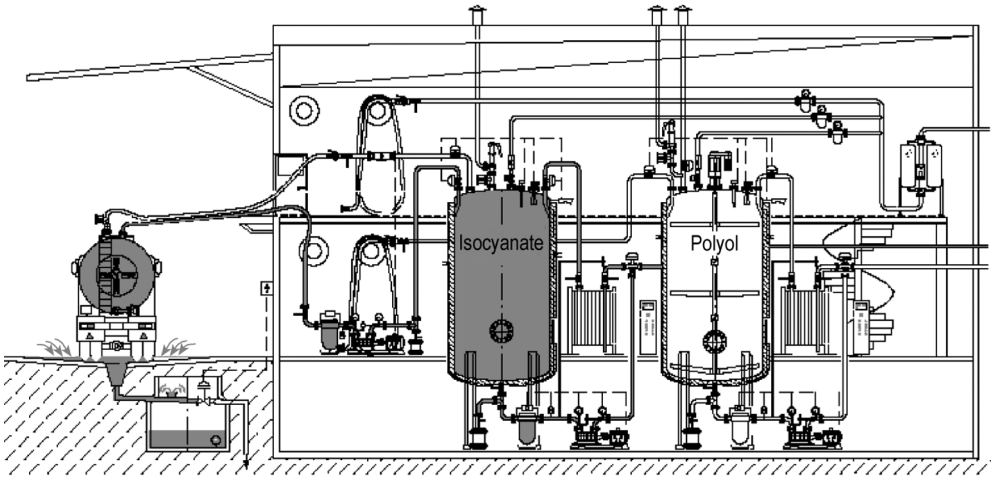


Figure 5. Tank truck unloading and storage tanks

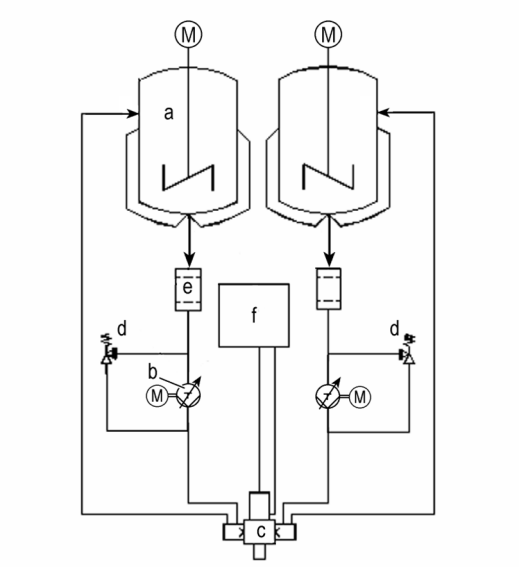


Figure 6. Principle of a high-pressure machine (circulation system)
a) Working tank; b) Metering pump; c) Mixing head; d) Safety valve; e) Filter; f) Hydraulic unit

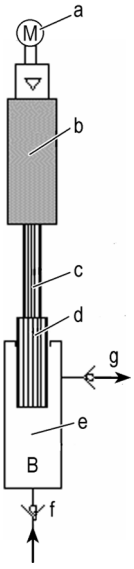


Figure 8. Plunger pump
a) Stepping motor; b) Hydraulic cylinder; c) Hydraulic piston; d) Metering piston; e) Metering cylinder; f) Stop valve: feeding side; g) Stop valve: delivery side

metering pumps (b) to the most important part of the machine, the mixing head (c), which delivers the liquid reaction mixture.

Depending on the PUR system to be processed, precision metering pumps of various outputs (up to 150 L/min) and pressure ranges (up to 250 bar) are used. The pumps must always satisfy extremely high requirements for metering accuracy in order to maintain a certain reaction mixture. In addition to conventional gear pumps and in-line piston pumps, which have been established in PUR technology for many years, axial piston pumps (Fig. 7) and, for systems containing fillers and reinforcements, slow-running single-cylinder positive-displacement pumps are used (Fig. 8).

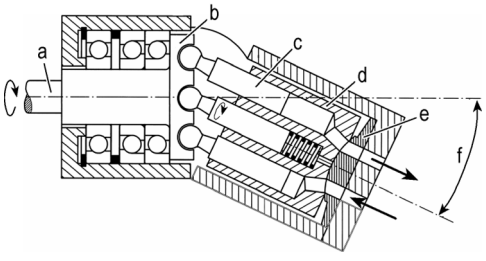


Figure 7. Axial piston pump
a) Shaft; b) Rod plate; c) Piston; d) Cylinder unit; e) Cam plate; f) Angle of inclination to adjust volume flow rate

Two types of mixing principles exist: low-pressure mixing heads with an agitator (3–40 bar) and high-pressure mixing heads (100–250 bar). In mixing heads with an agitator, the raw materials entering the upper part of the mixing chamber are intensively mixed on their way to the outlet by rotating, variable-speed agitators. Agitators include spiked, paddle, or screw agitators, propellers, or turbine impellers. After the end of the shot the agitators are cleaned with a rinsing medium. High-pressure mixing heads operate according to the countercurrent injection principle. The component streams are injected into the mixing chamber via nozzles (Fig. 9) and are mixed by virtue of the kinetic energy used and the chaotic flow behavior created [179].

In controlled-circulation mixing heads, the raw material streams are changed from the "circulation position" (Fig. 10A) (tank → pump → mixing head → tank) to the "injection position" (Fig. 10 B). After injection has occurred, a piston cleans the remaining reaction mixture from the mixing chamber and outlet pipe. These are therefore known as self-cleaning mixing heads.

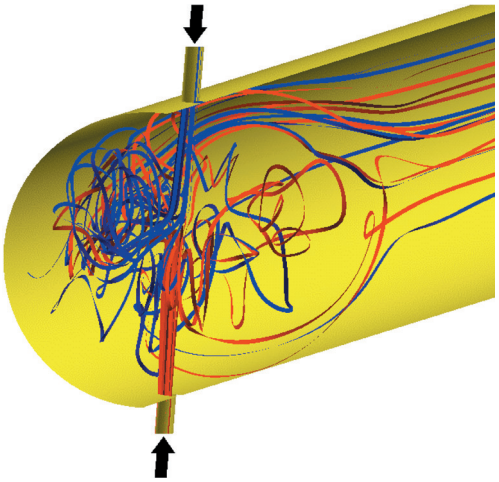


Figure 9. View into an impingement mixer during shot; visualization of streamlines

So-called L-shaped mixing heads are able to improve the homogeneity of the reaction mixture by a perpendicular deflection of the flow direction and simultaneous acceleration of the flow velocity (Fig. 11). Furthermore, the larger diameter of outlet tube compared with the dimension of the mixing tube allows the required laminar flow out of the mixing head.

6.3. Processing Plants

A two- or multicomponent metering and mixing machine is part of each processing plant. Further equipment and machines define the kind of processing plant.

In continuous plants, semifinished products are produced in the form of blocks, slabs, boards, profiles, etc. The scheme in Figure 12 depicts a plant for the continuous production of foam slabs. Four components are metered, mixed with an agitator mixing head, and poured onto the conveyor belt. The bottom and side paper are used to keep the conveyor belt clean and to avoid sticking of the foam to the conveyor belt during rising and curing. Figure 13 is a three-dimensional view of a plant for the manufacture of rectangular slab stocks.

A three-dimensional drawing of a plant for manufacturing metal sandwich panels (Fig. 14) gives an impression of how large and complex PUR plants can be. The length over all stations of processing steps in this case is ca. 350 m.

Plants for producing moldings operate batchwise. The example in Figure 15 shows a top view of a processing plant: On the left side is the wet part of the plant with a total of six components; a robot handles the high-pressure mixing head, and two clamping units are available for pouring into open moulds.

A distinction can be made between plants with movable (Fig. 16) and those with stationary molds (Fig. 17). Movable molds are supplied by a single mixing head, whereas in RIM plants, several mixing heads are used, each of them being permanently assigned to one (stationary) mold. The plants are preferably automatically controlled with electronic equipment.

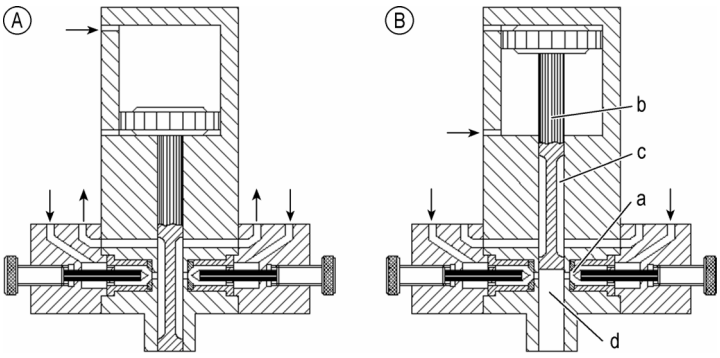


Figure 10. Circulating-groove mixing head
A) Circulation/cleaning; B) Mixing
a) Nozzle; b) Piston; c) Groove; d) Outlet tube

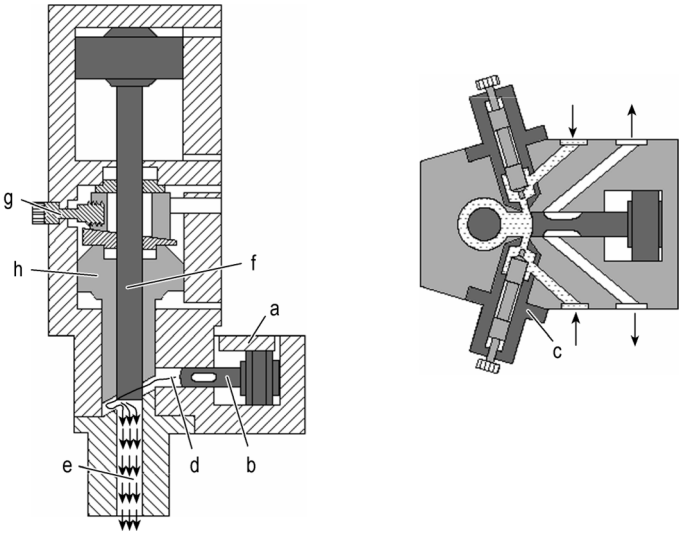


Figure 11. L-shaped mixing head with ring throttle (type Hennecke)
a) Impingement mixer; b) Actuating piston; c) Injection nozzle; d) Mixing chamber; e) Outlet tube; f) Cleaning piston; g) Adjustment of ring throttle; h) Ring throttle

7. Foams

Whilst the reaction of isocyanates with water in most PUR applications is an unwanted side reaction, for foams this reaction is of utmost importance, due to the two reaction products formed. These are CO_2, which acts as the blowing agent for foam formation, and the more or less crystalline polyurea domains, which control cell opening and act as reinforcing filler in the PUR backbone. This chemical blowing process was supplemented in the early 1960s by a physical blowing process using low-boiling liquids as blowing agents. These liquids are vaporized by the heat of reaction of the polyaddition reaction between isocyanates and polyols and/or water. The blowing agent vapor is trapped in the viscous reaction mixture and thus leads to the cellular structure of the foam. Since foam formation is a very sensitive and complex process of interdependent chemical, physical, and rheological processes, specific additives and catalysts are required (see Section 3.5).

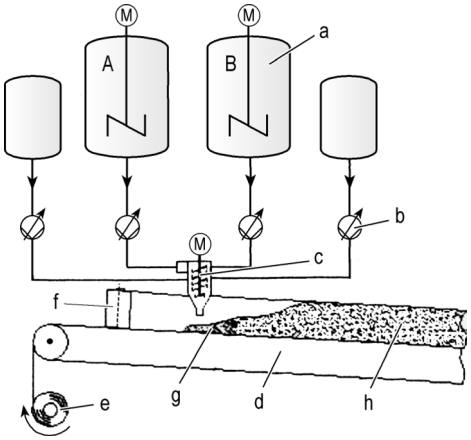


Figure 12. Principle of a plant for continuous production of foam slabs
a) Working tank; b) Metering pump; c) Agitator mixing head; d) Conveyor; e) Bottom paper; f) Side paper; g) Rising foam; h) Cured foam

PUR foams are generally divided into flexible, rigid, and semiflexible products. Integral skin foams, which have a densified surface layer forming an elastomerlike skin and a foamed core, are described in Section 7.4.

Polyols with a relatively high molecular mass (2000–8000 g/mol) and a nominal functionality of 2–6 yield flexible foams. Combinations of these polyols with low molecular mass glycols or amines as chain extenders and preferably polyisocyanates with a functionality of more than two yield semiflexible foams. Highly branched polyols, e.g., polyethers based on sorbitol or sucrose, with a relatively low molecular mass (<1000 g/mol) are the basis of rigid foams.

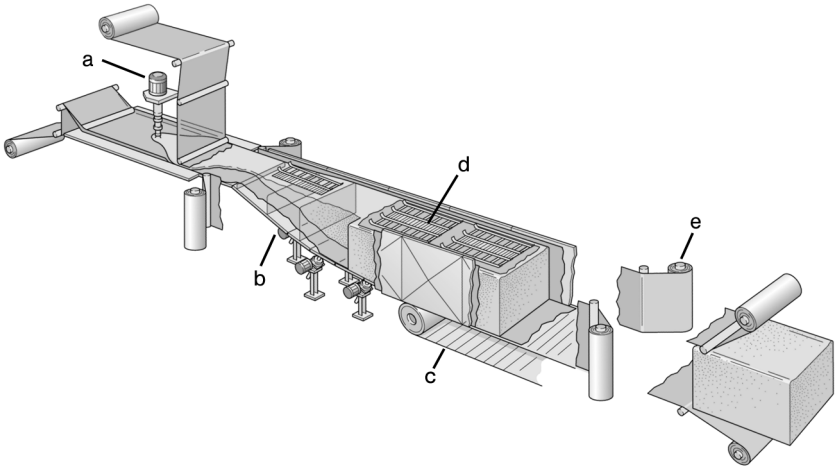


Figure 13. Plant for the manufacture of rectangular slab stocks (Quadro-Foamat-Machine: QFM, source Hennecke)
a) Agitator mixing head; b) Fall plate path adapted to foam expansion; c) Conveyor; d) Device to keep block shape rectangular; e) Paper winch

For all these classes of foams different types of manufacturing processes may be applied. An alternative way of classifying foams is therefore based upon the manufacturing process.

Depending on the processing, a distinction is made between molded foam and slabstock foam. Besides these most prominent groups of flexible foams, other foam types include cavity-filling foam (e.g., filling of cavities in car bodies for acoustical or reinforcing purposes) and spray foam (e.g., for thermal insulation of roofs). The term "filling foam" essentially refers to semiflexible foams behind appropriate overlays, e.g., flexible plastic sheets, films, etc.

7.1. Flexible Foams

Most flexible foams are produced continuously as slabs or batchwise by molding. They are

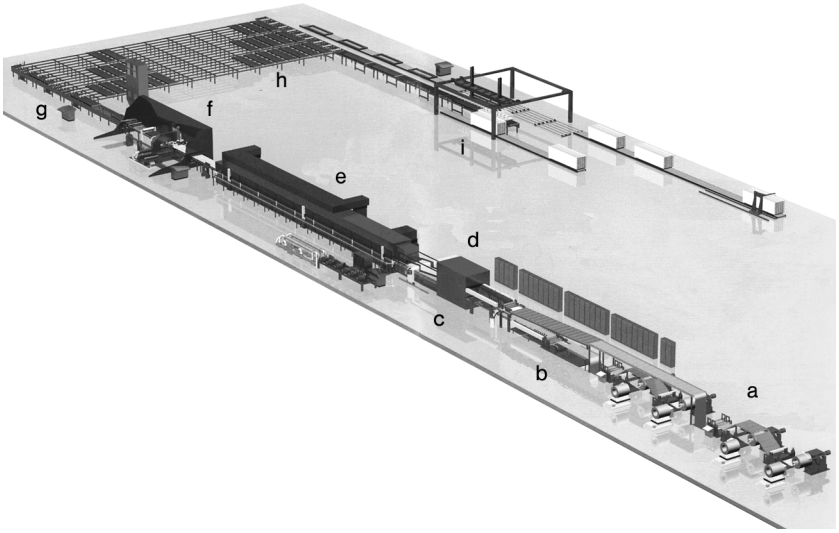


Figure 14. Plant for the manufacture of metal sandwich panels (source Hennecke)
a) Uncoiling station; b) Profiling machine; c) Heater; d) Twin-head foaming portal; e) Laminator; f) Cutting machine/bandsaw; g) Turn over system for roof elements; h) Cooling section; i) Stacker

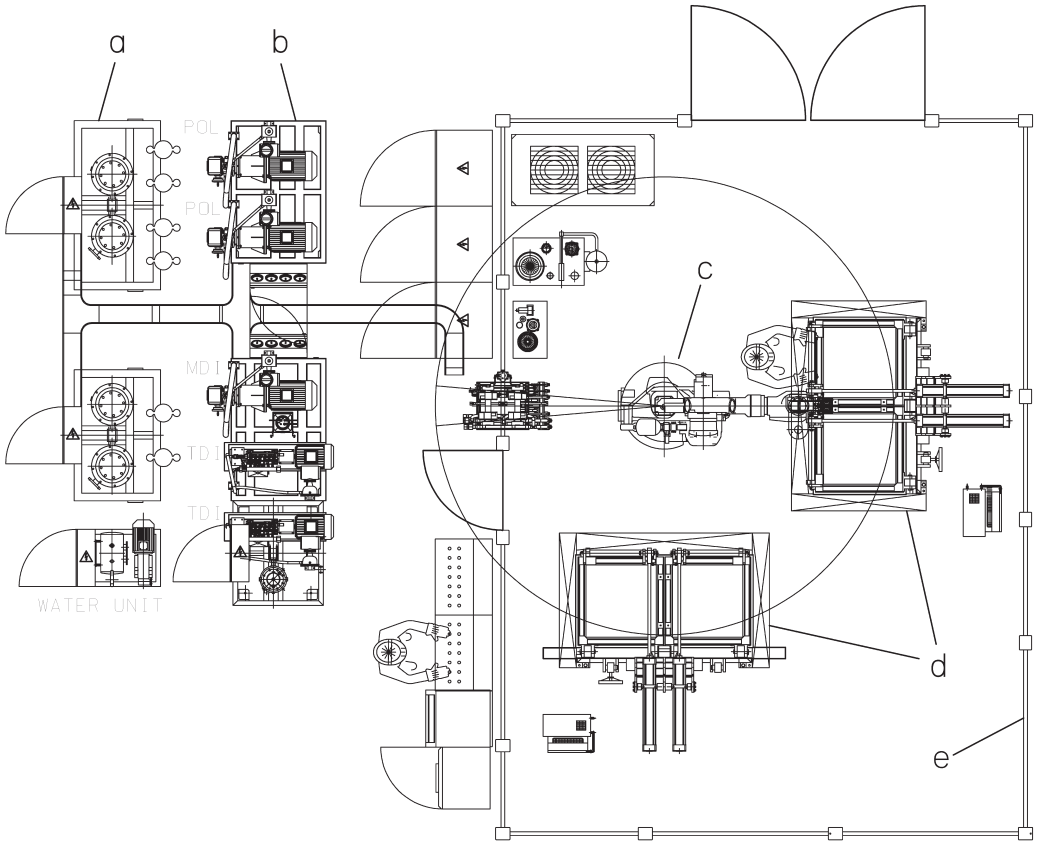


Figure 15. Layout of a plant for producing moldings by open-mold filling technology
a) Tank unit; b) Pump unit; c) Robot with mixing head; d) Clamping units; e) Protective guard

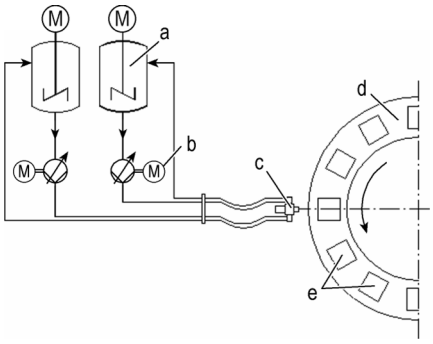


Figure 16. Principle of a plant with movable molds and stationary mixing head
a) Working tank; b) Metering pump; c) Mixing head; d) Turntable; e) Molds

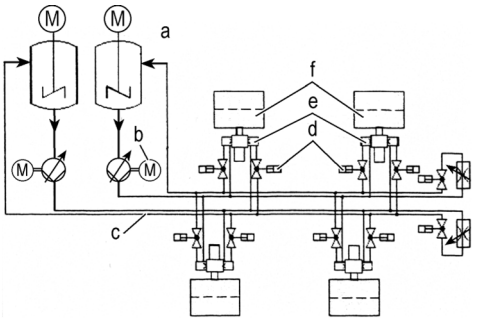


Figure 17. Principle of a RIM plant
a) Working tank; b) Metering pump; c) Circulation system; d) Selection valves; e) Mixing heads; f) Clamping units with tools

characterized by reversible deformability and an open-cell structure, associated with air permeability.

7.1.1. Flexible Slabstock Foam

7.1.1.1. Raw Materials

Based on different chemistries on the polyol side, three fundamentally different types of slabstock have to be considered: Polyester foams, made from polyester polyols, conventional polyether foam, made from polyether polyols with mainly secondary OH groups and high-resilient (HR) foamf, made from polyether foams with mainly primary OH groups.

The isocyanate used for polyester foams is usually TDI 65 (see Section 3.1.1) or blends of TDI 65 and TDI 80; the typical isocyanate for polyether foams is TDI 80. High-resilient slab stock foam is produced from polyethers and TDI 80, both optionally modified.

Main components (parts by weight) of a formulation for flexible polyester foam:

Polyester polyol (OH no. 65), e.g., Desmophen 2200	100
TDI 65 and/or TDI 80, e.g., Desmodur T65, Desmodur T80	variable
Index	95
Water	2.5–4.8
Amine catalyst	0.3–0.6
Foam stabilizer	0.7–1.3

Main components (parts by weight) of a formulation for flexible polyether foam:

Polyether polyol (OH no. 48), e.g., Arcol 1108	100
TDI 80, e.g., Desmodur T80	variable
Index	98–115
Water	2.0–4.5
Amine catalyst	0.15
Tin dioctanoate	0.12–0.28
Foam stabilizer	0.6–1.5

Main components (parts by weight) of a formulation for high-resilient (HR) flexible foam:

Grafted polyol (OH no. 28), e.g., Desmophen 7653	100
TDI 80, e.g., Desmodur T80	variable
Index factor	95–113
Water	1.5–4.0
Amine catalyst	0.10–0.20
Diethanolamine	0.8–1.5
Tin dioctanoate	0.1–0.35
Foam stabilizer	0.3–1.0

The polyesters (M_r 2000–3000 g/mol) are usually based on adipic acid and linear glycols (e.g., diethylene glycol), or triols (glycerol or trimethylolpropane) if slight branching is desired.

The polyethers used (M_r 1000–6000 g/mol) are di- and/or triols with a varying propylene oxide/ethylene oxide ratio, which is tailored to the foam's application. An important factor for polyether foaming is a well-balanced ratio of the metal and amine catalysts, which controls the simultaneous reactions of the NCO group with hydroxyl groups (polyurethane reaction) and with water (blowing reaction). If the polyurethane reaction rate predominates, the foam may shrink due to the formation of a high proportion of closed cells. If the water reaction proceeds too rapidly, the carbon dioxide formed cannot be contained in the cells; splits result and the foam can even collapse.

High-resilient foams are produced from highly reactive grafted polyethers which contain a high proportion of primary OH groups (from ethylene oxide). Grafting is achieved by in situ polymerization of styrene and acrylonitrile to form a stable SAN suspension in the polyol. Another class of grafted polyols is based on the polyaddition of TDI and hydrazine to yield PHD polyols which contain suspended polyhydrazodicarbonamide/polyurea particles. If highly functional (pre-cross-linked) modified TDI types are used, unmodified polyols can be applied, but due to advantages in foam processing, this approach has been generally replaced by grafted-polyol technology.

7.1.1.2. Production

The raw materials are processed in fully continuous plants to give flexible foam slabs up to 220 cm wide, 120 cm high, and of any length. Depending on the slab dimensions, internal temperatures of up to 165 °C are reached as a result of the exothermic reaction. This temperature must not be exceeded, otherwise severe scorching and even self-ignition of open-celled foam may occur. The foaming process is completed after ca. 3 min, and final curing takes

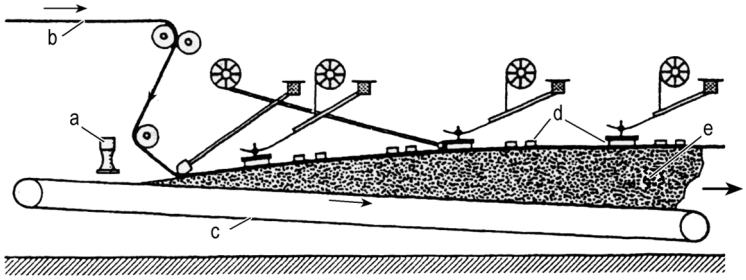


Figure 18. Principle of a plant for production of rectangular flexible foam slab stocks
a) Covering paper; b) Skids; c) Mixing head; d) Conveyor belt; e) Foam

from about 10–12 h up to 72 h, depending on the foam type. The slabs are therefore stored in curing storage facilities until they have cooled and attained their final mechanical properties, so that they can be transferred to further processing, fabrication, etc. The length of the slabs varies from 10 m (short slabs) to 120 m (long slabs). To minimize trimming losses of the foam buns, which would be dome-shaped under free-rise conditions, various technologies are applied to produce rectangular slabs.

Figure 18 shows the principle of a rectangular slabstock plant (Hennecke Planibloc process) [180]. A cover is applied to the rising foam. The pressure of the skids avoids the development of the usual slab dome without the foam becoming compacted. Besides a rectangular slab cross section, this process gives an increased yield of foam due to partial foaming of the mixture at the slab surface, which would otherwise form the surface skin.

In other processes a polyethylene film is drawn up to the slab sides in synchronization with the rising movement of the foam (Draka-Petzetakis) [181, 182]; or the reaction mixture is discharged into a trough with a sloping bottom, in which it rises and then flows off over a downward incline (fall plates) onto the conveyor (Maxfoam) [183]. A more recent development (Multiflex, Quadrofoamat, see Fig. 13) combines the fall plates with liquid laydown principles.

The application of reduced air pressure during the foaming process (variable-pressure foaming, Beamech [184]) or the introduction of carbon dioxide into the mixing chamber (e.g., Multistream (Fig. 19) and Novaflex (Fig. 20), Hennecke [185]) has allowed for the complete

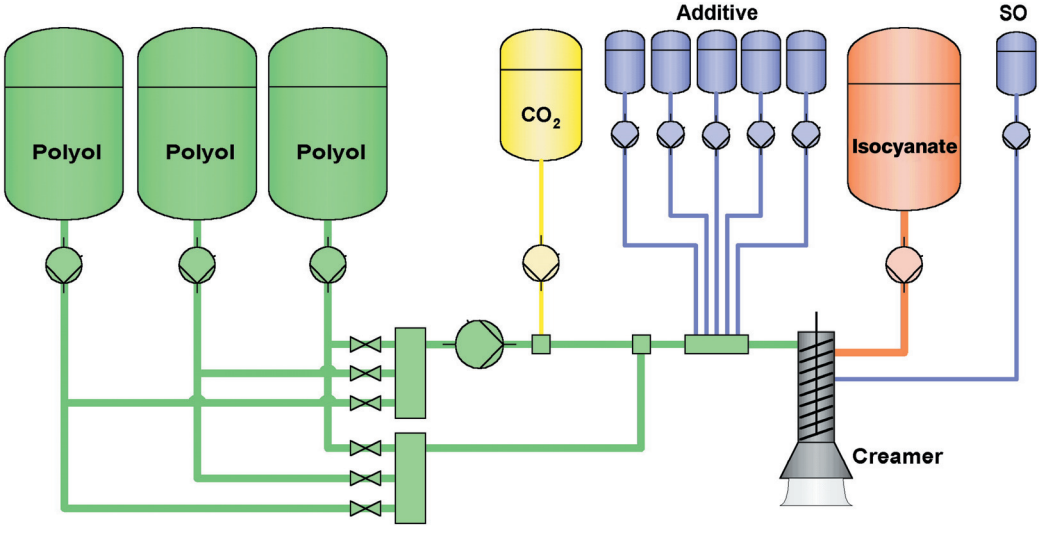


Figure 19. Multistream (Hennecke)

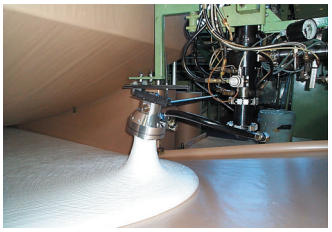


Figure 20. Novaflex creamer (Hennecke)

elimination of other physical blowing agents such as CFCs.

Rectangular blocks can also simply be produced batchwise by introducing the reaction mixture into metal or wooden boxes and at a given time putting a floating cover on the rising foam. In addition to primitive methods ("box foam"), mechanized box processes are also offered for this purpose with relatively low investment costs and a processing capacity of up to 1000 t/a (e.g., Hennecke Bloc-Foamat BFM 100). Special versions of these batch plants are available so that different ambient pressures can be applied during the foaming stage (e.g., Hennecke Megafoam).

In addition to the production of blocks with a rectangular cross-section, continuously produced blocks with a round cross section (diameter ca. 120 cm) have become industrially important (Reeves Brothers, General Foam [186, 187]). These buns can be peeled seamlessly.

7.1.1.3. Properties

The mechanical properties of the foam are largely determined by the raw materials and the formulation used and by its apparent density. For flexible foam slabstocks, the usual densities are 20–40 kg/m^3, but extremely light and extremely heavy types of foam (from 16 kg/m^3 and up to 130 kg/m^3) can be produced industrially for special fields. The choice of density is determined by the specific application of the foam: the higher the density, the better the properties or the lower the fatigue of the foam when in continuous use.

The hardness (measured as compressive strength at 40 % compression) is an important characteristic of PUR foams (Table 4). The hardness can be varied within wide limits by altering the formulation. Considerably softer conventional foams are obtained, e.g., by including polyethers of high ethylene oxide

Table 4. Relation between apparent density and compressive strength of various grades of flexible foam slab stock

Flexible foam system	Apparent density (ISO 845), kg/m^3	Compressive strength at 40 % compression (ISO 3386), kPa
Polyester foam, based on Desmophen 2200B/ Desmodur T65	35	6.5
Polyether foam, based on Polyether 10WF15/ Desmodur T80/T65	36	6.0
Polyether foam, based on Arcol 1108/ Desmodur T80	36	4.5
HR slab stock foam, based on Desmophen 7619W /Desmodur T80	34	2.7

content and special additives. Hardness control is also possible through the index or the addition of grafted polyols.

Apart from the hardness, other characteristic values can be derived from the hysteresis loop (Fig. 21). The slope of the loading curve and the area enclosed by the loading and unloading

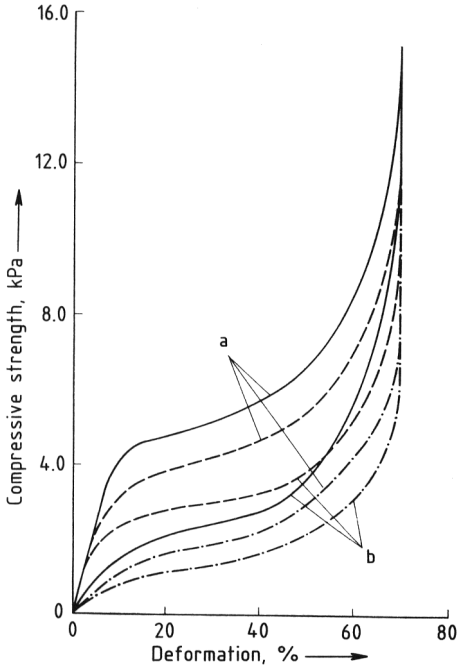


Figure 21. Hysteresis loops of different grades of flexible foam slab stock (apparent density 35 kg/m^3)
a) Loading lines; b) Unloading lines
— Polyester-based foam; – – – Polyether-based foam; –·–·– HR foam

Table 5. Mechanical properties of various grades of flexible foam slabstock

Flexible foam system	Tensile strength (ISO 1798), kPa	Elongation at break (ISO 1798), %	Compressive set (after 90% deformation; ISO 1856), %
Polyester foams	160 – 220	100 – 400	5 – 15
Polyether foams	100 – 180	100 – 400	2 – 10
HR slabstock foams	50 – 120	80 – 200	2 – 10

curves (hysteresis) are measures of the elasticity and energy absorption of the foam: the closer the curves are together, the more elastic the foam; and the larger the area, the better the energy absorption or damping properties of the foam. HR slabstock foam has the best elasticity, followed by polyether foam and polyester foam.

Some important mechanical properties are summarized in Table 5 to demonstrate their range of values. Table 6 shows the values for fatigue in continuous use under the conditions of short-duration tests.

The following list contains some additional properties of flexible PUR slabstock foams:

Thermal conductivity: 0.033–0.040 W m^{-1} K^{-1} (at 0–70 °C and densities of 20–70 kg/m^3)

Temperature stability: from −40 to +80 °C without embrittlement.

Open-cell character (see also reticulation capability): 98–100 % with respect to air permeability, not with respect to resistance to air flow.

Chemical resistance to acids and alkalis: polyether foam has a better resistance to acids and alkalis than polyester foam.

Chemical resistance to organic solvents: polyester foam shows a better resistance to organic solvents than polyether foam.

Chemical resistance to atmospheric oxygen: oxygen attacks foam slab stocks only superficially without harming the serviceability. Polyether foam is more easily oxidized than polyester foam. However, if aromatic polyisocyanates and polyether polyols are used for foam production, the foam will decompose over time if exposed to oxygen and light.

Combustibility (see Section 14.4): Flexible slabstock PURs are combustible, like all organic (carbon-containing) materials. By addition of suitable flame retardants the combustion behavior of foams can be adjusted to meet several flammability standards such as MVSS 302, BS 5852 part 2 Crib V, or even Fire Class B1 (DIN 4102). Also a post-treatment with latices containing flame retardants is possible, in particular if demanding tests have to be met. Besides flame retardants, the type of foam (polyester, conventional, or high resilient) is important if certain flammability standards have to be met.

Bactericidal and fungicidal treatment is possible by including appropriate additives in the formulation or by post-treatment.

Table 6. Change of hardness on ageing of various grades of flexible foam slab stock

Flexible foam system	Apparent density (ISO 845), kg/m^3	Decrease of indentation load deflection (ISO 3385), %	Decrease of compressive strength (5 d , 90°C, 95% rel. hum.), %
Polyester foams	25	43	35
	35	29	40
	45	26	40
Polyether foams	20	34	10
	25	29	14
	35	19	18
	50	16	16
HR slabstock foams	25	24	8
	35	18	13
	45	16	18

Reticulation capability (see also open-cell character): the flow resistance can be greatly reduced by using chemical or physical processes (Chemotronics) to remove residual cell membranes (filter foams).

Physiological aspects: According to extensive studies (both dermatological and oral toxicity in animals), flexible PUR foam of defined composition is physiologically harmless.

7.1.1.4. Trimming and Processing

Various possibilities and machines are available for processing the cured slabstock foam to finished articles. The simplest processes for foam blanks are horizontal-cutting (e.g., long-block cutting/peeling), vertical cutting, and angular cutting. These are carried out with continuously rotating knives.

Profile cutting in the form of copy cutting and punching, compression cutting, and milling is used for further forming. With profile cutting tailor-made cuts can be made by following prefabricated templates or drawings (Fig. 22).

Compression-cutting is a special variant of profile-cutting. All these processes exploit the easy deformability and excellent recovery of PUR flexible foam (Fig. 23).

Advances in foam trimming equipment such as fully automated CNC processing lines allow for economical conversion of foam buns into very sophisticated contoured parts (Fig. 24). At the same time, trim losses are minimized by specific software [188].

Form milling is used for rounding edges on seat backs and armrests as well as on seat pads. Due to the large variety of milling tools, any shape is possible (Fig. 25).

Other post-treatment methods include reticulation, impregnation, compression, welding, cementing, laminating with textiles or films by flame lamination or adhesive bonding, quilting, and covering.

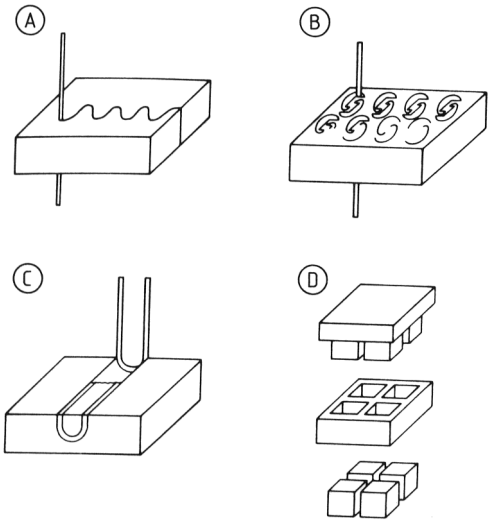


Figure 22. Cutting methods and punching
A) Hot-wire cutting; B) Copy cutting; C) Profile cutting; D) Punching

The trimmed-off foam is flaked in suitable mills. The flakes can be used as filling material or are bonded to form flake-composite blocks, referred to as rebonded foam. These composite blocks are then fabricated similarly to normal foam slab stocks (see Section 14.3).

7.1.1.5. Applications

The variety of properties and the continuous development of new foam grades and further processing techniques have made slabstock indispensable for many applications.

For furniture, the use of polyether foams extends from complete foam upholstery to the simple seat cushion. Very comfortable cushioning is achieved by combining types with different properties (e.g., density, hardness, or elasticity).

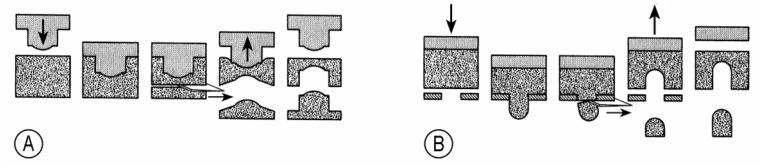


Figure 23. Compression cutting
A) Convoluting process; B) Skiving process

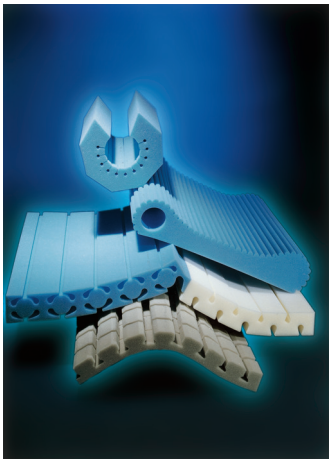


Figure 24. Contoured parts, produced by different trimming technologies

Full PUR foam mattresses at present account for approximately one-third of all mattresses sold in Europe. The relative low weight (e.g., versus latex foam) and the freedom of design by combining various foam types (high resilient, conventional, viscoelastic) and grades (density, hardness) in conjunction with advanced cutting systems have turned these mattresses into high-tech applications. All required grades of hardness are available, from the child's to the intervertebral disk mattress. Even in steel-spring mattresses, a layer of slabstock foam is used as cushioning and lining material.

An important field of application for slabstock foam is the lamination of fabrics. Polyester foams are preferred to polyether foams due to their melting properties and their specific cell structure. The foams can be bonded on one or two sides with textile widths by adhesive or flame lamination and are widely used for automotive interior trim applications such as seat covers or headliners.

Other applications in automotive industry are sun visor fillings, which can be manufactured from semirigid polyester foams, and sound-absorption materials for passenger, engine, and trunk compartments. PUR foams are also used as sealing and filter materials in the ventilation system. All foams for automobiles must satisfy the fire test MVSS 302 (see Section 14.4). Depending on the density and the chemical nature of the PUR foam (HR or conventional foam) flame retardants must be added to the foam formulation to meet this requirement.

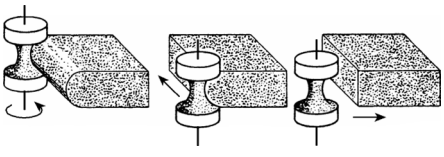


Figure 25. Shaping of flexible foam by milling

In the clothing industry the above-mentioned laminated fabrics are incorporated into jackets and coats. Other applications are paddings in ski and sports boots and underlinings in the purse-making industry.

Flexible PUR foam is particularly suitable as a packaging material for fragile goods. Because of the variety of cutting processes, extremely complicated shapes can be produced for the transportation of goods.

The main application in the household sector is sponges. They are produced from both polyether and polyester foam in very diverse colors and shapes. They can be fine- or coarse-pored and range from extremely flexible to almost rigid. The foam's hydrophilicity can be increased by using special additives. The range of uses in the household includes adhesive, sealing, and jointing tapes as well as undercarpet padding, doormats, and cleaning brushes. Special grades can be obtained by bonding with thermoplastic films by high-frequency welding.

The ability of flexible foams to absorb airborne noise efficiently is exploited for noise abatement. The low thermal conductivity of flexible block foams is used for the thermal insulation of heat accumulators and pipes. For use as filter material, e.g., in ventilation and air-conditioning systems or as dust filter in breathing masks, the flow resistance of the foam must be reduced by post-treatment. Depending on technical requirements, the foam can also be used as a filter for liquids. Since the foams do not absorb X rays, they are an ideal material for the comfortable support of parts of the body during X ray exposure.

7.1.2. Molded Flexible Foam

The foam molding process is used when it is impossible or uneconomic to produce a complex geometry by trimming slabstock foam, or

when the incorporation of metal inserts (for fastening cushioning units or coverings) or even steel springs (for furniture applications) is desired. A distinction is made between hot-cure molded foam and cold-cure molded foam.

7.1.2.1. Production

To produce hot-cure foam, trifunctional polyethers with a low content of highly reactive primary OH groups in the molecular mass range of 3000–5000 g/mol are reacted with toluene diisocyanate (TDI) with ca. 80 % of the 2,4′ isomer, e.g., Desmodur T80. The blowing agent is carbon dioxide, which is formed by the water-isocyanate reaction. Polyether polysiloxanes are employed for stabilizing the foam and due to the lower reactivity of the polyols, tin dioctanoate or other tin compounds are used to catalyze the polyurethane reaction, amines are used to catalyze the blowing reaction, and rather high mold temperatures must be applied. The hardness of the foams can be adjusted by adding grafted polyols for increased load-bearing properties or by using special polyols or additives for softer grades. The resulting foam is open-celled and does not require crushing for cell opening.

Cold-cure foams are produced from trifunctional polyethers with enhanced reactivity (high proportion of primary OH groups) in the molecular mass range of 5000–6000 g/mol and grafted polyols. A variety of different isocyanates are used, usually with a functionality exceeding two (modified TDI types, blends of TDI and higher functional MDI; special MDI types). If pure TDI 80 is applied, polyethers with a functionality slightly higher than three are usually used (e.g., Hyperlite). No further blowing agents are used; the carbon dioxide formed from the reaction of water with isocyanate is the sole blowing agent. Due to the higher reactivity of the polyols no metal catalysts are required for curing, and the mold temperatures are relatively low (“cold” cure) compared to hot-cure foam. On demolding the cold-cure foam is closed-celled and must be mechanically crushed to avoid shrinkage and to achieve consistent physical properties.

7.1.2.2. Molding Process

The molding methods for hot- and cold-cure foam systems differ sharply from each other.

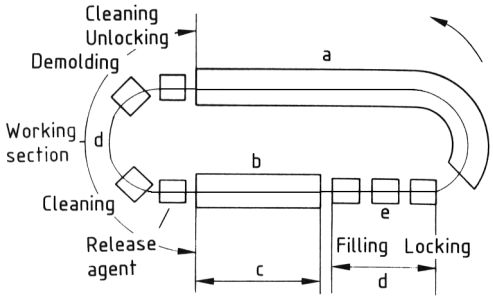


Figure 26. Plant for hot-cure moldings
a) Oven (160–250°C); b) Recirculating air/water bath; c) Cooling section; d) Working section; e) Inserts

This is mainly because external heat must be supplied to a hot-cure molded foam to cure the foam’s surface fast enough.

Figure 26 shows the individual process steps of the hot-cure foam molding process. This production sequence has a cycle time of ca. 20–25 min, depending on the nature and size of the foam parts.

The molds consist of black iron plate (wall thickness 1.5–2.0 mm), aluminum sheet (wall thickness 4–6 mm), or cast aluminum (wall thickness 6–10 mm). Since the foaming process for this foam type must proceed unpressurized, good mold venting is necessary. The arrangement of the vent holes is determined experimentally. In manufacturing the molds, a volume loss during the curing process of ca. 2 % must be taken into consideration. The precise value is specific for the formulation and must be determined experimentally. Release agents are mainly aqueous wax or soap dispersions. High- or low-pressure machines, operating batchwise, are used for metering the raw materials. The molds are usually heated by hot-air ovens. The heating capacity of the ovens for the full-cure process must be adapted to the mold material and the required cycle time. After removing the molded foam parts, the molds are cooled by water or cold air to the loading temperature.

The curing process can be shortened by rapid adjustment of the internal wall temperature of the mold to ca. 120 °C after the end of the rising time. In this case, the molds are heated directly with liquid heating media to conserve energy.

Cold-cure foam systems require much lower mold temperatures. To achieve the optimum quality of the foam skin, the molds are adjusted

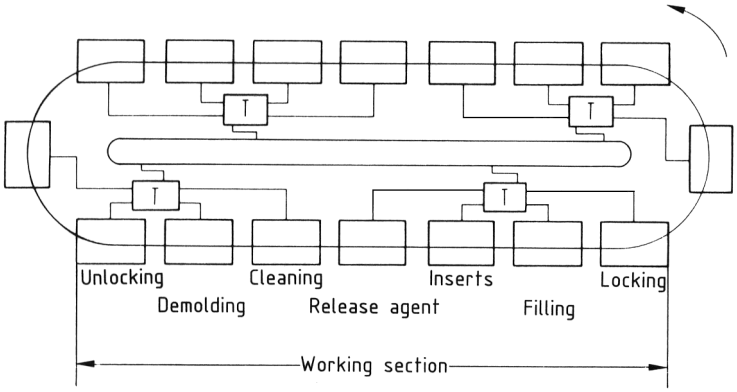


Figure 27. Plant for cold-cure moldings
T = thermostatting units

to the optimum temperature for the mold material and the release agent (between 40 and 65 °C). Cooling equipment is not required (Fig. 27). Depending on the combination of polyols, the isocyanate, the catalyst package, and the shape of the cavity, the foam can be demolded after 2–6 min.

In contrast to open-celled, hot-cure molded foam, the closed cells of cold-cure foam parts must be mechanically opened. This can be achieved by roller crushers with counter-rotating rollers, compressing the parts to a fraction of their original height, or by fast alteration of the ambient pressure in a pressure chamber.

One hour after demolding, cold-cure molded foams have reached only 50–80 % of their final hardness. Therefore, cold-cure foam parts need to be handled with care in the first few hours after production. Depending on the chemistry and the climatic conditions, final properties are achieved after 5–12 h (for comparison: a hot-cure foam will reach its final hardness within the first 2 h after demolding).

The foam molds must be designed for an internal mold overpressure of 0.3–0.6 bar. When fabricating the master patterns for the mold replica, a loss in volume of the molded part of up to 2 % must be taken into account.

Larger plants (greater space requirement, more molds) are required for the production of hot-cure foam than for cold-cure foam, owing to both the heating/cooling cycle and the longer mold holdup times of ca. 12 min compared to 4–8 min for cold-cure foam. Under ideal conditions, hot-cure molded foam has the advantage of a lower molding mass compared to cold foams at the same compression-load deflection.

7.1.2.3. Properties

Hot-cure and cold-cure foams differ fundamentally in their mechanical properties. The lowest densities can be achieved with hot-cure foam. At the same density, a hot-cure foam will usually provide a higher hardness. However, due to higher venting losses, savings in material for a hot-molded piece of foam are significantly lower than expected based on the simple comparison of apparent densities. The compression load deflection curves of molded foams can be compared with that of free-rise flexible foams (Section 7.1.1.3): the characteristics of hot-cure molded foam are similar to those of conventional slabstock foam; cold-cure molded foam can be compared with HR slabstock. The hysteresis curves show that cold-cure foam has a higher elasticity (narrower hysteresis loop) than molded parts from hot-cure foam. Table 7 gives a general overview of the properties of hot- and cold-cure foams.

With a cold-cure foam cushion, greater comfort is experienced due to its higher elasticity. However, for an automobile seat this higher elasticity means a reduced damping of the vehicle's vibrations. Since the construction of the seat (full foam or combination of foam and springs) and the damping behavior of the vehicle structure must be matched, the question whether to use hot-cure or cold-cure molded foam must be decided for each individual case. A second and more basic difference between

Table 7. Average properties for seat grades of flexible molded foams

Property	Hot-cure foam	Cold-cure foam	
	HC	TDI based HR-T	MDI based HR-M
Apparent density (EN-ISO 845), kg/m^3	28 – 40	35 – 50	45 – 65
CLD-Hardness at 40 % (EN-ISO 3386-1), kPa	3 – 7	2 – 8	4 – 12
Compression set 50 %, 70 °C, 22 h (EN-ISO 1856), %	2 – 4	4 – 8	4 – 8
Elongation (EN-ISO 1798), %	120 – 160	100 – 150	90 – 120
Tensile strength (EN-ISO 1798), kPa	80 – 140	130 – 200	100 – 160
Tear strength (ASTM D 3574-F), N/m	200 – 400	200 – 450	160 – 250
Humid ageing (OEM specific)	very good	good	good – very good
Hysteresis (Energy Dissipation)	high	low	medium

hot- and cold-cure foam is their fire behavior. Cold-cure foams down to a density of ca. 35 kg/m^3 usually meet the fire standards of the automobile industry, even without added flame retardants. For hot-molded foam, flame retardants must be used.

7.1.2.4. Applications

Flexible molded foams are principally used in all kinds of seat pads, seat cushions, backrests, bench seats, headrests, etc. in passenger cars (see Fig. 35), motorcycles, and commercial vehicles, aircraft, and railways. Another important area of application in the automotive industry is sound abatement. Flexible molded foam is used either on its own for absorption of airborne noise or as a composite in conjunction with a heavy layer (EPDM, EVA, or PUR elastomers filled with, e.g., barium sulfate) or as backfilling foam on the vehicle's floor cover. These composites may act either as sound barriers or can be tailored to dampen structureborne noise. In addition, flexible molded foams are used in the furniture industry, e.g., for office chairs, armrests, and in specific combinations with steel springs, which are incorporated into the molded foam. Sealing lips for passenger car tail lamps and for filters can also be produced from molded foams.

7.2. Semirigid Foams

7.2.1. Applications

Semirigid foams are used primarily for improving inner safety and comfort in automobiles. Combined with an external layer of ABS/PVS or PUR skin and a metal or plastic carrier, they are used to produce instrument panels (dash boards), door and pillar covers, armrests, and consoles. The foam has a density range of 80–180 kg/m^3 in the finished part. Key properties are long-term adhesion to skin and carrier, a uniform, fine cell structure, low emission, and high resistance to aging and heat.

Special grades (EA foams) are optimized for energy absorption. On impact, they dissipate the kinetic energy by deformation and thus protect the passengers in a crash (Fig. 28).

7.2.2. Production

Parts made of semirigid foam are produced mostly in a two-step process. First, the preformed skin (ABS/PVC by thermoforming or PUR by spraying) is positioned in the cavity of

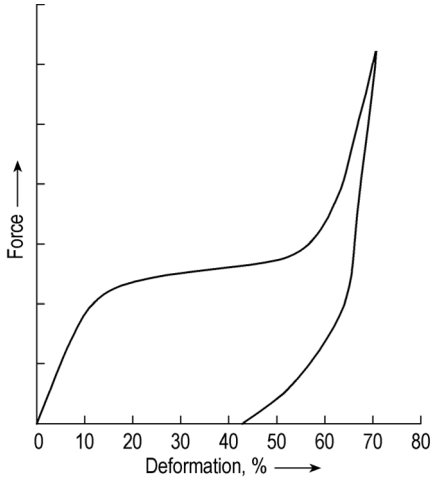


Figure 28. Dynamic force–deformation characteristics of a semi-rigid PUR foam

the mold. A plastic or metal carrier is fixed on the lid of the mold. In the second step, the mold is closed and the semirigid foam is injected. Alternately, the semirigid foam is spread in the open mold and the lid is closed before the foam expands.

The two PUR components are mixed by high-pressure machines. The molds are made from aluminum, often coated with epoxy resin. If the foam has contact to the surface of a mold, a wax-based release agent must be used. The demold times are between 1 and 6 min, depending on the size, thickness, and geometry of the parts and on the reactivity of the foam system.

7.2.3. Properties

Semirigid foams are mostly open-celled and have a higher compression load deflection and lower elasticity than flexible foams. Typical properties are:

Apparent density (ISO 845)	80–180 kg/m^3
Tensile strength (ISO 1798)	300–400 kPa
Elongation at break (ISO 1798)	30–60 %
Compression load deflection at 40 % compression (ISO 3386)	80–200 kPa
Compression set at 50 % compression (ISO 1856) 22h at 70 °C	< 10 %

The dynamic impact characteristics (Fig. 28) are important for the dampening and energy absorbing behavior.

7.3. Rigid Foams

Rigid foam is in most cases a closed-cell material that is used for thermal insulation. Besides providing thermal insulation the foam may also have to bear mechanical loads in some applications. Composite structures in which the self-adhesive effect is used to bond the foam to a substrate during the foaming process are often found in the field of rigid foam. This reinforcing sandwich-effect improves the mechanical properties significantly.

Rigid foam is used in many ways. The main applications for rigid foam are appliances (refrigerators, freezers), insulation boards (with and without facings), composite panels (mostly with metal facings), pipe insulation (as insulating shells or as composites), insulated containers, and in situ foam (spray foam).

7.3.1. Raw Materials

Rigid PURs require a highly cross-linked molecular structure. To achieve this, raw materials with high functionalities and low molecular weight are preferred on the polyol and on the isocyanate side. Therefore, short-chain polyether polyols and polymeric MDI are the materials of choice. Low molecular weight polyester polyols are also used.

Typical polyether polyols (see Section 3.2.1) are produced from a highly functional starter molecule (sucrose, sorbitol, glycerol, diethylene glycol, ethylenediamine, and others) or mixtures thereof by adding alkylene oxides, mainly propylene oxide but sometimes ethylene oxide. The resulting products are viscous liquids.

The *polyester polyols* (see Section 3.2.2) are typically based on aromatic acids like phthalic acid. (Di)ethylene glycol is mostly used as alcoholic component. Glycerol or other highly functional alcohol components may be used to increase the functionality. However, the use of starting materials with higher functionalities is limited because of the increasing viscosities of the resulting products.

The *polymeric* MDI types (see Section 3.1.1) that are used have functionalities in the range of roughly 2.5 to 3.5, corresponding to viscosities of about 100 to 1000 mPa · s at 25 °C.

Blowing agents (see Section 3.5) are not only used to create the foam. Since the blowing agent remains inside the closed cells it has a strong influence on the thermal conductivity of the resulting foam. The choice of the blowing agent depends on the most important criteria in the respective application, such as the lowest possible thermal conductivity, processability, or relationship between cost and performance. In most cases, a combination of a physical blowing agent (a low-boiling liquid or a gas) and a chemical blowing agent (mostly carbon dioxide formed by the chemical reaction of water with isocyanate) is used. While, according to the Montreal Protocol, the use of chlorine-containing halogenated hydrocarbons is still allowed in certain areas of the world, the use of these products in Western Europe is banned. Here only fluorinated hydrocarbons such as

tetrafluoroethane (R 134a), pentafluoropropane (R 245fa), and pentafluorobutane (R 365mfc) may be used. Hydrocarbons such as n-, iso-, and cyclopentane or mixtures with other hydrocarbons like propane or butane are widely used, despite their flammability. Methods for a safe handling of these products are industrially available and installed. All these blowing agents have very small coefficients of diffusion; they remain within the foam during its lifetime. Where no (metallic) facings are provided, the thermal conductivity increases very slowly because of air diffusing into the foam. Therefore, in some applications, e.g., the construction industry, increments are added to the measured values of the thermal conductivity to take this ageing process into account. In this way it is ensured that a sufficient level of insulation is installed.

Catalysts (see Section 3.5), sometimes called activators, are used to control the foaming process. Products used as catalysts are tertiary amines, organometallic compounds, and alkali metal and quarternary ammonium salts of carboxylic acids. The products may be classified according to their performance-without really being able to draw sharp lines-as blowing, gel, and trimerization catalysts. A few examples taken from a wide range of products are given here: bis[2-(N,N-dimethylamino)ethyl]ether and *N*, *N*-bis(*N*′,*N*′-dimethylaminoethyl)methylamine as blowing catalysts; triethylenediamine (dissolved) and dibutyltin dilaurate as gel catalysts and potassium acetate (dissolved) and 1,3,5-tris(3-(dimethylamino)propyl)hexahydrotriazine as trimerization catalysts.

Foam stabilizers (see Section 3.5), also called surfactants, are required to prevent the small bubbles in the liquid reaction mixture from coagulating. Fine-celled foams can be prepared by using these products. To produce foams with a fine cell structure, some air (or other inert gases) may be dispersed into the polyol component or into the reaction mixture for nucleation. A fine cell structure is important for a low thermal conductivity. Chemically, most of the products used in the industry are polyether-modified polysiloxanes. The structural variations possible by using different polyethers and different polysiloxanes lead to the great number of products available on the market, optimized for various purposes. Some of these purposes are: flowability (describes the expansion of the foam into narrow cavities), adhesion to facings (the force required to remove the facing), fine cell structure (small cells of similar size), and flammability (resistivity to flames or high temperatures).

Flame retardants (see Section 3.5) are used to make the foams less flammable. The methods for testing flammability are manifold. However, official requirements regarding flammability are in place for some applications, e.g., in the construction industry. Since PUR foams are based on organic molecules, it is only possible to achieve certain flammability classifications within the group of flammable materials. Flame retardants used in the field are usually substances based on halogens and/or phosphorus. Some products have OH groups, so they can react with isocyanate and are incorporated into the macromolecule; others are nonreactive. Examples of reactive flame retardants are polyethers made from dibromobutenediol and epichlorohydrin or brominated aromatic polyester polyols. Examples of nonreactive flame-retardants are tris(2-chloroisopropyl)phosphate, diphenyl cresyl phosphate, and dimethyl propyl phosphonate. Apart from red phosphorus, which is used in the production of rigid slabstock foam by low-pressure mixing, solid flame retardants have hardly been used in the field of rigid foams. A technique has been developed for processing solid flame retardants continuously on high-pressure machines [189].

7.3.2. Processing

Mixtures of the raw materials mentioned above are processed to produce rigid foams. The foaming process is described and monitored by periods of time taken from the start of mixing:

The *cream time* is the time until the reaction mixture starts to expand. At this point in time, the exothermic reaction has heated the reaction mixture to a temperature at which the blowing agent is starting to evaporate. The gas formed remains in the reaction mixture and forms small bubbles that grow with increasing temperature and further formation of gas.

When the cross-linking of the polymer has progressed to the point where the liquid reaction mixture starts turning into a solid the *gel time*

can be observed. This is mostly done by prodding the foam with a small stick. When fibers of polymer are pulled from the rising foam the gel time has been reached.

After that the foam continues to rise to its final height (*rise time*).

The *tack-free time* is the time required for the surface of the foam to lose its tackiness. The tack-free time may occur before or after the rise time.

The time required to cool down the foam depends on its thickness. For slabs 1 m in height it takes more than 24 h until ambient temperature is reached in the core. In all processes the foam applies pressure on the compartment in which it is contained. To keep the parts produced within their specified dimensions, the molds must withstand this pressure until the foam has reached a minimum strength and the part can be demolded (demold time). In continuous processes, the line speed needs to be adjusted to keep the foam in the machine for the time required to cure sufficiently. For thicker parts the demold times are longer than for thinner parts, and therefore the line speeds in a continuous production are slower for thicker parts.

Preblending some of the components-usually into the polyol side-for easier operation can be done at different levels. It can be performed by the raw material supplier or by the processor. This depends mostly on the variability required for the respective process (e.g., adjusting reactivity in continuous processes).

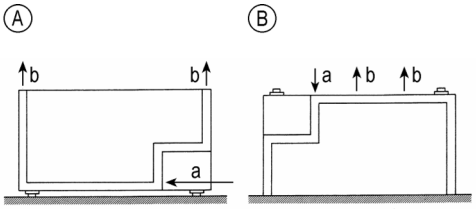


Figure 29. Principle of filling refrigerator cabinets
A) Door opening on top; B) Door opening on bottom
a) Pour-in opening; b) Ventilation openings

A discontinuous process (sometimes called a one-shot process) is used in cases where particular cavities are to be filled, such as in the production of refrigerators, freezers, insulated containers, and certain sandwich panels. Figure 29 shows the principle of filling refrigerator cabinets.

Figure 30 shows the discontinuous production of sandwich panels in a multistage press using the mixing head pull technique.

In most of these applications only one type of reaction mixture is used for the whole production range. Here all the necessary components are preblended into the polyol so that only two components, i.e, this polyol formulation and the isocyanate component, must be provided. The components are tempered and metered to the mixing head by high-pressure pumps. The mixing itself is performed by using the high-pressure impingement mixing technique. The amount of reaction mixture necessary to fill the cavity is determined by the volume of the cavity

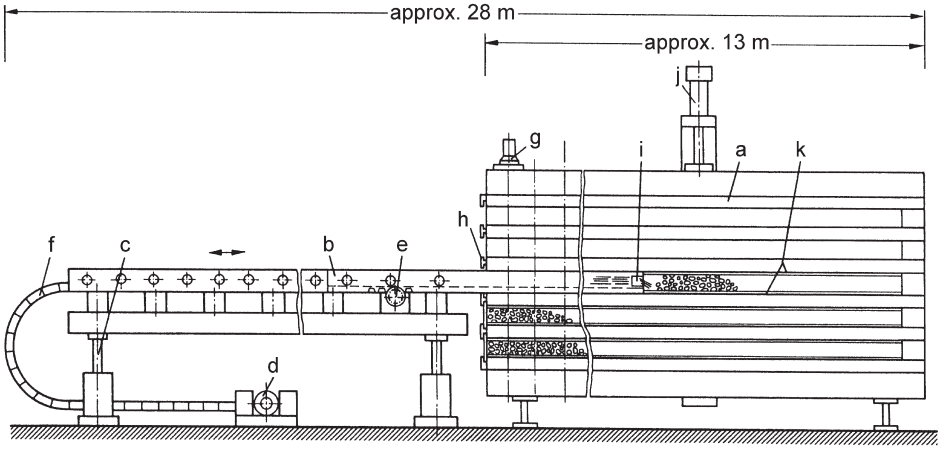


Figure 30. Production line for the discontinuous production of PUR composite elements
a) Plates of the press; b) Carrier on rolls for the hoses leading to the mixing head; c) Lifting device; d) Foam machine; e) Driving elements for horizontal movement; f) Cable holder; g) Device for closing the press; h) Closing cap for each unit; i) Mixing head with hoses; j) Opening device; k) Metal facers

and the density of the foam. The duration of the dosage is then given by the output of the pumps. This shot time must be shorter than the cream time to avoid pumping liquid reaction mixture into an already expanding foam. In so doing, the foam would be partially destroyed with negative effects on all of its properties.

In the continuous production of composite panels and insulation boards on double conveyor belts, the high-pressure impingement mixing technique is also used in most cases. The principle of this process is shown in Figure 31. Here the low weight of the mixing head and the hoses leading to it enable the oscillating of the mixing head across the moving bottom facing for an even distribution of the reaction mixture.

In the special case of the production of insulation boards on high-speed laminators at line speeds of up to 60 m/min, the high-pressure impingement mixing technique is used in most cases, but without oscillating the mixing head. The oscillation frequencies to ensure an even distribution of the reaction mixture on the bottom facing would be too high.

Here even distribution is achieved by passing the reaction mixture through a narrow gap between the top and the bottom facing (calibration technique). By this technique the small voids near the top facing that occur with the oscillating mixing head technique are eliminated. In all these applications it is necessary to adjust the reactivity of the reaction mixture according to the thickness of the board or panel. Also the amount of blowing agent must be adjusted. This means that the degree of preblending is lower than in a discontinuous process. Catalyst, blowing agent, and possibly other additives are metered separately into the polyol stream. Thus, only two components are finally led to the mixing head, keeping the moving weight low for the oscillation.

In the continuous production of rigid slabstock foam low-pressure mixing is used due to the high output. Here the components are metered into a mixing chamber and mixed by a mechanical stirrer. Separate metering of the components into the mixing head can be used. Preparing a polyol component containing all necessary components is also possible and allows for a certain quality control prior to foaming.

7.3.3. Properties

The most important property of rigid PUR foams is its low thermal conductivity, which is the lowest among the different insulation materials available by a significant amount. This allows for a smaller thickness of the insulating layer to achieve the same insulation value. The thermal conductivity of closed-cell PUR foams in the density range 25–60 kg/m^3 depends not so much on the apparent density (usually the thermal conductivity increases slightly with increasing density) but is dominated by the thermal conductivity of the blowing gas. The thermal conductivity can initially be near 0.020 W m^{-1} K^{-1}, and after ageing (cell gas diffusion) typically is in the range of 0.025–0.030 W m^{-1} K^{-1}.

The adhesion to substrates is important for composite constructions. The force needed to remove the foam from the substrate is the criterion used to judge adhesion.

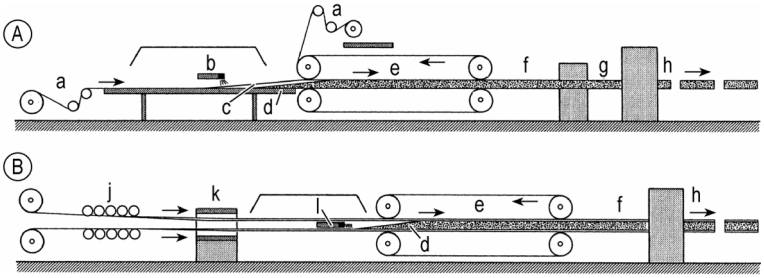


Figure 31. Principle of the continuous production of insulation board
A) With flexible facings; B) With profiled metal facings
a) Unwinding device; b) Lay-down with mixing head; c) Means for folding paper; d) Foaming reaction mixture; e) Compression; f) Cooling area; g) Longitudinal cutting; h) Transverse cutting; i) Coil unwinding; j) Corrugation rolls; k) Heating elements; l) Gate with moving high-pressure impingement mixing head

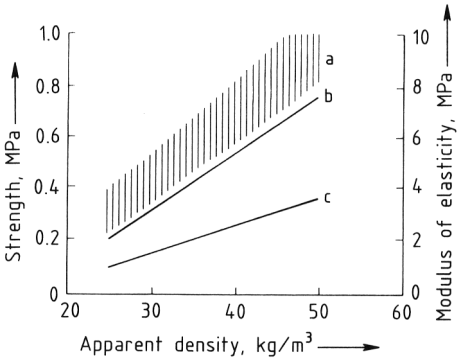


Figure 32. Relationship between typical properties and apparent density of rigid PUR foam (values at room temperature)
a) Modulus of elasticity; b) Tensile strength; c) Compression strength

Mechanical properties like compressive strength, tear strength, and shear strength are also important in load-bearing applications. Their values strongly depend on the density and the cell structure (Fig. 32).

Dimensional stability must be given under the conditions of use of the respective application. Dimensional stability is tested at low temperatures (e.g., for freezers) and at high temperatures (e.g., for hot water tanks).

Flammability is a very important property of the foam or the composite or both, depending on the test that needs to be passed. Various test methods are in place, most of them in the construction and transportation industries. For example, a harmonized test for the construction industry has been introduced in the EU. The new test procedure comprises a test on the foam (small burner) and the single burning item (SBI) test on the final product under end-use conditions. Other test procedures, e.g., those set up by insurance companies, are also in place.

For the different applications the importance of the various properties is prioritized differently.

For appliances (commercial and domestic refrigerators, freezers, hot water tanks), a low thermal conductivity is of top priority. In these applications a maximum useable space is desired at minimum or given outer dimensions. For this reason, the thickness of the insulation is limited, and only with a foam that offers low thermal conductivity can the energy consumption be minimized. Dimensional stability at low and high temperatures is the other important property here. In the low temperature applications the foam also fulfils a structural task, it forms a type of sandwich structure with the inliner and the outer facing.

Preinsulated pipes are mostly used for district heating. Here the thermal conductivity and the lifetime expectancy are the important properties. Accelerated ageing tests at elevated temperatures are performed to ensure a lifetime of, for example, at least 30 years according to EN 253.

Insulation boards, predominantly those with facings (aluminum foil, mineral fleece, papers) produced on double conveyor belts, also require low thermal conductivity and dimensional stability. On larger insulated areas, e.g., flat roofs, shrinkage would lead to areas without insulation due to gaps between the boards, while swelling might make the boards lift up and break the protective cover. For decorative boards also the appearance is important. Wrinkled facings, mostly aluminum foil, or sink marks due to voids under the facing are unacceptable here. Since most of the products are used in construction, flammability is also an important property.

Composite panels, mostly produced continuously on double conveyor belts with profiled steel sheets as facings, are mainly used in the construction of walls and roofs of large buildings like warehouses or factory buildings. The prefabricated self-supporting panels are attached to a bearing frame construction, so that the complete wall or roof can be put together very fast. The most important properties here are adhesion of the facings, dimensional stability, flammability, and thermal conductivity. The appearance is also important, especially for panels in facades. The thickness of the panels depends on the use of the building. For cold storage houses, where goods are stored at −40 °C, panels up to 24 cm thick are used. The thickness of panels for factories (from about 20 to 100 mm) depends mostly on the local climate. Discontinuously produced panels may have locks for connecting panels with one another that are incorporated into the foam during the foaming process. These panels can be used without bearing constructions, e.g., for walk-in-coolers. Another application is the use of panels in roll-up doors; large ones for truck entrances in industrial buildings, and small ones for private garages.

Slabstock foam is made for applications in very different fields. A few examples are given

here: low-temperature insulation (liquid gas tanks, also in ships); refrigerated containments for lorries, where the foam is covered with glass reinforced plastic; insulation for parts that are difficult to mold such as valves and flanges (here the foam is mechanically shaped); wedge-shaped boards to give flat roofs a slope; and others. Different properties are required in these different applications, so rigid slabstock foam is a specialty field. Foams with a range of densities from about 30 to over 200 kg/m^3, different flammability classifications, foams with glass fiber reinforcements, and other variations are found here.

7.3.4. Special Types

Foam from pressurized cans, mainly one-component-foam, is used for mounting and fixing applications such as windows and doorframes. Here all the raw materials, including blowing agent and isocyanate, are blended in the can to form a prepolymer with residual NCO groups. The propellant, that is, liquid under pressure, acts first as thinner for the prepolymer. When expelled the propellant acts as blowing agent to produce the foam. The foam itself is usually an open-cell product.

A few special types of open-cell foam exist, such as thermoformable rigid foam that is used in passenger car headliners, foam for flower-arranging purposes, and packaging foam. Recently some attempts have been taken to evacuate open cell foam to reduce the thermal conductivity even further. One problem here is to find suitable facings that ensure that the vacuum is maintained during the lifetime of the product.

In certain cases the foam must be applied in situ. Two methods are predominant: spraying and layer-by-layer application. Spray foam is mostly used for the industrial insulation of storage tanks or in the insulation of buildings. While spray foam on walls is only for insulation, foam on roofs is also applied for sealing purposes. Two-component systems are used here. The components are fed through heated hoses to the mixing head, which is designed like a spray gun. The reactivity of these systems is so high that the foam cures within a few seconds. In layer-by-layer application the reaction mixture is poured between two substrates, e.g., the outside of a tank and the casing. This method is used where the application of the foam in a factory is not possible, e.g., because of the size of the tank. Here also two-component systems are used. In both cases special attention must be paid to temperature and humidity conditions. Foams should not be applied on cold or moist surfaces. Otherwise, problems with bonding the foam to the substrate may result.

Polyisocyanurate (PIR) foams [190–195], more precisely to be understood as polyisocyanurate-modified PUR foams, are products in which isocyanurate structures are incorporated into the macromolecule. These structures are formed due to the reaction of excess isocyanate with itself. Special (trimerization) catalysts are required. Three NCO groups form the cyclic isocyanurate structure, which shows a higher decomposition temperature than PUR groups. Therefore, these foams are used where flammability or heat resistance is an issue. However, this highly cross-linked structure increases the brittleness of the foams. The overall cross-linking density is controlled by the use of low-functionality polyols. In the continuous production of insulation boards on double conveyor belts, which is the major application for this type of foam, the PIR structure is usually combined with (aromatic) polyester polyols. The higher decomposition temperatures of esters compared to ethers also leads to an additional positive effect on the flammability of the foam. In the manufacturing of these foams, special attention must be paid to the temperature of the laminator because the trimerization only takes place at temperatures above 60 °C. Apart from the reduction of brittleness the polyols have the task of heating the reaction mixture by their exothermic reaction with isocyanate. When the required temperature is reached, the trimerization starts, which can often be observed as a second phase in the expansion of the foam.

7.4. Integral Skin Foams and RIM Materials [196–198]

Integral skin or self-skinning foams are products with a cellular core and a cell-free surface that are formed in a mold in a single operation (Fig. 33). Parts made by the reaction injection molding (RIM) process are microcellular materials with a high surface quality that are mostly painted.

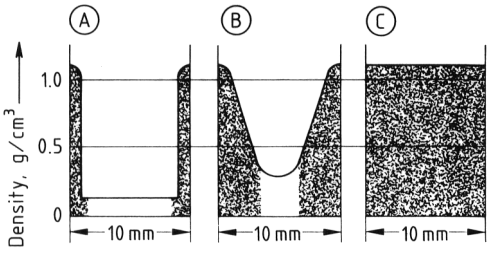


Figure 33. Principle of density distribution for integral foam boards of 10 mm thickness and various apparent densities:
A) 0.2 g/cm^3; B) 0.6 g/cm^3; C) 1.1 g/cm^3

7.4.1. Applications

Flexible self-skinning foams are used mainly in the automotive, furniture, and footwear industries. Typical automotive applications are steering wheels and gearshift knobs, but also armrests and headrests (Fig. 34). In the footwear industry, integral skin foams are used for soles of sport, leisure, and safety shoes.

RIM materials are used for exterior auto parts like fenders (Fig. 35A), panels, side protection and window encapsulation, but also for other exterior parts in agricultural machines or recreational vehicles like snowmobiles (Fig. 35B).

Rigid integral skin foams or RIM materials can be used in many different applications, mainly for structural parts. They can favorably compete with wood, thermoplastics, thermosets, and metals. They are used for furniture, skis, pump housings, window frames, decorative applications, and housings, just to name a few characteristic applications.

7.4.2. Production

Integral skin foams are mostly manufactured in metallic (aluminum) or epoxy molds. Skin formation is controlled by addition of a low-boiling solvent in amounts of about 2–10 wt %, relative to the polyol mixture. After the banning of CFCs and HCFCs, currently HFCs (hydrofluorocarbons) or alkanes are used. When using alkanes, special precautions must be taken because of their flammability.

Thermodynamic equilibrium between the liquid and gaseous phases of the blowing agent in the reaction mixture is crucial for the formation of the closed surface. The mold temperature is kept between 40 and 60 °C, and the reaction mixture in the vicinity of the mold surface has a lower temperature than the core (up to 140 °C). In the core the blowing agent vaporizes, while near the edge it condenses, with formation of the solid surface.

The quality of the surface depends very much on the quality of the mold, but precise control of the processing pressures and temperatures is also required.

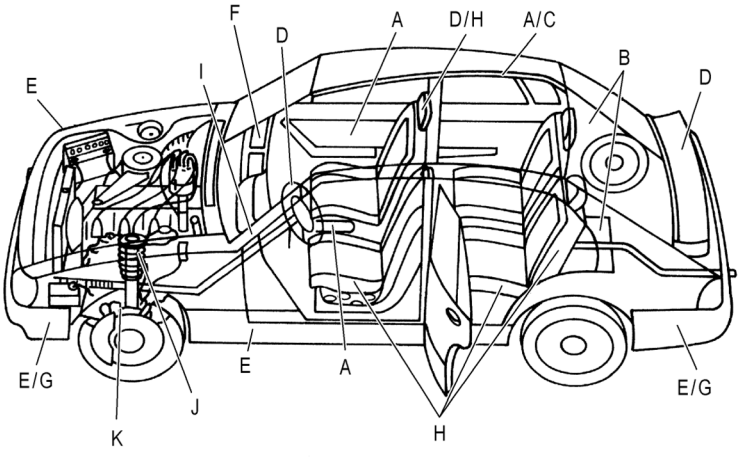


Figure 34. Use of PURs in the passenger car
A) Rigid integral foam; B) Rigid integral foam, glass-mat reinforced; C) Hot-moldable rigid foam; D) Semi-flexible integral foam; E) Semi-flexible integral foam, glass-fiber reinforced; F) Semi-flexible filling foam; G) Semi-flexible filling foam, impact-energy-absorbing ; H) Flexible molded foam; I) rigid foam; J) Hot-curing PUR elastomer; K) PUR rubber

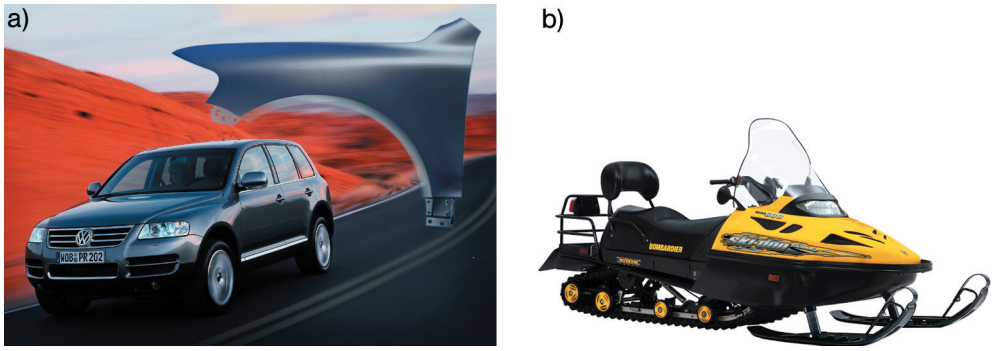


Figure 35. Use of integral skin foams and RIM materials
A) Fender of the VW Touareg; B) Snowmobile

In special cases formation of an integral skin is possible without the addition of physical blowing agents. For this, temperature-controlled carbon dioxide formation from the NCO/H_2O reaction must be achieved.

High-pressure metering and mixing units are necessary for manufacturing of RIM parts. The processing of these materials, which are mostly of high reactivity, also requires closed, metallic molds and a clamping unit. To obtain void-free parts without porosity the reaction mixture must enter the mold cavity through a gate designed to ensure laminar flow. Also, correct venting of the mold at the highest points and nucleation of the reaction mixture by air or nitrogen are important for good quality.

After demolding, the parts must be trimmed, and gate and flash must be removed. The surface is prepared for painting by removal of the release agent by washing or sanding.

7.4.3. Properties

Depending on the field of use, soft-elastic moldings have densities of 100–300 kg/m^3, flexible molded articles 400–600 kg/m^3, and the relatively hard, microcellular elastomers 900–1100 kg/m^3.

Technical data for a typical soft integral skin foam of low density:

Density (ISO 845)	400 kg/m^3
Shore A hardness (DIN 53505)	35
Tensile strength (DIN 53504)	0.8 MPa
Elongation at break (DIN 53504)	85 %
Tear resistance (ISO 34)	1.4 kN/m
Compression set (25 %/70 h, RT; ISO 1856)	2.5 %

Mechanical properties of a flexible molding of medium density used in the footwear industry (e.g., polyester system):

Density (ISO 845)	500–600 kg/m^3
Shore A hardness (DIN 53505)	ca. 50
Tensile strength (ISO 1798)	6–8 MPa
Elongation at break (ISO 1798)	450–550 %
Tear propagation strength (ISO 34)	10–15 kN/m
Abrasion loss (DIN 53516)	50–100 mg

Mechanical properties of a microcellular elastomer molding of high density (e.g., automotive body parts):

Density (ISO 845)	1100 ± 50 kg/m^3
Shore D hardness (DIN 53505)	64 ± 3
Tensile strength (DIN 53504)	35 ± 3 MPa
Elongation at break (DIN 53504)	300 ± 30 %
Tear propagation strength with cut (ISO 34)	80 ± 10 kN/m
Modulus of elasticity according to Roelig	
at –30 °C	1400 ± 100 MPa
at + 20 °C	600 ± 50 MPa
at + 65 °C	360 ± 30 MPa

The technical data of rigid integral skin foams depend very much on the density, which can be anywhere between 150 and 1100 kg/m^3. Typical properties of a low-density rigid integral skin foam, as used for imitation wood follow:

Density (ISO 845)	400 kg/m^3
Shore D hardness (DIN 53505)	58
Flexural strength (ISO 178)	20 MPa
Flexural modulus of elasticity (ISO 178)	520 MPa
Impact strength (ISO 6603)	10 KJ/m^2
Heat deflection temperature (ISO 75)	90 °C

High-density rigid RIM materials, which are typically used at wall thickness between 3 and 5 mm, have the following characteristics:

Density (ISO 1183)	1100 kg/m^3
Shore D hardness (DIN 53505)	76
Flexural strength (ISO 178)	25–45 MPa
Flexural modulus of elasticity (ISO 178)	2000 MPa
Tensile strength (ISO 527)	53 MPa
Elongation at break (ISO 527)	14 %
Impact strength (ISO 179)	45 KJ/m^2
Heat deflection temperature (ISO 75)	115 °C

When flame retardancy tests are also considered, RIM materials are capable of passing burning tests such as UL 94 V-0 (Underwriters' Laboratories) or B2 (DIN 4102) by the addition of flame retardants.

Both flexible and rigid RIM materials can be reinforced with short or long glass or mineral fibers and also glass mats or mats made of natural fibers. These composite materials show considerably higher stiffness and especially impact strength.

8. Noncellular Polyurethanes

Although the term "noncellular" is unambiguous, the terminology of the products treated in this chapter requires explanation. "Cellular Vulkollan," well known from the early days of PURs, already breached the borderline of precise definition. In practice, this material was not considered a "foam," although it can be undoubtedly classified as a foam from a strictly physical viewpoint because of its cellular structure, however small the few cells may be. The RIM technology has made the definitions even less distinct due to the terminology of "microcellular elastomers" on the one hand and "solid integral parts" on the other. In this chapter the problem of definition is solved as follows: All products which are based on a formulation that usually leads to a foam are classified as "foams," even if cell-free solid materials can be obtained by raising the apparent density (less blowing agent). Similarly, products which are based on formulations that usually result in noncellular materials are classified as noncellular PUR, even though they may be cellular, and these materials are treated in this chapter.

There are two different processing technologies for manufacturing these noncellular PURs. Liquid, low molecular mass raw material systems are converted to high molecular mass products by the reaction of the polyol and polyisocyanate components by cold or hot curing. Linear, high-molecular-mass raw material systems are either thermoplastically processable pellets or urethane rubber are processed by vulcanization technology.

8.1. Cast Elastomers

Cast elastomers are mostly solid, noncellular materials, produced in a low-pressure casting process from ester or ether prepolymers of MDI, TDI, and NDI (see Section 3.1.1) and a cross-linker such as butanediol. If water-containing cross-linkers are used, cellular elastomers can also be obtained.

8.1.1. Applications

The highest quality elastomers are those derived from NDI [Tradenames: Vulkollan (Bayer MaterialScience), Cellasto (Elastogran)]. They are used where materials must meet extremely high requirements regarding durability and mechanical properties. Examples are high-load rolls and wheels for forklift trucks and machines, hydraulic seals, membranes, valve seats and balls, scrapers, and sieves. Cellular NDI-based elastomers are widely used in the automotive industry for bouncers and spring supports (Figs. 34 and 36).

Hot-curing elastomers based on MDI or TDI are used, e.g., for bottle stars in automatic filling machines, cutting wheels for fiber production, roll covers for the paper and printing industry, and wheels for in-line skates and skateboards.

Cold-curing PUR elastomers are used as binders for the surface of playgrounds and sport tracks. These surfaces are very durable, require little maintenance, can be used under all weather conditions, and reduce the risk of injuries. Other applications are seals for stoneware pipes, polishing disks, protective edges, and permanent fenders for boats. Cold-cure elastomers can also be sprayed on concrete or metal for corrosion protection and are used for the surfacing of bridges, parking decks, and terraces and for lining of wagons and trucks.

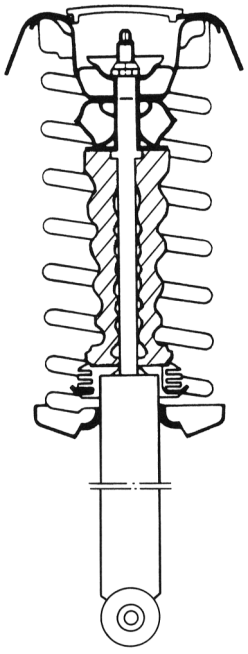


Figure 36. Use of cellular Vulkollan as supplementary spring in the passenger car

8.1.2. Production

The raw materials used are low molecular mass glycols or amines, polyester or polyether polyols, and (modified) MDI-, TDI-, or NDI-type isocyanates.

The elastomers can be manufactured in a two-step or a one-step procedure. Figure 37 shows a typical line for the production of high-quality elastomers, as is used for NDI-based high-performance materials. The system passes through several stages: dehydration of the polyester (a), production of prepolymer from polyester and diisocyanate (b), degassing of the feed component (c), admixing of cross-linking agent (d), atmospheric-pressure casting in open molds (e, f), and fully curing the molding at 100–300 °C for several hours (g). This processing technique even allows the production of voluminous and thick-walled parts in relatively simple, inexpensive molds with low energy consumption. Depending on the system to be cast, steel, aluminum, and in special cases plastics or wood can be used as the mold material.

For MDI and TDI stable prepolymers are commercially available, so that a one-step process can be used. The reactivity of the raw materials varies widely. Casting times between 2 and 60 min can be realized.

Cold-casting systems are usually processed with a casting machine. For some formulations that have a sufficiently long pot life, the starting components can also be hand mixed and cast. In

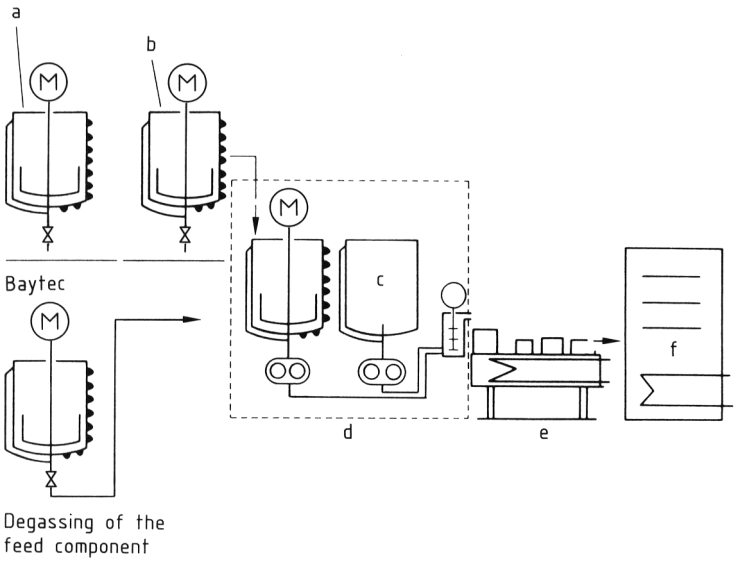


Figure 37. Flow chart for production of high-quality elastomer (e.g., Vulkollan/Baytec)
a) Dehydrogenation of the polyester; b) Prepolymer production; c) Cross-linker; d) Casting machine; e) Mold frame; f) Heating oven (thermal posttreatment)

this case the charge volumes are limited to a few liters. The reaction mixtures cure, without an external heat supply, within widely differing cure times, from less than 10 min to a maximum of 24 h. The castings reach their final strength after ca. 7 d storage at room temperature.

8.1.3. Properties

NDI-based elastomers have a temperature range for continuous use between −30 and +80 °C. At temperatures below 0 °C the material becomes increasingly hard and inelastic, though there is no danger of fracture. Embrittlement occurs only at very low temperatures (below −30 °C).

NDI elastomer (Vulkollan) is resistant to mineral oils, grease, gasoline, and most organic solvents. Gasoline and some solvents cause some swelling, but this does not impair its mechanical properties if the solvents are able to re-evaporate. Concentrated acids, alkalis, and other hydrolyzing media attack NDI elastomers. By incorporating additives or using special polyesters the hydrolytic stability can be increased so that the service life of the elastomers becomes adequate for a variety of uses even under extreme conditions. Mechanical properties of NDI elastomers are listed in Table 8.

Cellular NDI elastomers can be produced with densities of 300–700 kg/m^3 and are characterized by their high capability of absorbing energy on impact. The material can be compressed by up to 80 % of the original volume without damage. Damping units with various compression deformation characteristics can be manufactured from cellular Vulkollan by varying its apparent density, preferably in the range 300–600 kg/m^3.

Hot-casting systems with a base other than NDI are produced with Shore hardness grades from ca. 55A to 65D. The other mechanical properties and the chemical stability are basically comparable with those of NDI elastomers without reaching the same levels, especially in dynamic stability. They do not, however, reach the high values of Vulkollan in all points, as is also clear from the lower dynamic stability under load. MDI and TDI elastomers cannot replace Vulkollan but are used as supplementary products, primarily in fields where the high quality of Vulkollan is not absolutely necessary, where a system with long casting time is advantageous for producing large-volume and thick-walled moldings, and where short demolding times are desirable for producing large series.

Cold-curing products have a good elasticity, high flexibility, and a variable Shore hardness in the range of ca. 20A to 65D. They are highly resistant to aging and microorganisms and are not attacked by dilute acids and alkalis, mineral oils, soaps, or detergents. Organic solvents cause various degrees of swelling.

8.2. Thermoplastic Polyurethane Elastomers (TPU)

See also Thermoplastic Elastomers - Thermoplastic Polyurethane Elastomers, → Thermoplastic Elastomers, Chap. 2.

Production. Diisocyanate (usually MDI), polyols (polyester and polyether polyols), chain extenders (butanediol), and the necessary auxiliaries are reacted in continuous plants via mixing heads or in reaction extruders. After

Table 8. Mechanical properties of a hot-casting system (e.g., Vulkollan)*

Property	Vulkollan type			
	18/40	18	30	50
Shore hardness A/D (DIN 53505)	68/20	83/31	92/36	96/58
Density (ISO 1183), kg/m^3	1.25	1.25	1.26	1.26
Abrasion loss** (DIN 53516), mm^3	45 – 50	45 – 50	40 – 50	43 – 48
Tear propagation strength according to Graves (ISO 34), kN/m	20 – 30	40 – 55	67 – 85	85 – 96
Impact resilience (DIN 53512), %	48 – 55	45 – 50	45 – 50	45 – 50
Tensile strength (DIN 53504), MPa	42 – 49	50 – 60	37 – 45	40 – 43
Elongation at break (DIN 53504), %	600 – 700	630 – 750	550 – 650	330 – 370

* The properties listed here can only be regarded as approximate. For Vulkollan articles on the market, the quality characteristics specified by the manufacturer are applicable.

** Relative to abrasion-resistant grade of natural rubber (= 100).

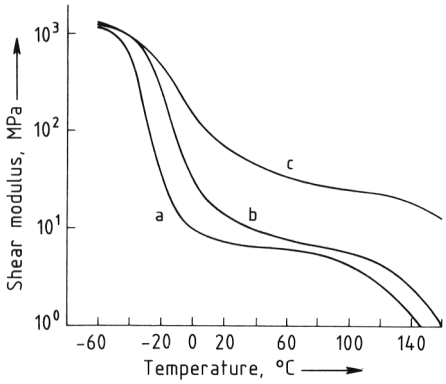


Figure 38. Shear modulus for various TPUs (e.g., Desmopan)
a) Type 385; b) Type 790; c) Type 460

solidifying, the product is processed further to pellets. The TPU can be processed further by, e.g., injection molding, extrusion, calendering, or blow molding to give finished or semi-finished products.

Properties. The principle of "tailor-made plastics" applies to the properties of thermoplastic PURs, as to all PURs. A very wide range of properties is available by careful choice of the starting materials. This is shown in Figures 38 and 39 as well as Table 9 for three selected examples.

Uses. The TPUs are valued as high-grade polymeric materials in many industrial branches for a great variety of constructional parts. Table 10 shows examples of their use in relation to their

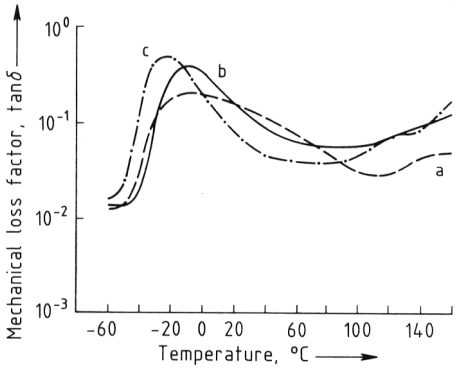


Figure 39. Mechanical loss factor for various TPUs (e.g., Desmopan)
a) Type 385; b) Type 790; c) Type 460

Table 9. Mechanical properties of different types of TPU (e.g., Desmopan)

Property	Desmopan system		
	385	460	790
Shore hardness A/D (ISO 868)	86/33	97/59	92/42
Density (ISO 1183), kg/m^3	1200	1210	1210
Tensile strength (ISO 527-1/-3), MPa	40	35	55
Elongation at break (ISO 527-1/-3), %	450	350	450
Tear propagation resistance (ISO 34-1), kN/m	80	120	85
Impact resilience (ISO 4662), %	42	35	32
Abrasion loss (ISO 4669), mm^3	30	40	30

Shore hardness. Glass-fiber reinforced types are used for bodywork units.

9. Polyurethane Coatings [199–201]

See also → Paints and Coatings, 2. Chap. 9.

PUR coatings offer a large variety of outstanding properties, which make them suitable for many high-performance applications. PUR coatings have polymeric structures with urethane, urea, biuret, or allophanate coupling groups. They are generated either from reactive systems by polyaddition of oligomeric polyisocyanates with polyol components, or from high molecular mass adducts which are further cross-linked by physical drying or other mechanisms. The nature of the isocyanate building blocks (aliphatic or aromatic) and the structure of the backbone are important. Film mechanical properties are dependent on the structure of the polymer (segmented, interpenetrated networks) and cross-link density. PUR coatings are available solvent-borne and, as a result of the trend to reduced emission systems (low VOC), as high-

Table 10. Typical applications for different grades of TPU

Hardness range		Uses
Shore A	Shore D	
75 – 90	< 35	membranes, seals, damping units, sieve units, hoses, cable sheatings
90 – 95	35 – 45	animal identification markings, roll coverings, toothed belts, sport shoe soles
> 95	45 – 55	seals, flanges, rolls, pneumatic hoses
	55 – 70	bearings, bushes, connectors, ball sockets, seals, coupling units, ski bootlegs, heel pieces

solids, waterborne, solvent-free, and powder systems. Important PUR systems are summarized below.

Two-component coatings are the most important (solvent-borne) PUR paint systems. The primary component is always polyisocyanate (mainly HDI, IPDI, or TDI derivatives). The other component consists of polyols (polyester, polyacrylic) or amines or a mixture thereof and any additional ingredients such as pigments or solvents. The reactive components must be kept separate. Mixing, preferably of an equimolar equivalent, is done immediately before application. The coatings system can be applied by all conventional coating methods, but preferably by spraying or, industrially, with automatic two-component equipment. The solids contents of the coatings are usually higher than with standard coatings and can reach 80 % (pigmented high-solids), depending on the formulation. Curing takes place at ambient temperature, but can be accelerated by heat. Outstanding film properties such as high mechanical resistance, high chemical resistance, and, with aliphatic polyisocyanates, excellent lightfastness and weather resistance, open up a broad range of uses. Major areas of application are transportation (large motor and rail vehicles, aircraft, automobile finishes and refinishes), the building sector (wood and mineral substrates), industrial paints, and steel construction.

One-component coatings include air-drying and stoving systems. The most important are solvent-borne, isocyanate-terminated prepolymers of higher molecular weight made from aromatic or aliphatic isocyanates (MDI, TDI, HDI, IPDI) with polyols. They react with atmospheric moisture to form urea linking groups. Although the final properties are comparable to those of two-component PURs, curing of these systems is slower, which limits their use mainly to wood-flooring coatings, corrosion protection, and applications on mineral surfaces.

The reaction of TDI or IPDI with polyol-modified drying or semi-drying oils generates urethane alkyds, which can be cured oxidatively (by air drying) like alkyds.

The isocyanate groups of prepolymers can be reacted with agents containing, e.g., acidic CH or NH groups to form blocked isocyanates (see Section 3.1.3). Their mixtures with polyols are stable at room temperature, but react at elevated temperatures (120–220 °C, depending on the nature of the blocking agent). The resulting films have a very high mechanical resistance. They are particularly important for automotive finishes, industrial goods and coil coating.

Powder coatings consist of a combination of solid polyols (mostly polyester or polyacrylate polyols) and solid blocked polyisocyanates as the cross-linker. ε-Caprolactam was the most commonly used blocking agent but is being replaced by other blocking agents. An alternative method, avoiding the use of an added blocking agent is the dimerization of the isocyanate groups to uretdiones. During stoving (10–25 min at 150–210 °C) isocyanate groups are liberated and undergo cross-linking. PUR powder systems are used in many industrial applications.

Waterborne coatings are growing continuously in importance, due to the requirement that emissions should be reduced. A variety of systems are available, comparable to solvent-borne coatings. One-component systems are based on self-emulsifying polyurethane or polyurethane-polyurea dispersions. They are manufactured by processes which allow the production, in contrast to solvent-borne PURs, of any molecular weight without having a significant impact on viscosity, and with only small contents of solvents or no solvent at all. These products are used in physically dried films for more flexible substrates like textile, paper, and plastics. One-component polyurethane/polyacrylate dispersions based on aliphatic or aromatic isocyanates are used for coating parquet flooring. In addition, UV-curing PUR acrylate dispersions are used in industrial wood and furniture finishes.

One-component stoving systems contain blocked polyisocyanates emulsified in OH- or NH-containing dispersions (epoxy polyester, acrylic). Important applications are automotive coatings (electrodeposition coating, primer surfacer) and other industrial coatings.

Reactive waterborne two-component systems are based on polyisocyanates (HDI, IPDI) and aqueous OH-functional dispersions (polyacrylate, polyester, polyester polyurethane). Self-emulsifying polyisocyanates reduce interfacial tension between the components and ease homogenization. The film properties are influenced by the extent of side reactions, which can occur in the presence of water. The main

applications of these reactive systems are in all types of industrial, wood, and plastic coatings.

10. Polyurethane Adhesives [202–204]

See also → Adhesives, 1. General

PUR adhesives exhibit unique properties due to their wide variety of compositions, their excellent adhesion to most polar substrates (ability to form hydrogen bonds), and the possibility of chemical cross-linking.

To achieve good cohesive strength of the adhesive bond, high molecular weight polymers are necessary. On the other hand, for good adhesion to the substrate, efficient wetting of the surface is essential. This can be done either by "liquefying" the polymer by the use of solvents, aqueous dispersions, or heat or by in situ polyaddition of low-viscosity polyols and polyisocyanates to give high molecular weight products. Depending on the application, the adhesives can be differentiated as follows:

Solvent-borne adhesives are made by dissolving granules of a linear high molecular weight OH-terminated PUR in a solvent like methyl ethyl ketone, acetone, ethyl acetate, or mixtures thereof to a solids content of up to 15–20 %. The PUR building blocks are crystalline polyester diols or polycaprolactones, aromatic diisocyanates (mainly MDI or TDI), and possibly a low molecular weight chain extender like butanediol or hexanediol. After evaporation of the solvent a nonblocking adhesive film results on the substrate. Due to the crystalline nature of the polyester soft segment, this adhesive film can be thermally reactivated at temperatures between 50 and 80 °C, and in this tacky state bond formation to a second coated and activated substrate can be achieved. On cooling down again, recrystallization leads to high initial and final bond strength ("physical setting"). To improve properties such as heat resistance, resistance to solvents, water, oils, or plastisizers, two-component processing is possible. This is achieved by adding a solvent-based triisocyanate (e.g., Desmodur R-Series, Bayer MaterialScience, cf. Section 3.1.1) to the adhesive solution shortly before application, which results in chemical cross-linking by reaction with the OH groups of the base polymer and other isocyanate-reactive groups on the substrate (including water). The main application for this kind of adhesive is in the footwear industry (bonding shoe soles to uppers).

Waterborne adhesives usually consist of a 40–50 wt. % aqueous dispersion of a high molecular weight PUR made by the acetone or the prepolymer mixing process. Besides crystalline polyester diols, aliphatic isocyanates such as HDI or IPDI and ionic or hydrophilic groups containing chain extenders are used as starting materials. Properties and processing are comparable to those of solvent-borne adhesives. Cross-linking can be achieved by using solvent-free emulsifiable polyisocyanates (e.g.- Desmodur D series, Bayer MaterialScience). The main applications are in sport shoe fabrication, the furniture industry (MDF kitchen cabinet door lamination with PVC films), and the automotive industry (lamination of interior trim parts with films).

Hot-melt adhesives are available in nonreactive and reactive form. The starting materials for nonreactive systems are similar to those used for solvent-borne adhesives, but instead of dissolving the granules, these are either directly extruded onto the substrate or (co)extruded to form hot-melt films or fleeces. Another possibility for bringing the adhesive polymer into intimate contact with the substrate (without using solvents or water as a carrier) is cold grinding of the granules. The resulting powders (particle size < 600 μm) can be easily brought onto the surface by scatter coating. Common to all these nonreactive hot melt application forms is the (in this case only one-component) processing by the thermo-activation procedure described above. Application fields are textile and film lamination.

Reactive hot melts are prepolymers of a crystalline or high-T_g polyester with an excess of a diisocyanate (mostly MDI-based). They are applied at temperatures of 60–80 °C higher than the melting point of the soft segment and combine the aforementioned advantages of physical setting and chemical cross-linking (NCO/water reaction). Typical application areas are bookbinding, woodworking, packaging, and the automotive and construction industries.

Reactive adhesives can be divided into one- and two-component systems. One-component reactive adhesives liquid at room temperature

are NCO-terminated prepolymers of (usually) polyether polyols and an excess of an aromatic polyisocyanate (mainly MDI derivatives). Setting occurs by reaction with humidity and therefore requires at least one porous substrate. Applications are foam rebonding, rubber crumb bonding, and in the construction and transportation fields.

Two-component reactive adhesives consist of a liquid polyether polyol (or a low-viscosity polyester polyol) and a polyisocyanate (mainly polymeric MDI). The two components are either mixed and applied immediately before use by an automatic machine or by using a handheld double cartridge/static mixer combination. A broad spectrum of polyisocyanates and polyols is available, and the mixing ratio of the two components can be varied over a wide range. Thus, it is possible to design the adhesive for the individual substrate/bond requirements, e.g., from flexible to rigid. Application fields are again transport and construction, and flexible packaging/film lamination (no porous substrate necessary).

11. Polyurethane Fibers [205]

See also → Fibers, 6. Polyurethane Fibers

Synthetic fibers containing at least 85 wt % of high molecular weight segmented PUR [206] are known as Elastane or in the USA as Spandex. The segmented structure (see Section 4.2) gives these fibers high elasticity and makes them easy to stretch. The properties are determined not only by the raw materials used, but also by the synthesis conditions, the spinning process, and the post-treatment.

Compared to rubber fibers, the PUR fibers exhibit superior properties such as the ability to form fine filaments, good colorability and chemical resistance, and high resistance to physical impact.

They are produced by a two step process. In the first step, long-chain diols are reacted with aromatic diisocyanates; in the second step, the high-melting urethane and/or urea groups which are necessary for the high-level properties are introduced by chain extension with short-chain diols or diamines (see Section 4.2) [207–211].

In industrial production, usually poly(tetraethylene glycol) [212, 213], manufactured by ring-opening polymerization of tetrahydrofuran, is used as the long-chain polyol. In some cases, copolyethers of tetrahydrofuran and 3-methyltetrahydrofuran are used [214]. If polyesters are used as diols, they are usually based on adipic acid and mixtures of ethylene glycol, propylene gylcol, butylene glycol, and/or 1,6-hexandiol.

Aromatic diisocyanates, mainly 4,4′-MDI and in some cases 2,4-TDI, are used exclusively. Due to its unsymmetrical structure, 2,4-TDI leads to a weaker segmented structure and therefore to lower thermostability. Aliphatic diisocyanates, e.g., HDI, are only used in small amounts as modifiers.

Chain extension with diamines usually gives high-performance Elastane [215–218]. Mostly primary cycloaliphatic or aliphatic diamines such as ethylenediamine and 1,2-propylenediamine are used. Modification of the hard segments is achieved by adding small amounts of, e.g., 1,3-diaminocyclohexane.

12. Polyurethanes and Isocyanates as Binders [219]

Panels and molded parts made of wood chips, fibers, and veneers are used extensively in the furniture, building, packaging, and automotive industries. These products are produced under heat and pressure by using a variety of organic binders. PURs are excellent starting materials for composite binders and are used extensively in their production. They are classified according to binder type as polyurethane and polyurea bonding agents.

Polyurethane bonding can be accomplished with one-component moisture-curing systems or two-component ambient-cure systems. The latter can be adjusted in reactivity to meet processing conditions.

PUR dispersions are also utilized in special cases. In addition to adhesion, PUR dispersions exhibit excellent film-forming properties. This is an especially important characteristic for the sizing of glass fibers. PUR dispersions meet very specific requirements regarding film formation and glass adhesion, critical for “matrix” bonding. The properties of glass-reinforced plastic depend to a high degree on the adhesion of the polymer to the surface of the glass fibers.

In polyurea bonding, polyisocyanates are transformed into polyureas at high temperatures

in the presence of moisture and, if necessary, catalysts. In addition to the physical adhesion properties of polyureas, there is also the possibility of adhesion by way of chemical reactions between polyisocyanate and reactive groups of the substrate material. Compared to the PUR binders, polyureas are more rigid and hydrophobic.

Binders based on polymeric diphenylmethane diisocyanate (PMDI) have been industrially used in the wood composite industry since 1973. PMDI binders are used worldwide in the manufacture of particleboard, oriented strand board (OSB), laminated strand lumber (LSL), medium-density fiberboard (MDF), and other specially engineered wood composites, as well as panel products based on annual plants, e.g., straw and sugar cane bagasse. The manufacture of straw-based panels was indeed first made possible with PMDI binders.

The success of PMDI binders in the wood and straw composites industry has its origin in the unique properties of the polyurea bond.

Moisture resistance: polyurea is highly crosslinked, chemically stable, and hydrolytically resistant. PMDI binders are one of two binders listed in the European standard for particleboard EN 312-3/5, option 2 that require no special testing to prove hydrolytic resistance.

Dimensional stability: polyurea is also hydrophobic and lends wooden panels improved dimensional stability. This was demonstrated on particleboard during three years of outdoor exposure, where they showed the lowest moisture absorbance and weight changes. This favorable behavior was also confirmed by long-term stress bending (creep testing) under severe conditions of 40 °C and 95 % R.H.

Emission-free: PMDI wood binders contain no formaldehyde. The resultant polyurea bond in the finished panel is free from emissions.

High-strength properties: The excellent adhesion properties of polyurea and the deep anchoring of the bond in the wood structure leads to the high strengths of the different wood composite panels.

During the manufacture and processing of rigid PUR foams, cutting and milling about 5–25 % of scrap is generated. Utilization of this scrap is possible by bonding it into panels or molded parts with varying properties. This can technically be realized with the aid of the hot-press technique employing PMDI binders, analogous to the manufacture of wood composites. The physical and mechanical properties of articles made from rigid PUR foam scrap can be varied over a wide range. The properties depend upon the type and pretreatment of the raw material, the amount of bonding agent, and the density.

Cork granulates and remilled rubber waste, especially peeled tire tread from the recapping process, as well as recovered scrap from milling of frozen old tires, can be converted with PUR bonding agents to composite materials. The bonding agents are isocyanate-terminated, one-component, moisture-curing prepolymers or reactive two-component systems. They form elastic films during curing. The prepolymers are synthesized from long-chain linear or slightly branched polyethers and MDI types or toluene diisocyanate and/or from mixtures of both. The one-component prepolymers generally have an NCO content of ca. 10 % and a viscosity of 1500 to 3000 mPa · s at 23 °C.

The most important properties are elasticity, flexibility, damping capacity and void content. They can be varied over a broad range through the shape and size of the rubber particles, type and amount of binder, and degree of compaction.

13. Special Products

PURs are particularly suitable as wall materials for microcapsules (see also → Microencapsulation). Capsules can be impermeable or permeable to the core material. The capsule wall is usually produced by interfacial reaction of multifunctional isocyanates or NCO prepolymers and multifunctional amines at an oil/water interface. The microcapsules have a diameter of 1 to 5000 μm, depending on the droplet size of the emulsion used for polymer formation. The capsules are used for a wide variety of purposes, e.g., for the production of carbonless copying paper or for the delayed release of plant-protection products.

Polyoxazolidinone polyisocyanurates are produced from polyisocyanates and epoxy resins in the presence of special catalysts (see Chap. 2). They have high fire resistance, high

long-term heat resistance, and excellent electrical insulation properties [220, 221].

Water-soluble PURs are of interest as retaining agents and dyeing auxiliaries, thickeners, paper-sizing agents, and other sizers.

Oligourethanes with unsaturated (e.g., acrylate) groups can be cured by UV radiation in the presence of photoinitiators [222]. Systems based on acrylate groups containing blocked NCO prepolymers have been developed. They can be cured either by heat or by radiation (dual curing [223–227]) and are used especially for automotive refinishing paint.

14. Safety and Ecology

PUR-containing products have become an essential part of modern living. For production and processing of all of these varieties of PUR, it is estimated that worldwide well over 500 000 people are handling PUR raw materials every day. For the toxicology of the raw materials, see also → Isocyanates, Organic, Chap. 10. and → Polyoxyalkylenes, Chap. 4.

Health, safety, and environmental aspects, especially for MDI and TDI (see Section 3.1.2), are described in [228].

14.1. Safety Precautions when Handling the Raw Materials

When building and operating plants for producing PUR, all laws, decrees, and regulations in force for chemical plants must be observed. Many years' experience in handling the raw and auxiliary materials for PUR has shown that these products can be handled safely. It is a prerequisite for this, however, that the persons working with them are supplied with all the necessary information and above all, that the required technical and personal protective equipment is available and used.

All isocyanates, activators, and most alkanes and haloalkanes are regarded as products having acute or chronic harmful properties.

Di- and polyisocyanates have only a moderately acute oral and cutaneous toxicity. Di- and polyisocyanates are known to have allergenic potential, and the human health risk due to the acute or chronic effect of isocyanate vapors and aerosols (of liquid and dust forms) is considerably higher. Therefore, it is of extreme importance that appropriate safety measures, e.g., protective clothing and ventilation, are provided.

Table 11. German air concentration limits (according to TRGS 900) for typical polyisocyanates (see Section 3.1)

Isocyanate	Air concentration limit	
	ppm	mg/m^3
TDI (2,4-/2,6-)	0.005	0.035
MDI	0.005	0.050
NDI	0.010	0.087
HDI	0.005	0.035
IPDI	0.010	0.092
H12-MDI	0.005	0.054

Occupational exposure limits have been set in many countries. As examples, the currently (2003) MAK values for Germany are listed in Table 11.

The vapor pressures of the industrially most important isocyanates at their usual processing temperatures are listed in Table 12.

Many years' experience in handling the various isocyanates has shown that very effective air-extraction systems must be present at all workplaces where TDI is processed at room temperature or MDI and NDI at temperatures above 40 °C. If, for any reason, the aforementioned maximum value at the workplace is exceeded (e.g., on construction sites), the persons present in the working area must be protected against inhaling isocyanates, wherever possible by wearing suitable masks. TRGS 430 is a special German guideline on how to analyze and monitor isocyanates at workplaces where PURs are produced or processed.

More information can be obtained from literature available from the isocyanate producers, or their associations e.g.,

ISOPA: http://www.isopa.org
API: http://www.polyurethane.org/

Table 12. Vapor pressures of the industrially most important isocyanates at processing temperature

Isocyanate	Processing temp., °C	Vapor pressure, Pa	Conc. of saturated vapor, mg/m^3
TDI (2,4-/2,6-)	25	3	255.5
PMDI	25	$< 10^{-2}$	< 0.1
MDI	42	6×10^{-2}	0.65
NDI	130	ca. 120	7850

Polyols have been well studied with respect to their toxicity and, if used according to relevant regulations, do not present an industrial hygiene problem. Aminopolyethers are moderately irritating to the eyes and skin, and thus contact with them should be avoided.

Auxiliary Materials. The ready-to-use polyol preparations, which are used to a large extent nowadays, contain the auxiliary materials necessary for PUR production (especially activators, emulsifiers, and stabilizers) in quantities of up to ca. 1.5 wt %. Toxicological studies have shown that these small quantities of the auxiliary materials scarcely affect the biological behavior of the polyols.

Polyols and polyol preparations have an exceptionally low vapor pressure; a health hazard via inhalation is therefore not to be expected. If, however, they contain readily volatile aliphatic amines as activators, an unpleasant odor can be expected.

For the *tertiary amines* used as catalysts, occupational threshold values in air (MAK) defined by the German TRGS 900 (2003) are available only in some cases, e.g., triethylamine: 1 mL/m^3 (ppm) corresponding to an eight-hour average value of 4 mg/m^3. However, the intense odor of most tertiary amines gives a clear warning of excessive concentrations.

Low-boiling chlorofluoroalkanes were used as blowing agents for producing rigid and flexible foams in the past. Since these substances are suspected of damaging the ozone layer, their use was phased out in the late 1980s. These substances have therefore been replaced by alkanes and to some extent by partly halogenated alkanes, because the blowing process cannot be carried out with carbon dioxide (from the NCO/H_2O reaction) in all cases. Since direct contact of partly halogenated alkanes and alkanes with the skin leads to intense defatting and roughness, it is important to wear impermeable gloves and to take good care of the skin. The inhalation of vapors from these blowing agents in high concentrations can lead to intoxication.

14.2. Emissions, Accidental Release, and Waste Disposal [229]

The emission of PUR raw materials into the atmosphere during production and processing is usually small. In special cases (e.g., filling of storage tanks, flexible foam slabstock production), measures to reduce emissions are advisable or required. Since a certain concentration limit of a harmful substance must not be exceeded in the air at the workplace, the air is extracted at the processing plant, and this is one source of emissions. The volatility of the raw materials determines the extent of emission. Hence blowing agents (e.g., carbon dioxide, halogenated hydrocarbons, hydrocarbons) and tertiary amines are the main constituents, whereas isocyanates normally do not play a significant role. Since the carbon dioxide formed from the reaction of water with isocyanate is a natural constituent of air, it presents no problem. The other blowing agents are discharged into the atmosphere in varying quantities depending on the foam type. The emissions of volatile organic chemicals are being increasingly regulated in industrialized countries. National regulations must be observed.

During storage, tank-filling, and transportation of PUR raw materials, discharge due to accidents or leaks cannot be entirely ruled out. Should this happen, as a standard precaution, the accidentally released raw material should be prevented from entering soil or water by suitable measures (e.g., covering sewers). Spilled product should be covered with a liquid-binding material such as a chemical binder based on hydrated calcium silicate (e.g., Hybilat), sand, or sawdust. This can then be transferred to a waste container. In the case of spilled isocyanates, the liquid-binding material should be moist and the material in the waste container stored under moist conditions in a secure place in the open air. The lid of the container must not be tightly sealed because of danger of bursting (CO_2 evolution). The polluted areas must then be decontaminated (see below). In all cases, the waste collected in the containers is best disposed of by incineration in a suitable facility (see below). In the unlikely event that a large pool of escaped isocyanate has formed, all unauthorized persons should be kept away from the scene of the accident. Persons downwind should be evacuated. Further evaporation of isocyanate can be prevented very effectively by covering the pool with protein foam. Large quantities of liquids can be pumped into waste containers, before the procedure given above is applied to the remaining residues.

Nevertheless, in the case that isocyanate raw materials have leaked into the soil or water, inert polyurea is the major end product of their reaction with water. According to a three-month soil study with ^{14}C-labeled TDI and MDI, degradation products (e.g., amines) were at no time detected in the aqueous extract.

An experimental pond study indicated low environmental risk arising from spillage of polymeric MDI into a natural aquatic ecosystem. No direct ecotoxic effects and no bioaccumulation of MDI or MDA were observed. Furthermore no MDI or MDA could be detected in water.

Waste Disposal. Liquid or solid PUR production wastes which are not completely reacted are categorized as hazardous waste and should not be dumped but burned in industrial waste incineration facilities, equipped with state-of-the-art flue-gas scrubbing.

Drum decontamination. Any isocyanates residue in "empty" containers that are to be sent for reconditioning or disposal can be rendered harmless with a special neutralizing solution (for formulations, see the specialist literature). The same solution can also be used to decontaminate clothing, equipment and floors. Fully cured PUR end-product wastes, such as trimming waste from flexible foam slabs, can be recycled or recovered (see below). Wastes for which no utilization is yet possible can have their energy content recovered in appropriate incineration plants or can be disposed of in landfill sites, as a last resort (and as long as local regulations do not exclude organic materials from landfilling).

14.3. Recycling/Recovery of Polyurethanes

Because of their excellent durability, PURs in general contribute significantly to a long service life of the products containing them. This is an important contribution to waste minimization. To handle PUR wastes that cannot be prevented, technologies for recycling or recovery have been developed by many industrial associations, joint ventures, and cooperations between producers and users of raw materials throughout the world, e.g., the Polyurethane Recycle and Recovery Council (PURRC, USA), European Isocyanate and Polyol Producers Association (ISOPA, Europe), Tecpol (Germany), and the Japan Urethane Industrial Institute (JUII, Japan). The most appropriate method may vary from case to case, and depends on the properties of the PUR, the intended application, and the related capacity of the market for the recycled material, and very much on logistical, economic, and ecological factors. After all, recycling should not only serve to minimize waste; it ought to contribute also to the saving of resources and to the reduction of environmental burdens. Only then can recycling be counted as a contribution to sustainable development. Currently, the following possibilities for recycling/recovery of PUR exist.

Mechanical Recycling. Mechanical (or physical) recycling of PURs means one of the many forms of "particle recycling." The rebonding of flexible foam or adhesive pressing of rigid foam, for example, involves binding roughly 90 wt % of particles with about 10 wt % PUR binders under heat and pressure. Particle bonding uses up to 70 wt % PUR as the matrix for any kind of particles (e.g., rubber chips for sports ground surfaces). PUR powder can be incorporated into new PUR articles at a loading of round about 20 wt %. PUR powders/particles are also being reused as oil binders.

Feedstock Recycling/Chemical Recycling. Large-scale feedstock recycling processes recover oil and gas products from mixed plastic waste streams of a hundred thousand tons per year or more, of which PUR materials can be one constituent. These processes include pyrolysis, hydrogenation, synthesis gas generation, and reduction of iron ore in blast furnaces. When smaller, but pure streams of particular polymers are available, "chemical recycling" processes can be applied. It is thus possible to obtain liquid degradation products from PURs that are suitable, together with new material, for the manufacture of new PURs. For example glycolysis has been applied more often in favorable case where a suitable application for the glycolysate has been identified. Much research has resulted in several process variations [230]. Some of them include purification and chemical processing of the regenerate before use in PUR applications. Observation of appropriate industrial hygiene and safety is essential, because hazardous substances could be formed.

Energy Recovery. Combustion, or incineration with the recovery of energy, is currently the most effective way to reduce the volume of organic material which otherwise would have to be sent to landfill. Combustion is suitable for all materials for which material recycling is ruled out on ecological or economic grounds or simply because of logistical difficulties. Rotary kilns, fluidized beds, and mass burning equipment, for example, have been shown to be suitable for combustion of plastic scrap. These processes are applied, e.g., in cement production, in industrial power stations, and in municipal solid waste combustors. The heat content of PURs (lower heating value 24–30 MJ/kg) is comparable to that of coal. Numerous test runs have shown that this energy content is recovered in an environmentally sound manner in modern plants equipped with state-of-the-art flue-gas treatment facilities.

14.4. Fire Performance of Polyurethanes [128], [231]

The fire performance of a product is characterized at the various stages of a fire by the parameters ignitability, flame spread, and heat release, and by phenomena such as smoke density and the toxic potency of the combustion products. The dripping behavior, the amount of debris in general, and the corrosive effect of effluents are also determined. Fire test methods differ greatly from country to country, and also depend on the field of application. Different requirements exist, e.g., for the electrical, transportation, furniture, and building sectors. Fire testing, classification and regulatory requirements are very complex and reference must be made to summarizing literature.

In general, the fire hazards posed by a PUR foam and its fire effluents are comparable to those of natural materials like wool and wood. The chemical composition of the material is not

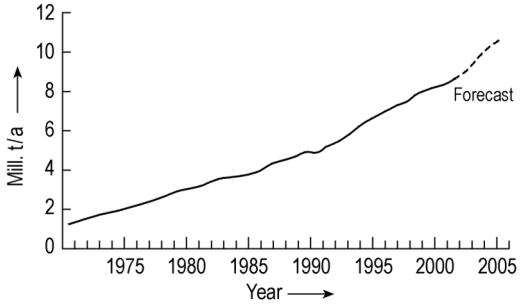


Figure 40. World PUR consumption

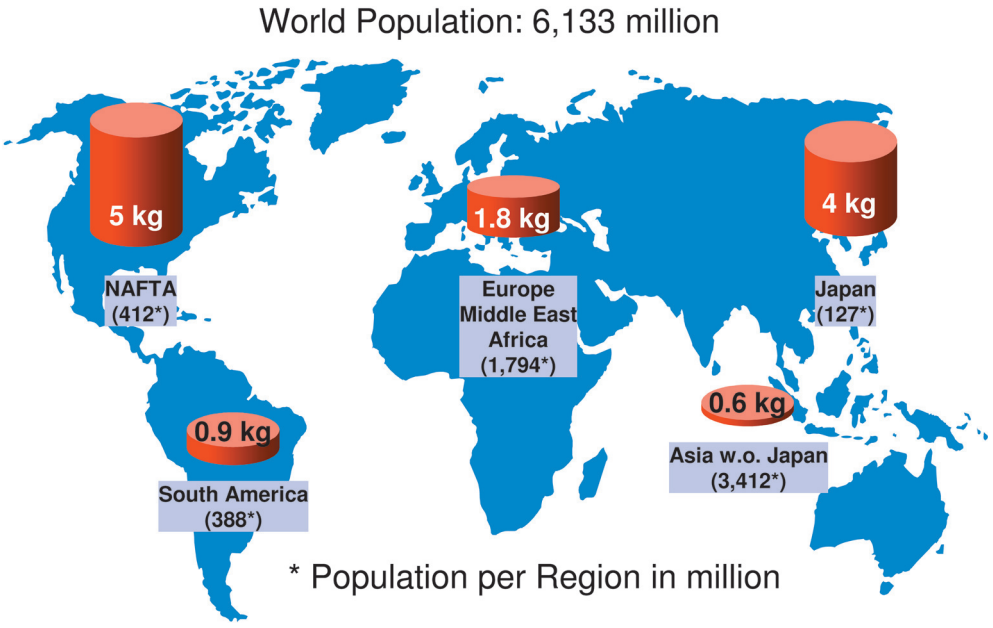


Figure 41. PUR per capita consumption 2001 by regions

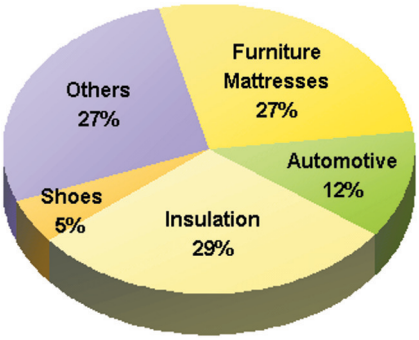


Figure 42. World PUR consumption 2004 by applications (total: 10×10^6 t/a)

the main determining factor. The behavior of the material in fires depends on, e.g., the relative surface of the material (e.g., massive wood compared to sawdust), the combination of materials, thermal conductivity, nature, duration, and intensity of ignition sources, and ventilation.

The qualitative and quantitative composition of fire effluents depends on the decomposition conditions (temperature and ventilation) as well as the amount of material involved. Comparative tests taking into account different stages of a fire have confirmed that the toxicity of fire effluents from PUR products is similar to that of other natural products like wood, cork, and wool. Fire effluents of natural and artificial organic products always pose a toxic hazard irrespective of the type of burning material.

As effluents from PUR do not differ greatly from natural materials, a similar effect on the environment is assumed. Due to their reactivity, isocyanates are rapidly decomposed photochemically or converted chemically.

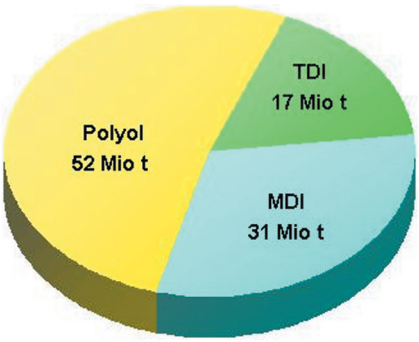


Figure 43. World PUR consumption 2004 by raw materials (total: 10×10^6 Mio t/a)

Table 13. Trade names of raw materials (exemplary)

Type	Tradename	Company
Isocyanates	Caradate	Shell
	Cosmonate	Mitsui Takeda
	Desmodur	Bayer MaterialScience
	Isonate	DOW
	Lupranate	BASF
	Mondur	Bayer MaterialScience
	Rubinate	Huntsman
	Suprasec	Huntsman
	Takenate	Mitsui Takeda
	Tedimon	DOW
	Voranate	DOW
Polyols	Acclaim	Bayer MaterialScience
	Actcol	Mitsui Takeda
	Arcol	Bayer MaterialScience
	Caradol	Shell
	Daltolac	Huntsman
	Desmophen	Bayer MaterialScience
	Isonol	DOW
	Jeffol	Huntsman
	Lupranol	BASF
	Luprapren	BASF
	Multranol	Bayer MaterialScience
	Pluracol	BASF
	Rubinol	Huntsman
	Tercarol	DOW
	Voranol	DOW
Catalysts	DABCO	Air Products
	Desmorapid	Bayer MaterialScience
	Jeffcat	Huntsman
	Niax	Witco
	Polycat	Air Products
	Toyocat	Tosoh

A special fire risk from PUR is not evident: risk of ignition and flame spread as well as emissions mainly depend on the scenario and the amount of burning material, and are not determined by the specific material involved.

15. Economic Aspects

Even though PUR makes up only for ca. 6 % of the total consumption of plastics, the annual production reached the 10×10^6 t level in 2004. The growth rate since 1970 (Fig. 40) on average exceeded 5 % and thus grew faster than GDP. The fastest growing market over the last few years was Asia, in particular China with growth rates exceeding 10 %.

Figures from 2001 show that there is still a big difference in per capita consumption between the regions (Fig. 41), which allows an optimistic outlook for further development.

Figure 42 gives an overview of the main application areas of PURs and Figure 43 the split for the basic raw materials MDI, TDI, and polyethers.

Table 13 lists trade names of raw materials.

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Poly(Vinyl Chloride)

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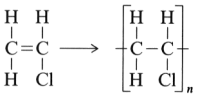
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1. Introduction

Poly(vinyl chloride), PVC, a polymer prepared from vinyl chloride monomer (VCM),



where n = 700–1 500, holds a unique position amongst all the polymers produced today. It is relatively inexpensive and is used in such a wide range of applications that its versatility is almost unlimited. However, if it were discovered today it would probably be shelved as a somewhat intractable and thermally unstable material. How can this apparent contradiction be explained?

The uniqueness of PVC is considered in the sections: Morphology (Section 1.1), versatility (Section 1.2), and molecular structure (Section 1.3).

1.1. Morphology

As made, PVC is particulate in nature and comes in two main sizes depending on the process used. Suspension and mass polymerizations give grains (particles) of 100–180 μm in diameter, whereas the emulsion process affords

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a latex of particle size 0.1–3.0 μm. The latter is dried to yield friable grain-like structures of 5–50 μm.

Because of this unique particulate structure, the most frequently used word in the vocabulary of the PVC technologist is morphology. In no other polymer is it as important as it is in PVC.

In its polymerization, a growing PVC chain becomes insoluble in VCM above a chain length of about 10 units [6], PVC is essentially insoluble in its monomer, and the process is thus classified as a precipitation suspension polymerization. However, PVC is heavily swollen and partly solvated by the monomer to the extent of 27 wt% [7], and this has a major influence on the polymerization itself (see Section 4.1) as well as on the final properties and end uses of PVC. Hence, the way the PVC separates from the monomer, its future growth mechanism, and the swelling of the polymer by the monomer are critically important in its formation, handling, and subsequent processing.

1.2. Versatility

Poly(vinyl chloride) is a generic name. Each producer makes a range of PVC polymers that vary in morphology and in molecular mass, depending on the intended end use. In industry, the *K*-value and viscosity number are used to represent molecular mass, and producers often reflect these parameters in the grade codes used to define different products (e.g., S 68/173 refers to a suspension type material with a *K*-value of 68, and VY 110/57 to a resin with a viscosity number of 110). The calculation of the *K*-value is given in [8] and the relationship between these parameters and molecular mass in [9].

PVC with $K = 66$–68 can be processed in rigid formulations to give pipes, conduit, sheet, and window profiles; $K = 65$–71 in flexible formulations for flexible sheet, flooring, wallpapers, cable coverings, hoses, tubing, and medical products, and PVC with low *K*-values (55–60) in formulations for injection molding of pipe and conduit fittings, integral electrical plugs, and blow molding of bottles and other containers.

In contrast, poly(methyl methacrylate) of even very high molecular mass is still soluble in its monomer and produces only glass-like solid beads at the end of polymerization that have no internal morphology and as such are limited to a narrow range of end uses (e.g., moldings for optical applications, such as covers for car lights and illuminated signs).

1.3. Molecular Structure

Amongst the range of polymeric materials produced today PVC is unique because the bulky chlorine atom imparts a strongly polar nature to the PVC polymer chain, and the essentially syndiotactic conformation of the repeat unit in the chain leads to a limited level of crystallinity [10]. This results in good mechanical properties, particularly stiffness at low wall thickness, high melt viscosity at relatively low molecular mass, and the ability to maintain good mechanical properties even when highly plasticized. This enables a wide range of softness and flexibility to be achieved and hence leads to an even wider variety of end uses.

2. Physical and Chemical Properties

2.1. Vinyl Chloride Monomer

Vinyl chloride monomer (VCM), *bp* −13.4°C, is a gas at room temperature and pressure. Therefore, it is handled as a compressed volatile liquid in all polymerization operations. Its vapor pressure over the typical polymerization temperature range of 50 to 70°C is 800–1 250 kPa. As a result, PVC polymerization reactors are thick-walled jacketed steel vessels with a pressure rating of 1 725 kPa. VCM is slightly soluble in water (0.11 wt% at 20°C). Whereas this has some influence on the suspension polymerization process, it is critically important to the success of the emulsion polymerization process described in Section 4.3. The polymerization of VCM is strongly exothermic, and its specific heat and heat of evaporation of 1.352 kJ kg^{-1} K^{-1} and 20.6 kJ/mol, respectively, allow the use of a condenser to remove the heat of reaction as well as the more conventional jacketed vessel systems. Its explosive limits in air are 4–22 vol%, and plant design, particularly when handling unreacted VCM in the recovery system, must be designed and operated accordingly.

Table 1. Typical properties of rigid PVC (UPVC)

Property	Test	Value
Tensile strength at 23°C, MPa	ISO 527	55
Tensile modulus (1% strain, 100 s), GPa	ISO 527	2.7–3.0
Tensile modulus (1% strain, 3 years), GPa	ISO 527	1.7
Izod impact, ft lb/in	ISO 180	2 (unmodified) 10 (modified)
Specific gravity	ISO 1183	1.38–1.50
Coefficient of linear thermal expansion, K^{-1}	BS 4618 : 3.1	6×10^{-5}
Coefficient of thermal conductivity, $Wm^{-1}\ K^{-1}$		0.14
Flammability (oxygen index)	ASTM D2863 (Fenimore Martin)	45
Weathering resistance		very good (especially white)
Resistance to concentrated mineral acids (at 20°C)		excellent
Maximum continuous operating temperature	field experience	60°C

Further physical and chemical properties of VCM are given in → Chloroethanes and Chloroethylenes.

2.2. Poly(Vinyl Chloride)

Poly(vinyl chloride) (PVC) is always mixed with heat stabilizers, lubricants, plasticizers, fillers, and other additives to make processing possible, all of which can influence its physical and mechanical properties. Table 1 lists properties of rigid (unplasticized) PVC with a total additives content of <10%. Table 2 list properties of flexible (plasticized) PVC where the range of physical properties varies widely, depending on the plasticizer content. This can vary between 20 and 100 phr so as guide properties typical of a plasticizer content of 50 phr are given.

In addition, the *K*-value (molecular mass) of the PVC can also influence properties significantly (see Section 4.1.4.3).

Table 2. Typical properties of flexible PVC

Property	Test	Value
Tensile strength, MPa	ISO 527	7.5–30
Elongation at break, %	ISO 527	140–400
Shore hardness (A)	ISO 868	5–100
Specific gravity	ISO 1183	1.19–1.68
Cold flex temperature,°C	BS 2782 159B	−20 to −60
Volume resistivity at 23°C, Ω · cm	BS 2782 202A	10^{10}–10^{15}
Ageing resistance	field experience	excellent
Ozone resistance	field experience	very good

PVC has extremely good chemical resistance to all but low molecular mass chlorinated solvents. Therefore, it is widely used in the construction and lining of chemical plants.

3. Resources and Raw Materials

VCM is produced industrially by two main reactions:

1. Hydrochlorination of acetylene
2. Thermal cracking of 1,2-dichloroethane produced by direct chlorination or oxychlorination of ethylene in a balanced process. More than 90% of the VCM produced is based on this route, full details are given in → Chloroethanes and Chloroethylenes, Section 2.1.

In an ideal situation, a PVC plant is fully integrated, beginning with ethylene and chlorine (salt), but various levels of integration are employed worldwide. Stand-alone PVC plants, supplied with VCM by sea, road, or rail, are well known as are those making the bulk of their VCM requirements from scratch on site, with supplementary supplies of 1,2-dichloroethane for cracking to satisfy peak demand. Finally, there are fully integrated plants that have the benefit of uninterrupted supplies of base raw materials (ethylene and salt) and where the monomer is supplied by pipeline at a significant cost benefit. It can cost up to 65 €/t to transport VCM within continental Western Europe depending on distance and type of freight used, i.e., road, rail, or ship.

4. Production

There are three main processes used for the commercial production of PVC: Suspension (providing 80% of world production), emulsion (12%) and mass, also called bulk (8%).

4.1. Suspension Polymerization of Vinyl Chloride

4.1.1. Introduction

The layout of a typical suspension PVC plant is shown in Figure 1.

The suspension polymerization process is essentially a bulk polymerization process carried out in millions of small "reactors" (droplets). Liquid vinyl chloride under its autogenous vapor pressure is dispersed in water by vigorous stirring in a reactor (autoclave) of 25–150 m^3 capacity, fitted with a jacket and/or condenser for heat removal and baffles for optimum agitation. This results in the formation of droplets of average diameter 30–40 μm that are stabilized against coalescence by one or more protective colloids (granulating agent). The other essential ingredient is a monomer-soluble free radical initiator.

The formulations charged to the reactors (otherwise known as autoclaves, kettles, or polymerizers) are normally referred to as recipes. A basic recipe for suspension processes can be simply water, VCM, initiator, and suspension agent, for example:

VCM	100 parts
Water	90–130 parts
Protective colloid	0.05–0.15 parts
Initiator	0.03–0.08 parts

These quantities vary depending on the PVC grade, reactor size, plant type, etc.

Whereas this produces particulate PVC, it is unlikely to have the optimum morphology. This is only achieved if other additives are employed, such as oxygen, buffers, secondary or tertiary granulating agents, chain-transfer or chain-extending agents, comonomers, antioxidants, together with the right level of agitation and homogenization and the correct charging procedure and timing for each additive addition. A combination of just the right number and degree of the above parameters to achieve the optimum morphology usually determines the quality of a PVC grade.

After charging, the reactor contents are heated to the reaction temperature of 45–75°C. Reactors are 80–95% full at this stage. Heat causes some of the initiator to decompose into free radicals, and the monomer in the droplets begins to polymerize. The strongly exothermic reaction (−1 540 kJ/kg) is controlled

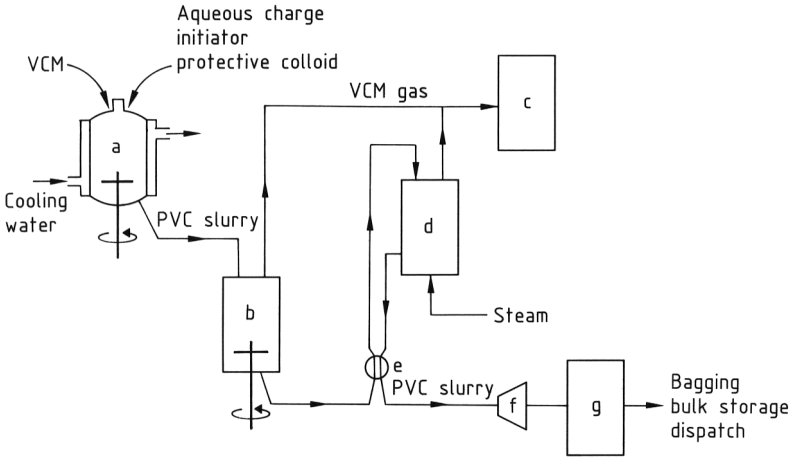


Figure 1. Suspension PVC plant
a) Reactor; b) Blowdown vessel; c) VCM recovery plant; d) Stripping column; e) Heat exchanger; f) Centrifuge; g) Driers

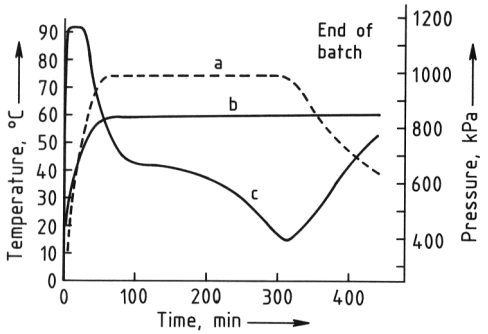


Figure 2. Reaction profile for a typical suspension polymerization
a) Pressure; b) Batch temperature; c) Jacket temperature

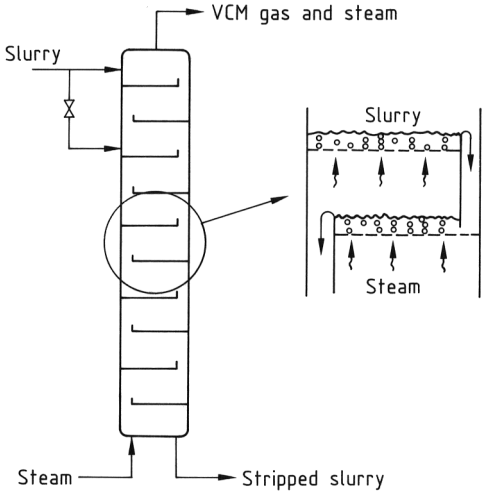


Figure 3. Stripping column

by removing heat via the jacket and/or by boil-off into a condenser from which the condensed monomer is returned to the reactor.

Progress of the reaction in a jacketed reactor can be followed by continuously monitoring the water temperature in the jacket because the flow rate is constant and a constant batch temperature is maintained by progressively reducing the cooling water temperature (see Fig. 2).

Although PVC is insoluble in its monomer (see Section 1.1) the polymer is swollen by ca. 27 wt% VCM to form a coherent gel [7]. Therefore, as the conversion increases towards 70% and beyond, the pressure in the reactor starts to fall; slowly at first, but then much more rapidly as the last of the free liquid monomer is consumed. Polymerization continues in the gel phase, very rapidly at first because chain termination is hindered by lack of mobility of the growing chain, but, as conversion increases beyond 80–85%, monomer starvation rapidly reduces the rate.

The reaction is terminated at a predetermined pressure by either adding a chain terminator and/or venting off the unreacted monomer to the recovery plant. After venting, the resin in the aqueous slurry can still contain 2–3% unreacted monomer, which is removed by stripping, either batchwise (as in older plants) or continuously in a column. The batch is discharged from the reactor to a feed vessel and then fed continuously through a stripper column (Fig. 3). The unreacted monomer is recovered, liquefied, and reused in later polymerizations. After passing through a heat exchanger, the slurry is fed to a continuous centrifuge to give a wet-cake with 20–30% moisture content. The remaining water is then removed by conventional flash and/or fluid-bed drying to give a dry, free-flowing powder with a residual VCM content below 1 ppm.

4.1.2. Additives

Water. The water used in the process should be demineralized (i.e., of low conductivity) because ionic species, especially sodium ions, can affect the performance of other additives, such as protective colloids and influence final polymer properties, such as volume resistivity.

Protective Colloids (Granulating Agents). The protective colloids used in the suspension polymerization process are of two types: Primary and secondary. The main function of the primary granulating agents is to control grain size, but they also affect porosity and other morphological properties. The demand for polymers with reduced residual VCM levels and better plasticizer adsorption led to the need for higher and more uniform porosity within each grain and this is achieved by using a secondary stabilizer in addition to the primary.

Although a wide variety of surface active materials have been or are still used, the

Table 3. Typical primary and secondary protective colloids used in the suspension polymerization of vinyl chloride

Trade name	Manufacturer	Degree of hydrolysis	Viscosity of 4% aqueous solution, mPa · s
Primaries			
Alcotex 72.5/B72	Synthomer	71.5–73.5	5.5–7.5
Alcotex 78	Synthomer	76–79	5.5–7.5
Denka W–20N	Denka	78–81	37–43
Denka MP-10	Denka	70–74	9–13
Denka HS-80	Denka	78–81	30–43
Denka B-24	Denka	86–89	40–48
Inovol PA 4	Ineos	79–81	30–6
Inovol PA 6	Ineos	70.5–72.5	4.5–6.0
Inovol PA 7	Ineos	87–89	40–50
Poval L8	Kuraray	69.5–72.5	5.0–5.8
Poval L9	Kuraray	70–72	6.0–6.5
Poval L10	Kuraray	71–73	5.5–7.5
Gohsenol KP08	Nippon Gohsei	71–75	6–9
Gohsenol KH17	Nippon Gohsei	78.5–81.5	32–38
Gohsenol KH20	Nippon Gohsei	78.5–81.5	44–52
Gohsenol GH20	Nippon Gohsei	86.5–89	40–46
Secondaries			*Solvent Base*
Alcotex 552P	Synthomer	54–57	aqueous
Polivic S202	3V-Sigma	47	methanolic
Polivic S404W	3V-Sigma	55	aqueous
Poval LM10HD	Kuraray	38–42	solid
Gohsenol LL02	Nippon Gohsei	45–51	solid
Gohsenol LW-200	Nippon Gohsei	46–53	aqueous
Inovol SA4	Ineos	54–56	aqueous
Tego SML 20 (sorbitan monolaurate)	Evonik Industries		liquid, no solvent

substances most commonly used today are cellulose ether derivatives and partially hydrolyzed poly(vinyl acetates) or poly(vinyl alcohols) (PVAs). The latter are usually preferred and are used alone or in combination with the cellulose type, which they are gradually replacing. Typical PVA protective colloids are listed in Table 3.

As PVA primary granulating agents are prepared by alkaline hydrolysis of poly(vinyl acetates), they are complex mixtures containing fractions with different degrees of hydrolysis and molecular mass and having a block distribution of the OH groups [11]. Because of this complexity suspension processes need fine-tuning around the chosen agent because decreasing the average degree of hydrolysis of the PVA increases the porosity of the PVC grains and affects the grain size, as shown in Figure 4. This behavior is used in conjunction with agitation to achieve the optimum size and porosity. Below 70% hydrolysis, the PVAs are insoluble in water and lose their ability to stabilize the VCM droplets adequately thus, the normal range of PVA granulating agents used are in the range 70 to 85%.

Many surfactants of low molecular mass have been claimed as useful secondary stabilizers but in practice, few can be used without adverse side effects. One exception is the nonionic sorbitan monolaurate. Again, PVAs are much more widely used. However, this family is prepared by acid hydrolysis of low molecular mass poly(vinyl acetates) and has a random distribution of acetate groups [11]. Initially these materials, which are insoluble in water, were prepared as methanolic solutions (e.g., Polivic S 202) but aqueous-based, low-hydrolysis PVAs (e.g., Alcotex 55, and Polivic S 404 W), which are safer to handle and are environmentally more acceptable, have been developed and are now widely used in the industry. Typical secondary protective colloids are listed in Table 3.

The use of secondary granulating agents affects the mean grain size and grain-size distribution thus the concentration of the primary must be adjusted to compensate. Because each

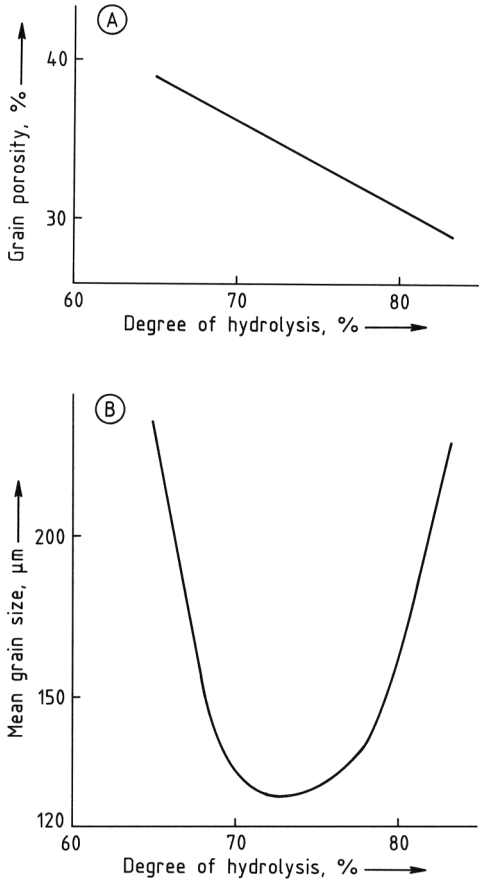


Figure 4. The effect of the degree of hydrolysis of poly (vinyl acetate) on PVC grain properties
A) Grain porosity; B) Mean grain size

producer uses autoclaves of different size and shape, equipped with different agitation and baffle systems, with or without condensers, and makes many different types of resin, no absolute formula is available that determines the magnitude of this change in primary concentration; this must be developed in-house by the suspension polymerization technologist.

Initiators. A range of initiators have been used, but relative few are widely employed. At one time benzoyl peroxide and azo initiators were typically used, but diacetyl peroxides, peroxydicarbonates (PDC), and alkyl peroxyesters are now preferred. Typical initiators are listed in Table 4.

The half-life $t_{1/2}$ at a particular temperature is the main factor that determines the choice of an initiator for a given PVC grade. The initiator should have a half-life of ca. 2 h at reaction temperature to optimize reaction time. Because the best plant output is obtained when the reaction profile is as square as possible (see Section 4.1.3) two initiators of different activity are often chosen to try to achieve this ideal. The more reactive initiator is used to start the polymerization but then as this exhausts itself the slower one takes over to completion. When preparing *K* 70–80 resins at temperatures at or below 52°C, a peroxydicarbonate (e.g., **4**, **5**, **6**, **7** or **8**) is used as the primary initiator, with an active initiator, such as **11** helping to bolster the slow initial rate which is obtained at these low temperatures. In the intermediate range of *K* 63–68 a single peroxydicarbonate (PDC) is usually sufficient, but at or below *K* 60 the PDC needs the extra radical flux of a slow initiator to prevent exhaustion of the reaction, so a less active diacyl peroxide, such as **3** is used as a secondary.

Three other factors are also important: Water solubility, storage and handling, and reactor fouling.

The initiators' water solubility can affect their efficiency by making them more susceptible to hydrolysis and can affect their distribution between VCM droplets; the higher the solubility the more homogeneous the distribution.

The ease of storage and handling has a major influence on the acceptability of an initiator to a PVC producer. In general the shorter the half-life of the initiator, the more unstable it is, and the lower its self-decomposition temperature. The stability also depends on the radical energy and physical form. Solid crystalline initiators, such as **7** (BCHPC) are more stable than their liquid analogues, e.g., **4** (EHPC). Many of the more active initiators must to be stored under refrigeration that tends to restrict their acceptability. Liquid initiators have the advantage that they can be automatically metered into reactors, which is essential in larger computer-controlled plants. However, the current trend is to use initiators as finely divided aqueous dispersions. This has the advantage of improving their homogeneity of distribution throughout the VCM droplets,

Table 4. Initiators for suspension or mass polymerization of VCM

No.	Name	Storage temperature[a], °C	M_r	Supplied form	$T_{1/2}$, °C[b]			$t_{1/2}$, min[c]		
					10 h	1 h	6 min	50°C	60°C	70°C
	Diacyl peroxides									
1	Dioctanoyl peroxide	10	314	solid or solution	57	75	94		700	190
2	Didecanoyl peroxide	10	343	Solid	63	80	100		700	190
3	Dilauroyl peroxide	30	398	solid	62	80	99		850	220
	Peroxydicarbonates									
4	Bis(2-ethylhexyl) peroxydicarbonate	−15	346	solution	47	64	83	250	70	21
5	Dicyclohexyl peroxydicarbonate	10	286	solid	44	59	76	250	58	16
6	Dicetyl peroxydicarbonate	20	571	solid or dispersion	48	65	84	320	70	20
7	Bis(4-*tert*-butyl cyclohexyl) peroxydicarbonate	20	398	solid or dispersion	47	64	83	250	60	18
8	Dimyristyl peroxydicarbonate	15	515	solid or suspension	48	65	84	320	70	20
	Alkyl peroxyesters									
9	*tert*-Butyl peroxyneodecanoate	−10	244	solution	46	64	84	250	70	25
10	*tert*-Amyl peroxyneodecanoate	−15	258	solution	43	61	81	560	180	55
11	Cumyl peroxyneodecanoate	−20	306	solution	38	56	75	100	30	9
12	*tert*-Butyl peroxypivalate	−5	174	solution	57	75	94	700	200	70
	Azo initiator									
13	Azobisisobutyronitrile (AIBN)	25	164	solution	64	82	101		500	170

[a] Maximum.
[b] Temperature at which $t_{1/2}$ = 10 h, 1 h, or 6 min, as indicated.
[c] Approximate.

allows them to be added at any time or temperature during the charging procedure, and renders them very safe to handle because their heat of decomposition is less than the heat of evaporation of the carrier. Dispersion of 25–40% are typical, and systems must be carefully designed to ensure complete homogenization of the dispersion is maintained and accurate metering achieved. As the water solubility of the initiator increases the tendency to cause reactor fouling also increases. This is of increasing importance as more and more processes switch from the open to the closed mode of operation (see Section 4.1.4.4).

4.1.3. Kinetics

The kinetic profile seen in Figure 2 is typical of many VCM suspension polymerizations conducted at the lower end of the temperature range and exhibits the classical acceleration with conversion as shown by the gradually decreasing jacket temperature. At higher temperatures, the reaction rate is more constant and a square-wave profile is obtained. Three different phases in the reaction can be identified:

Low Conversion (< 5%). Polymerization occurs largely in the monomer phase because the quantity of polymer produced is so small. Only this early stage follows classical kinetics where the rate of polymerization is dependent on the square root of the initiator concentration:

$$\frac{-\mathrm{d}[M]}{\mathrm{d}t} = \frac{k_p[M] \cdot k_d[I]^{1/2}}{k_t}$$

where

$[M]$ monomer concentration
$[I]$ initiator concentration
k_p propagation rate constant
k_d initiator decomposition rate constant
k_t termination rate constant

As the amount of polymer phase increases with conversion, the rate deviates more and more from this equation due to a decrease in k_t. A full description of the models used to explain the deviations from ideality is given in [12, 13].

Medium Conversion (5–65%). Polymerization continues in both the free monomer and polymer–monomer gel phases. This region shows the classical acceleration with increasing conversion [14]. Because termination occurs primarily by the diffusion together and collision of

two bulky macroradicals, it is considerably slower in the viscous polymer phase. As a result, the termination rate constant is dramatically reduced and the rate of polymerization in this phase is much faster. As the amount of polymer phase increases, the rate of polymerization accelerates.

High Conversion (> 65%). No free monomer is left to maintain the autogenous pressure, which falls, and polymerization occurs in the polymer gel phase of rapidly increasing viscosity as the remaining VCM is consumed. Hence, the rate of polymerization increases still further to reach a maximum just after the pressure drop but then decreases progressively due to increasing monomer starvation. When the instantaneous polymerization rate falls below the overall rate of reaction, the batch is terminated, either by venting off unreacted VCM to the recovery plant or by adding a chain terminator and then venting. Depending on the properties required, a conversion of 70–95% is chosen. It is uneconomic to continue to very high conversion, and as properties, such as plasticizer absorption, dry up rate (i.e., the time taken to achieve a free-flowing PVC–plasticizer dry blend), and initial color–heat stability deteriorate rapidly above 85–90% conversion, most flexible resins are stopped at around 85% and rigid resins at around 90% conversion.

4.1.4. Morphology

The morphology of each PVC grain is the main parameter controlling the quality of a PVC resin. This subject covers mean grain size, grain size distribution, and, most important of all, porosity (cold plasticizer absorption) and bulk density, which are closely interrelated.

4.1.4.1. Control of Grain Size

At the beginning of the batch, the bulk vinyl chloride phase is broken down into droplets of 30–40 μm mean size under the influence of agitation and by the presence of the water-soluble protective colloid, which is adsorbed at the monomer–water interface. As polymerization proceeds, graft copolymerization of PVC onto the interfacial layer of protective colloid reduces its mobility and protective ability, and droplet coalescence begins to occur at around 4–5% conversion. As the conversion increases, changes in the surface layer of the droplet due to further polymerization suppress the droplet coalescence step, which ceases at 20% conversion, and the grain size remains largely constant for the remainder of the polymerization. Altering the stirrer speed after this point has no further effect on the mean grain size (MGS) [15] of the final product, which is controlled to between 100 and 180 μm, depending on resin type, by a combination of initial agitator speed and protective colloid(s) concentration and type.

Polymerizations with high concentrations of colloid and less agitation give spherical grains of low porosity (≤ 10%) and very high bulk density (≥ 700 g/L) and are of little interest, generally due to problems of VCM removal and poor gelation. Flexible resins are made with a low MGS (100–130 μm), rigid polymers higher (150–180 μm), and low *K* resins with intermediate size (130–160 μm).

In extreme cases, it is possible to stabilize the droplets to such a degree that no coalescence occurs. Specialized VCM–vinyl acetate copolymers for gramophone record production fall into this category as do blending resins (30 μm MGS) for use as viscosity depressants in plastisols (see Section 4.3).

As well as achieving the desired MGS it is equally important to control the size distribution. A Gaussian distribution is normally produced and it is important to make this as narrow as possible because a coarse fraction (> 250 μm) can give rise to fisheyes (dispersion faults) and make VCM removal difficult as well as resulting in loss of yield due to screen rejects, whereas fines (< 60 μm) can be lost in aqueous and gaseous effluent or cause powder flow problems.

4.1.4.2. Control of Porosity and Bulk Density

Porosity in PVC grains is created by a complex series of interrelated steps in the formation and growth of the submicroscopic structure within each droplet and also depends on the unique nature of the VCM–PVC system.

PVC is insoluble in its monomer, and the growing oligomers start to precipitate when the chain length exceeds 10 monomer limits [6]. This initial precipitation results in the formation of microdomains about 15–20 nm in diameter

[17]. This occurs at as low as 0.001% conversion [17]. The microdomains rapidly become unstable and aggregate to form domains (primary particle nuclei) of about 0.1 μm diameter. After this stage, no further domains are formed and the number of primary particles is fixed. All new PVC radicals that are produced in the monomer phase collide with and are precipitated onto the vast existing surface area of primary particles before a new domain can be formed. Because the existing PVC phase is swollen with monomer and contains initiator, initiator radicals, and growing chains undergoing chain transfer, primary particles grow rapidly by accretion of new microradicals and microdomains as well as by gel-phase polymerization. They in turn become unstable and a final agglomeration step to form 1–2 μm primary particle aggregates takes place. By the end of the polymerization the primary particles have grown to 1 μm within the aggregates, which themselves have grown to 2–5 μm. The whole mechanism is shown in diagrammatic form in Figure 5 and discussed in detail in [18].

The arrangement of the aggregates of primary particles within each monomer droplet has a major influence on the morphology of the final PVC grain. The conversion of VCM of density 0.85 g/cm^3 at 52°C to PVC of 1.4 g/cm^3 produces a volume contraction of 39%. If the polymerizing droplets contract totally, the final

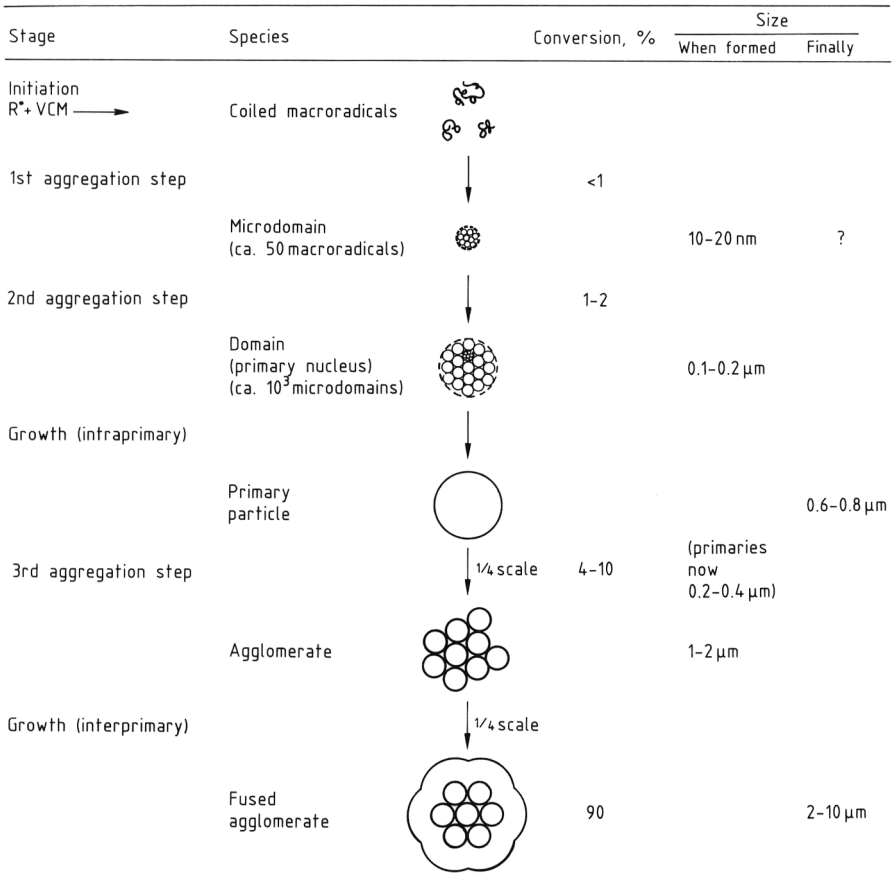


Figure 5. Schematic representation of the mechanism of VCM polymerization (from [18], courtesy of Elsevier Applied Science Publishers)

grain has no porosity. If, however, the contraction is prevented totally, the final grain porosity can be as high as 39%. Therefore, the better the three-dimensional spatial arrangement of the aggregates relative to one another is, the higher the achieved porosity.

The main aim of the polymer technologist is to create the best possible spatial network of aggregates relative to one another so that a network is formed that is strong enough to resist droplet contraction and hence maximize porosity. The sooner this is achieved in the polymerization, the better the porosity attained. In practice, 34–35% is easily achievable. At ca. 65–70% conversion, all of the free monomer is consumed, and the only VCM remaining is that swelling the polymer gel (27%), in the vapor space, and dissolved in the water. At this stage, the voids in the grain (the porosity) are filled with batch water, so that the quantity of water in interstitial spaces between the grains is reduced and a significant increase in slurry viscosity is observed because less mobilizing water is available to separate the grains.

The control of bulk density or apparent density (AD) is more important than even porosity to the processor. The latter is concerned with charge size and cycle times in high-speed mixers, output rates, motor torque, and degree of gelation in extruders, and mechanical properties of the article being produced. These parameters are dependent on AD. The reason for introducing the control of porosity before control of AD is that the latter is very heavily influenced by the former. Apparent density depends on porosity, grain shape, and grain size distribution in order of priority and is best described by examining the packing fraction (PF) concept, i.e., the ability of the somewhat irregular PVC grains to fill a space to the maximum efficiency.

$$\mathrm{PF} = \frac{(1 + 0.014 \cdot \mathrm{CPA})(\mathrm{AD} \cdot 0.1)}{1.4}$$

CPA	cold plasticizer absorption (porosity)
AD	apparent density

Most extruders used in processing PVC are of the twin-screw type, and these operate like a simple pump: Increasing the feed rate by 10% (10% higher AD) increases the discharge or output rate by 8–9% (see Chap. 8 in [14]). In practice, controlling porosity is relatively easy because a number of effective secondary stabilizers are available. Maximizing the AD is much more difficult because control of grain shape comes from a complex interaction of both agitation and choice of primary and secondary granulating agents together with in-house expertise of charging techniques and use of other additives. A range of grain shapes that can be produced is shown in Figure 6.

In practice typical property targets for porosity and AD are:

- For flexible resins (*K* 70): Porosity of ≥ 30% and AD of ≥ 500 g/L
- For rigid extrusion resins (*K* 66–68): Porosity 20% and AD 580 g/L
- For bottle resins (*K* 57–60): Porosity 18–20% and AD 560 g/L

4.1.4.3. *K*-Value (Molecular Mass)

PVC is again rather unique in its relationship between reaction temperature and *K*-value. With PVC the rate of polymer formation by chain–chain termination is small due to the influence of gel phase polymerization described above. Instead, because chain transfer to monomer is a predominant step in the polymerization of VCM, the length of the polymer chain (degree of polymerization, DP) is determined by the ratio of the rate of chain propagation to chain transfer:

$$\mathrm{DP} = \frac{\text{Rate of propagation}}{\text{Rate of chain transfer}} = \frac{k_p[R_n][M]}{k_{tr}[R_n][M]} = \frac{k_p}{k_{tr}} \quad (1)$$

$[M]$	monomer concentration
$[R_n]$	radical concentration
k_p	propagation rate constant
k_{tr}	chain-transfer rate constant

As k_p and k_{tr} depend only on temperature, the molecular mass of PVC is controlled by the reaction temperature (see Fig. 7).

If a particularly low molecular mass polymer is required or if a reactor's pressure rating is too low to operate at very high temperatures, an

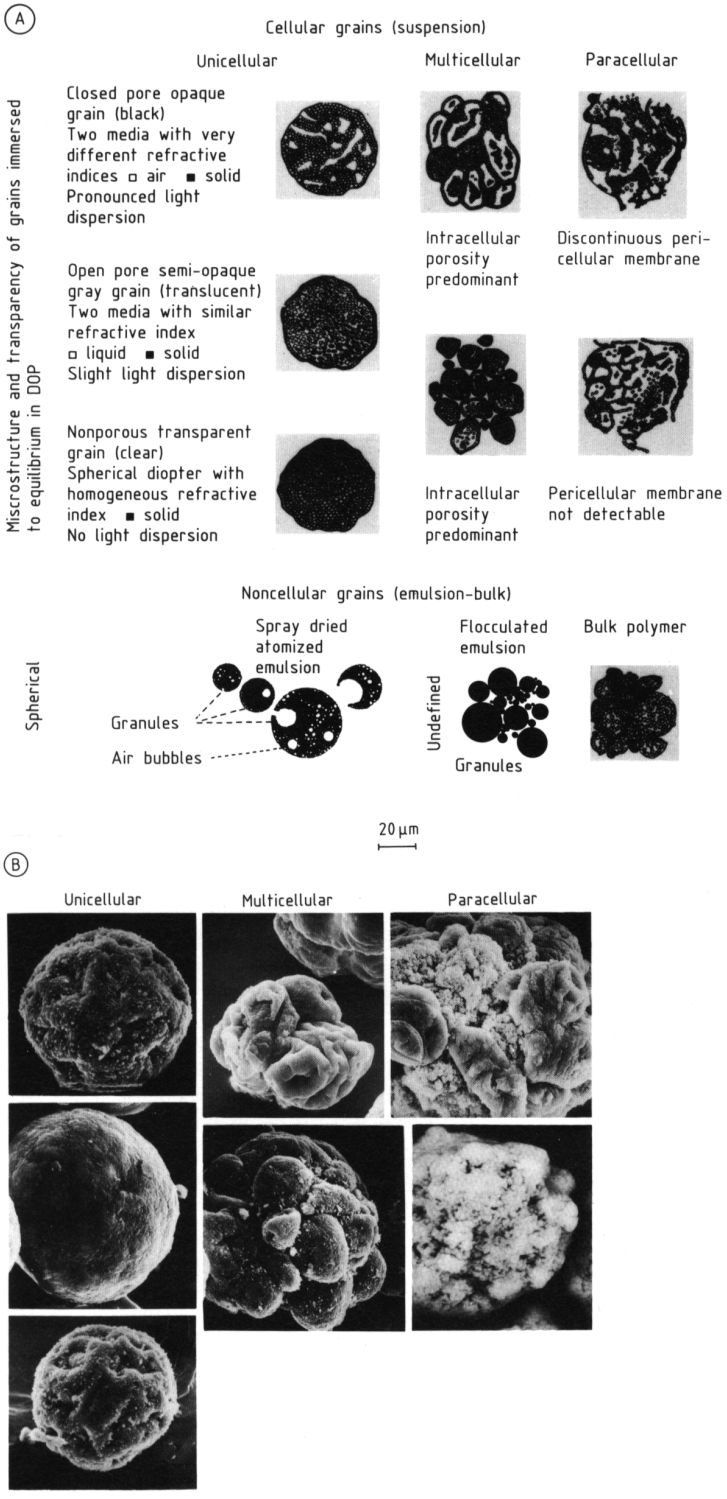


Figure 6. A) Classification of PVC grains; B) Typical cellular PVC grains — layout as in Figure 6 A From [18], courtesy of Elsevier Applied Science Publishers

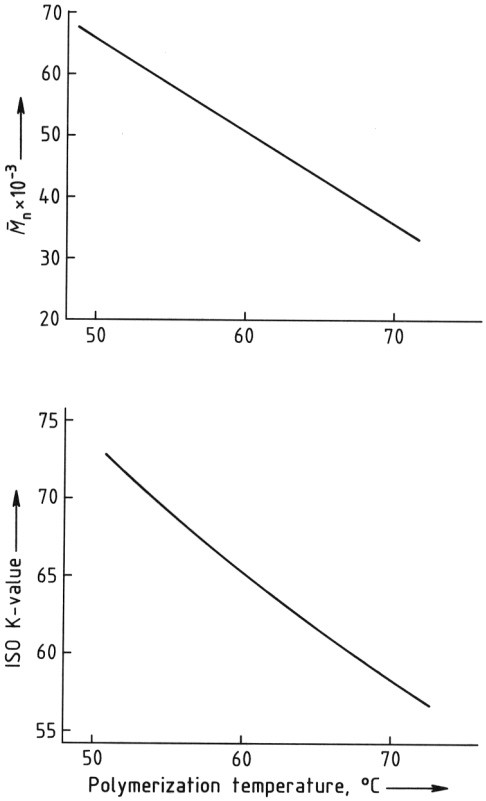


Figure 7. The effect of temperature on molecular mass and *K*-value

additional chain-transfer agent can be employed. This reduces the molecular mass by increasing the chain-transfer rate constant above that for monomer alone in Equation 1. As a result, DP decreases, depending on the quantity of chain transfer agent used.

The general *K*-value range of commercial resins is *K* 55 to *K* 75, with a few producers providing speciality resins outside this range to *K* 50 and *K* 80 and with just one or two *K* 90–100 polymers being available. Despite the relatively narrow *K*-value/molecular mass range of most commercial resins (see Table 5), the polar nature of the PVC chain gives rise to a considerable melt viscosity span. Mechanical properties increase slightly with increasing *K*-value so wherever possible the highest *K*-value polymer is used. However, the power and mechanical robustness of equipment and the complicated melt flow pattern requirements in molds often restrict the *K*-value that can be used. For example, most bottles are made from *K* 57 polymers, some from *K* 60, but this is the limit for the application because bottles are blow molded thus restricting the melt viscosity that can be handled.

4.1.4.4. Problem Areas

There are relatively few problems in the operation of the suspension polymerization process. However, to obtain the best possible quality and consistency some points need special attention.

In the past, reactor fouling was bad and mechanical cleaning between each batch essential. With the advent of clean-wall technology, high-pressure rinse systems, and improved recipes it is now possible to operate in a closed manner, thereby reducing problems of VCM exposure (see Chap. 5 in [14]). Reactor opening for cleaning is reduced to once in several hundred batches. It is essential to ensure that the reactor is rendered completely free of polymer between batches because this is the most common cause of fisheyes. Equally important is to ensure there is no chance of cross-grade contamination in the downstream operations of slurry handling, stripping, drying, and storage. Contamination of the product by foreign substances is eliminated by good housekeeping and plant management together with the right choice of metals of construction and design. Stainless steel is widely used in many sections of PVC plants.

4.2. Bulk or Mass Polymerization of Vinyl Chloride

The mass polymerization process is virtually identical to that taking place within each monomer droplet in the suspension process. As such, the mechanism and kinetics are very similar to those described in Section 4.1.3. The major difference is in the mechanical operation of the process.

About 10% of world PVC production is provided by the mass process. The process was developed by Pechiney St. Gobain (PSG). All mass producers are licensees of the PSG technology. The process is carried out in two stages:

1. In the first stage, monomer and initiator are charged and vigorously agitated in a vertical,

Table 5. Correlation of various PVC molecular mass (expressions)*

European methods						Japanese method	American methods				
Viscosity number ISO/R 174 (1974)	**Specific viscosity 0.5 g/ 100 mL cyclohexanone at 25°C**	***K*-value 0.5 g/ 100 mL^{-1} cyclohexanoe at 25°C**	**Relative viscosity 0.5 g/ 100 mL ethylene dichloride at 25°C**	**Specific viscosity 1.0 g/ 100 mL cyclohexanone at 25°C**	***K*-value 1.0 g/ 100 mL cyclohexanone at 25°C**	**Polymerization degree JIS K 6721**	**Inherent viscosity ASTM D 1243-58 T (method A)**	**Specific viscosity ASTM D 1243-58 T (method B)**	**Specific viscosity 0.2 g/ 100 mL cyclohexanone at 30°C**	**Specific viscosity 0.4 g/ 100 mL nitrobenzene at 25°C**	**Approximate number-average molecular mass**
70	0.35	53.9	1.304	0.70	54	560	0.62	0.239	0.13	0.24	36 000
73	0.37	55	1.316	0.74	55	600	0.65	0.25	0.14	0.25	
77	0.38	56.1	1.329	0.77	57	640	0.67	0.264	0.145	0.26	40 000
80	0.40	57.2	1.342	0.80	58	680	0.70	0.275	0.15	0.27	
83	0.42	58.3	1.355	0.83	59	720	0.73	0.285	0.155	0.29	
87	0.44	59.5	1.369	0.86	60	760	0.75	0.3	0.16	0.30	45 000
90	0.45	60.6	1.383	0.87	61	800	0.78	0.31	0.17	0.31	
94	0.47	61.9	1.397	0.92	62	840	0.80	0.32	0.175	0.32	50 000
98	0.49	62.9	1.412	0.95	63	885	0.83	0.33	0.18	0.33	
102	0.51	64	1.427	0.98	64	930	0.85	0.34	0.19	0.34	
105	0.53	65.2	1.443	1.01	65	975	0.83	0.36	0.195	0.35	55 000
109	0.55	66.3	1.458	1.04	66	1025	0.91	0.37	0.20	0.36	
113	0.57	67.4	1.474	1.07	67	1070	0.92	0.38	0.205	0.37	
117	0.59	68.5	1.491	1.10	68	1120	0.95	0.39	0.21	0.39	60 000
121	0.61	69.7	1.508	1.13	69	1175	0.99	0.40	0.22	0.39	
125	0.63	70.5	1.525	1.16	70	1230	1.01	0.41	0.225	0.41	64 000
130	0.65	71.2	1.543	1.19	70.5	1300	1.03	0.43	0.23	0.43	
134	0.67	72.2	1.562	1.22	71	1350	1.06	0.44	0.235	0.44	
138	0.69	73.0	1.581	1.25	72	1420	1.08	0.45	0.24	0.46	70 000
142	0.71	74.0	1.60	1.28	73	1490	1.11	0.46	0.25	0.48	
145	0.73	74.5	1.62	1.31	74	1570	1.13	0.47	0.255	0.49	73 000
149	0.75	75.5	1.64			1650	1.16	0.49	0.26	0.50	
153	0.77	76.3	1.661			1720	1.18	0.50	0.27	0.51	
157	0.79	77.0	1.682			1810	1.21	0.51	0.275	0.52	
161	0.81	77.5	1.704			1900	1.23	0.53	0.28	0.53	80 000
165	0.83	78.5	1.726			1980	1.26	0.54	0.29	0.54	82 000

* From [65], courtesy of Elsevier Applied Science Publishers.

stainless-steel autoclave (prepolymerizer) of 8–25 m^3 capacity, fitted with a water-cooled jacket and condenser. Rapid polymerization takes place at 62–75°C to give ca. 100 μm aggregated spherical flocs composed of 0.1 μm primary particles, which form the basis or seeds of the final PVC grain. Conversion is taken to 7–12% in ca. 30 min, by which time the initiator used is exhausted.

2. The slurry from the prepolymerizer is discharged into the second-stage reactor, which has a volume of 12–50 m^3, with fresh initiator and more VCM. Up to five second-stages can be fed from one prepolymerizer. In the second stage, the 0.1 μm primary particles making up each seed grow in size and fuse together to give the final grain of PVC of 130–160 μm diameter. As the conversion increases the physical nature changes from a wet powder at ca. 20% to a dry one at 40% conversion. The heat of polymerization is removed from the growing grains by evaporation of the VCM and condensation on the cooled wall of the reactor or in a water-cooled reflex condenser(s). The second stage takes 3–9 h, depending on *K*-value.

Originally, the second stage reactor was a horizontal jacketed vessel with one or more condensers, agitated by slowly rotating (6–10 rpm) ribbon blenders with some blades set very close to the reactor wall to keep it clean. However, it proved difficult to discharge and clean the reactor to a sufficiently high standard to prevent the formation of fisheyes (dispersion faults) in PVC grades intended for plasticized applications [19]. The product can contain up to 10% of coarse material that must be sieved out and recovered by grinding, milling, and reclassifying.

In 1978, this led to the development of a vertical second-stage reactor of up to 50 m^3 capacity fitted with two independent agitators designed to overcome the above discharge problems. However, there has been little interest in this development and all recent investment in new PVC plants has been in the suspension process. In theory, the mass process should be cheaper because it does not need a drying stage. However, as it is a two-stage process, it is difficult to remove traces of unreacted monomer, and it gives a significant amount of oversized material, all of which offset its advantages.

Several of the smaller and older mass-polymerization plants have closed because they find it more difficult to meet increasingly stringent environmental standards and are becoming less competitive compared to suspension-polymerization plants on the basis of production rate.

The mass process is discussed in more detail in [19, 20].

4.3. Emulsion Polymerization of Vinyl Chloride

4.3.1. Introduction

The emulsion polymerization process involves the polymerization of monomer in an aqueous medium containing surfactant and a water-soluble initiator, producing PVC latices. PVC latices are colloidal dispersions of spherical particles, ranging in size between 0.1 and 3.0 μm. Most PVC latices are spray dried and then milled to obtain fine powders, made up of agglomerates of latex particles. When mixed with plasticizers they disperse readily to form stable suspensions. During mixing most of the agglomerates are broken down into the original latex particles. Such dispersion of fine particles in plasticizers are known as plastisols or pastes, and the powder is called dispersion or paste polymer. The surfactant layer around the particle surface prevents their adsorbing the plasticizer at room temperature thus they can be used as liquids and may then be spread on to fabric or other substrates, poured on molds, or deposited on formers to produce flooring, wall covering, artificial leather, balls, toys, or protective gloves. There are other grades of PVC polymers, produced by emulsion polymerization, that do not form plastisols and that are used as blends with suspension PVC grades for extrusion application or in the manufacture of battery separator plates. These so-called emulsion polymers are of only minor economic interest. Sales in latex form are very limited; latices are used in water-based paints, printing inks, and impregnated fabrics. The total

Table 6. World emulsion PVC production in 2012

Region	Production, 10^3 t	Percentage
Europe	820	32
NAFTA	220	11
Asien without China	595	22
China	580	28
South America	65	4
Rest of the world	60	3
Total capacity	2 340	100

production capacity of emulsion PVC is given in Table 6.

4.3.2. Emulsion Polymerization Processes

The ways to produce PVC latices are:

- The classic emulsion polymerization, in which the particle size and particle size distribution are controlled by a water-soluble initiator and a surfactant [21–25]. They are monodisperse with a particle size typically less than 0.1 μm.
- Seeded emulsion polymerization, in which the particle size distribution of the final latex depends on the amount and the size of the latex used as seed and on the amount of surfactant and the way in which it is added [26, 27]. A typical material has 0.2 and 1.2 μm particles (see Fig. 8).

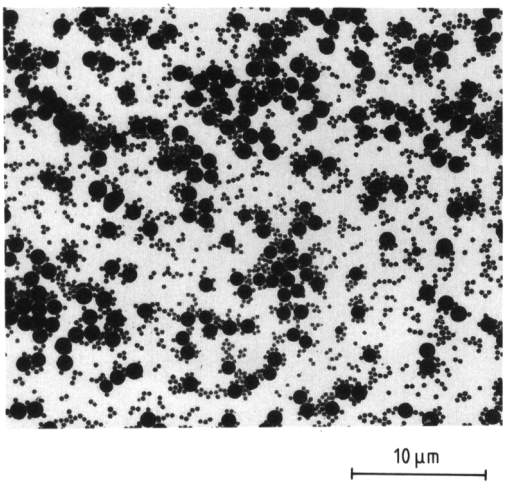


Figure 8. Electron micrograph of latex particles obtained by seeded emulsion polymerization

- Microsuspension polymerization, in which a monomer-soluble initiator is used. Polymerization takes place within the fine droplets in which the monomer is dispersed by passing a coarse emulsion of monomer, initiator, and surfactant through a mechanical homogenizer [28–30]. The resulting particle size distribution is Gaussian between 0.2 and 1.2 μm.
- Polymerization of fine emulsions achieved by using a combination of a typical surfactant, such as sodium dodecyl sulfate and a long-chain fatty alcohol. This gives rise to spontaneous emulsification of the monomer into very fine droplets. In this case, the polymerization can be carried out by using a water-soluble or a monomer-soluble initiator [31]. The latex particle size distribution is the same as for microsuspension polymerization.

The industrial polymerization techniques used for carrying out these processes are:

- Batch polymerization where all the monomer is charged at the beginning
- Semibatch or semicontinuous polymerization, with the monomer added in stages or continuously as reaction proceeds
- Continuous polymerization where monomer and other components are fed continuously into the reactor and the latex is withdrawn from the bottom of the reactor

All these processes are in current use to achieve a wide range of latex characteristics, which are related to the rheological properties of the PVC plastisols [32].

4.3.3. Description of the Batch Process

The emulsion polymerization of PVC consists of the following stages:

1. Polymerization
2. VCM removal
3. Latex storage
4. Drying
5. Milling
6. Packing and storage.

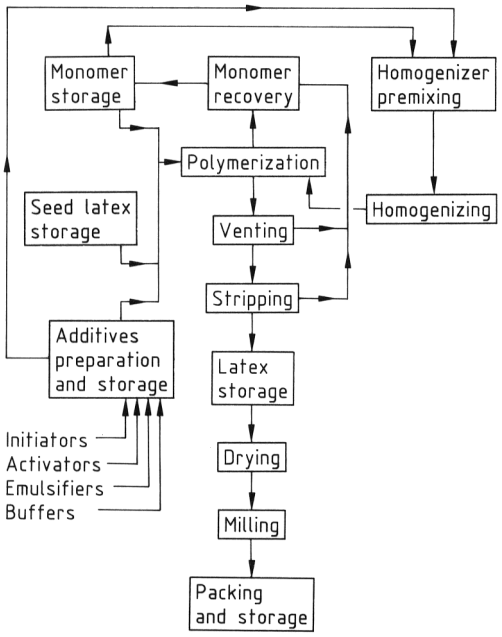


Figure 9. Schematic representation of the stages required for a plant which produces all emulsion, seeded, and microsuspension grades

Figure 9 shows a schematic representation of the stages required for a plant that produces all the emulsion, seeded, and microsuspension grades.

A recipe for a simple batch emulsion polymerization (in parts by weight) is:

Demineralized water	110–140
Vinyl chloride	100
Emulsifier	0.1–1
Initiator	0.1–0.2

The polymerization takes place in an autoclave resistant to the VCM vapor pressure. Pressures of 6.4–10.0 bar correspond to polymerization temperatures of 40–60°C, depending on the desired molecular mass. The polymerization reaction is strongly exothermic with a heat of polymerization of −1 534 kJ/kg. Heat removal can be a problem as the size of the autoclave increases because the ratio between surface area and volume becomes less favorable. For this reason, industrial plants commonly use water cooling and external condensers. Modern plants use autoclaves with capacities ranging between 30 and 80 m^3. Large autoclaves can present agitation problems because low shear rates are required to maintain mechanical stability of the latex and to avoid coagulation.

Initiators. Although organic peroxides slightly soluble in water, such as methyl ethyl ketone peroxide and 1-hydroperoxy-1′-hydroxydicyclohexyl peroxide can be used, the most widely used initiators are ammonium or potassium peroxosulfate. Their decomposition in aqueous solution is first order with respect to the peroxosulfate ion concentration [33]. The rate may be increased significantly by using a reducing agent. Redox catalysis involves the use of transition metal ions, such as copper or iron [34]. The systems widely used in emulsion polymerization of vinyl chloride are potassium peroxosulfate–sodium bisulfate–copper or iron. Redox systems can also be used in microsuspension, an example is dilauroyl peroxide–copper–ascorbic acid [35].

Emulsifiers are very important in the emulsion polymerization of vinyl chloride because they determine not only the latex characteristics but also the properties of the final product [36–38]. Moreover, the nature and the concentration of the emulsifier, together with the agitation, are major parameters controlling the mechanical stability of the latex during polymerization and handling, and the major cause of reactor wall encrustation and lump formation. Because the latex is dried by spray drying, the emulsifier remains in the resin and can influence properties of the product, such as the flowability of the powder, plastisol formation, the viscosity of the plastisol, and the properties of the final article such as heat stability, water adsorption, and coat adhesion. For this reason a wide variety of emulsifiers are used. During polymerization, anionic types are usually used, whereas nonionics are generally added to the latex after polymerization. Typical emulsifiers are the sodium salts of alkyl sulfates, alkyl sulfonates, alkylbenzenesulfonates, dialkyl sulfosuccinates, alkyl ethoxysulfates, fatty acid soaps, alkyl phenol ethoxylates, and fatty acid ethoxylates.

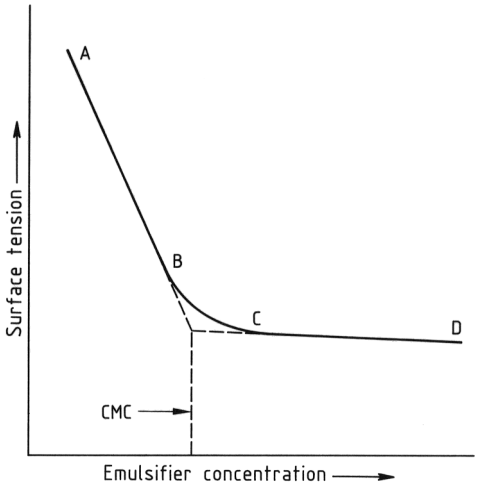


Figure 10. Dependence of surface tension on emulsifier concentration

Particle Formation. Emulsifiers are characterized by the critical concentration at which their molecules aggregate to form micelles [39, 40]. In Figure 10 a plot of surface tension versus emulsifier concentration is shown; the point at which the curve exhibits a marked change is known as the critical micelle concentration (CMC). Conventional emulsion polymerization is carried out at a concentration above the CMC. In this way, particle formation is controlled by the micelles, which solubilize the monomer by swelling and become the loci of polymerization. The nucleation phase stops when the micelles disappear, and the emulsifier is absorbed on to the surface of the particles. Depending on the balance between the hydrophilic and hydrophobic part of the molecule, each emulsifier plays a specific role in the emulsion polymerization, as they have different CMC values, surface covering powers, and stabilizing effects.

VCM Removal. The polymerization is terminated at 90% conversion and is followed by the venting of unreacted monomer to a gas holder. After degassing, the latex contains 3% vinyl chloride and further reductions must be made to fulfill legal requirements for environmental protection. The residual VCM is removed by stripping under vacuum in a stripping vessel. Although VCM loss from particles by diffusion is fast, VCM removal from an emulsion is much more difficult than from suspension slurries as the surfactants lead to large amounts of foam formation. Continuous processes using a thin-film evaporator or which spray the latex into an evacuated chamber against a countercurrent stream of gas reduce considerably the problems of foaming and coagulation [41–44]. The residual vinyl chloride monomer content of the latex after stripping ranges between 200 and 2 000 ppm, depending on the type of latex and the operating conditions.

Drying and Milling. Although there are several different techniques to separate polymer from water, such as freeze drying, drum drying, or coagulation followed by centrifugation, the most widely used is spray drying because this confers a special structure to the dried particle that is important for the production of plastisols. A fine spray of latex is introduced into a hot air stream where evaporation takes place.

The spray is obtained by various types of atomizers, such as:

- Spinning disks or wheels rotating at 15 000–20 000 rpm
- Single pressure nozzles operating at 100–500 bar
- Two-fluid pressure nozzles using compressed air up to 4 bar as atomizing fluid [45]

The drying air temperature at the inlet is 150–240°C and at the outlet, 55–80°C, depending on the quality of the required product and the type of latex. By varying the drying conditions it is possible to change the resin characteristics, and hence its use, even from a typical paste grade to a general-purpose emulsion resin, e.g., for rigid extrusion. The dry powder consists of spherical aggregates, with the size usually ranging from 1 to 100 μm diameter with an average of 30–40 μm. The aggregates are called secondary particles, to distinguish them from those of the latex, which are known as primary particles. The way the aggregates form is complex and depends on many parameters, such as primary particle size, type and amount of emulsifier, mean residence time in the drying chamber, droplet size of the spray, and temperature

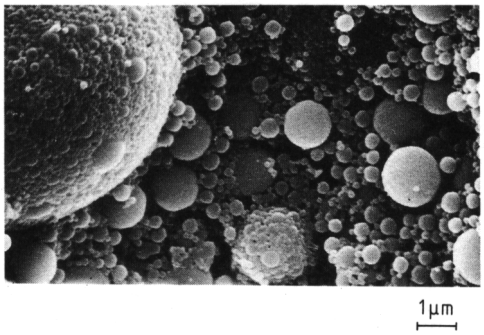


Figure 11. Scanning electron micrograph of spray-dried PVC particles produced from bimodal seeded latex

[11]. Figure 11 shows a scanning electron micrograph of spray-dried PVC particles formed from bimodal seeded latex.

Plastisol-grade resins, usually made from multimodal latex (i.e., with a Gaussian particle size distribution), are milled to reduce the size of the coarse fraction, which can cause problems in coating applications of the plastisol. Generally, the viscosity of the plastisol increases when the polymer has been milled, so it is desirable to reduce milling as far as possible and to use air classification to remove the coarse fraction (> 65 μm) under control. In industrial production, air classifiers or mills or a combination of both are used. After milling, the average particle size of the resin is in the range of 5–15 μm.

Polymers for rigid extrusion and for manufacturing plate separators in batteries are sold in unmilled form. Resins are characterized by analysis of molecular mass, emulsifier and salt content, pH of aqueous extract, granulometry, and viscosity and rheological behavior of the pastes.

4.3.4. Plastisols

Plastisols, commonly called pastes, are dispersions of PVC powders in plasticizers. A wide range of plasticizers are used in plastisol formulations, but the most widely used are C_4–C_{12} esters, such as phthalates, adipates, azelates, sebacates, trimellitates, and phosphates. Chlorinated paraffins are used as secondary plasticizers. A good plasticizer should have low volatility, low color value, neutral reaction, resistance to hydrolysis, insolubility in water, flame resistance, and nontoxicity. As no plasticizer can satisfy all these properties, several plasticizers are mixed to achieve the desired properties of the final product. Table 7 shows the influence of plasticizers on plastisol properties; Table 8, the influence of plasticizers on final product properties; and Table 9, the influence of resin characteristics on plastisol and final product properties.

Table 7. Influence of plasticizers on plastisol properties

Plastisol properties	Plasticizers*
Low fusion temperature	DBP, BBP, TCP
Low viscosity	DOA, DOS, DIPA
High viscosity	BBP, TCP, polymerics
High fusion temperature	DIDA, DOZ, DTDP, DOS, polymerics

* DBP = dibutyl phthalate, BBP = butyl benzyl phthalate, TCP = Tricresyl phthalate, DOA = Dioctyl adipate, DOS = Dioctyl sebacate, DIDA = Diisodecyl adipate, DOZ = Dioctyl azelate, DTDP = Ditridecyl phthalate.

The amount of plasticizer used in plastisol formulations plays a major role in determining the hardness and flexibility of the end product and can vary from 40 to 130 phr. In Figure 12, the influence of plasticizer content on plastisol viscosity is shown.

The other essential ingredients in plastisol formulations are:

- Heat stabilizers, which generally are the same compounds used for suspension polymers
- Dyes and pigments suitable for coloring plastisols; the most widely used is titanium dioxide

Table 8. Influence of plasticizers on final product properties

Product properties	Plasticizers
Flame retardancy	phosphates, chlorinated paraffins
Light and heat resistance	epoxy plasticizers
Low-temperature flexibility	adipates, azelates, sebacates, straight-chain phthalates
Low volatility	polymerics, trimellitates, linear phthalates, epoxy plasticizers
Stain resistance	butyl benzyl phthalate
Low migration	polymerics, trimellitates

Table 9. Influence of resin characteristics on plastisol and final product properties*

Plastisol and product properties	Effect of resin characteristics			
	Molecular mass	Particle size	Particle size distribution	Emulsifier type and quantity
Paste making		S	S	S
Plastisol viscosity		S	S	S
Air release				S
Gelation	M	M	M	S
Fusion	S			
Mechanical properties	S			
Gloss	M	S	M	
Transparency		S		S
Foaming	S	M		S
Fogging				S
Streaking flow		S		
Water resistance				S

* M = moderate effect; S = strong effect.

- Fillers, generally inorganic materials, such as calcium carbonate, barite, silicate, kaolin, or china clay, are used primarily to lower costs and also to impart special properties such as hardness, abrasion resistance, and no sticking
- Blowing agents for foamed PVC production, such as azodicarbonamide
- UV adsorbers to prevent the decomposition action of sunlight
- Esters of poly(ethylene glycol), phosphate esters, and fatty acid amines and amides are usually employed as antistatic agents

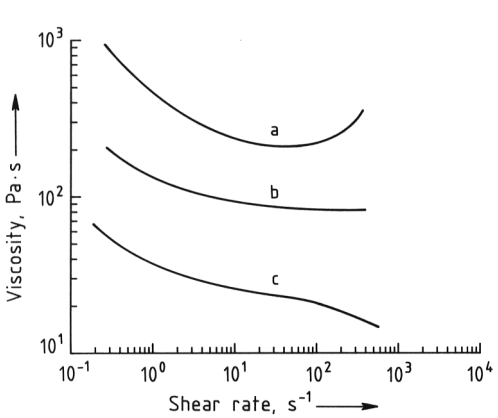


Figure 12. Influence of plasticizer content on plastisol viscosity
a) PVC/DINP = 100/40; b) PVC/DINP = 100/50; c) PVC/DINP = 100/60
DINP = diisononyl phthalate

- Viscosity depressants, such as white spirit, poly(ethylene glycol) monolaurate, alkylphenols, low molecular mass paraffins
- Extender resin or filler polymer; a PVC grade of spherical form, made by the suspension process and therefore cheaper than dispersion resin, which is used to reduce cost and viscosity of the plastisol [47, 48]

The influence of plastisol ingredients on the final product characteristics is shown in Table 10.

4.3.5. Polymer–Plasticizer Interaction

Figure 13 illustrates the types of dependence of viscosity on shear rate;

- Newtonian (viscosity is independent of shear rate)
- Pseudoplastic (viscosity decreases as shear rate increases)
- Dilatant (viscosity increases with increasing shear rate)

Over a wide range of shear rate, a plastisol may exhibit all three types of behavior because the viscosity of plastisols rarely displays true Newtonian behavior. At low shear rates, they are generally pseudoplastic, at intermediate values they show dilatancy, and may sometimes become pseudoplastic again at higher shear

Table 10. Influence of plastisol ingredients on the final product characteristics*

Characteristics	Filler	Pigment	Stabilizers	Quantity of plasticizer	Plasticizer type	Resin
Tensile properties	M			S	M	S
Flexibility	M			S	M	
Hardness	M			S	M	
Low-temperature bending resistance	M			S	S	M
Gloss	S	S				S
Volatility				S	S	
Extraction				S	S	
Color	S	S	M			
Light resistance		S	S		M	
Cost	S		M	M	M	

* M = moderate effect; S = strong effect.

rates, as shown in Figure 14. There is no certainty on the exact mechanism as the rheology of PVC plastisols is complex and affected by many factors such as:

- Polymer/plasticizer mixing ratio
- Type of plasticizer and its interaction with polymer
- Particle size and their distribution of primary particles
- Structure, shape, porosity, and surface of the secondary particles
- Surfactants, added during polymerization or in the paste
- Molecular mass and molecular mass distribution
- Paste-making conditions such as mixing temperature, time, and intensity [49].

4.3.6. Gelation and Fusion

Gelation is defined as the change from liquid to semisolid state, and fusion, when an homogeneous phase at molecular level between polymer and plasticizer is reached. These processes have been examined by determining viscosity changes of the liquid system, the tensile strength, and changes in complex viscosity and viscoelastic properties over the temperature range 25–200°C.

At the beginning of heating, plasticizer viscosity decreases, as does the plastisol viscosity. At the same time, polymer particles adsorb

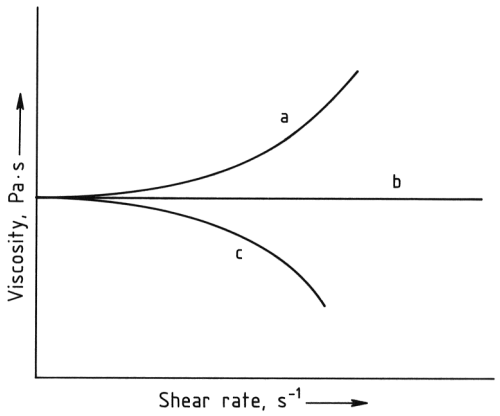


Figure 13. Effect of shear rate on dilatant (a), Newtonian (b), and pseudoplastic (c) fluids

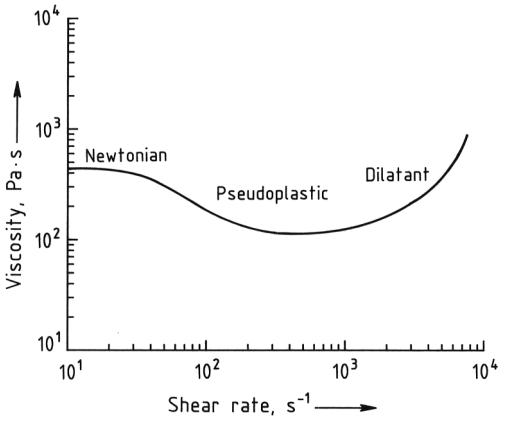


Figure 14. Effect of shear rate on the PVC plastisol viscosity (PVC/DINP = 100/50 at T = 25°C)

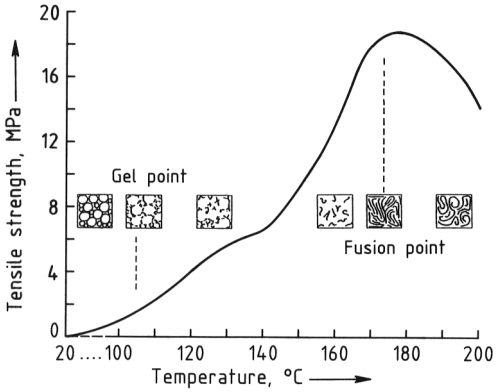


Figure 15. Changes in morphology and mechanical properties of PVC plastisol during gelation and fusion

plasticizer and swell, reducing the fraction of liquid plasticizer, and the viscosity then increases rapidly. When the liquid phase is completely absorbed by the particles, the system becomes dry. As the process continues, the interparticle boundaries disappear and the polymer chains become increasingly entangled and development of the physical properties begins. At this point, the gelation stage is complete and the fusion process starts, as illustrated in Figure 15. Further heating of plastisol makes the polymer flow into a continuous mass. The melt viscosity, after having reached a maximum, starts to decrease and the process passes through the fusion stage. Morphology of the particles, particle size, particle size distribution, and molecular mass of the resin affect the viscosity behavior. Low molecular mass resin starts the gelation phase earlier and completes the gelation process at lower temperature. The same result is obtained by using plasticizers with higher solvating action, whereas larger particle size increases gelation temperature or time because it slows the penetration of the plasticizer into the resin [50].

4.3.7. Applications

Vinyl plastisols can be applied by spread coating, knife coating, roll coating, molding, dipping, and spraying; the most widely used application is coating.

Coating. Vinyl plastisol can be used to coat paper, fabrics, metals, felt, and glass fibers to produce wallpapers, floor coverings, vinyl leather, conveyor belts, and tarpaulins. Each application needs its own formulation, in which the appropriate resin grade and plasticizer must be used to give the required rheological characteristics. In the case of fabric coating where direct spreading is employed, it is important to avoid penetration of plastisol into the fabric; therefore, the viscosity behavior of the paste must be strongly pseudoplastic at low shear rate and have moderate viscosity at high shear rate. In wallpapers, where thin coatings are applied, a low-viscosity resin with Newtonian behavior is required. In production of floor coverings, three or even four coatings are applied: An impregnation layer to saturate the fibers, one or two foam coats, and a wear layer with high mechanical strength. Each coat, which needs different grade resin to achieve the required properties, is gelled at 150°C before application of the next layer. When the last coat is applied, the entire coating is fused in an oven at 200°C. The foam layer can be chemically or mechanically foamed [51]. Usually mechanical embossing is used to create surface textures and apply colored patterns.

Dipping. The product, mainly work, household, and surgical gloves, is obtained by dipping metal or ceramic molds or an article to be coated into the plastisol and then withdrawing it, draining it, and then curing it in an oven.

Molding is used for producing hollow articles such as balls, dolls, and toys. The process requires a plastisol with low viscosity at low shear rate that has a short gelation time and is easy to deaerate. In rotational molding, the plastisol is poured into a cold mold that rotates around two perpendicular axes while entering an oven where it is heated with air to 200–250°C. After gelation and fusion, the mold is cooled in a water bath.

Further information is given in [32, 39, 40, 45, 48, 52–54].

4.4. Chlorinated Poly(Vinyl Chloride), CPVC

The softening point (heat distortion temperature or T_g) of PVC can be increased by chlorination of the polymer, either in a solvent or as a

suspension. The normal chlorine content of 56.7% is raised to 63–68%, depending on type, and this increases the softening point from ca. 78–83°C (depending on formulation) to at least 120°C.

The older method involves chlorination of the PVC dissolved in a chlorinated solvent, but the process is expensive because of the need for an extensive solvent recovery system. However, it has the benefit of yielding a homogeneous material. The product is difficult to handle physically because of its very low bulk density.

The most common commercial process in use today disperses the PVC grains in water and swells them with a chlorinated hydrocarbon. The reactor is degassed to remove oxygen and heated to reaction temperature (50–60°C); chlorine is added continuously, and the system irradiated with UV light to produce chlorine radicals. Hydrogen chloride is produced as a byproduct and is removed at the end by washing with an inorganic base, after which the product is dried [55]. The degree of chlorination is variable, with the surface layers of the grains being preferentially treated.

CPVC is less thermally stable than conventional PVC and requires higher temperatures to develop good mechanical properties. Hence, it is difficult to process and quite expensive, but blends with suspension PVC can be used to achieve a specific softening point. CPVC products have not been very successful commercially but have found a specific niche in the market. They are used for hot-water systems in mobile homes in the United States and for the manufacture of fibers, for use in thermal underwear, in France.

5. Environmental Protection

Potential problem areas associated with the production, handling, and use of PVC are small if a few simple measures to avoid environmental contact and pollution are followed.

Losses of VCM from polymerization plants have been reduced to extremely low levels following conversion to closed-lid operation as a result of the toxicological problems discussed in Chapter 10 in [14]. Although modern column strippers reduce VCM levels in PVC to less than 10 ppm, a small quantity of VCM is lost from the drier section. The older batch strippers present more of a problem because they cannot achieve such low residual VCM contents.

PVC powder can be lost in centrifuge and scrubber effluent and by overfilling stock tanks and from pipeline leaks. It is important that all plant drains that are likely to contain PVC are directed to settling pits where flocculation treatment can be used so that the final discharge is free of PVC. All wet waste is collected and reclaimed as second- or third-grade material for use in noncritical applications, such as one-trip horticultural products and fencing.

Powder losses from drier stacks can be minimized by ensuring that drier cyclones are adequately sized to the air conveying rates used. Some modern plants use bag filter systems to meet current regulations that restrict the amount of PVC dust loss to 50 mg/m^3 air [56].

Compared to other polymers and typical metals PVC requires less energy per unit weight for its production [57]. Whereas plastics in general are blamed for long-lasting litter problems, it is significant that only 12% of PVC is used for consumables, whereas 64% is incorporated into products with an expected useful life of 15 years or more. Disposal is therefore less of an immediate problem than is often thought.

As landfill sites are used up more municipal waste is being incinerated. Though inherently nonflammable, PVC burns in an existing fire to release hydrogen chloride gas, which can be scrubbed out satisfactorily. Fears about the increased release of dioxins during incineration due to the presence of PVC in waste have proved to be unfounded [58].

6. Quality Specifications and Analysis

All PVC producers test a number of parameters on every batch produced as part of routine quality control operation. These include *K*-value, mean grain size and grain size distribution, apparent density, porosity, contamination, dispersion, color and heat stability, and residual VCM content. Most plants use statistical process control techniques to ensure that product consistency from batch to batch meets the stringent requirements of today's customers. It is

difficult to give a typical testing regime because every plant makes batches of different size, has slurry-blending facilities of differing degrees of sophistication, and has hoppers of different capacity on their drying plants. For a modern plant operating large autoclaves there is considerable testing of each polymerization batch (wet stage) together with additional testing of the dried and blended material as a cross check.

In-house tests have been collected and correlated by national and international standards organizations to make them universally applicable. ISO has defined tests and standards set up by other organizations, such as the ASTM and DIN so that ISO methods are now widely accepted worldwide. ASTM D 1755 defines a system for classifying general purpose (mass and suspension) and dispersion (paste) resins [59].

7. Storage and Transportation

Most plants handle more than 80% of their production in bulk, and storage and supply in 25 kg bags is diminishing all the time as customers convert. After drying, the material is conveyed by blow-eggs (vessels in which the powder is pressurized and fluidized) of 2–15 t capacity via pipeline to the silo farm where it is stored in silos of capacity 100–500 t. PVC is discharged either directly or via a smaller loading hopper into 20 t road tankers, the most popular form of PVC transportation. Sometimes big-bags made of woven polypropylene are used for 1 t lots of PVC, and 20 t ISO metal containers are used for long distance deliveries. PVC is not a difficult material to handle and the logistics side of the operation is straightforward. It is essential to prevent cross-contamination of the PVC by other products and thorough intertrip cleaning is essential, because many operators use their tankers for back carriage of a wide range of products, many of which are nonpolymeric.

8. Processing and End Uses

Due to its unique combination of properties, PVC is never handled on its own. Instead, a complex formulation incorporating several additives is used. A typical base formulation contains: PVC resin, heat stabilizer(s), internal lubricant(s), external lubricant(s), processing aid, and additionally, impact modifier, filler (s), pigment, UV stabilizer, as well as primary and secondary plasticizers (for flexible applications; see → Plasticizers).

PVC is intrinsically unstable because of molecular defects in some of the polymer chains [60, 61], and when subjected to heat they initiate a self-accelerating dehydrochlorination reaction. Stabilizers neutralize the HCl produced and introduce nucleophilic substitution reactions that prevent further degradation [60, 61] (see also → Plastics, Additives, Chap. 4).

The Ca–Zn stabilizer family is becoming increasingly popular as objections to the use of heavy-metal systems increases. In Europe withdrawal of cadmium stabilizers was planned for the end of 2001, and although it has been shown that use of the highly effective lead stabilizers is safe, adverse publicity will slowly erode their market position. Table 11 gives a summary of the *heat stabilizers* in regular use.

The polar, highly viscous PVC melt sticks easily to metal walls of extruder barrels, calenders, mills, etc. thus an *external lubricant* is employed to assist the smooth passage of the melt. *Internal lubricants* help to reduce melt viscosity and prevent overheating and thus help to ensure good color of the final product. *Processing aids* improve the surface appearance of extruded sections and reduce melt defects, such as screw memory, where the helical nature of the screw can be seen as regular ripples in the pipe surface. Many other additives can be used, e.g., *impact modifiers* for bottles and *UV stabilizers* as well as *fillers* (e.g., TiO_2) for house sidings and window frames to ensure the best possible in-service performance or longevity.

In all extrusion and some other conversion processes, the PVC grain is not broken down to its constituent primary particles [62], unlike emulsion PVC processing (see Section 4.3.6). Instead, the suspension grains (150 μm) gradually lose their original form by fusion and elongation under the influence of heat, pressure, and shear so that in badly processed PVC grain memory can be detected by optical microscopy of cross sections of extrudates [62]. In practice,

Table 11. Heat stabilizers for PVC

Stabilizer	Properties
Lead stabilizers	
Lead soaps	Good heat stability
Lead salts	Sulfur staining
Liquid lead complex	Lead phosphites give good light stability
Lead one-pack systems	Kickers for chemical blown foam
Tin stabilizers	
Organo sulfur tin	Excellent heat stability, good clarity; poor light stability
Organo tin carboxylates	Medium heat stability
Excellent light stability	
Barium–zinc stabilizers	
Ba–Zn liquid	Good heat and light stability on high-quality grades; general-purpose stabilizers.
Calcium–zinc stabilizers	
Ca–Zn soaps	Low toxicity
Ca–Zn liquid	Medium heat and light stability
Organic co-stabilizers	
Thiourea derivatives	Synergistic effects with epoxy plasticizer and/or Ca–Zn, Ba–Zn
Indol derivatives	
Amino crotonic acid esters	
Diketones	
Organic phosphites	
Antioxidants	
Epoxidized soybean oil (ESBO)	Synergistic effect with Ca–Zn and Ba–Zn
Epoxy esters	

converters take great care to ensure that the degree of gelation (i.e., lack of grain memory) in the final PVC article is very high. Degree of gelation can be measured by determining the degree of attack by a poor solvent, such as acetone or methylene chloride or by measurement of flow pressure to assess the strength and elasticity of partially fused material directly [63].

The enormous subject of processing, including different aspects, such as formulations, types of processing equipment, gelation, rheology, and mechanical properties is covered more widely in [62, 64–68].

The versatility of PVC can be gauged by the very broad summary of typical end uses given in Table 12.

9. Economic Aspects

Fear of litigation, the need to handle VCM (a known carcinogen), and reduced funding have all but eliminated fundamental research into

Table 12. Typical end uses for PVC

Application	Rigid PVC	Flexible PVC
Construction	window frames, gutters, pipes, cars, housesiding, ports, roofing	waterproof membranes, cable insulation, roof lining, greenhouses
Domestic	curtain rails, drawer sides, laminates, audio and video tape cases, records	flooring, wall coverings, shower curtains, leather cloth, hosepipes
Packaging	bottles, blister packs, transparent packs and punnets	cling film
Transport	car seat backs	under seal, roof linings, leather cloth upholstery, wiring insulation, window seals, decorative trim
Medical		oxygen tents, bags and tubing for blood transfusions, drips and dialysis liquids
Clothing	safety equipment	waterproofs for fishermen and emergency services, life-jackets, shoes, wellington boots, aprons and baby pants
Others	floppy-disk covers, credit cards	conveyor belts, inflatables, sports goods, toys

VCM polymerization. Work on processing of PVC continues, but at a much reduced level. Many companies have scaled down R & D and process development, and raw materials suppliers are now increasingly responsible for technological developments.

Since the early 1990s, the main trend in the PVC industry has been consolidation and amalgamation. Some well-known companies, including pioneers from the 1940s (e.g., B F Goodrich/GEON, ICI, and Chisso) have disappeared through acquisition, and many others have formed larger conglomerates to survive. The current feeling in the industry is that a minimum capacity of 500 000 t/a is required for a viable operation.

Strong investment in new plant near the peak of the economic cycle has resulted in overcapacity, weakened prices, lower company profits, and economic casualties, just as it did around 1990. Since the 2000s, the sharp increase of feedstock as well as energy costs has speeded up the process of restructuring the industry as a general trend in the more mature markets like North America and Europe, but also in Japan. Changes in the European PVC scene are summarized in Figure 16.

Table 13 lists the regional capacities (in 10^3 t/a) of the top ten producers, which represent 36% of the world capacity of 53.4×10^6 t/a. World production was 37.5×10^6 t (70% of capacity) in 2012.

Since around 1990, China has emerged as a major force on the global PVC market, and its tremendous import capacity has had a large impact on the world price/consumption relationship in the beginning. Especially since 2000, the Chinese market has been determined by a substantial increase of capacity, reaching a share of approx. 44% of the total global capacity (23.4×10^6 t/a). Of the installed capacity, approx. 81% are calcium carbide based and only 19% ethylene based.

In 2010, the Chinese production volume was approx. 10.8×10^6 t (utilization approx. 62%) and increased in 2012 to approx. 13.1×10^6 t (utilization reduced to 56%).

In 2010, there were 92 PVC producers in China, of those

- 21 sites with $> 3 \times 10^5$ t/a capacity
- 48 sites with $> 1 \times 10^5$ t/a and $< 3 \times 10^5$ t/a capacity
- 23 sites with $< 1 \times 10^5$ t/a capacity

Between 2008 and 2012 the domestic demand grew 8.5% p.a. and the domestic production output by 8.0% p.a. in China.

World PVC production was 37.5×10^6 t/a in 2012, and growth ranged from 0 (Europe) to +8% (China). Overall, long-term growth worldwide is estimated at approx. 4%. Table 14 summarizes the world supply–demand balance.

10. Toxicology and Occupational Health

Vinyl Chloride Monomer (VCM). Because vinyl chloride boils at −13°C, it is handled as a compressed liquid. It has a vapor density greater than air, thus, precautions are taken in design not to contain the vapor in restricted areas. Protection of reactors by relief valves or bursting disks and double-valve isolation of all lines containing VCM are basic precautions taken in the design and construction of any PVC plant vessel that contains monomer. The gas is explosive between 3.6 and 25 vol% with air and 12 vol% oxygen is required for ignition [69]. Therefore, a special series of working conditions must be satisfied in the working environment and great care is always taken to purge lines, pumps, valves, etc. before any maintenance work is started. Thorough documentation (e.g., clearance to work certificates) is always used to ensure proper isolation of plant equipment before any entry. The whole plant is contained within a "red-fence" area where smoking is not permitted and where all electrical equipment is of a gas-tight and "flame-free" construction.

VCM has a narcotic effect at 8–12 vol% concentration and can cause death at higher concentrations [69]. Therefore, early VCM and PVC plants were designed to avoid build-up of gas above 1 000 ppm in the atmosphere. VCM has a pleasant ethereal smell that is first noticed at concentrations of 500–2 000 ppm.

Exposure to VCM has been shown to lead to two distinct problems. In the mid 1960s it became clear that a number of workers involved

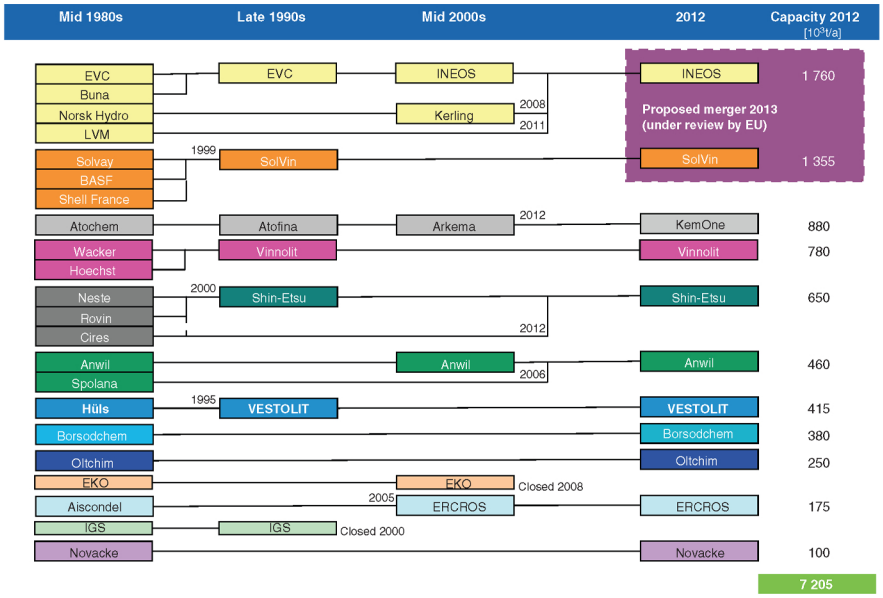


Figure 16. Evolution of the PVC industry in Western Europe

Table 13. Regional capacities (in 10^3 t/a) of the top ten PVC producers in 2012

Company	S. America	Asia	NAFTA	Europe	Total
Shin-Etsu	0	650	2 650	650	3 950
Formosa	0	1 775	1 525	0	3 300
Solvay	560	280	0	1 355	2 195
Oxy-Vinyls	0	0	1 930	0	1 930
Ineos	0	0	0	1 760	1 760
Axiall	0	0	1 330	0	1 330
LG Chem	0	1 260	0	0	1 260
Westlake	0	130	770	0	900
KemOne	0	0	0	885	885
Mexichem	390	0	480	0	880

The top 10 producers represent about 34.4% of world capacity of 53.3×10^9 t. World production in 2012 was 37.4×10^9 t (70% utilization).

PVC Production Plants:

Consumption of PVC Resin	Number of Plants
$> 3 \times 10^5$ t/a	21
$> 1 \times 10^5$ t/a	48
$< 1 \times 10^5$ t/a	23

Between 2008 and 2012
Domestic output of PVC increased 8% in yearly average.
Domestic consumption increased 15% in yearly average.
Imported quantities of PVC increased to 20% in yearly average.
PVC usage 2012 (kg/capita) is given below.

Europe (EU 28)	9.2
Eastern Europe/CIS	4.7
Turkey	11.3
Northeast Asia (without China)	12.1
Southeast Asia	2.8
China	10.2
India Subcontinent	1.5
Africa/Middle East	6.0
Oceania	5.5
North America	12.7
South America	4.2

Table 14. World supply/demand balance for PVC in 2012 (in 10^3 t/a)

	Capacity	Operating rate, %	Production	Imports	Exports	Consumption
N. America	8 040	86	6 900	90	2 520	4 470
S. America	2 350	80	1 860	950	240	2 570
European Union	7 260	80	5 780	170	1 200	4 750
Eastern Europe	950	86	820	650	20	1 450
Middle East/Turkey	1 250	65	800	1 280	70	2 010
China	23 430	56	13 120	1 130	350	13 900
Northeast Asia without China	5 630	78	4 370	110	1 660	2 820
Southeast Asia	2 320	90	2 090	320	660	1 750
Africa	625	63	400	670	70	1 000
Indian Subcontinent	1 510	88	1 330	1 210	0	2 540
Others	0	–	0	210	0	210
Total World	53 365	70	37 470	6 790	6 790	37 470

in reactor cleaning suffered from a bone condition called acroosteolysis (AOL), which affects mainly the hands and feet. Removal of the worker from exposure to VCM leads to an almost complete recovery. Since improvements to ventilating reactors and the introduction of high-pressure water cleaning the incidence of AOL has ceased [70]. A study of long-term exposure of rats to 30 000 ppm VCM did not reproduce any sign of AOL but they did develop cancers in various sites [71].

Subsequently, an extensive study with a wide range of dose conditions relating to occupational exposure was begun in 1971 at the Institute of Oncology in Bologna [72]. This showed that a very rare liver cancer, angiosarcoma could be formed in rats at levels of 250–500 ppm VCM. The first correlation between exposure to VCM and cancer in humans was made in 1973 when three workers at a plant in Louisville, Kentucky were shown to have died from angiosarcoma [73]. Since then other cases have been identified, all of which involved workers exposed to high concentrations of VCM as reactor cleaners or charging operators. As the period between first exposure to VCM and the appearance of angiosarcoma is 20 to 25 years it is likely that the incidence of the disease will soon decrease following improvements made to operation of PVC plants since 1973.

The knowledge that VCM is a human carcinogen has led to the introduction of very stringent controls by governmental and regulatory authorities to limit the exposure of workers and the general public to the monomer. In the United States, OSHA has set an 8-h TWA of 1 ppm VCM. During a shift, an employee's exposure must not exceed 5 ppm over a period of 15 min or less [74]. The European regulations, EC directive 2004/37/EC, require an annual average of < 3 ppm in the plant's airspace with alarm values of 15 ppm over 1 h, 20 ppm over 20 min, and 30 ppm over 2 min. Several Eu Member States and companies set somewhat lower levels, typically 1 ppm [75].

Poly (Vinyl Chloride). Strict limits have been set for the quantity of residual VCM in processed PVC articles intended for use in food contact applications.

In 1979, the EC set an upper limit of 1.0 ppm in the article and 10 ppb in the food. In 1986, the FDA suggested levels of ≤ 5 ppb in rigid and ≤ 10 ppb in plasticized PVC articles in food contact applications. To ensure that these limits are met PVC producers aim for these concentrations in the polymer grains themselves so that any further loss during processing ensures even greater safety.

There is little evidence that PVC powder itself causes any significant medical problems but steps are always taken to reduce powder emissions because of its nuisance value.

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Polyvinyl Compounds, Others

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1. Poly(Vinyl Alcohol)

In 1924, W. O. Herrmann and W. Haehnel [1] were the first to prepare poly(vinyl alcohol) by saponifying poly(vinyl esters) with stoichiometric amounts of caustic soda solution. At about the same time, work was resumed in the Hoechst Works of the IG Farbenindustrie on the saponification of poly(vinyl ester) derivatives such as poly(vinyl chloroacetate), which F. Klatte and E. Zacharias had begun in 1912 in the Chemische Fabrik Griesheim Elektron.

In 1932, W. O. Herrmann, W. Haehnel, and H. Berg [2] discovered that poly(vinyl alcohol) can be prepared from poly(vinyl esters) by transesterification with absolute alcohols in the presence of catalytic amounts of alkali. The transesterification principle is still used today by all poly(vinyl alcohol) producers. Work on the conversion of poly(vinyl acetate) to poly(vinyl alcohol) contributed substantially to the proof of Staudinger's theory of the structure of macromolecules [3].

In the transesterification of poly(vinyl acetate) to poly(vinyl alcohol), products with different acetyl group contents can be obtained depending on production conditions. The range of commercial poly(vinyl alcohols) extends from fully saponified types to products with degrees of hydrolysis of ca. 70 mol %.

In addition to these poly(vinyl alcohols), which dominate the market, saponification products of vinyl acetate–ethylene copolymers are also commercially important [4]. Numerous saponification products of other vinyl acetate copolymers (e.g., with other vinyl esters, longer-chain α-olefins, vinyl ethers, vinyl halides, acrylate and methacrylate esters, and unsaturated acids, nitriles, and amides) are described in [5].

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1.1. Structure and Crystallinity

Poly(vinyl alcohol) contains mainly 1,3-diol units. The content of 1,2-diol units in poly(vinyl alcohols) obtained by hydrolysis of poly(vinyl acetates) is <1 – 2%. The content of 1,2-diol sequences can be reduced by lowering the polymerization temperature of vinyl acetate [6] or using other vinyl esters such as vinyl formate [7] or vinyl benzoate [8]. The content of 1,2-diol units influences some properties of poly (vinyl alcohols) (e.g., the degree of swelling of films in water [9]).

Carboxyl and carbonyl end groups are more abundant than initiator end groups in poly(vinyl alcohols) [10]. Poly(vinyl alcohol) is slightly branched as a result of chain transfer reactions occurring during the polymerization of vinyl acetate [11]; → Poly(Vinyl Esters).

In partially saponified poly(vinyl alcohols) the acetyl groups can be distributed statistically or blockwise, depending on production conditions. The nature of the acetyl group distribution influences important properties of poly(vinyl alcohols), such as the melting point [11], the surface tension of aqueous solutions [12], and the emulsifying and protective-colloid properties [13].

The stereochemistry of poly(vinyl alcohols) is fixed during the polymerization of vinyl monomers. It is determined from the position and intensity in the ^{1}H NMR spectrum of the hydroxyl proton signal, which consists of three doublets assigned to syndiotactic (S), atactic (A), and isotactic (I) triads of poly(vinyl alcohol) [14, 15]. According to this, poly(vinyl alcohol) obtained by radical polymerization of vinyl acetate followed by hydrolysis is predominantly atactic in structure (24% I, 44% A, 32% S).

Stereochemically more uniform poly(vinyl alcohols) are obtained when the initial polymer is either poly(vinyl trifluoroacetate) (23% I, 36% A, 40% S) or poly(vinyl *tert*-butyl ether) (55% I, 32% A, 13% S). Poly(vinyl alcohols) of different tacticity have different properties. For example, in acetalization (see Chap. 2), the isotactic sequences react first, and the highest stability toward water is shown by syndiotactic poly(vinyl alcohols) [16].

Poly(vinyl alcohol) is a crystalline polymer (for X-ray structure, see [17] for the X-ray structure). The degree of crystallinity depends strongly on the structure and previous history of the poly(vinyl alcohol). Acetyl groups and other incorporated groups of any kind lower the crystallizability [18]. The degree of crystallinity of fully saponified poly(vinyl alcohols) is increased by heat treatment, which also lowers their solubility in water [19]. This effect is less marked for poly(vinyl alcohols) that contain acetyl groups.

1.2. Production

Since the monomer of poly(vinyl alcohol), vinyl alcohol, is nonexistent — the tautomeric equilibrium lies on the acetaldehyde side — only indirect methods are available for the production of poly(vinyl alcohol).

Attempts to prepare poly(vinyl alcohol) by polyaldol condensation of acetaldehyde have had little success up to now [20]. Polymerization of the metal vinyl compounds (which are relatively complicated to prepare), followed by saponification, leads in general to poly(vinyl alcohols) of low molecular mass [21, 22].

The most important manufacturing process for poly(vinyl alcohol), which is used worldwide, is the polymerization of vinyl esters or ethers, with subsequent saponification or transesterification. The preferred starting material is vinyl acetate, but derivatives of vinyl acetate (such as vinyl mono- and dichloroacetate, vinyl bromoacetate [23], and vinyl trifluoroacetate [24]), vinyl esters of other carboxylic acids (such as vinyl formate [25], vinyl butyrate [26], and vinyl benzoate [27]) and vinyl ethers (such as benzyl vinyl ether [28]) can also be used. The hydrolysis of poly(vinyl acetate) is easily controllable, and no side reactions occur.

Production Conditions. Since the properties of poly(vinyl alcohols) depend primarily on their molecular mass and residual content of acetyl groups, industrial production processes are optimized for the precise control of these two characteristics.

The preferred process for the production of poly(vinyl acetate) for further processing to poly (vinyl alcohol) is polymerization in methanol.

Factors determining the molecular mass of poly(vinyl acetate) and, accordingly, of poly

(vinyl alcohol) are the polymerization temperature, vinyl acetate–methanol ratio, and polymerization conversion [29]. Lowering the polymerization temperature, the proportion of methanol, and the conversion increases molecular mass.

In general, poly(vinyl acetate) should be as free as possible of monomeric vinyl acetate because the latter is cosaponified. Any acetaldehyde formed colors the poly(vinyl alcohol) yellow in alkaline saponification as a result of aldehyde resin formation and acetalizes it in acid saponification.

Conversion of poly(vinyl acetate) to poly (vinyl alcohol) can be carried out in solution, suspension, or emulsion with alkaline or acidic catalysts. The preferred process is transesterification in methanol in the presence of catalytic amounts of sodium methoxide, with formation of poly(vinyl alcohol) and methyl acetate.

Hydrolysis conditions influence the structure of the poly(vinyl alcohol) formed. By varying catalyst concentration, reaction temperature, and the reaction time, the content of residual acetyl groups can be adjusted practically at will. The nature of the distribution of the remaining acetyl groups in partially saponified poly(vinyl alcohol) is determined by the choice of catalyst and by the solvent. Thus, in alkaline saponification the residual acetyl groups are distributed largely blockwise [30], and in acidic saponification largely statistically [31].

If methyl acetate [31, 32] or benzene [18] is added to methanol in transesterification, poly (vinyl alcohols) with increased block formation by the remaining acetyl groups are obtained. In aqueous solution with acid catalysis, equilibrium conditions occur. The degree of saponification can be adjusted by the addition of different amounts of acetic acid [33]. Partly acetylated poly(vinyl alcohols) prepared by reacetylation of fully saponified products in homogeneous aqueous systems have a completely statistical distribution of the acetyl groups [31].

Poly(vinyl alcohol) is manufactured in both batch and continuous processes. For the continuous polymerization of vinyl acetate in methanol, high molecular masses can be achieved only with relatively low methanol content and low vinyl acetate conversion [34]. Part of the vinyl acetate must therefore be recycled.

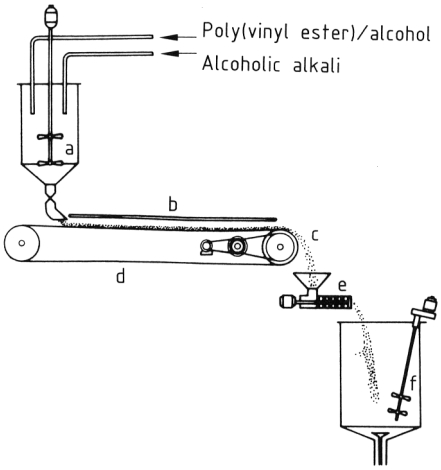


Figure 1. Belt saponification process for poly(vinyl alcohol) [38, 39]
a) Mixing vessel; b) Cover plate; c) Discharge; d) Conveyor belt; e) Mill; f) Washing vessel

In the alkaline hydrolysis of poly(vinyl acetate) in methanol, a highly swollen gel is formed initially. Then, toward the end of saponification this swollen gel contracts and releases solvent (syneresis), becoming a tough gel of poly(vinyl alcohol).

An example of a continuous process is the belt saponification of Shawinigan Chemicals (Fig. 1) [35, 36].

Suspension- or solution-polymerized poly (vinyl acetate) is mixed with methanolic alkali in a mixing vessel to give a 30% methanolic solution, which is fed to a conveyor belt, where it remains until syneresis begins. The gel is ground in a mill, neutralized with acid, washed with methanol, separated from the mother liquor, and dried. The mother liquor, consisting of excess acid, methanol, and methyl acetate, is worked up in further process stages.

Saponification in a kneader is an example of a discontinuous process (Fig. 2) [37, 38]. Poly (vinyl acetate) is dissolved in methanol in a kneader, and the amount of sodium methylate in methanol required for the desired degree of saponification is added. The transesterification process at 20–30°C usually lasts about 8 h. Then the mixture of methanol and methyl acetate is

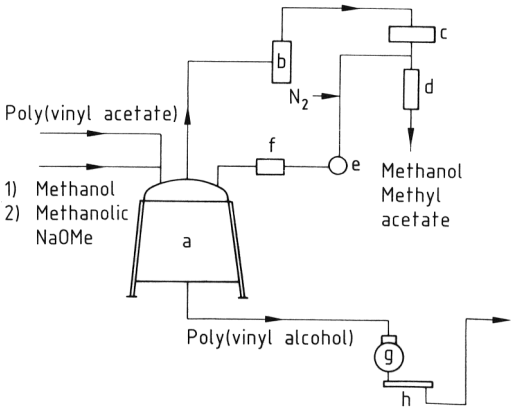


Figure 2. Manufacture of poly(vinyl alcohol) in a kneader [37, 40]
a) Kneader; b) Dust separator; c) Trap; d) Cooler; e) Blower; f) Heater; g) Mill; h) Sieve.

driven from the kneader at 60–70°C with a nitrogen stream, and poly(vinyl alcohol) is fed to subsequent processing stages.

Subsequent process stages [39, 40] include separation of vinyl acetate from partly reacted solution polymers in stripping columns, separation of the saponification mother liquor into methyl acetate and methanol, hydrolytic cleavage of methyl acetate with subsequent distillation of methanol and acetic acid, and drying of poly(vinyl alcohol), which can be carried out batchwise or continuously.

Trade Names. Poly(vinyl alcohol) is supplied by manufacturers under different trade names: Mowiol (Hoechst, Germany), Polyviol (Wacker Chemie, Germany), Rhodoviol (Rhône-Poulenc, France), Alcotex (Revertex, England), Polivinol (Rhodiatoce, Italy), Denka Poval (Denki Kagaku Kogyo, Japan), Gohsenol (Nippon Gohsei, Japan), Kurashiki Poval (Kuraray, Japan), Shinetsu Poval (Shinetsu Chem. Ind., Japan), Unitika Poval (Unitika, Japan), Elvanol (Du Pont, US), Gelvatol (Shawinigan Resins, US), Lemol (Borden, US).

Storage and transport of poly(vinyl alcohol) require no special precautions: the polymers must merely be protected from the effects of moisture and heat.

Wastewater Problems. Poly(vinyl alcohol) is degradable in sewage treatment plants with an adapted biological clarification stage. However, when discharged into receiving waters it is degraded only with difficulty, as shown by the 5-d BOD values. Tests showed that fish (guppies) are not harmed, even at a poly(vinyl alcohol) concentration of 500 mg/L of water [41].

1.3. Properties

Physical Properties. Normal commercial poly (vinyl alcohols) are white to yellowish and are supplied as powder and granules. The main factors influencing physical properties are the degrees of polymerization and hydrolysis. Most commercial products fall into two main groups: those with a degree of hydrolysis of about 98 mol% of the acetyl groups, and those with a degree of hydrolysis of 87–89 mol%. Both groups include products with degrees of polymerization from ca. 500 to 2500. Data such as the viscosity of the aqueous poly(vinyl alcohol) solutions, the molecular mass of the precursor poly(vinyl acetates), and the degree of hydrolysis or ester number are frequently used by manufacturers of poly(vinyl alcohol) to characterize their products.

The melting point and glass transition temperature depend not only on the content and distribution of acetyl groups but also on the tacticity and water content. For fully saponified poly(vinyl alcohols) a melting point of 228 °C and a glass transition temperature of 85 °C are reported [42]. Prolonged heating of dry poly (vinyl alcohol) above 110 °C can lead to evolution of gaseous cleavage products.

Poly(vinyl alcohol) Solutions. Water is the most important solvent for poly(vinyl alcohol). Certain polar solvents such as diethylenetriamine [43], dimethyl sulfoxide [44], formamide, dimethylformamide, and hexamethylphosphoric triamide [45] are relatively good solvents. The rate of dissolution in water increases with decreasing degree of polymerization and degree of hydrolysis. The degree of polymerization has a greater effect with fully saponified than with partially saponified poly (vinyl alcohols). Poly(vinyl alcohols) with

degree of hydrolysis below 88% dissolve better in water at low than at elevated temperature [46].

Poly(vinyl alcohol) solutions are obtained by stirring poly(vinyl alcohol) into water at ca. 90 °C. Industrially they are produced in indirectly heated dissolving tanks or by introducing steam into poly(vinyl alcohol) suspensions. For prolonged storage, solutions must be stabilized against microbial attack by adding preservatives.

The viscosity of aqueous solutions depends on the degrees of polymerization and hydrolysis of poly(vinyl alcohols) as well as on the concentration and temperature. Fully saponified poly(vinyl alcohols) yield more viscous solutions than partially saponified poly(vinyl alcohols) at the same degree of polymerization [46]. Concentrated solutions of highly saponified poly(vinyl alcohols) undergo a viscosity increase on prolonged standing, which can be reversed by heating.

Many inorganic salts, especially sulfates and phosphates, precipitate poly(vinyl alcohols) from aqueous solutions [42]. Boric acid and borax act as thickeners [47]. The conductivity of aqueous poly(vinyl alcohol) solutions depends on their electrolyte content, which is carried over from the precipitation process: for 10% solutions it is ca. 0.1–0.7 mS/cm [48].

Chemical Properties. Poly(vinyl alcohol) undergoes the chemical reactions expected of a polyglycol with secondary hydroxyl groups. The most important are the formation of esters, ethers, and acetals [42, 49, 50]. Only a few typical reactions are mentioned here. Examples of inorganic esters are poly(vinyl nitrates), phosphates, and sulfates. Organic esters can be obtained by reaction with acid anhydrides or acid chlorides. The cinnamate esters are important for the production of light-sensitive polymers [51]. Many poly(vinyl alcohol) ethers have been described. The products of the reaction of poly(vinyl alcohol) with ethylene oxide are suitable for the production of films with good solubility in cold water. Of the reaction products of poly(vinyl alcohol) and aldehydes, poly(vinyl butyrals) have attained importance as raw materials in the manufacture of safety glass.

1.4. Uses, Toxicology, and Economic Aspects

Protective Colloid in Emulsion and Suspension Polymerization. Poly(vinyl alcohol) has proved outstandingly effective as a protective colloid for the production of plastic dispersions, especially of poly(vinyl acetate) homo- and copolymers, and as a suspension stabilizer. By selection of suitable types and combination with emulsifiers, dispersions with extremely varied properties can be produced, most of which are used in adhesives [31, 52–55].

Adhesives. Poly(vinyl alcohol) is used in aqueous solution, alone or in combination with plastic dispersions, for packaging adhesives, cigarette adhesives, and moistenable gumming [56].

Sizes. The most important field of application in the textile industry is the sizing sector. Poly (vinyl alcohol) is an excellent raw material for the sizing of stable fiber yarns and filaments [56–59].

Paper Industry. Applications in the paper industry are surface sizing and the production of coated papers and special papers with specific barrier properties. Poly(vinyl alcohol) has excellent pigment binding power and is a good carrier for optical brighteners [60–63].

Other Uses. Poly(vinyl alcohol) is used for bonding all kinds of nonwoven fabrics, especially glass fiber; as temporary bonding agents for special ceramics; in secondary brighteners in electroplating and electroforming; for the production of protective lacquers and decorator sizing and solvent-resistant dipped products, such as gloves and aprons; for the modification of surface coating formulations; as a release agent for cast resin moldings; in the production of photoresists for the printing industry and of highly absorbent sponges; and in binders and thickeners for cosmetics.

Poly(vinyl alcohol) is also very suitable for the thermoplastic production of packaging films with graded water solubility. Good plasticizers for poly(vinyl alcohol) are ethylene glycol, glycerol, trimethylolpropane, neopentyl glycol, poly(ethylene glycols) with molecular masses

up to ca. 400, and ethoxylated phosphate esters. Films of plasticized poly(vinyl alcohols) are practically impermeable to nitrogen, oxygen, and carbon dioxide [64]. Saponification products of vinyl acetate copolymers (e.g., with ethylene or long-chain α-olefins) are also used in the film sector [60, 64].

Toxicology. In testing poly(vinyl alcohol) for toxicity and for compatibility with skin and mucous membranes, no negative effects were found in animals (LD_{50}; 90-d feeding test on rats; FDA patch test; dermal application) [48].

Economic Aspects. The worldwide production capacities (in 10^3 t/a) are as follows:

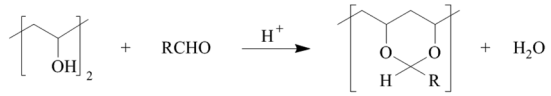
World	650
Japan	239
United States	127
Western Europe	60

2. Poly(Vinyl Acetals)

Robert Fuss, Florian Mummy

2.1. General Aspects

The first poly(vinyl acetal) was obtained by W. HAEHNEL and W. O. HERRMANN in 1924 by the reaction of poly(vinyl alcohol) with benzaldehyde in concentrated hydrochloric acid [65]. In the following years, more methods were developed, in which the reactions were carried out in concentrated acids and anhydrous solvents. In 1929, H. HOPF and E. KÜHN succeeded in acetalizing aqueous poly(vinyl alcohol) solutions in the presence of dilute acid [66]. Shortly afterwards, G. KRÄNZLEIN et al. reacted poly(vinyl acetate) with aldehydes with simultaneous saponification and acetalization to give poly(vinyl acetals) [67].



Vinyl alcohol Aldehyde Vinyl acetal

Poly(vinyl acetals) are terpolymers consisting of the following repeating units: vinyl acetate, vinyl alcohol, and vinyl acetals. There are poly(vinyl acetals) of different compositions, polarities, and molecular masses.

Poly(vinyl acetals) serve as very versatile and high-performance materials. They are characterized by their excellent mechanical and adhesive properties, optical clarity (of films), and good process ability.

2.1.1. Properties and Analysis

Analytical data typically quoted are:

- Grade/grade name
- Viscosity (commonly as a 10 wt.% solution in ethanol); note: different viscosity measurement systems may be utilized
- Residual hydroxyl content (also known as residual poly(vinyl alcohol)), in wt% and/or mol%
- Residual acetate content, in wt% and/or mol%
- Glass transition temperature T_g
- Solids

Solubility. Poly(vinyl acetals) are soluble in organic solvents such as alcohols, glycol ethers, ethers, Cellosolve, ketones, and others. Depending on their polarity, some grades are even soluble in hydrocarbon compounds such as toluene or xylene (highly acetalized products). Solubility in certain esters is also possible, in this case, ethyl lactate is the solvent of choice. Other solvents are terpineol, butyl carbitol, acetic acid, and dimethyl sulfoxide.

Poly(vinyl acetals) are thermoplastic polymers and may be extruded with or without plasticizers.

Particle size and density. Poly(vinyl acetals) are produced as powders (≈50–≈150 μm particle sizes) or compacted or granular materials and are white (colorless) to slightly yellow. Densities for powders are above 1.0 g/cm^3, but bulk densities are in the magnitude of 0.2–0.4 g/cm^3.

Molecular Mass Distribution (M_n/M_w) There is no existing standard for measuring the

molecular masses of poly(vinyl acetals). The reason for this is that there is no standard poly (vinyl acetal) polymer available (different from numerous other polymers). Data quoted in some publications simply refer to PMMA standards. Thus, for the same poly(vinyl acetal) polymer, data varying up to a factor of three can be found.

Viscosities (measured as 10 wt% or 5 wt% ethanolic solutions; higher molecular mass materials are often quoted in 5 wt% solutions) range typically from 10 to 300 mPa s. Some specialty products of either higher or lower viscosity levels may also be available. At the same total solids amount, depending on the solvent used, e.g., ethanol versus isopropyl alcohol, greatly varying solutions viscosities of the same poly(vinyl acetal) are obtained. In addition, by employing the same total solids amount and the same solvent but different dissolving techniques (e.g., stirrer bar, dissolver, rotating rolls), different solution viscosities are encountered. Viscosity data of poly(vinyl acetals) may only be compared if the same solvent, concentration, temperature, solution preparation technology, and viscosity measurement method are employed.

Glass transition temperatures T_g of poly(vinyl acetals) depend on the type of aldehyde or ketone employed. Short aliphatic chains (using e.g. formaldehyde (T_g = 108°C), or acetaldehyde) give rise to values T_g > 100°C. Longer aliphatic chains (e.g., butyraldehyde) lead to T_g of approximately 63–73°C, also depending on the degree of conversion (at the same chain length of the polymer backbone). The softening point of the polymers vary in the range between 100°C and 240°C (determined by the ring-and-ball method, according to ISO 4625), mostly depending on the length of the polymer backbone.

2.1.2. Synthesis and Reactions

As most aldehydes and many ketones react with vinyl alcohol homo- and copolymers, a large number of poly(vinyl acetals) may be obtained. Poly(vinyl acetals) are specialty chemicals produced only by a limited number of producers. The chemical variety of possible poly(vinyl acetals) is rather high (numerous different poly(vinyl alcohols) are available as well as a variety of different aldehydes and ketones).

Poly(vinyl butyral) is the predominant commercial product. Of minor importance and volumes are poly(vinyl formal) and poly(vinyl acetaldehyde) as well as mixed aldehydes, the latter ones being produced by using two different aldehydes in the same reaction.

The synthesis of poly(vinyl acetals) is somewhat more demanding than that of other polymers, which are produced in very high volumes by, e.g., a single-step polymerization reaction starting from the corresponding monomer (→ Polymerization Processes, 1. Fundamentals).

Characteristic parameters used in the production of poly(vinyl acetals) are:

- Degree of polymerization
- Molecular mass distribution
- Residual hydroxyl and acetate contents
- Degree of acetalization

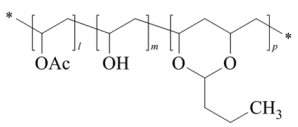
During the acetalization reaction starting from poly(vinyl alcohol), only the parameters residual hydroxyl content and degree of acetalization change. Degree of polymerization, molecular mass distribution, and residual acetate content remain unchanged and, hence, are determined by the choice of starting poly(vinyl alcohol). The poly(vinyl alcohols) used to produce poly(vinyl acetals) always contain residual vinyl acetate units (generally 1–8 wt%).

Poly(vinyl acetals) may differ in the degree of acetalization, which can vary within broad ranges and strongly influences the polymer properties, especially strength, solubility, and adhesiveness. According to Flory [68], for statistical reasons, no more than 81.6% of the alcohol groups in poly(vinyl alcohol) can react with aldehydes, given the underlying poly(vinyl alcohol) also contains 1,2-glycol bonds. For acetal formation, 1,3-glycol units react leading to the characteristic cyclic 1,5-acetal. This is the case for most commercial poly(vinyl alcohols).

The acetalization reaction is assumed to be exclusively intramolecular (i.e., it proceeds without cross-linking). Therefore, only in the reaction of poly(vinyl alcohol) with formaldehyde cross-linking can be produced relatively

easily, although even in this case, intramolecular acetalization is preferred. In the reaction with higher aldehydes, intermolecular acetalization is much more difficult or impossible [69].

Consequently, single aldehyde- or ketone-based poly(vinyl acetals) are terpolymers of the formula:



where *l*, *m*, and *p* can vary over wide ranges, and the alcohol, acetal (here: butyral), and acetate groups are generally distributed statistically. Although indications are that poly (vinyl acetals) with block (partially ordered) structures can be prepared, little is known about such structures.

In the reaction of formaldehyde with poly (vinyl alcohol), isotactic vinyl alcohol units, which give *cis* rings on acetalization, react more readily than syndiotactic vinyl alcohol units, which give more highly strained *trans* rings [70]. Therefore, in the acetalization of poly(vinyl alcohol), the isotactic vinyl alcohol units react first and the syndiotactic units remain. Individual acetalization processes appear to differ, however, so, e.g., poly(vinyl butyrals) of the same empirical composition can vary not only in the blocklike or statistical arrangement of their repeating units but also in the tacticity of the residual vinyl alcohol sequences. The properties of poly(vinyl acetals) are affected as a result. For example, syndiotactic vinyl alcohol polymers exhibit pronounced intermolecular hydrogen bonding, which is the reason for their high strength and poor solubility.

In poly(vinyl butyrals), the ratio between the hydrophobic and hydrophilic polymer units is variable within wide limits. The hydrophobic vinyl butyral units give the polymer good thermoplastic process ability, solubility in numerous solvents, elasticity, and toughness, as well as compatibility with many resins and plasticizers. The hydrophilic vinyl alcohol units are responsible for the high adhesion to inorganic materials such as glass and metals, high strength, cross-linking ability [71], and anticorrosive action.

Examples for cross-linking reactions include reactions with phenolic resins, epoxy resins, melamine resins, polyisocyanates, and dialdehydes.

Like all acetals, poly(vinyl acetals) are able to undergo acid-induced hydrolysis. If oxygen is also present, peroxidic oxidation can cause cleavage of the polymeric chain and increase the acidity of the polymer so that the decomposition accelerates autocatalytically.

Poly(vinyl acetals) can be stabilized effectively by the addition of alkali [72]. Poly(vinyl acetals) are also sensitive to oxidation in neutral or alkaline medium especially in the presence of UV light. In this case, stabilization with antioxidants, in addition to alkali, is advisable. Of the numerous antioxidants proposed [73], phenols and its derivatives have proved effective [74], whereas phosphites [75] or triazole derivatives [76] are effective as co-stabilizers.

Poly(vinyl butyral) powders may be stored over prolonged periods of time if kept under controlled conditions. Appropriate storage conditions consist of a dry, cool and dark environment. Manufacturers therefore recommend a storage period not exceeding 12 months.

2.2. Production

Raw Materials. The principal raw materials for poly(vinyl acetals) are poly(vinyl acetate) or poly(vinyl alcohol) and aldehydes or ketones. Most common aldehydes such as acetaldehyde or *n*-butyraldehyde are used. Basically, all types of aldehydes or ketones may be employed. However, C-1 to C-4 aldehydes have mostly been employed as they are sufficiently miscible with water (see Figs. 4 and 5). Use of formaldehyde has been greatly discontinued as a result of safety reasons (toxicity). Use of long-chain aliphatic aldehydes gives rise to remarkably different properties of the resulting products. In poly(vinyl acetals) produced from long-chain aliphatic aldehydes, compatibility with plasticizers as used for poly(vinyl acetals) film may be positively influenced. In addition, use of plasticizer and its possible migration may be reduced.

The starting materials should be pure and colorless. Commercial products may generally be used without further purification.

The poly(vinyl alcohol) must not contain insoluble components. The aqueous poly(vinyl alcohol) solution must therefore be filtered before acetalization. Although technical-grade formaldehyde can be used directly for acetalization, butyraldehyde should be purified by distillation and stored under nitrogen. It must not contain more than 2% impurities, especially other aldehydes and acids. The inorganic acids used for acetalization should be free of heavy metals.

Production Processes. Although there are a variety of potential methods for the manufacture of vinyl acetale polymers, only two different processes and their variants are commercially used [77–82]. In the *aqueous process*, the acetal is precipitated during the reaction of an aldehyde with poly(vinyl alcohol). In the *solution process*, the acetal formation takes place in an organic solvent. The subsequent reaction cascade of hydrolysis and acetalization can be performed either as a sequential or concurrent process [83].

The production processes are exemplified for poly(vinyl butyral) in Section 2.6.2.

The effect of production conditions on polymer properties is described in [84].

2.3. Uses

Owing to their transparency, elasticity, and good adhesion, poly(vinyl acetals) find various usage such as in laminated glass, as raw materials for surface coatings and primers, as a binder in ceramics and printing inks, and as adhesives. See Sections 2.6.3 and also Section 2.7.4 for a detailed list.

2.4. Environmental Issues, Safety, and Health

Poly(vinyl acetals) consist of carbon, hydrogen and oxygen. Under atmospheric combustion conditions, they burn with virtually no residue to produce carbon dioxide and water. For this reason poly(vinyl acetals) pose no disposal problems.

The U.S. Food and Drug Administration regulated poly(vinyl butyral) resins and classified them as indirect food additives [85, 86]. Poly(vinyl butyral) resin is considered nontoxic by single-dose oral ingestion ($LD_{50} > 10.0$ g/kg for rats) and is especially suitable for use in food packaging. The use of poly(vinyl butyral) in this area is governed by:

- EU regulation No. 0010/2011 of January 2011 on plastic materials and articles intended for contact with food (Plastic Implementation Measures, PIM Regulation),
- Council of Europe, Resolution RESAP (2004) 1, formerly AP (96) 5, on surface coatings intended for contact with foodstuffs (list of authorized monomers and starting substances in Appendix II, List 1),
- U.S. Food and Drug Administration 21 CFR
  - § 175.105 Adhesives
  - § 175.300 Resinous and polymeric coatings
  - § 176.170 Components of paper and paperboards in contact with aqueous and fatty foods.

Unformulated poly(vinyl butyral) and poly (vinyl formal) resins have flash points above 370°C. The lower explosive limit for PVB dust in air is 20 g/m^3.

2.5. Economic Aspects

Capacity. Global production capacities for poly(vinyl butyrals) are in the magnitude of 200 000 t/a (2014). Approximately 90% of the poly(vinyl butyral) production is plasticized and subsequently extruded into poly(vinyl butyral) films to be used for architectural safety glass and automotive applications. Minor use concerns applications in photovoltaics. As poly(vinyl butyrals) films contain plasticizers, the global production capacities for poly(vinyl butyral) films are in the magnitude of 225 000 t/a.

Less than 10% of the resins are used for non-interlayer applications.

Many producers are backward integrated and produce their own poly(vinyl alcohol) raw materials to be used for the production of poly(vinyl acetals).

Depending on grade in the United States and Europe, the price for nonfilm poly(vinyl butyral) resin is in range of € 5–20 per kilogram (2014).

Producers of poly(vinyl butyral) resin for nonfilm applications are Kuraray (Mowital, Pioloform) and Eastman (Butvar), as well as Chang Chun, Kingboard, and Micro Inks. Major producers of poly(vinyl butyral) interlayers are Kuraray (Trosifol, Butacite), Sekisui (S-LEC) and Eastman (Saflex) and since 2006 Chang Chun (Winlite).

The regional consumption of poly(vinyl butyral) is pictured in Figure 3. A total of 60% is utilized in Western Europe and the United States of America. In Asia Japan and China are the largest users. In the recent years China showed the largest consumption growth now reaching a total of some 12% of the global demand.

Commercial Products. Poly(vinyl butyrals) are commercially the most important poly(vinyl acetals). They are produced in numerous types, differing in molecular masses and composition. Additivation is possible but not always stated. Additives used concern oxidation and UV-light stabilization.

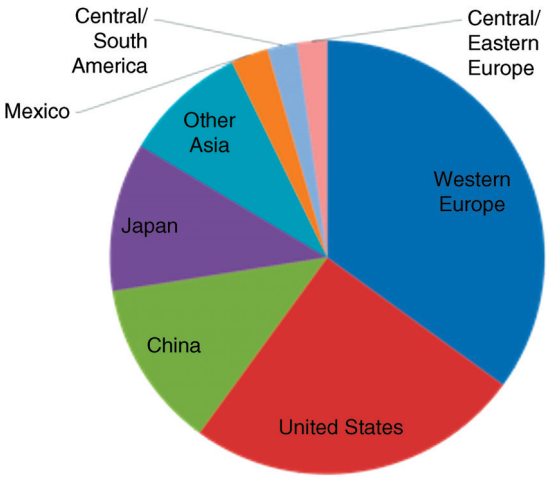


Figure 3. World consumption of poly(vinyl butyral) resin (2012)

Poly(vinyl butyral) is mostly sold as a powder. Other forms of delivery include compacted powders and granules. Next to bags (10–15 kg), deliveries in super sacks are also common. The most important manufacturers are Kuraray (Mowital, Pioloform), Eastman (Butvar), Chang Chun and Sekisui (S-lec).

As raw material for conversion into films, poly(vinyl butyral) is sold by a limited number of producers including Kuraray, DE, US, KR (Trosifol, Butacite); Eastman, US (Saflex), and Sekisui, JP (S-Lec), Chang Chun Group, TW, (Winlite) as well as Kingboard, CN.

Other forms of commercial product consist of partially acetalized poly(vinyl alcohols) that are still water-soluble. Such products are sold, e.g., from Sekisui under their trade name S-LEC K.

High-plasticizer containing poly(vinyl acetal) dispersions are also commercially available.

2.6. Poly(Vinyl Butyral)

2.6.1. Properties

Poly(vinyl butyrals) are amorphous and transparent. At low degrees of acetalization they are water-soluble. Like vinyl alcohol–vinyl acetate copolymers, they are good dispersants [87]. Also like these copolymers, their solubility in water decreases with increasing temperature [88].

Table 1 lists the composition and some average properties of various poly(vinyl butyrals), derived from product information pamphlets [85, 86, 89]. It roughly demonstrates the effects of molar mass on rheological, thermal, and mechanical properties. In detail, the softening temperature is between 105 and 155°C and increases accordingly with the molecular mass. Also the stiffness (determined by the tensile strength) increases with the chain length of the polymeric backbone. In addition, the effect of the proportion of vinyl alcohol units in the polymer is evident: with increasing vinyl alcohol content the intermolecular forces increase, and the strength and modulus of elasticity rise as do the softening point and the glass transition temperature.

Table 1. Properties of poly(vinyl butyrals) with various percentages of vinyl alcohol units and various molar masses [85, 86, 89]

Vinyl alcohol units, wt%	Molar mass, g/mol[a]	Viscosity, mPa s[b]	Water absorption in 24 h,%[c]	Tensile strength, 10^3 psi[d]	Elongation at break,%[e]	Flow temperature, °C[f]	Modulus of elasticity, 10^5 psi[g]	Glass transition temperature, °C[h]
17.5–20.0	170–250	1600–2500	0.5	7.0–8.0	70	145–155	3.3–3.4	72–78
17.5–20.0	120–150	800–1300	0.5	7.0–8.0	75	135–145	3.3–3.4	72–78
11.5–13.5	90–120	200–450	0.3	4.6–5.6	110	110–115	2.8–2.9	62–72
18.5–20.5	70–100	200–400	0.5	5.7–6.7	100	125–130	3.0–3.1	72–78
11.0–13.5	50–80	75–200	0.3	4.6–5.6	110	110–115	2.8–2.9	62–72
18.0–20.0	40–70	75–200	0.5	5.6–6.6	110	105–110	3.1–3.2	72–78

[a] Molecular mass (mass average in thousands) determined by size exclusion chromatography with low-angle laser-light scattering (SEC/LALLS) in THF.
[b] 10% by weight: 95% ethanol at 25°C using an Ostwald-Cannon-Fenske Viscometer.
[c] According to ASTM D 570-59aT.
[d] According to ASTM D 638-58T.
[e] According to ASTM D 638-58T.
[f] According to ASTM D 569-59.
[g] According to ASTM D 638-58T.
[h] Determined by differential scanning calorimetry over a range of 30–100°C on dried granular resin.

2.6.2. Production

For the commercial production of poly(vinyl butyrals), only those processes that start from poly(vinyl alcohol) isolated before acetalization are significant. Two important processes exist. One begins with aqueous poly(vinyl alcohol) solutions, which are reacted with *n*-butyraldehyde in the presence of mineral acid. After passage through a highly viscous intermediate stage, the polymer precipitates as fine grains. The reaction is then completed heterogeneously.

In the second process, an alcoholic poly (vinyl alcohol) suspension is acetalized. A homogeneous poly(vinyl butyral) solution is obtained that can be freed from insolubles by filtration.

Aqueous Process. In the aqueous process (Fig. 4) [77, 78], poly(vinyl alcohol) is dissolved in water and acidified with a mineral acid and reacted with butyraldehyde. As the condensation reaction proceeds and the acetals are formed, the number of hydroxyl groups present in the starting poly(vinyl alcohol) is reduced. This leads to a continuously decreasing solubility of the newly formed polymer in water. Finally the product produced becomes completely water-insoluble; the degree of acetalization at this stage is approximately 30%. However, once the product precipitates, the desired conversion is not yet accomplished. After a certain post-reaction time, sometimes in combination with heat treatment, this now heterogeneous system brings the reaction to completion. The final product is obtained as an aqueous dispersion of fine particles. This production process is characterized by a batch as well as continuous mode.

The prepared poly(vinyl alcohol) solution is charged into an acetalization vessel (up to 50 m^3 in size) and the process is batchwise. There are usually a number of such acetalization vessels running in sequences. Subsequently, the obtained acidic product slurry is worked up continuously. This work-up procedure includes thorough washing to remove the acid employed. Note: Acetals are formed under acidic conditions, however, they are not stable under acid conditions (back reaction). Being washed to neutral poly(vinyl acetals), they may be stabilized by adding an alkali, such as, e.g., sodium or potassium hydroxide. Finally the powdery material is dried and packed. Both normal bags as well as super sacks are available. In some cases, other packaging units such as full containers with polymeric inliners are used.

Solution Process. In the solution process (Fig. 5) [79–81], poly(vinyl acetate) is saponified by transesterification in the presence of ethanol and a mineral acid catalyst to obtain poly(vinyl alcohol). The ethanol and formed

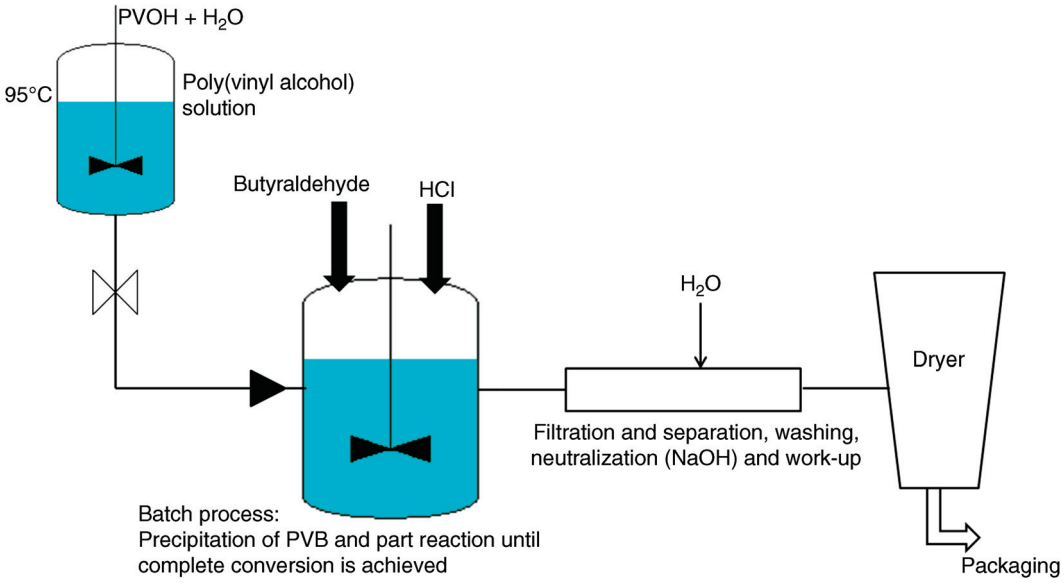


Figure 4. Aqueous process
PVOH = Poly(vinyl alcohol); PVB = Poly(vinyl butyrate)

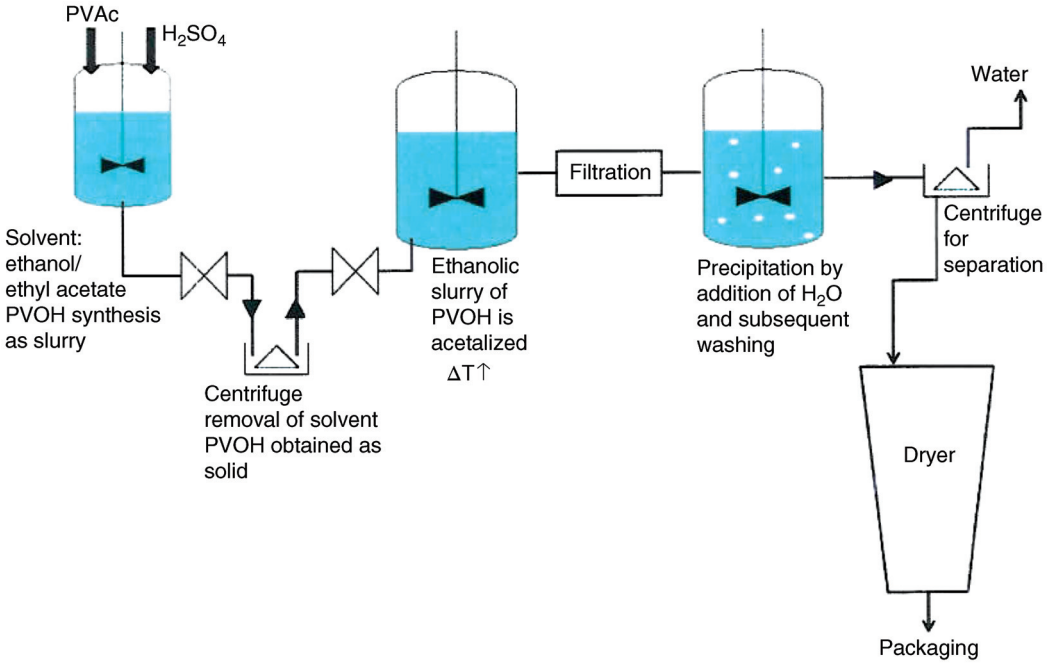


Figure 5. Solvent-based process
PVOH = Poly(vinyl alcohol); PVAc = Poly(vinyl acetate), ΔT = Rising temperature

ethyl acetate are removed from the solid by centrifugation. As the final poly(vinyl butyrate) polymer needs to have a low acetate content, the acetalization reaction cannot be performed concurrently. Poly(vinyl alcohol) is acetalized in a separate reaction unit, after being redispersed with ethanol, heated with butyraldehyde and the acid catalyst. As the acetalization proceeds, the obtained poly(vinyl acetal) becomes more and more soluble in the solvent used. Finally a homogeneous poly(vinyl butyral) solution is obtained that can be freed from insolubles by filtration. Upon completion, the obtained poly (vinyl acetal) is removed from the solvent. The major aspects of this process are the costly precipitation of the polymer and the need to recover the solvent.

In both processes the acid catalyst is neutralized upon completion of the reaction using typically sodium or potassium hydroxide, and several washing steps are necessary to remove traces of the catalyst, salts and to achieve a more alkaline resin pH to improve the resin's thermal stability [77, 90, 91].

Acetalization in Water. A small-scale synthesis may be conducted as follows:

An aqueous solution of poly(vinyl alcohol) with a polymer concentration of about 9% is heated to 95°C and slowly cooled. During cooling, butyraldehyde is added at 40°C and at a temperature of about 12°C, the hydrochloric acid (16%) is slowly added. The product starts precipitating already during acid dosage.

After 15 min, the suspension is heated to 70°C and held at this temperature for 2 h to complete the acetalization reaction. The suspension is filtered off and washed several times with deionized water at room temperature.

For stabilization, the washed polymer is suspended in water containing sodium carbonate and stirred at 70°C for 2 h. Finally, the product is rinsed several times with water and dried at 50°C overnight in a vacuum oven.

2.6.3. Uses

***Laminated Glass* [92].** The most important use of poly(vinyl butyral) (PVB) films is manufacture-laminated safety glass [93].

Such PVB films consist of approximately 80–70% PVB and 20–30% plasticizer. Residual hydroxyl groups mostly determine the polarity of the polymer thus resulting in adequate compatibilities of the two components. Their compatibility with plasticizers such as esters of phthalic, sebacic, ricinoleic, and citric acids is good [94]. Other important plasticizers in PVB films are ethers and esters of ethylene glycol, and esters of its oligomers with butyric or hexanoic acid. Dihexyl adipate is also used as a plasticizer for PVB films [95]. The commonly used plasticizer Hexamoll DINCH (1,2-cyclohexane dicarboxylic acid diisononyl ester) in PVB films is even suitable for food contact applications. Currently the most frequently used plasticizer in PVB films is triethylene glycol-bis-2-ethylhexanoate (3G8) [94-28-0] (suppliers: Oxea, Germany; Eastman, US).

The refractive indices of such PVB films (refractive index: 1.48) are in the same range of those of glass (1.46–1.52). Owing to the residual hydroxyl groups, adhesion to polar substrates is pronounced. Because of their flexibility, both curvatures of glass and little glass imperfections may be offset using PVB films [96].

The safety functionality derives from a well-balanced adhesion of the film to glass [97]. Upon impact dissipation of energy is achieved as the PVB film delaminates from the glass, thus reducing the velocity (energy) of the intruding object. If the sheet adheres too firmly to the glass, it is overstretched and tears when the glass breaks resulting in puncturing of the composite. Therefore, the adhesion must be adequately controlled so that when the glass breaks the sheet detaches slightly and a larger area absorbs the impact energy. The adhesion is fine-tuned by use of anti-adhesion additives. Suitable compounds are, e.g., various potassium salts such as potassium acetate [98]. However, the adhesion must remain sufficiently high to hold splinters of glass which have become completely detached from the laminate.

In automotives, next to windscreen applications sidelight as well as sun and moon roof applications are fields of use. In addition, switchable (smart) windows are on the way. In the manufacture of automobile windshields a sheet thickness of approximately 0.8 mm is generally used, whereas for structural or bullet-proof glass, thinner but multiple sheets may

be utilized. The surface of the sheet is structured by various techniques [99]. This reduces the tendency to stick together and facilitates deaeration during production of the glass composite. To completely prevent sticking, the sheet is either dusted with sodium hydrogen carbonate, which must be washed off prior to producing the composite, or cooled below 10°C.

In manufacturing the composite [100], sheets are laid between two or more sheets of glass and subjected in an autoclave to a special pressure and temperature program [101].

Plasticized PVB films for the production of automobile windshields and structural or bullet-proof glass are produced, for example, by the following companies: Kuraray (Trosifol, Butacite), Eastman (Saflex), and Sekisui Chem. Ind. (S-lec).

Advanced-Performance Poly(Vinyl Acetal) Films. Next to safety-glass applications poly (vinyl acetal) films providing additional features or functionalities have been developed. Such additional functionalities include special reflective properties by means of doping poly(vinyl acetal) films with IR reflective nanoparticles. Whereas the optical transparency is hardly impaired, reflection of sunlight is achieved yielding less headload in, e.g., vehicles.

Single and multi-layered poly(vinyl acetal) films have been made available focusing on superior sound isolation in buildings and cars.

A further advancement is concerned with switchable windows (smart windows) [102]. Such systems are divided into active (switchable) and passive (self-switching/automatic) systems. In both systems transparent and translucent devices are possible.

In self-switching systems the window changes transparency due to increased (outside) temperatures (thermochromic windows). Tinting is completely reversible and upon cooling returns to non-tinted status (Pleotint, US).

Active systems are switchable by, e.g., change of a potential differences. Switching may be complete (full tinting) or interrupted at any intermediate state (electrochromic; suspended particle devices or gasochromic systems) (Switchmaterials, CAN; EControl-Glas GmbH & Co. KG, DE; SageGlass, US; View Inc.; US).

Poly(vinyl acetals) are used either as matrix material for such compositions (e.g., in the case of thermochromic) and are laminated between, e.g., glass. Other systems use both, poly(vinyl acetal) material as a matrix material as well as poly(vinyl acetal) film for (glass) lamination [103].

Surface Coatings and Primers. Because of their elasticity and good adhesion, PVBs are important raw materials for paints, particularly for metal coatings. They are frequently combined with phenolic, alkyd, epoxy, urea, or melamine resins. The low-acetalized and lower molecular mass types, in particular, show good compatibility with these resins. When the coatings are heat-treated ("baked"), cross-linking occurs [104].

PVBs are outstandingly effective as primers with high corrosion protection. The coatings are abrasion resistant and adhere very well. The coated plates can be welded easily [86, 105].

Wash primer formulations with PVB form a good foundation for various types of topcoats [106–108]. Wash primers provide good adhesion to metal surfaces and stabilize the metal surface by continuously releasing of anti-corrosion ions. Wash primers with phosphoric acid and zinc chromate show very good anti-corrosion performance. However, owing to toxicity concerns related to chromates, other zinc-containing pigments have been developed. Mostly a system consisting of zinc molybdate [109] and phosphate pigments [110] is recommended. The problems associated with volatile organic solvents can be eliminated, as there are waterborne PVB dispersions that can also be employed in wash primer formulations [111].

Adhesives. (→ Adhesives, 2. Applications) Poly(vinyl acetal) resins are mainly consumed in high-performance thermosetting adhesives and in thermoplastic hot-melt formulations. PVB is also found in reflective films for license plates and road signs where PVB is the matrix for the glass beads [112–114]. PVB in formulations with plasticizers, waxes, and/or combination with other co-resins is utilized to make hot-melt adhesives [115]. Structural adhesives can be obtained when PVB is cured with, e.g., epoxy resins to give a thermoset material.

***Ceramics* [116].** As a temporary binder poly (vinyl acetal) is used in the manufacture of especially electronic ceramics. Next to superior dispersion, purity and binding properties a very reproducible burning out behavior (shrinkage) favors the use of poly(vinyl acetal). Poly(vinyl butyral) is completely burned out above 450°C (depending on molecular mass and atmosphere employed, N_2 vs. O_2).

Of major importance for electronic ceramic applications are sufficiently high mechanical stabilities for ever thinner ceramic layers in the green sheet stage (non-burned-out state; e.g., manufacturing of multi-layered ceramic capacitors MLCCs) as well as nonresidual (ash-free) burning out performance. Presence of foreign matters and metal ions derived from the temporary binder may render electronic ceramics unusable.

Printing Inks and Toners. PVB resin is an important binder in the formulation of printing inks [117]. Due to good solubility in mild solvents it is applied in several solvent-based formulations like for flexographic, gravure, screen and inkjet printing applications. As a binder PVB improves flexibility, adhesion, and toughness [106, 118–120]. Flexographic and gravure printing are the dominant fields in the market for printing of flexible packaging that are mainly processed in the food processing industry.

In addition to printing inks PVB is also beneficial as binder for toner formulations [106, 121]. The role of PVB is to increase viscosity, to improve the film formation in the fuser station and to prevent blocking. PVB also enhances the overall performance of the toner by minimizing the amount of fines without decreasing the flow properties.

X-Ray Imaging. Owing to their remarkable optical properties, poly(vinyl acetals) are also employed in medical devices such as X-ray imaging films. After exposure to irradiation such films are mostly developed dry. Such films consist of numerous layers where different poly (vinyl acetals) provide next to perfect optical performance additional features such as adhesion or dispersion (e.g. of silver particles). Companies producing such products include Carestream, US; Konica-Minolta, JP as well as Agfa, BE.

Poly(Vinyl Butyral) Dispersions. Poly(vinyl butyral) may be dispersed in the aqueous phase only with huge amounts of emulsifiers and dispersants. This way pollution of the environment by solvents is avoided. Nevertheless, such dispersions have minor importance because of the mentioned high emulsifier content, which impairs the adhesive properties and water resistance of coatings. Poly(vinyl butyral) dispersions can be produced by acetalization of aqueous poly(vinyl alcohol) solutions in the presence of emulsifier or by emulsification of poly(vinyl butyral). The latter process is commercially feasible. The utilization of higher molecular mass poly(vinyl acetals) is preferred, which are kneaded in the presence of high amounts of plasticizers and dispersants by shear mechanical force. Once a homogeneous mixture is obtained, careful dilution with water follows until the final dispersion is obtained. Next to virgin poly(vinyl acetal) also post-consumer poly(vinyl acetals) are utilized in the manufacture of poly (vinyl acetal) dispersions. The achieved quality levels are strongly depending on the starting materials employed. Usually the poly(vinyl acetal) content of such dispersions is in the magnitude of some 25%. High energy consumption as well as tough production conditions and equipment renders this production process to a rather niche one (producers: PPG, US; Eastman, US; Shark Solutions, DK).

In addition partly acetalized and hence water-soluble poly(vinyl acetals) are also commercially available. These waterborne products differ greatly in their performance when compared to fully, non-water-soluble poly (vinyl acetals).

Single-Serve Packaging. Unfavorable volume-to-surface ratios are obtained for small (food) packaging containers. Packaging of (oxygen) sensitive products requires gas barrier materials for sufficient product protection. Use of a combination of gas barrier providing polymers such as poly(vinyl alcohol) and poly (vinyl acetal) have been made available. Whereas the barrier material is water-sensitive, the poly(vinyl acetal)-based top coat provides sufficient moisture and mechanical protection to the container. The container materials may be based on polar (e.g., poly(ethylene terephthalate) or oriented poly(ethylene therephthalate))

or nonpolar (PE, PP) polymers. Barrier performance systems are available for various climatic conditions of use (producer: Container Corporation of Canada, CAN) [122, 123].

Other uses for which poly(vinyl butyrals) have been proposed are temporary, strippable coatings [124]; powder coatings [125]; and blends with other polymers.

2.7. Poly(Vinyl Formal)

The importance of poly(vinyl formal) is limited.

2.7.1. Production

Since the commercially important poly(vinyl formals) contain a relatively large number of vinyl acetate units, a single-stage process for manufacturing directly from poly(vinyl acetate) is particularly suitable.

In the processes developed in the United States [126, 127], 1000 parts by weight of poly (vinyl acetate) are dissolved in 2000 parts of pure acetic acid; a mixture of 875 parts of 30% formalin and 70 parts of concentrated sulfuric acid is added; and the mixture is stirred for 6 h at 85°C. After the mixture is cooled to 50°C and the sulfuric acid is neutralized, poly(vinyl formal) is precipitated with water and washed. A pale yellow powder is obtained. Instead of acetic acid, Hoechst [128] recommended the use of ethyl acetate, optionally mixed with methanol.

By altering the proportions of starting materials and varying reaction conditions, numerous types of poly(vinyl formal) can easily be produced. For the reaction mechanism, see [129, 130].

2.7.2. Commercial Products

Poly(vinyl formals) were marketed by Wacker-Chemie under the name Pioloform F and by Monsanto Chemical Company in St. Louis, Missouri under the name Formvar. The latter manufacturing unit of Monsanto was sold and Formvar is now distributed under the name "Vinylec" by SPI Supplies. The Wacker unit was purchased by Kuraray in 2008 and production of poly(vinyl formals) discontinued.

2.7.3. Properties [85, 131]

Commercial poly(vinyl formal) powders in contrast to formalized fibers from poly(vinyl alcohol), are not cross-linked. Individual types differ in molecular mass, which is usually between 15 000 and 45 000, and in the proportion of vinyl acetate units, which is usually 10 – 30 wt% of the polymer. The proportion of vinyl alcohol units is between 5 and 9 wt%.

The viscosity of polymer solutions increases not only with increasing molecular mass but also with increasing poly(vinyl alcohol) content. At the same time, the glass transition temperature increases from approximately 75 to 95°C. The softening temperature is between 140 and 170°C, depending on molecular mass. The tensile strength of the polymers is up to 70 MPa with a fracture strain of 30–70%. Depending on the type of stabilization, polymers can withstand temperatures of 120 – 150°C for up to one hour. The solubility in polar solvents increases with increasing proportion of poly (vinyl acetate). Poly(vinyl formals) are insoluble in hydrocarbons and alcohols, but soluble in mixtures of alcohols and aromatic hydrocarbons.

2.7.4. Uses

The most important use of poly(vinyl formal) is in the production of coatings for electrical wires [85], in which the poly(vinyl formal) is combined with phenolic resins. The coatings, which are cured at elevated temperatures are insoluble, tough, and resistant to abrasion and heat, and also have very good insulating properties [132, 133]. Its use in adhesive joints [91, 134] and metal coating [85] is less important.

The use of poly(vinyl formal) for foamed plastics has frequently been proposed. To produce such foamed plastics, an aqueous solution of poly(vinyl alcohol) is foamed and formalized in the presence of a water-soluble substance such as starch or sodium chloride. After washing out, an insoluble soft and spongy material is obtained [135, 136].

2.7.5. Toxicity

Poly(vinyl formals) are nontoxic provided there are no traces of residual formaldehyde.

Poly(vinyl formals) are therefore permitted for coatings that come in contact with food [85, 131].

2.8. Other Poly(Vinyl Acetals)

The numerous aldehydes that have been reacted with poly(vinyl alcohol) include furfural, benzaldehyde, crotonaldehyde, halogenated aldehydes, cyanopropionaldehyde, nitrobenzaldehyde, and glyoxylic acid. However, such poly(vinyl acetal) products have not reached economic importance. Poly(vinyl acetaldehyde acetal), on the other hand, temporarily played a role in Germany and Canada, but was displaced by poly(vinyl butyral) [137].

Studies of poly(vinyl acetals) from aliphatic C_2–C_8 aldehydes with different acetal contents in the presence and absence of plasticizers [138] have shown that the glass transition temperature decreases with increasing chain length of the aldehyde component. At the same time the poly (vinyl acetals) become softer and more hydrophobic.

Of the poly(vinyl acetals) from substituted aldehydes, the sodium salt of poly(vinyl butyral sulfonic acid) was produced commercially but has long since been abandoned (Afrilan, Hoechst). The substance was water-soluble and was employed in sizing. It was produced by passing sulfur dioxide into an aqueous solution of poly(vinyl alcohol) in the presence of crotonaldehyde at 0°C and subsequent heating the solution. Sulfurous acid was added to crotonaldehyde simultaneously with acetalization, and the sulfonic acid formed acted as the catalyst for the acetalization, so that further addition of acid was unnecessary [139].

3. Poly(*N*-Vinyllactams) and Poly(*N*-Vinylamines)

3.1. Polyvinylpyrrolidone

When *N*-vinylpyrrolidone and other *N*-vinyl compounds became commercially available by Reppe vinylation of lactams in about 1940, the polymers were soon produced on an industrial scale. Polyvinylpyrrolidone is used as an auxiliary in cosmetics and pharmaceuticals.



N-Vinylpyrrolidone

Production. Only radical polymerization is important. *N*-vinylpyrrolidone (*mp* 13.9°C, *bp* at 1.3 kPa 90 – 93°C) is usually polymerized batchwise in aqueous solution with hydrogen peroxide as initiator and regulator. The average molecular mass can be adjusted by varying the quantity of hydrogen peroxide: with 0.05% hydrogen peroxide, molecular masses of ca. 750 000 are obtained; with 3%, ca. 25 000. With increasing quantity of hydrogen peroxide the polymerization rate increases. The rate also increases with increasing concentration of *N*-vinylpyrrolidone in the aqueous solution, reaches a maximum at 40 – 60% monomer content, and then decreases. Due to the viscosity of the final polymer solution the concentration is adjusted within a range between 10% at high molecular mass and 60% at low. To control polymerization, the monomer solution must be added slowly to the polymerization mixture with cooling. Polymerization is complete after 6–12 h. The ready saponifiability of *N*-vinylpyrrolidone in aqueous acidic solution is a problem. Aqueous solutions containing monomeric *N*-vinylpyrrolidone should therefore always be neutral to basic. The pH value is best controlled with ammonia, which also activates the polymerization reaction [140].

Polyvinylpyrrolidone can be obtained as a white powder from polymer solutions by drum or spray drying. Because it is highly hygroscopic it must be protected from moisture during extended storage.

Polymerization can also be carried out in organic solvents. The initiators preferably used then are organic peroxides or azocompounds, preferably alkyl hydroperoxides, dialkyl peroxides, and peroxy esters [141]. The polymerization temperature is chosen according to the decomposition temperature of the initiator, but the polymerization rate also depends on the nature of the solvent [142, 143].

Bulk polymerization [144] and polymerization in suspension [145] have no commercial importance.

N-Vinylpyrrolidone can be copolymerized with many other vinyl compounds such as acrylic acid [144, 146, 147], methacrylates esters [140, 148], and methacrylamide [149]; for the Q and e values, see [150]. The most important are the polymers with vinyl esters [149, 151, 152], whose properties lie between those of the pure polymers.

When *N*-vinylpyrrolidone is heated for several hours with hydroxides and alkoxides of the alkali and alkaline earth metals [153], an insoluble polymer slightly swellable by water is formed in a spontaneous reaction. This polymer is also formed on heating *N*-vinylpyrrolidone with divinyl compounds in the absence of atmospheric oxygen [154] and is known as popcorn polymer [155].

Commercial Products. Polyvinylpyrrolidones with an average molecular mass of 2500 to 750 000 are on the market.

Trade names are Kollidon, Luviskol, Albigen A, and Divergan (BASF); PVP and Plasdone (General Aniline and Film Corp.); Collacral and Luviskol VA (copolymers with vinyl esters, BASF); PVP/VA (copolymers with vinyl acetate, General Aniline and Film Corp.); Polyclar and Polyplasdone XL (insoluble polyvinylpyrrolidone, General Aniline and Film Corp.).

Properties. Polyvinylpyrrolidone is a white powder. The glass transition temperature depends on the water content; extrapolation to 0% water content gives a glass transition temperature of 175°C. The mean molecular mass can be adjusted in the range of 1000 to 10^6.

Polyvinylpyrrolidone is highly hygroscopic, absorbing ca. 30% water at 60% humidity. It dissolves readily in water, and aqueous solutions are stable to electrolyte addition. The viscosity of the solution decreases with increasing temperature and with strong shearing [156].

Polyvinylpyrrolidone dissolves readily in polar solvents such as alcohols, amines, acids, and chlorinated hydrocarbons. It is insoluble in esters, ethers, ketones, and hydrocarbons. Completely anhydrous polyvinylpyrrolidone is also soluble in toluene.

Polyvinylpyrrolidone can be precipitated from aqueous solution by dropwise addition to acetone and from solution in organic solvents by addition of diethyl ether.

Polyvinylpyrrolidone has good compatibility with numerous film formers, water-soluble binders, and plasticizers. On solution casting, a clear, high-gloss, hard film is formed.

The polymer is chemically inert. The lactam group is saponified only by the action of concentrated acids, with the formation of poly[vinyl (γ-amino)butyric acid] [157].

With some substances such as iodine, polyphenols, tannin, dyes, and toxins, polyvinylpyrrolidone forms complexes [158]. Frequently, only a reversible association occurs. The protective colloid action is utilized in dispersions and in suspension polymerization.

For qualitative analysis [159], aqueous ammonium cobalt thiocyanate solutions are added to an acidic aqueous polyvinylpyrrolidone solution. The flocculation of a bright blue complex indicates polyvinylpyrrolidone. The IR spectrum is also suitable for identification. To determine concentration, the brownish red polyvinylpyrrolidone–iodine complex can be analyzed colorimetrically.

Uses. In cosmetics, polyvinylpyrrolidone and some copolymers, especially with vinyl acetate, are used as film formers in setting lotions and hairsprays. Fairly high molecular mass polyvinylpyrrolidone is used as a thickening agent and protective colloid in cosmetic emulsions. Its use as a blood plasma substitute has been abandoned.

In pharmacy, polyvinylpyrrolidone has a wide spectrum of applications: as a solubilizer, as a crystallization retarder, for detoxification, for reducing the irritant action and toxicity of certain substances, as a tablet binding and coating agent, as a suspension stabilizer, and as a dispersant for pigments in tablet-coating suspensions. The polyvinylpyrrolidone (PVP) complex with iodine, PVP-iodine, is used as a disinfectant and does not show the side effects of elementary iodine [160]. The insoluble and slightly water-swellable popcorn polymer is used as a tablet-disintegrating agent.

Polyvinylpyrrolidone and PVP-iodine are described in a series of pharmacopoeias (e.g., in the U.S.).

Since polyvinylpyrrolidone forms complexes with tannins it is used for the clarification of beer and other beverages. The cross-linked, insoluble popcorn polymer is particularly suitable [161].

Polyvinylpyrrolidone forms hard, transparent, strongly adherent films on glass, metal, plastics, and cellulose, and is used in the adhesives industry as a binder and water-soluble hot-melt adhesive.

Polyvinylpyrrolidone is also used as an auxiliary in textile finishes, as a dye acceptor for synthetic fibers, as a leveling and stripping agent for dyes, as a thickener for printing inks and latex paints, as a dispersant in laundry detergents, as a protective colloid in the emulsion and suspension polymerization of many polymers, and as a water-binding agent for the concentration of protein solutions [162].

Toxicology. Polyvinylpyrrolidone is chemically and biologically largely indifferent [163, 164] with regard to both acute toxicity and skin irritation.

In feeding tests on rats with radioactively labeled polyvinylpyrrolidone of average molecular mass 40 000, more than 99% was excreted through the intestinal tract [163]. Even when large amounts of polyvinylpyrrolidone were fed for years, no harm to experimental animals was established. Swelling of the lymph nodes, which can be interpreted as a transition stage in the excretion of polyvinylpyrrolidone, was observed only with dogs; no indications of accumulation or extensive degenerative changes to organs were detected.

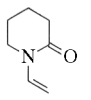
Carcinogenicity of polyvinylpyrrolidone was not observed in any of the experimental procedures [165]. On the basis of extensive experience on humans as well as on the results of further experimental studies on animals with parenteral or oral administration, no evidence of carcinogenic risk to humans was found [166].

More than one million people have shown good tolerance for polyvinylpyrrolidone infusions as a blood plasma substitute without side effects. However, the high molecular mass fractions of polyvinylpyrrolidone, with molecular masses above 40 000, are excreted slowly or not at all. Polyvinylpyrrolidone is therefore no longer used for infusions because the low molecular masses types do not have a plasma-expander action. Animal experiments have shown that larger molecules are stored in the cells of the reticuloendothelial system of the spleen, the liver, and the lymph nodes, as well as in bone marrow. However, during such polyvinylpyrrolidone storage, neither morphological nor functional damage has been observed [167].

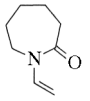
On the basis of inhalation tests on female volunteers with six different kinds of hairspray that caused no pathological changes of any kind [168], the FDA reported that the normal use of aerosol hairsprays containing PVP and PVP – vinyl alcohol as film formers is not accompanied by a health risk.

3.2. Polymers of other *N*-Vinyllactams

In the addition to polyvinylpyrrolidone, the polymers of other *N*-vinyllactams such as *N*-vinylpiperidone [162] and *N*-vinylcaprolactam [169] are known.



N-Vinylpiperidone



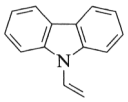
N-Vinylcaprolactam

These polymers have better solubility than polyvinylpyrrolidone in organic solvents such as aromatic hydrocarbons, ketones, and aliphatic hydrocarbons. Polyvinylcaprolactam is readily soluble in cold water: the higher its average molecular mass, the better is its solubility. In warm water (30–40°C), polyvinylcaprolactam precipitates from solution.

Vinylcaprolactam can be polymerized in bulk [170] or in solution. The polymers are used for gluing woven synthetic textiles and as components of lubricating oils [171]. The copolymers with ethylene are used as coatings for textiles and paper, and as adhesives [172].

3.3. Polyvinylamines

Poly(N-vinylcarbazole) is a transparent thermoplastic material. The glass transition temperature is 211°C and the glass point 173°C. It starts to decompose only above 300°C [173].



Vinylcarbazole

Poly(*N*-vinylcarbazole) dissolves in aromatic and chlorinated hydrocarbons and in tetrahydrofuran. It swells in benzene-containing fuels and is insoluble in water, dilute acid and alkali, aliphatic hydrocarbons, and alcohols.

The electrical properties are unusual. Photoconductivity depends on the molecular mass [174]; doping effects are observed upon addition of various substances such as 1,5-diaminonaphthalene, tetracyanoethylene, or anthracene [175]. The existence of traps for electronic charge carriers (electrons and defect electrons) has been demonstrated [176]. For the mechanism of conductivity, see [177].

Before polymerization, *N*-vinylcarbazole (*mp* 63–64°C, *bp* at 0.3 kPa 155°C) should be purified by distillation or recrystallization. When handling *N*-vinylcarbazole, safety instructions should be observed [178], because it has very strong sensitizing properties. No harmful side effects are known for monomer-free poly(*N*-vinylcarbazole).

For radical polymerization in bulk, azo initiators or peroxides are used [179, 180]. Suspension polymerization in water [181] or methanol [182] is also known. Cationic polymerization of *N*-vinylcarbazole proceeds easily, but whether polymerization in the presence of benzoyl peroxide occurs via a radical or a cationic route is unknown [183]. Cationic polymerization has a rate constant five times higher than radical polymerization and is used for the production of low molecular mass polymers [184].

Radical copolymerization with other vinyl compounds such as styrene, acrylonitrile, vinyl esters, and acrylate esters has been described, and a Q value of 0.28 and an e of −1.49 are given [185]. The stereospecific polymerization of *N*-vinylcarbazole is also known [186].

Because its softening point is ca. 200°C, polyvinylcarbazole was formerly used for moldings that are exposed to elevated temperature. Fibers and films have also been manufactured from polyvinylcarbazole [187]. Today, it is used as a heat-resistant insulator in radio and radar technology and in capacitor manufacture [188]. Because of its photoconductivity it is important for the manufacture of electrostatic photocopiers and television recording tubes [189].

Commercial Product: Luvican (BASF).

Polyvinylimidazole. Because of the second nitrogen atom, polymers of *N*-vinylimidazole have a basic character. The solubility therefore depends on the degree of protonation. Unquaternized polyvinylimidazole is soluble in organic solvents such as alcohol, but in water it is only swellable. It dissolves in acids, with salt formation. Quaternized polyvinylimidazole is water soluble. Depending on the length of the alkyl group used in quaternization, polymers with different hydrophobic–hydrophilic character are obtained [190].

N-Vinylimidazole (*bp* 190–193°C) and *N*-vinylimidazoles quaternized with alkyl halides or dialkyl sulfates can be polymerized by the radical mechanism using azo initiators and peroxides. Copolymerization with acrylamide, acrylates, butadiene, styrene, *N*-vinylpyrrolidone, and vinyl acetate has been described: values of 0.1 and 0.24 have been given for Q, and −0.91 and −1.73 for e [191].



N-Vinylimidazole

Polyvinylimidazole and copolymers are used as hairdressing preparations, antistatic agents for hydrophobic plastics, liquid detergents, and in the production of hydrogels.

Other Vinylamines. Because of their instability, aliphatic vinylamines can be prepared

only with difficulty, and the corresponding polyvinylamines are obtainable only by indirect routes [192]. Cyclic amines such as carbazole and imidazole, indole, and pyrrole, on the other hand, can easily be converted to *N*-vinylamines by Reppe vinylation.

Polymers of 2-vinylpyridine and 4-vinylpyridine have also been produced. 4-Vinylpyridine can be copolymerized with other vinyl compounds such as styrene and vinyl chloride; values of 1.91 for Q, and −0.51 for e are given [193]. Polyvinylpyridines have been studied as polymeric reagents in organic synthesis, catalysts, and ion exchangers.

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Poly(Vinyl Esters)

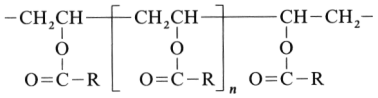
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1. Introduction

Poly(vinyl esters) are polymers with structural units of the general formula:



They are synthesized by polymerization of vinyl ester monomers CH_2= CH−O−CO−R.

In addition to vinyl ester homopolymers, co- and terpolymers of mixed vinyl esters or of vinyl esters and other comonomers are also important industrially.

Poly(vinyl acetate) and vinyl acetate copolymers are the most important poly(vinyl esters).

In 1912 and 1913 Klatte synthesized the first poly(vinyl esters): poly(vinyl chloroacetate) (R = CH_2Cl) and poly(vinyl acetate) (R = CH_3) [1].

2. Raw Materials

Vinyl Esters. Vinyl acetate is predominantly produced by acetoxylation of ethylene with acetic acid on palladium catalysts. Vinyl esters of ≥ C_3 acids are produced by addition of acetylene to the acid, or by palladium- or mercury-catalyzed transvinylation of vinyl acetate (see → Vinyl Esters).

On an industrial scale vinyl acetate (R = CH_3), vinyl propionate (R = CH_2CH_3), vinyl pivalate[R = $C(CH_3)_3$], vinyl 2-ethylhexanoate [R = $CH(C_2H_5) - (CH_2)_3CH_3$], vinyl laurate [R = $(CH_2)_{10}CH_3$], VeoVa 10 [R = $C(CH_3)R'_2$] and VeoVa 9 [R = $C(CH_3)R'_2$] are used for the production of polymers. VeoVa 9 and VeoVa 10 are the vinyl esters of versatic acids — synthetic tertiary carboxylic acids with nine or ten carbon atoms (see → Carboxylic Acids, Aliphatic, Chap. 10.). Previously, vinyl chloroacetate, vinyl isobutyrate, vinyl caproate, vinyl isononanate, vinyl stearate, VeoVa 911, and vinyl benzoate were also used in industry for a time or were envisaged for this purpose.

Data for the industrially most important monomers are summarized in Table 1. High-purity monomers are required for the reproducible production of polymers. The content of other components can be determined by gas chromatography. The purity determination of vinyl acetate is standardized in ASTM standards [2]. Impurities which are particularly disruptive are those which severely inhibit polymerization, such as crotonaldehyde and vinylacetylene, or compounds that act as chain-transfer agents, such as acetic acid, acetaldehyde, acetone, benzene, or toluene [3], [4]. Impurities with two readily copolymerizable double bonds, such as

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Table 1. Physical data for industrial vinyl esters

	Vinyl acetate	Vinyl propionate	Vinyl pivalate	Vinyl 2-ethyl-hexanoate	VeoVa 9	VeoVa 10	Vinyl laurate
CAS no.	[*108-05-4*]	[*105-38-4*]	[*3377-92-2*]	[*94-04-2*]	[*54423-67-5*]	[*51000-52-3*]	[*2146-71-6*]
Vinyl ester content, %	≥ 99.9[a]	≥ 99.9[b]	99.4[c]	99.5[c]	99.4	> 98.0	99.4 ± 0.1
Water (DIN 51 777), %	≤ 0.03[a]	≤ 0.1[b]	< 0.10	< 0.10	< 0.1[d]	≤ 0.1[d]	< 0.005
Acid content, %	≤ 0.0005	≤ 0.03[b]	< 0.10	< 0.10	< 0.3	≤ 0.2	< 0.5[e]
Color number (ISO 6271)	≤ 5	≤ 10[b]	20	< 20	< 20	< 15	≤ 10
Inhibitor content, ppm	3 – 20	10[b]	9 – 13	6 – 10	5 ± 2[d]	5 ± 2[d]	without[e]
bp, °C	72 – 73[a]	ca. 95	112.1	185.6	185 – 200	136 (13.3 kPa)	254
Vapor pressure, kPa							
at 20 °C	12	4.58	2.412	0.057	< 0.1	< 0.1	
at 50 °C	42.6	19.63					0.01
at 70 °C					1.2	0.7	0.38
Flash point (DIN 51 755), °C	− 8	4.5[i]	14[i]	65	45	75[h]	136
Upper/lower explosion limit (vapor in air at 20 °C), vol %	2.6/13.4	1.8[j] – 13.5[k]	n.d.	n.d.	0.7/n.d.	n.d.	0.5/n.d.
Solubility in water at 25 °C, %	0.9[f]	0.6	0.08	< 0.01	< 0.1	< 0.1	< 0.1
Solubility of water in vinyl ester at 25 °C, %	2.3[f]	0.8	n.d.	n.d.	< 0.06	< 0.05	< 0.1
Heat of polymerisation, kJ/kg	1035.8	882			ca. 522	ca. 485	n.d.
T_g of homopolymer[g], °C	33	− 7 (33)	+ 70 (33)	− 36 (33)	60 (28)	− 3 (28)	− 53[l]

[a] Hoechst specification.
[b] BASF specification.
[c] Union Carbide Specification.
[d] Shell specification.
[e] Values from Wacker Chemie.
[f] At 20 °C.
[g] Values depend on measurement method; values in parentheses give T_g of poly(vinyl acetate) when same method is used.
[h] DIN 51 758 (PM).
[i] Tag closed cup (ASTM D56 – 61).
[j] At 4 °C.
[k] At 41.5 °C.
[l] Extrapolated from copolymer data. n.d. = not determined.

vinyl crotonate, also cause problems because they can lead to cross-linking reactions and thus to the formation of insoluble polymers. Monomers used for emulsion polymerization must be completely free from previously formed polymer.

To prevent polymerization during storage and transport, 3 – 20 ppm of a phenolic compound such as hydroquinone or hydroquinone monomethyl ether is used as an inhibitor. The inhibitors generally need not to be removed before polymerization, since they can be rendered inactive during polymerization by using a sufficiently large amount of initiator.

To assess the purity and the suitability for polymer production, particularly in the case of vinyl acetate, a simple polymerization test [5] is used. A given quantity of monomer is warmed with 0.5 % benzoyl peroxide (relative to monomer) to 70 °C under defined conditions, and the time elapsing until the start of polymerization is recorded. The delay in comparison with pure, inhibitor-free monomer is a measure of the impurity content or of the amount of inhibitor added for stabilization.

Initiators. In industrial poly(vinyl ester) processes polymerization is initiated by radical initiators. Other processes, such as photopolymerization, radiation-induced polymerization, and the use of organometallic compounds as initiators have not achieved importance.

Azo compounds (e.g., azobisisobutyronitrile), diacyl peroxides (e.g., dibenzoyl peroxide and dilauryl peroxide), peroxyesters (e.g., *tert*-butyl peroxybenzoate and *tert*-butyl peroxyoctanoate), hydroperoxides (e.g., *tert*-butyl hydroperoxide and cumene hydroperoxide), and water-soluble inorganic peroxides (e.g., hydrogen peroxide, potassium, ammonium, or sodium peroxodisulfate) are used as radical initiators. Redox systems are also widely used, in which a peroxy compound is combined with a reducing agent (e.g., H_2O_2– ascorbic acid; H_2O_2– Fe^{2+},

ammonium peroxodisulfate – sodium sulfite, or *tert*-butyl hydroperoxide – sodium formaldehyde sulfoxalate) [6].

Initiators are chosen according to their solubility in the solvent or monomer, and the decomposition half-life of the substance or the redox combination under polymerization conditions.

Sufficient initiator must be used to oxidize any inhibitors present in the monomer, and to ensure a constant reaction rate in spite of continuous decomposition of the peroxide under the reaction conditions. High radical concentrations result in polymers of low molecular mass. Generally 0.1 – 1 % of an initiator based on the monomer is used. The initiator can be added at the start of the polymerization in one portion or added gradually during the course of the reaction.

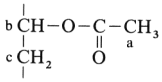
Molecular Mass Regulators. To regulate the molecular mass of the polymer, C_1 – C_4 alcohols, C_2 – C_4 aldehydes, thiols (> C_{10}), or chlorinated hydrocarbons (e.g., carbon tetrachloride) are used; for chain-transfer constants, see [7].

3. Polymer Structure

The kinetics of homo- and copolymerization of vinyl esters has been widely studied; for a summary, see [3]. Three features are particularly characteristic of the polymerization of vinyl acetate:

1. Very high reactivity of the vinyl acetate radical
2. Relatively low reactivity of vinyl acetate monomer towards attack by radicals
3. High chain-transfer constants of vinyl acetate, poly(vinyl acetate), and other polymers relative to the vinyl acetate radical or the growing chain

The differing reactivity of the radical and the monomer, which is also the case for other vinyl esters, makes the production of uniform copolymers from vinyl esters with comonomers that behave differently (e.g., where the monomer reacts more rapidly with radicals) difficult. For copolymerization parameters *r*, *q*, and *e*, see [7]. Chain-transfer reactions involving the monomer or the polymer results in products with a high degree of branching being formed in the polymerization of vinyl acetate. Three types of branching are observed in the final polymer:



The side chains can be bound to the main chain via an ester group (a) and also directly by a C–C bond (b and c). In the case of chain-transfer in (a), the side chains can be cleaved hydrolytically. The extent of side chain formation at positions (a), (b), and (c) depends strongly on the reaction conditions. The data vary between 97 % and 75 % for (a) [8–10]. The lowering of the average degree of polymerization occurring on saponification of polyvinylacetate, the reduction in the number of side chains in the polymer, and the broadening of the molecular mass distribution, which depends on the proportion of (a) branches, must be taken into consideration in the production of downstream products of poly(vinyl acetate) (see → Polyvinyl Compounds, Others).

In poly(vinyl acetate) the monomer units are linked predominantly head-to-tail. The proportion of head-to-head segments decreases with decreasing polymerization temperature [3].

4. Production

Homo- and copolymers of vinyl esters are produced both in the homogeneous phase by bulk or solution polymerization, and in the heterogeneous phase by suspension and emulsion polymerization.

4.1. Bulk Polymerization

Bulk polymerization can be carried out discontinuously by monomer addition in stirred reactors or continuously in tubular reactors. The monomers are heated to the reaction temperature in the presence of monomer-soluble initiators. The heat of reaction can be removed for low-boiling monomers by a reflux

condenser, and in all other cases through the reactor wall. The process is limited to polymers with low to medium molecular mass. Molecular mass and melt viscosity must be sufficiently low at the end of the reaction that the product can be removed from the reactor without difficulty.

Discontinuous processes for poly(vinyl acetate) with a molecular mass of $M_w = 35\ 000$ have been described. The molecular mass can be controlled by addition of regulators [11]. A similar process is used for the production of graft copolymers from poly(ethylene glycol) and vinyl acetate [12].

Poly(vinyl acetate) with $M_w = 300\ 000$ is obtained in tubular reactors, which give almost quantitative polymerization [11].

Terpolymers can be produced from VeoVa 10, styrene, and maleic or acrylic esters by substance polymerization at 155 – 170 °C [13]. Vinyl acetate – ethylene copolymers with an ethylene content of > 60 % are produced by using the high-pressure polyethylene process (see → Polyethylene).

4.2. Solution Polymerization

Solution polymerization allows the production of polymers with a more uniform structure and lower degree of branching in a simpler process. The removal of the heat of reaction is less problematic than in bulk polymerization, since the reaction can be carried out under reflux at the boiling point of the solvent or one of the monomers. The degree of polymerization depends on the nature and amount of solvent [14].

A process which allows the production of relatively uniform, high molecular mass poly(vinyl acetate) is solution polymerization with relatively low conversion. The unreacted vinyl acetate acts as an additional solvent. The reaction is stopped at a conversion of, for example, 50 % by adding an inhibitor, and unreacted monomer is removed.

Poly(vinyl acetate) which is to be further processed to poly(vinyl alcohol) [7], is generally produced in methanolic solution. Use of *tert*-butanol permits the production of high molecular mass solution polymers because of its low chain-transfer constants relative to the vinyl acetate radical. This is exploited industrially in the production of vinyl acetate – ethylene copolymers with an ethylene content of 50 – 70 % (see → Rubber, 6. Synthesis by Radical and Other Mechanisms). Solution polymerization can be carried out as a discontinuous process in simple stirred reactors, which operate under pressure (for vinyl acetate – ethylene) or pressureless, depending on the monomer used and the reaction conditions; or continuously in a tubular reactor or a cascade of stirred reactors, which are particularly suitable for this process.

4.3. Suspension (Bead) Polymerization

In suspension polymerization the monomer, usually vinyl acetate, is suspended in water by stirring together with a monomer-soluble initiator, and heated to the boiling point of the vinyl acetate – water azeotrope for polymerization. The polymer is produced as beads (diameter ca. 0.2 – 3 mm) and can easily be separated after cooling, and dried. Suspension polymerization combines the advantages of bulk and solution polymerizations: heat removal during polymerization is straightforward, and the product can be easily isolated and handled, and is free of solvent. Suspending agents are used to stabilize the two-phase system of water and the monomer or the solution of polymer formed in the monomer during the reaction. In the older literature a large number of active substances are described, including neutral electrolytes such as phosphates, water-soluble polymers such as modified starch, poly(vinyl alcohol), polyacrylamide, polyvinylpyrrolidone, copolymers with carboxyl groups such as styrene – maleic acid copolymers [11], or crotonic acid – vinyl acetate copolymers.

Apart from the nature of the suspending agent, the shape of the reactor, the stirrer speed, and the stirrer geometry significantly affect the stability of the system and the particle size distribution of the beads formed.

4.4. Emulsion Polymerization

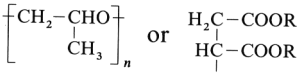
Emulsion polymerization is the most important process for the production of vinyl ester homo- and copolymers. The emulsions, which contain water as the continuous and the polymers as the dispersed phase, are mainly used in the liquid form. Smaller amounts are converted to the

polymer by spray-drying to give a powder which can be redispersed in water.

The properties of the product are determined not only by polymer composition and structure, but also by the stabilizing additives used in production, and by the particle size and particle size distribution of the dispersed polymer phase.

In the production of poly(vinyl ester) emulsions three types of stabilizer are used:

1. Water-soluble, polymeric protective colloids, such as poly(vinyl alcohol) [15], [16], [17], hydroxyethyl cellulose, polyvinylpyrrolidone [18], poly(*N*-vinylamides) [19], or starch.
2. Anionic emulsifiers that contain hydrophilic groups such as $-SO_3^-$, $-OSO_3^-$, $-(OCH_2-CH_2)_n-SO_3^-$, or $-OPO_3^{2-}$, in addition to a hydrophobic group. The hydrophobic part of the molecule can consist of C_{12} – C_{24} alkyl or alkylaryl groups,



Typical compounds of this type are dodecylbenzenesulfonate, sodium laurylsulfate, and dioctyl sulfosuccinate. Ethylene sulfonate is an anionic stabilizer [20] that leads to formation of high molecular mass polymers with $-SO_3Na$ groups by incorporation into the polymer.
3. Nonionic emulsifiers with hydrophobic groups and polyether chains as hydrophilic groups. Oxyethylation products of nonylphenol, isooctylphenol, C_{12} – C_{18} fatty alcohols, or low molecular mass poly(propylene oxide) are most widely used. The degree of oxyethylation is 4 – 50.

Protective colloids usually give emulsions with an average particle size of ca. 1 – 10 μm. Ionic emulsifiers give an average particle diameter of 0.1 – 0.3 μm. With a combination of the two types the average particle diameter is ca. 0.2 –2 μm.

The choice of emulsifiers or protective colloids depends on the desired properties of the emulsions. There is a range of known relationships between the emulsifier/protective colloid system, the amount of emulsifier or protective colloid, the polymerization reaction conditions, and the polymer properties [7], [21], [22]. However, they have not yet led to a general theory for the choice of emulsifiers and protective colloids. Therefore, for the production of new poly(vinyl ester) emulsions the most favorable emulsifiers and protective colloids and the optimal concentration must be determined experimentally.

The protective colloid most thoroughly investigated and most often used is poly(vinyl alcohol). Its emulsifying action is strongly dependent on the content of residual acetyl groups. It decreases with decreasing acetyl group content, as does the reaction rate of the emulsion polymerization [23]. Poly(vinyl alcohols) with a residual acetyl content of 0 – 12 % are generally used for the emulsion polymerization of vinyl esters. During polymerization, part of the poly(vinyl acetate) is grafted on to the poly(vinyl alcohol). In peroxodisulfate-initiated polymerization, the content of graft polymer increases with increasing molecular mass and increasing acetyl group content of the poly(vinyl alcohol) [24]. It is also strongly dependent on the initiator. With H_2O_2 and azobisisobutyronitrile as initiators significantly less graft polymer is formed.

Kinetic investigations of the emulsion polymerization of vinyl esters are mainly concerned with vinyl acetate homo- and copolymerization in the presence of ionic emulsifiers [3], [25]. Because of the considerable water solubility of the monomer, in the case of vinyl acetate a mechanism of particle formation differing from that in the emulsion polymerization of other monomers has been discussed. It is assumed that polymerization initially takes place in aqueous solution since the rate is almost independent of the emulsifier concentration [7], [25–27]. In contrast, experiments on emulsion polymerization of water-insoluble vinyl esters of long- chain carboxylic acids have shown, that here the behavior is similar to that of other hydrophobic monomers such as styrene.

For emulsion polymerization with protective colloids ideas about the stabilizing effect are mainly qualitative. It is assumed that high molecular mass hydrophilic protective colloids are adsorbed as loops on the surface of the particles and stabilize them by forming a hydrate layer.

Discontinuous Polymerization. On an industrial scale, discontinuous emulsion processes predominate. In batch processes the total

quantity of monomer is heated to the polymerization temperature with the aqueous solution of the protective colloid or emulsifier and the initiator required to form the final emulsion. In the addition process the monomer or, in the production of copolymers, a monomer mixture is added to the total aqueous phase during the course of polymerization. A special case of the addition process is the preemulsion technique, in which part of the aqueous phase is charged to the reactor and a preemulsion is formed from the other part and the monomer. This preemulsion is then added during the course of polymerization.

After polymerization is complete, the emulsion formed is cooled, treated if necessary with stabilizing additives, plasticizers, or by pH adjustment, and then removed from the reactor. The treatment can also be carried out in additional stirred vessels connected to the reactor.

In the discontinuous processes stirred vessels are used. The stirrer geometry and speed have a major influence on the quality of the emulsion. Anchor stirrers, propellers, impellers, and MIG stirrers are used. In the case of vinyl acetate homo- and copolymers produced at atmospheric pressure, the heat of reaction can be removed by a reflux condenser. For other vinyl esters, and for polymerization of vinyl acetate below its boiling point, jacket cooling or the use of internal or external heat exchangers is necessary.

If low-boiling or gaseous monomers such as ethylene or vinyl chloride are copolymerized with vinyl esters, stirred autoclaves must be used. The amount of ethylene which is copolymerized mainly depends on the ethylene pressure above the reaction medium but also on other process parameters such as reaction temperature and monomer concentration during polymerization [28], [29]. Addition processes [30] and batch processes [31] at ethylene pressures up to 100 bar have been described.

Continuous Processes. For the continuous production of poly(vinyl ester) emulsions, both atmospheric-pressure, and pressurized-vessel processes (for copolymerization with ethylene [32] or vinyl chloride) have been described. The monomers, initiators, emulsifiers and protective colloids, and water are fed, either together as a preemulsion or separately as aqueous and organic phases, to a tubular reactor [33], [34], a stirred-tank cascade, a continuous stirred-tank reactor, or a loop reactor with a circulating pump [35].

Construction Materials. Vinyl esters, poly (vinyl esters), and the additives and initiators used in their production are not very corrosive. To produce poly(vinyl esters) reactors made of stainless steel or glass-lined steel are used. For parts of the plant which only come into contact with the monomers, such as pipes and heat exchangers, aluminum can also be used. Copper and copper alloys should be avoided, since copper ions can inhibit polymerization even at very low concentrations [3].

5. Industrially Important Poly (Vinyl Esters)

The only industrially important homopolymers are poly(vinyl acetate) and, to a much lesser extent, poly(vinyl propionate). All vinyl esters which are accessible on an industrial scale are also used to prepare a large number of co- and terpolymers by combination with one another and with other monomers. In this group vinyl acetate is also by far the most important vinyl ester.

In the following the most important processes for the production of the individual polymers are denoted by letters as follows:

(B) Bulk polymerization
(S) Solution polymerization
(BS) Bead suspension polymerization
(G) Graft polymerization
(E) Emulsion polymerization

Polymers are produced from the following monomers by the methods shown:

Vinyl acetate (B, S, BS, E)
Vinyl acetate – dibutyl maleate (B, E) [36]
Vinyl acetate – *n*-butyl acrylate (E)
Vinyl acetate – 2-ethylhexyl acrylate (E)
Vinyl acetate – *n*-butyl acrylate – *N*-hydroxymethylacrylamide (E) [37]
Vinyl acetate – crotonic acid (S, E) [38]
Vinyl acetate – VeoVa 10 (B, E) [13]
Vinyl acetate – VeoVa 10 – acrylic acid (E) [13]

Vinyl acetate – VeoVa 10 – *n*-butyl acrylate (E)
Vinyl acetate – *N*-hydroxymethylacrylamide (E)
Vinyl acetate – vinyl laurate (B, E) [39]
Vinyl acetate – vinyl laurate – vinyl chloride (E) [40]
Vinyl acetate – ethylene (B, S, E)
Vinyl acetate – ethylene – vinyl chloride (E) [41]
Vinyl acetate – ethylene – acrylic ester (E)
Vinyl acetate – ethylene – acrylamide (E) [42]
Vinyl acetate – ethylene – *N*-hydroxymethylacrylamide (E) [43]
Vinyl acetate – crotonic acid grafted on polyglycol (G) [12]
Vinyl acetate – *N*-vinylpyrrolidone (S)
Vinyl propionate (E)
Vinyl propionate – vinyl chloride (E)
Vinyl propionate – *tert*-butyl acrylate (E)
VeoVa 10 – vinyl chloride (E) [22]
VeoVa 10 – styrene – acrylic ester and/or maleate (B) [13]
VeoVa 10 – VeoVa 9 – methyl methacrylate – butyl acrylate (E)

VeoVa 10 can be completely or partly replaced by VeoVa 9 to achieve special properties.

6. Properties

Poly(Vinyl Acetate) Homopolymers. Poly (vinyl acetate) is amorphous, odorless, tasteless, and has high lightfastness, and weather resistance. The glass transition temperature (T_g = 28 °C) depends to a certain extent on the molecular mass [7]. For electrical, mechanical, and thermal properties, see [7]. The polymers are soluble in many esters, ketones, cyclic ethers, phenols, halogenated aliphatic hydrocarbons, methanol, 95 % ethanol, and 90 % isopropanol.

Commercial poly(vinyl acetate) emulsions with poly(vinyl alcohol) as the protective colloid usually have a particle size of ca.1 – 10 μm,a solids content of 40 – 65 %, and a viscosity range of 1 – 50 Pa · s. The latex particles are frequently aggregated to produce grape-like formations [44].

Emulsifier- containing homopolymer emulsions, some of which contain protective colloids such as hydroxyethyl cellulose, have lower particle size (0.1 – 2 μm).

The minimum film formation temperature of homopolymer emulsions, which is important for their applications, is 15 – 18 °C. Therefore, for many uses plasticizers, such as dibutyl phthalate, tricresyl phosphate, or auxiliary film formers, are added.

Coarse-particle emulsions stabilized with poly(vinyl alcohol) are mainly important as wood glues and adhesives. Fine- and medium-particle emulsions stabilized by emulsifiers are mainly used as binders for emulsion paints and textiles.

Vinyl Acetate Copolymers. The facile alkaline saponification of the ester groups in vinyl acetate homopolymers is a disadvantage in many applications, since the saponification products are hydrophilic and water sensitive. This low resistance to hydrolysis is one reason for combination with comonomers. The second is the glass transition temperature of 28 °C, which is too high for many uses (e.g., paints and adhesives) and renders the poly(vinyl acetate) too hard and inflexible at the usual temperatures of use. The glass transition temperature can be adjusted by the addition of plasticizers. However, for use where plasticizers are undesirable and increased resistance to saponification is required, softening comonomers are used, e.g., dibutyl maleate; *n*-butyl acrylate; 2-ethylhexyl acrylate; ethylene; or ethylene in combination with vinyl chloride, VeoVa 10, or vinyl laurate. The glass transition temperature is most effectively lowered by ethylene, vinyl laurate, and acrylic esters, while the resistance to alkali is best improved by ethylene, or ethylene combined with vinyl chloride or by VeoVa 10. Copolymerization with > 20 wt % VeoVa 9 increases the glass transition temperature and the resistance to alkali.

Since for a particular application of a copolymer, a narrow range for the glass transition temperature or for the minimum film formation temperature is required, the ratio of vinyl acetate to the comonomers can only be varied within certain limits. The additional use of VeoVa 9 in the pressureless production of emulsions or the additional use of vinyl chloride for high-pressure polymers allows the production of polymers with a desired glass transition temperature but

different vinyl acetate contents. For the evaluation of a copolymer it is critical that, at a monomer ratio required by the glass transition temperature, the other properties are favorable. For example, emulsions used as binders in paints must be stable towards alkalies. LINDEMANN [28] has determined the compositions necessary to achieve glass transition temperatures of + 10 °C, 0 °C, and − 10 °C for the most important comonomers used in the production of vinyl acetate copolymers. Saponification experiments on vinyl acetate copolymers have shown that vinyl acetate – ethylene, vinyl acetate – ethylene – vinyl chloride, vinyl acetate – VeoVa 10, and vinyl acetate – vinyl laurate – vinyl chloride, co- and terpolymers with 50 – 80 % vinyl acetate have particularly favorable properties for paints [41], [45–47]. Use of *N*-hydroxymethylacrylamide allows the production of cross-linkable vinyl acetate copolymers, and the use of crotonic acid gives water-soluble vinyl acetate copolymers with good film-forming properties.

Vinyl Proprionate Homopolymers. Poly(vinyl propionate) differs from poly(vinyl acetate) in its lower glass transition temperature (T_g − 7 °C) and its higher stability towards alkalies [47]. Under the same conditions vinyl propionate polymerizes more slowly than vinyl acetate and gives products with lower molecular mass [48]. Poly(vinyl propionate) is produced industrially by emulsion polymerization.

Vinyl Propionate Copolymers. For many applications the glass transition temperature of poly(vinyl propionate) is too low. To obtain industrially more desirable polymer properties (e.g., T_g, resistance to saponification, weather resistance) it is therefore more commonly used together with comonomers that raise the glass transition temperature. Vinyl propionate – vinyl chloride and vinyl propionate – *tert*-butyl acrylate copolymers are produced by emulsion polymerization. Coatings made from these polymers are relatively resistant to saponification and have good weather resistance.

VeoVa 10 and VeoVa 9 Polymers. Homopolymers of VeoVa 10 or VeoVa 9 have not yet achieved any importance. Copolymers with vinyl acetate (see above) and vinyl acetate and acrylic esters are the most important. A range of other co- and terpolymers have been described [22], [22]. VeoVa 10 – vinyl chloride copolymers in the ratio 2 : 1 to 1 : 2 can be produced by emulsion polymerization in stirred autoclaves. The polymers are very weather resistant and have a high pigment-binding capacity.

Styrene – VeoVa 10 – acrylic ester or maleic ester terpolymers are clear, colorless, saponification resistant, and, on copolymerization with monomers with functional groups, cross-linkable [49].

7. Quality Specifications, Trade Names, Storage and Transport, Wastewater

Quality Specifications. The applications of vinyl ester homo- and copolymers are so varied that uniform, generally valid quality specifications cannot be defined.

The content of unpolymerized monomers, which is generally < 0.5 % can be determined by GC [50], [51]. Molecular mass can be determined by light scattering or gel permeation chromatography.

For emulsions the determination of dry residue (ISO 1625), sieve residue (ISO 4576), pH value (ISO 1148), viscosity (ISO 3219 and ISO 2555), freeze/thaw resistance (ISO 1147), density (ISO 8962), minimum film formation temperature, and the white point (ISO 2115) is standardized. The size of the latex particles is determined by optical or electron microscopy, by light scattering [52], by the Marshall method [53], or by aerosol spectroscopy [54]. In Germany, for polymers subject to foodstuffs regulations, the chewing gum regulation [55], the cheese regulation [56], and Recommendation XIV [57] apply.

Trade Names and Producers. Airflex (Air Products); Appretan, Mowilith, Mowiton, Imperon-Binder (Hoechst); Emultex (Harlow Chemical Comp.); Everflex (Grace); Propiofan (BASF); Rhodopas (Rhone Poulenc Polymers); Uramul (DSM); Vinamul (Vinyl Products); Ucar (UCC); Vinavil (Montedison); Vinnapas, Vipolit (Wacker).

Storage and Transport. Poly(vinyl esters) are combustible, but not readily flammable. They are generally not corrosive.

For poly(vinyl ester) emulsions, transport and storage containers must be resistant towards the aqueous phase, including low molecular mass substances dissolved therein. Irreversible damage to emulsions can arise through external effects which change the composition or the state of colloidal distribution. For example water loss can result in skin formation on the surface.

Many emulsions are frost resistant. However some products coagulate when the aqueous phase freezes. Producers generally give information on the frost resistance of emulsions.

Undesired aggregation or coagulation of the latex particles can occur on strong shearing in unsuitable pumps or in spray nozzles.

Poly(vinyl ester) emulsions must frequently be protected against attack by microorganisms [58].

Wastewater. With the exception of the less widely used crotonic acid copolymers, the polymers are insoluble in water. They can, however, enter the wastewater system as emulsions. Poly (vinyl esters) are nontoxic but are degraded extremely slowly in water. Emulsions therefore must not be discharged directly into receiving waters. Wastewater that contains emulsion can generally be treated in biological sewage treatment plants. The polymer enters the sewage sludge.

8. Uses, Toxicology, and Economic Aspects

Uses. The most important uses of poly(vinyl esters) are in emulsion paints (→ Paints and Coatings, 2. Types, Section 4.4.→ Paints and Coatings, 2. Types, Section 4.5.) and adhesives (→ Abrasives.). Other uses include antinoise compounds, chewing gum bases, concrete additives, soil stabilization, glass fiber sizing material, binders for nonwoven fabrics, fibrous leather substitute, pigment printing pastes, coatings for undersides of carpets, cheese rinds, and coatings for paper.

For some uses (building, adhesives, paints) dispersion powders, which can be redispersed in water before use, are produced from the emulsions by spray drying [59]. Here vinyl acetate homopolymers, copolymers of vinyl acetate with ethylene, VeoVa 10, or with VeoVa 10 and acrylic esters stabilized with poly(vinyl alcohol) are predominantly used. The main advantage of these products lies in their ability to be stored without any problem, and that they can be combined with hydraulic binding agents as one- component systems [60].

Toxicology. A differentiation must be made between the polymers themselves and the other substances always present in the industrial products. All investigations published to date on poly(vinyl esters) refer to industrial products; they are therefore only valid for the composition used in each case.

There are no indications that the poly(vinyl esters) investigated are toxic by oral administration; poly(vinyl acetate) see [61]. Poly-(vinylesters) from C_2– C_{18} unbranched fatty acids are therefore permitted together with the comonomers listed individually in the corresponding regulations [55–57] and the accompanying substances for coating cheese and as additives for the production of chewing gum.

Economic Aspects. For the production of polymers based on vinyl esters there are no reliable statistical figures. The production capacity for vinyl acetate in 1990 (in 10^3 t/a) gives an indication of the order of magnitude [62], [63]:

	1991	1994
Western Europe	590	655
Germany	290	–
Eastern Europe	300	116
Former Soviet Union	115	–
North and South America	1480	1775
United States	1280	1500
Asia	930	953
Japan	570	–

The consumption of vinyl acetate is assumed to be ca. 800 000 t in the United States, ca. 660 000 t in Western Europe, and 550 000 t in Japan in 1990. The distribution of the consumption of vinyl acetate among the different products varies in the individual regions. In Western Europe the following quantities of vinyl acetate are consumed in the most important areas of use:

Poly(vinyl acetate) emulsions	ca. 430 000 t
Poly(vinyl alcohol)	ca. 120 000 t
Poly(vinyl acetal) and other uses	ca. 110 000 t

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Poly(Vinyl Ethers)

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1. Introduction

Industrially important poly(vinyl ethers) are compounds with the general formula: $(-CH_2CHOR-)_n$ where R is an alkyl group such as methyl, ethyl, isobutyl, or octadecyl.

Poly(vinyl ethers) were first prepared by Wislicenus, who in 1878 produced a balsam-like product from 700 mols of vinyl ethyl ether [*109-92-2*] and 1 mol of iodine [1]. This reaction was recognized as a chain reaction involving a cationic polymerization initiated by I^+ and chain growth via carbonium ions.

In the 1920s the monomeric vinyl ethers [2] became readily available by Reppe vinylation of alcohols with acetylene and grew in industrial importance. Their polymerization was researched systematically.

After 1930 vinyl ethers and poly(vinyl ethers) were produced on an industrial scale, initially at the Ludwigshafen works of the I. G. Farbenindustrie (now BASF), and since 1940 at the General Aniline and Film Corporation (GAF) in the United States, and later also by Union Carbide (UCC) in the United States.

Today (1991) poly(vinyl ether) homopolymers are only produced by BASF; UCC and GAF have ceased production. Poly(vinyl ether) homopolymers are used as raw materials for adhesives.

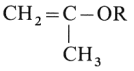
Copolymers of vinyl ethers with other monomers, such as maleic anhydride, vinyl chloride, or acrylic esters, are produced by GAF and BASF. They are used as auxiliary materials for adhesives and paints, and in many other industries. General information on poly(vinyl ethers) can be found in [3–5].

2. Production

Monomers. Poly(vinyl ethers) are produced exclusively by polymerization of vinyl ether monomers.

In addition to the vinylation of alcohols with acetylene, the vinylation of alcohols with ethylene also leads to alkyl vinyl ethers, according to patents of Union Oil of California [6]. However the process has not become established industrially.

The very reactive α-methylvinyl ethers [7]

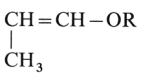


are only of academic interest.

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With both strong and weak initiators and independent of the polarity of the solvent used, they give polymers with syndiotactic structures [8].

The stereochemistry of the polymers from β-methylvinyl ethers



has been intensively investigated [9–15]. Polymers of vinyl ethers which are substituted at the alkyl group by, for example, chlorine [16], oxyethylene groups [17], a phthalimide group [18], an acetoxy group [19], a 9-carbazolyl group [20], a trifluoroalkyl group [21], or an acrylate or sorbate group [22], also have no industrial importance.

Of the industrially important vinyl ethers (methyl [*107-25-5*], ethyl [*109-92-2*], isobutyl [*109-53-5*], and octadecyl [*930-02-9*]), vinyl methyl ether has the greatest economic growth rate.

Initiators. *Anionic initiators* are unsuitable for the polymerization of vinyl ethers.

With *radical initiators* such as azoisobutyronitrile [23], peroxides [24], or redox systems [25], vinyl ethers polymerize to give homopolymers with a low reaction rate and a low degree of polymerization. However, copolymers from vinyl alkyl ethers and maleic anhydride in a molar ratio of 1 : 1 can be produced at a high rate with radical initiation, the polymer chains being constructed from both monomer units in a strictly alternating sequence.

Copolymers of vinyl ethers and vinyl chloride or vinyl ethers and acrylic esters contain a maximum of 50 mol % vinyl ether.

Cationic initiators are very suitable for the polymerization of vinyl ethers. They require high-purity monomers and solvents and clean apparatus; the absence of water is particularly important.

Friedel – Crafts catalysts, such as BF_3, $AlCl_3$, $SnCl_4$, or their complexes (e.g., BF_3 dietherate or BF_3 dihydrate), and also acidic aluminum sulfate, are widely used [26].

Other initiators such as halogens [27], protic acids [28], halogenated metal alkyls [29], cation-forming salts (e.g., $Ph_3C^+BF_4^-$) [30], Ziegler – Natta catalysts [31], and high-energy radiation [33], [33] are of theoretical interest.

Stereoregularity. Poly(vinyl ethers) were the first group of compounds in which the phenomenon of stereoregularity was recognized [35], [35]. Depending on the choice of polymerization conditions, either an amorphous or a crystalline polymer, which were later recognized as atactic or isotactic, can be produced from vinyl isobutyl ether [36]. For further details see [4].

Living Polymers. In 1984 it was discovered that in nonpolar solvents the initiator system HI – I_2 can convert vinyl isobutyl ether to living polymers [37]. The number-average molecular mass of the poly(vinyl isobutyl ether) increases with increasing monomer conversion, but is inversely proportional to the initial concentration of initiator. The molecular mass distribution is very narrow: the quotient of the weight-average and number-average molecular masses is close to 1, whereas for conventional poly (vinyl ethers) it is ca. 3. This interesting process is, however, not used commercially.

3. Industrial Processes

3.1. Batch Bulk Polymerization of Vinyl Methyl Ether

In one process 200 mL of an initiator solution (3 % boron trifluoride dihydrate in dioxane) is charged to a stirred-tank reactor containing 300 L vinyl methyl ether (*bp* 6 °C) at 12 °C. The reactor is cooled by jacket cooling and is equipped with a reflux condenser.

After the strongly exothermic polymerization is initiated, 5300 L vinyl methyl ether (in 10 h) and 6 L initiator solution (in 16 h) are continuously pumped into the stirred reactor against a regulated internal pressure of ca. 0.3 bar. The reactor temperature is ca. 15 °C. The heat of reaction (1400 kJ/kg monomer) is removed via the reactor jacket and the reflux condenser. Three hours after addition of the monomer is complete the temperature is increased to 60 °C, and 2 h later to 90 °C. After a further 2 h the reflux condenser is removed and the automatic cooling switched off. Two hours later the stirrer is switched off.

After a further 2 hours the reactor is degassed for 4 hours. The contents of the reactor are then either emptied out directly as a hot polymer melt or transferred to a mixer where they are converted into 50 – 70 % solutions with solvents such as water, ethanol, or toluene.

About 97 % of the monomeric vinyl methyl ether is converted to a light yellow soft resin, with $\bar{M}_w \approx 60\,000$ and $\bar{M}_n \approx 20\,000$ (commercial name Lutonal M 40). Polymers from vinyl ethyl ether (*bp* 36 °C) and vinyl isobutyl ether (*bp* 83 °C) can be produced analogously.

3.2. Continuous Bulk Polymerization of Vinyl Ethyl Ether

4600 mol/h (440 L/h) of vinyl ethyl ether and 0.4 mol/h of an initiator in solution are continuously pumped into a 2.5 m^3 stirred reactor. The reaction temperature is 98 °C, and the heat of reaction (ca. 1100 kJ/kg) is removed by jacket cooling and a reflux condenser.

The liquid level in the stirred reactor is kept constant by a siphon overflow. The polymer running out is collected in a larger receiver in which unreacted monomer is polymerized. The product is homogenized and then removed in batches as a viscous liquid. The molecular mass $\bar{M}_w$ is 3300 and $\bar{M}_n$, 1400 (commercial name Lutonal A 25). A viscous polymer with $\bar{M}_w = 17\,000$ can be produced analogously from vinyl isobutyl ether (commercial name Lutonal I 30).

3.3. Continuous Solution Polymerization of Vinyl Isobutyl Ether

The low-temperature polymerization of vinyl isobutyl ether in liquid propane on a conveyor belt [26] is no longer used due to poor economics.

3.4. Environmental Protection

The off-gases formed in the production of poly (vinyl ethers) are contaminated by solvent and monomer vapors; they are collected and incinerated. The off-gases from incineration are discharged to the atmosphere. In the market, solvent- containing poly(vinyl ether) products are declining in importance, while 100 % polymers and aqueous systems are exhibiting growth — a favorable tendency for environmental protection.

4. Properties and Uses

Consistency and Compatibility. Commercial poly(vinyl ethers) are highly viscous oils, soft adhesive resins, or nonadhesive elastomers, depending on the molecular mass. Poly(vinyl octadecyl ether) has a waxlike consistency.

Poly(vinyl ethers) are resistant to saponification by dilute acids and bases. Their solubility in water and organic solvents and their compatibility with other polymers depends on the nature of the alkyl group. For example, poly(vinyl methyl ether) (Lutonal M 40) is soluble in aromatic hydrocarbons, insoluble in aliphatic hydrocarbons, and soluble in alcohols and cold water. Formation of hydrogen bonds between the ether oxygen and water is responsible for the solubility in cold water. These bonds are destroyed on heating, and above 28 °C the polymer precipitates from aqueous solution.

Poly(vinyl methyl ether) forms clear films when mixed with many other polymers such as methyl cellulose, ethyl cellulose, nitrocellulose, epoxy resins, natural rubber, poly(vinyl acetate), vinyl acetate – vinyl chloride copolymers, and polystyrene. It can also be used as a plasticizer.

Poly(vinyl ethyl ether), a highly viscous oil, soft resin,or nonadhesive material,depending on the molecular mass, is soluble in ethers, esters, ketones, and hydrocarbons, but insoluble in water.

Poly(vinyl isobutyl ether) is produced as a highly viscous oil and as a soft resin, but also as a secondary emulsion in water for mixing with other aqueous polymer emulsions.

Poly(vinyl octadecyl ether) is a brittle solid which melts at 50 °C and is compatible with many waxes.

Uses. Uses of some commercial poly(vinyl ethers) are listed in Table 1.

The economically most important use of poly (vinyl ethers) is in the adhesives industry, mostly as modifying additives for other (cheaper) raw materials. Depending on the nature of the poly-(vinyl ether), adhesives for labels, for flexible tapes, or adhesives which stick well to polyethylene, on a moist

Table 1. Uses of poly(vinyl ethers)

Poly(vinyl ether)	Trade name	Consistency	Use
Methyl	Lutonal M 40	soft resin	raw material for adhesives
	ca. 50 % in water	highly viscous solution	plasticizer thickener heat sensitizer
	70 % in ethanol	highly viscous solution	raw material for adhesives
	70 % in toluene	highly viscous solution	raw material for paints
Ethyl	Lutonal A 25	highly viscous oil	raw material for paints auxiliary for printing inks
	Lutonal A 50	soft resin	raw material for adhesives
	70 % in naphtha	highly viscous solution	plasticizer
	70 % in ethanol	highly viscous solution	plasticizer
	70 % in toluene	highly viscous solution	plasticizer
	Lutonal A 100, ca. 25 % in hexane	highly viscous solution	raw material for adhesives
Isobutyl	Lutonal I 30	highly viscous oil	raw material for adhesives
	Lutonal I 60	soft resin	raw material for adhesives
	50 % in heavy naphtha	highly viscous solution	raw material for paints
	80 % in light naphtha	highly viscous solution	raw material for adhesives
	Lutonal I 60 D	medium-viscosity aqueous dispersion	raw material for adhesives
	Lutonal I 65 D	medium-viscosity aqueous dispersion	raw material for adhesives
Octadecyl	Luwax V	wax	polish for floors and other surfaces

background, or at low temperatures can be produced. For further information on the uses of poly(vinyl ethers) see [5], [38].

5. Copolymers

Vinyl ethers readily undergo cationic copolymerization with one another, but the resulting copolymers are unimportant industrially. Radically produced copolymers from vinyl ethers and other monomers contain a maximum of 50 mol % vinyl ether. Solutions (e.g., in ethyl acetate) or aqueous emulsions of radical copolymers containing up to 30 % vinyl isobutyl ether are used as raw materials for adhesives with special adhesive and compatibility properties. Copolymers with 75 % vinyl chloride and 25 % vinyl isobutyl ether are used as binding agents for ageing-resistant, flexible anticorrosion paints.

Copolymers of vinyl methyl ether and maleic anhydride are very versatile in their applications, being used as protective colloids, thickeners, pigment dispersants, film formers, and binding agents. Products of this type are produced by GAF (trade name Gantrez) and BASF (trade names Sokalan, Luviform, Lupasol) for use as detergent additives, in the paper and textile industries, in cosmetics, and in the production of microcapsules. For further information see [5]. GAF sells the copolymer as a white powder, which, on dissolving in water, forms a maleic acid – vinyl methyl ether copolymer and, on dissolving in an alcohol, a maleic acid half ester – vinyl methyl ether copolymer.

6. Toxicology

For the common poly(vinyl alkyl ethers) known for nearly 50 years (methyl, ethyl, isobutyl, and octadecyl), no effects which are hazardous to health have so far been found. In animal experiments they are classified as nonirritant to the skin and nonmutagenic. The oral toxicity LD_{50} (rat) is > 500 mg/kg.

The toxicity of organic poly(vinyl ether) solutions is determined essentially by the solvent. Toluene and *n*-hexane present in naphtha have a narcotic effect, irritate the eyes and skin, and can produce permanent damage to the nervous system. Good workplace ventilation is necessary.

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Poly(Vinylidene Chloride)

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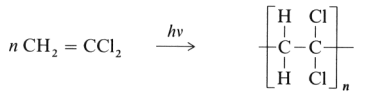
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1. Introduction

Vinylidene chloride (1,1-dichloroethylene), VDC, was first obtained by V. Regnault in 1838 by treating 1,1,2-trichloroethane with alcoholic caustic potash solution to produce a colorless, chemically impure liquid having a boiling point of 35–40°C, which was subsequently recognized as being impure VDC [2]. The processes used today are still based on this reaction (see → Chloroethanes and Chloroethylenes).

When VDC is stored and particularly when exposed to light (E. Baumann, 1872), a white precipitate is formed.



Vinylidene chloride — Poly(vinylidene chloride)

This precipitate was identified by Feisst and Staudinger (1930), who carried out the first systematic polymerization experiments [3, 4], as poly (vinylidene chloride) homopolymer. It was found that poly(vinylidene chloride) (PVDC) could not be processed thermoplastically because of its thermal instability. R. M. Wiley [5] succeeded in obtaining processable materials by copolymerization and plasticization. Because of the special properties of PVDC, this polymer was intensively researched and further developed in the 1930s (in the United States by Dow in particular, and in Europe by BASF). For further information on the historical development, see [6–12].

The first poly(vinylidene chlorides) were marketed more than 50 years ago. They were originally used mainly for resistant fibers and bristles. Coatings of PVDC were first applied in significant quantities around 1940 in the United States and in Germany. The first extruded shrink PVDC films for meat packaging also appeared at that time.

However, large-scale development of this class of products did not start until the 1950s when improved PVDC resins for coatings came onto the market; early examples of this class of high-grade polymers were the soluble Saran resins (F and B) and Saran dispersions of Dow and the Diofan dispersions of BASF.

All conventional commercial PVDC products are now copolymers of vinylidene chloride with small amounts of other monomers. The VDC content of these polymers is usually between 75 and 95%, and in special cases it is as low as 50% (e.g., VDC–vinyl chloride (VC) copolymers).

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2. Production

Vinylidene chloride is prepared commercially by dehydrochlorination of 1,1,2-trichloroethane in the presence of lime or caustic, as described in Figure 1. Commercial VDC is then stabilized with monomethyl ether of hydroquinone (MEHQ).

This inhibitor can be removed by distillation or by washing with aqueous caustic under an inert atmosphere at low temperatures. Without inhibitor, VDC should be stored at −10°C under an inert atmosphere, and used within 1 d.

Due to its asymmetric structure, VDC polymerizes readily at its double bonds; comonomers are used for modification. The main comonomers are methyl acrylate, ethyl acrylate, acrylonitrile, methyl methacrylate, butyl acrylate, and vinyl chloride.

Small amounts of unsaturated carboxylic acids or other products with adhesion-promoting groups are also used to obtain improved anchorage or other special coating properties.

Two processes are used to produce PVDC copolymers on an industrial scale, which are of comparable commercial importance: emulsion polymerization and suspension polymerization, also known as bead polymerization.

Vinylidene chloride polymerizes in the presence of ionic and radical initiators and Ziegler catalysts and under the influence of radiation. Ionic polymerization has the disadvantage that initiators such as butyllithium react with the polymer and accelerate its degradation. Therefore, only radical polymerization in aqueous systems has been of industrial interest.

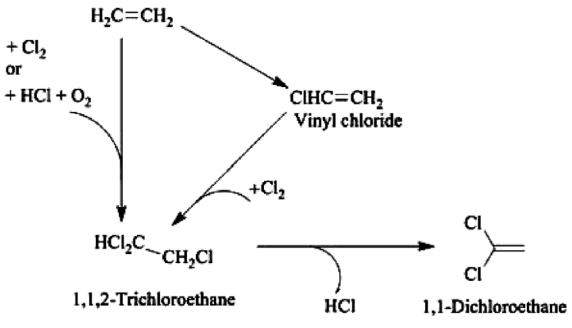


Figure 1. Synthesis of 1,1-dichloroethylene (VDC)

2.1. Emulsion Polymerization

VDC is polymerized by batch [14] or monomer-addition [15–19] processes. The mechanism of the polymerization cannot be described by the Smith–Ewart theory [20]. Typical polymerization processes require the following considerations:

Polymerization is preferably carried out at pH 1–4 to avoid attack by bases, and the operating temperature must be <80°C to suppress polymer degradation. Feed tanks, polymerization reactors, and monomer removal units are often made of glass-lined steel to avoid metallic impurities. If the reaction medium is buffered, the polymerization can also be carried out in stainless-steel reactors.

In VDC emulsion (co)polymerization, anionic emulsifiers such as sodium alkylarylsulfonates, alkyl esters of sodium sulfosuccinic acid, and fatty alcohol sulfates are used alone or in combination with nonionic surfactants such as ethoxylated alkylphenols. The usual initiators are peroxosulfates, hydrogen peroxide, organic hydroperoxides, peroxoborates, and peroxocarbonates in the presence of redox activators such as ascorbic acid, bisulfites, or formaldehyde sodium bisulfite. Redox systems are used to obtain high-molecular-mass products at low temperatures and acceptable space–time yields.

2.1.1. Batch Emulsion Polymerization [21]

Figure 2 shows a flow sheet for the production of VDC copolymers by batch emulsion polymerization.

1. VDC and comonomers are charged to a glass-lined reactor, equipped with a double jacket and containing a cold aqueous solution composed of the anionic or cationic surfactants, a water-soluble initiator, a redox activator, and different additives such as chain-transfer agents, buffer, etc. A delayed introduction of some highly reactive monomers is sometimes necessary. If the stirring is well suited, the surfactants form micelles when introduced over the critical micellar concentration and monomer droplets. By its (thermal- or redox-triggered) decomposition

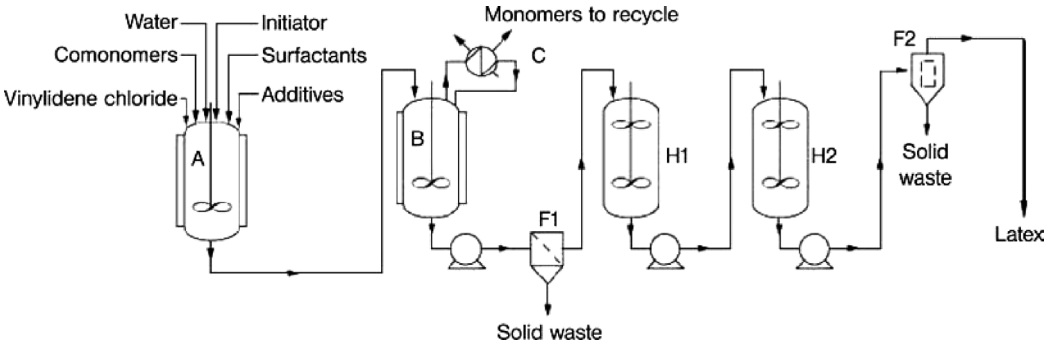


Figure 2. Flow sheet for the production of VDC copolymers by batch emulsion polymerization
A) Reactor; B) Degasser; C) Cyclone; F1, F2) Filter; H1) Buffer tank; H2) Storage tank

into radicals, the water soluble initiator provides a start of the polymerization in the aqueous phase. The newly created, water-soluble oligomers will further enter into a swollen micelle, thus creating particles, to continue the polymerization process. The gradual diffusion of monomers from the droplets to the particles, where the polymerization takes place, ensures the growth of the particles up to ca. 100–200 nm, which remain dispersed in the water phase. In some cases, it is necessary to introduce initiator gradually to keep the polymerization going. Surfactants may also be introduced throughout the polymerization in order to ensure the colloidal stability of the growing particles.

The heated double jacket allows a high increase in temperature of the media, which initiates the polymerization reaction. The exothermic nature of the latter must be carefully controlled by cold water supply in the jacket. In batch polymerization, the polymerization time can vary from 3–24 h, with polymerization temperatures from 30–80°C, leading to 95–98% final conversion [15]. Polymerization to completion of batch charges gives copolymers with broad comonomer distributions [22], except when the copolymerization parameters r_1 and r_2 equal 1, which is the case for VDC and methyl acrylate (MA) (see Table 1).

2. The copolymerization is considered as finished when the temperatures in the reactor and the double jacket are the same or when the pressure in the reactor decreases significantly, indicating the consumption of the monomers in the sky of the reactor. At the end of the polymerization, the reactor is degassed and the residual monomers are eliminated from the latex by stripping. The stripping of monomers can be done directly in the reactor or, better, in a dedicated reservoir called degasser, equipped with a double jacket and controlled in pressure. The latex is heated under reduced pressure. The combination of high temperature and low pressure causes evaporation of water which brings the unconverted monomers. The steams containing monomers are condensed, and the monomers are sent to an incinerator and the water treated before discharge.
3. The residual monomer content is strictly controlled to meet the requirements of the legislation (food contact safety) and even beyond. After the stripping, water or surfactants may be added to the latex to adjust the solid content or surface tension in order to meet sales specifications. The solid content of the latex is usually between 40 and 60%. The latex is then filtered to remove the flocs that have formed in the reactor, and then it is stored in reservoirs awaiting quality control. If the test results are positive, the product is

Table 1. Copolymerization parameters of vinylidene chloride with various comonomers

Comonomer	r_1	r_2	Temperature, °C
Styrene	0.14	2.0	60
Vinyl chloride	3.2	0.3	60
Acrylonitrile	0.37	0.91	60
Methyl acrylate	1.0	1.0	60–70
Methyl methacrylate	0.24	2.53	60
Vinyl acetate	6	0.1	68

transferred to a storage tank. Before shipping, the product is filtered again to remove any coagulated particles and analyzed (customer specifications).

2.1.2. Continuous-Feeding Emulsion Polymerization [21]

Figure 3 shows a flow sheet of the continuous-feeding emulsion polymerization process.

1. VDC, comonomers, water, surfactants, and additives are introduced in a premixing tank, which is maintained at 15°C in order to prevent thermal polymerization of the monomers. Controlled stirring of the mixture provides an emulsion of monomers in water. VDC, comonomers, and the aqueous phase can also be emulsified by using a nozzle before introduction in the reactor.
2. A given fraction of the emulsion (between 5 and 20% of the total load) is introduced in the reactor already containing a given amount of water (and, possibly, additives such as surfactants or electrolytes). A fraction of the initiator (redox system) is also introduced in the reactor, which is then heated. The polymerization starts with the fraction of monomers introduced in the reactor. This step of prepolymerization provides a seed consisting of very small particles (20–50 nm) and determines the number of particles (and thus the particle size) in the latex phase at the end of the polymerization. When the polymerization of the seed is finished, the rest of the emulsion is introduced in the reactor with a controlled flow. The monomers introduced in this way will swallow the seed particles, and the controlled introduction of the redox system (initiator and reductor) allows maintaining a high polymerization rate in the swollen seed particles. These particles will then grow progressively. However, this seed polymerization step can also be substituted by the introduction of a "ready-to-use" seed consisting of very small particles of, possibly, another polymer (e.g., polystyrene, poly(methyl methacrylate)).
3. At the end of the polymerization, the latex is transferred to a degasser. The injection of steam into the latex under a controlled reduced pressure results in the formation of foam. These foams made of latex and steam containing monomers climb in a stripping column. At the top of this column, a nozzle with a defined geometry causes the reduction of the foams in a cyclone. The latex is then redirected to the degasser and the steam containing monomers is removed by means of a vacuum circuit, condensed,

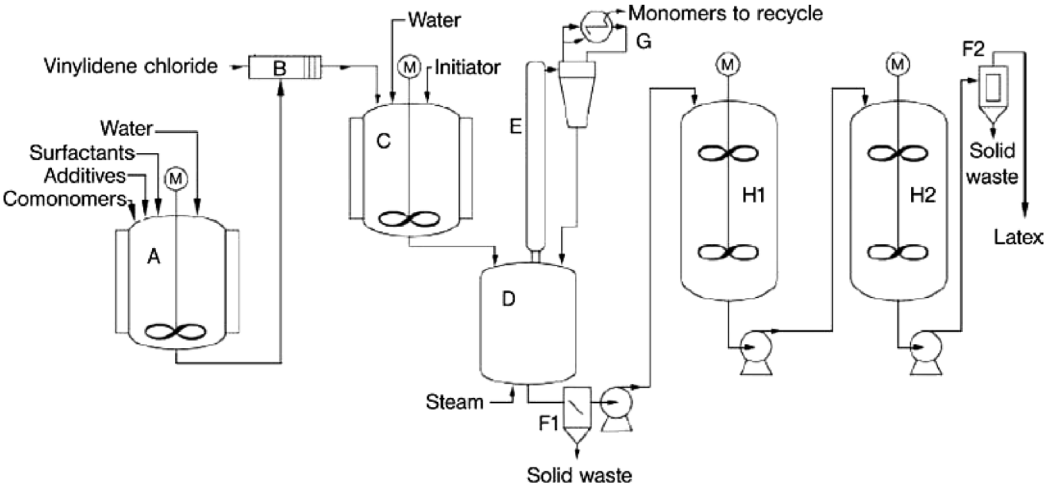


Figure 3. Flow sheet for the production of VDC copolymers by continuous-feeding emulsion polymerization
A) Premixing tank; B) Static mixer; C) Reactor; D) Stripper; E) Column; F1, F2) Filter; G) Cyclone, H1) Buffer tank; H2) Storage tank

and treated. The latex is recycled several times through the stripping column and the residual monomers are gradually eliminated. The good control of the process allows the extraction of the amount of water from the latex introduced by the steam. The latex is finally transferred to storage tanks.

Because the reaction is carried out under controlled conditions, copolymers manufactured by the continuous-addition process have uniform comonomer distribution [15–19]. The copolymers in the latex state are in an amorphous form and can be used directly as coating materials with good film-forming properties.

The principal VDC copolymers produced by emulsion polymerization are those with acrylonitrile and/or various (meth)acrylates [23–28], while VDC–vinyl chloride copolymers are produced in smaller volume [14, 29, 30]. The copolymers are used as dispersions with solids content of 50–60%.

2.1.3. Emulsion Polymerization for Soluble Resins [21]

Until the intermediate storage stage, the polymerization processes for soluble resins are similar to those for batch polymerization (see Fig. 2). The comonomers are generally acrylonitrile for soluble resins and vinyl chloride for extrudable resins.

After extraction of residual monomers, the latex is filtered and transferred to a buffer tank, which allows the feeding of a coagulation line. For coagulation, the dispersion is diluted to 30% solids content to lower its viscosity. Unlike the polymerization reaction, coagulation is a continuous process. The coagulation reactor is continuously fed from the buffer tank. In the case of latex containing anionic surfactants, salts of metallic cations are added to the latex under continuous stirring. These salts cause a significant decrease of the electric double layer which protects the particles covered by surfactants. The attractive forces between them become predominant and the latex coagulates.

The solid coagulates are successively transferred by overflowing to a series of temperature-regulated tanks. This series of stirred reactors allows for heat treatment of the grains formed. This treatment induces a partial crystallization of PVDC which limits sticky grains and facilitates further proceedings. A centrifugal dryer or a rotary filter is used to separate water from a cake of resin which was dried in a rotary dryer and overdried on a fluidized bed. Cyclones provide separation of powder and air. A vibrating screen allows the separation of large particles (which will be crushed and recycled) before storage and controls. Extrudable resins can be converted to premix by adding plasticizers and stabilizers. Since they are soluble resins, they are packed in rigid and flexible containers.

2.2. Suspension Polymerization [11, 12, 21]

Figure 4 shows a flow sheet of the suspension polymerization process.

1. The monomer mixture is dispersed in water under controlled stirring, with a small amount of dispersing agents such as poly (vinyl alcohol) or methyl cellulose added. By this, an aqueous dispersion of monomer droplets is formed, where the size of the polydispersity is governed by the stirring speed. As the dispersing agents prevent the droplets from coalescence, the stirring is the real driving force to maintain the dispersion. Indeed, the dispersion turns into a biphasic system if the stirring speed is not high enough to create shearing in the medium.

   Organic peroxides, peroxocarbonates, and azo compounds are used as initiators. Before polymerization, the initiators, which must be soluble in the monomers, must be distributed uniformly in the monomer mixture to avoid different rates of polymerization in the droplets. When the reactor temperature increases, the initiators undergo a thermal decay which generates radicals in the monomer droplets. As a consequence, each monomer droplet can be considered as bulk microreactor.

   As PVDC is not soluble in VDC, the created polymer chains precipitate in the droplets throughout the polymerization and self-assemble in a semicrystalline structure. At the end of the polymerization, the initial dispersion is converted to aqueous slurry

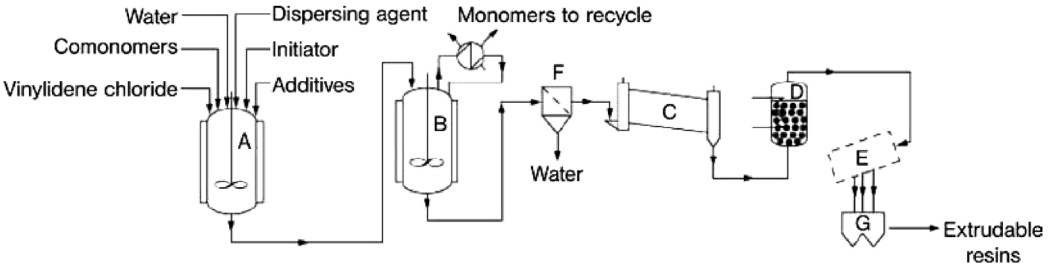


Figure 4. Flow sheet for the production of PVDC copolymers by suspension polymerization
A) Reactor; B) Stripper; C) Rotating dryer; D) Dryer with fluidized bed; E) Sieve; F) Filter; G) Storage tank

that contains hard, glassy suspended particles. These particles have diameters of 80–250 μm, and relatively narrow size polydispersity.

The polymerization temperature can vary from 60–80°C, leading to polymerization times of 8–30 h. The polymerization rate increases with increasing initiator concentration and temperature. The suspension agents influence the particle size distribution but also the porosity of the particles, and clarity and transparency of the processed products. Secondary suspension agents such as sorbitan monostearate improve the porosity and plasticizer absorption of the polymer powder.

2. After polymerization, the slurry is transferred to a stripper where residual monomers can be removed by steam treatment at reduced pressure. The monomer-free suspension enters intermediate tanks (in which several batches can be homogenized). After the transfer to theses buffer tanks, the polymer beads are separated from the aqueous phase by vacuum filtration on a rotary filter and washed on the same filter with water spray. A knife can take off the cake from the rotating filter, and the cake, of about 20% humidity, is transferred continuously to a rotating dryer.
3. Over-drying in a fluidized bed precedes the sieving. Controls and packaging in containers are made directly out of the fluidized bed.

The polymers made by suspension emulsion absorb plasticizers and stabilizers because of the highly porous internal structure of beads. They can be turned into ready-to-use premixes by the addition of various liquid or solid additives, which are needed during the extrusion process, in a dry mixer.

2.3. Comparison of the Processes [21]

On a commercial scale, heterogeneous polymerization of VDC is carried out by means of suspension and emulsion processes in the presence of radical sources.

Radiochemical and anionic initiations suffer from the impossibility of excluding polymer degradation, while cationic polymerization gives low-molecular-mass polymers. Ziegler polymerization of VDC has never been developed.

Homogeneous solution polymerization has not been described in patents. Bulk polymerization and precipitation polymerization in inert solvents such as cyclohexane or benzene cannot be controlled in practice owing to the associated engineering problems such as stirring and heat removal. In bulk polymerization, the reaction mixture thickens to a paste at 10–20% conversion. In the presence of inert solvents the reaction is too slow, only low molecular masses are attained, and the polymer must be freed of solvent.

Suspension polymerization in water can be well controlled but, especially in the case of VDC–VC copolymers, requires quite long reaction times to reach the high molecular masses attained in emulsion polymerization. Due to their low concentration of polymerization additives, suspension polymers are generally more stable and less sensitive to water.

The composition of the copolymer can be better controlled in emulsion polymerization by the metering in of monomer.

Suspension and emulsion polymerization are carried out in stirred, glass-lined or stainless-

steel autoclaves. Heat is supplied or removed by jacket heating or cooling. Before polymerization, the water and empty volume of the reactor are flushed free of oxygen, which strongly inhibits the polymerization. The water added must also be free of metallic impurities, or the thermal stability of the polymers is impaired.

Reproducible setting of a defined comonomer distribution in the polymer is more difficult in suspension polymerization than in emulsion polymerization. Unmodified batch operation [31], as well as temperature-programmed polymerization and the use of initiators with different decomposition rates [32], lead to a polymer mixture with heterogeneous polymer composition. In VDC–VC copolymerization, uniform monomer incorporation is achieved by continuously removing the less reactive monomer to maintain a constant volume ratio in the nonreacted monomer mixture [33]. The polymerization rate can be increased by stepwise polymerization with more active initiators such as peroxodicarbonates [34].

Suspension polymerization is mainly used to produce VDC–VC or VDC–MA copolymers [32, 35], which are suitable for injection molding and extrusion molding. Modified VDC–alkyl acrylate [36] and VDC–methyl acrylate copolymers [37] can be processed by blow molding.

2.4. Purity and Storage of the Monomers

The VDC monomer used for polymerization contains 200 ppm *p*-methoxyphenol or 0.6–0.8% phenol as a stabilizer. Polymerization is practically unaffected by *p*-methoxyphenol, while phenol must be removed before polymerization by distillation or alkaline extraction.

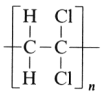
Vinylidene chloride is stored under a nitrogen protective atmosphere in nickel-plated or phenol-coated vessels. The oxygen content in the stock tank must not exceed 100 ppm.

On storage VDC can form peroxides, especially with nonstabilized VDC and oxygen. These peroxides can lead to spontaneous polymerization, but are also explosive in the presence of air or oxygen, even at low temperatures (−40°C). The peroxides can be detected by their pungent, acrid smell or by the formation of flocculent deposits of polymer. They are deactivated on storage under water, and can be destroyed by washing with a 5% solution of methanol in tetrachloroethylene. PVDC peroxide decomposes into phosgene and formaldehyde [13].

3. Structure and Properties [10–12]

3.1. Homopolymers

PVDC does not dissolve in monomeric VDC, and polymer and monomer are practically insoluble in water. VDC polymerizes in the presence of radical sources to give a linear, symmetrical macromolecule with head-to-tail structure and the repeat unit



The theoretical chlorine content of the polymer is 73.14%, although in practice chlorine contents of 72–73% are obtained.

The polymer chain is tightly packed in the solid state, and in the thermodynamically stable state it is highly crystalline (ca. 75%), indicating the absence of defects or branches. The crystallinity and rate of crystallization are influenced by the polymerization conditions, the mechanical and thermal treatment of the polymer, and, in the case of copolymers, the comonomer content.

The combination of high crystallinity and high density results in PVDC having very good barrier properties against gases and vapors and resistance to solvents.

The absolute molecular mass of PVDC cannot be determined by conventional methods due to the lack of a suitable solvent. Like other high-melting polymers, PVDC is sparingly soluble in most solvents. Only at temperatures of 130°C can 1% solutions be prepared in, e.g., 1,3-dibromopropane or bromobenzene. At room temperature PVDC dissolves only in polar solvents such as hexamethylphosphoric triamide or tetramethylene sulfoxide; amorphous PVDC dissolves in tetrahydrofuran.

The structure and solubility of PVDC are independent of the polymerization temperature.

PVDC decomposes at temperatures above 125°C, chiefly with elimination of hydrogen chloride and formation of polyene sequences. The degraded polymer is infusible, and the crystalline structure is destroyed [37]. The polymer is also degraded by the action of high-energy radiation, bases, and heavy-metal ions.

Some properties of PVDC are as follows:

Melting point	198–205°C
Glass transition temperature	− 19 to − 11°C
Amorphous density (25°C)	1.67–1.775 g/cm^3
Crystalline density (25°C)	1.80–1.97 g/cm^3
Degree of polymerization	100–10 000
M_w/M_n	1.5–2.0
Softening range	100–150°C
Ceiling temperature	350–400°C

3.2. Copolymers

Industrially important copolymers are those manufactured by radical polymerization of VDC with vinyl chloride, acrylonitrile, and (meth)acrylate esters. Table 1 lists the copolymerization parameters of VDC with the most important comonomers [10]. The Q and e values of VDC are $Q = 0.20$ and $e = 0.36$ [38].

Copolymers with high VDC content have lower melting points and, at least at low comonomer content, higher glass transition temperatures than the PVDC homopolymer. Figures 5 and 6 show the effect of the copolymer composition on the melting point and glass transition temperature.

VDC copolymers are more stable to degradation than pure PVDC. Comonomers interrupt the unstable poly(vinylidene chloride) chain. The copolymerization must therefore be conducted so that as few long PVDC sequences as possible are present in the copolymer. Furthermore, VDC–VC copolymers are more stable than PVDC since the chlorine–carbon bond is stronger in the vinyl chloride unit than in the VDC unit. Polar functional groups, however, weaken the chlorine–carbon bond, so that copolymers with polar functional groups such as the nitrile group are less stable due to neighboring group effects.

The mechanical properties of VDC copolymers depend on temperature, molecular mass, crystallinity, degree of orientation, and plasticizer content. With increasing crystallinity the strength increases, whereas toughness and elongation decrease. The above properties are improved by orientation.

Incorporation of vinyl chloride, for example, in the VDC polymer chain raises the glass

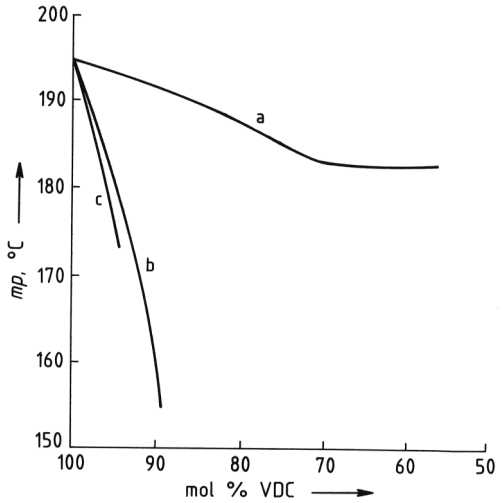


Figure 5. Dependence of melting point on copolymer composition
a) VDC–vinyl chloride; b) VDC–methyl acrylate; c) VDC–octyl acrylate

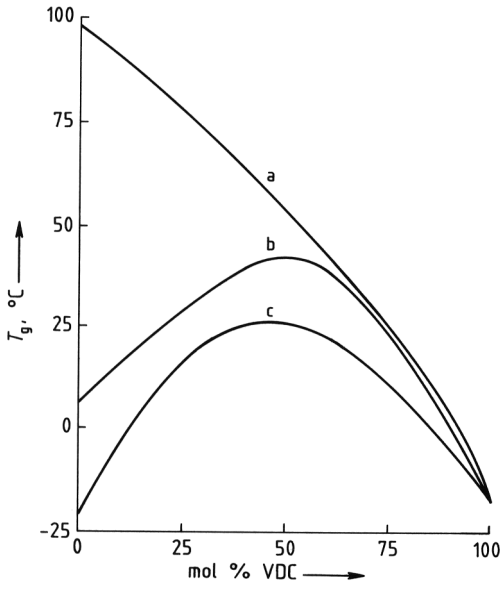


Figure 6. Dependence of glass transition temperature on copolymer composition
a) VDC–acrylonitrile; b) VDC–methyl acrylate;c) VDC–ethyl acrylate

transition temperature, which leads to less favorable low-temperature behavior (increased brittleness). The glass transition temperature can be lowered again without loss of strength properties by plasticization (2–10% plasticizer).

Crystallinity. The performance of PVDC films and coatings is greatly influenced by the high chlorine content of the polymers and especially their crystallinity.

The polymer molecule is very symmetrical if the proportion of VDC in the polymer is high, which leads to crystallization. The crystallinity is directly proportional to the mole fraction of VDC in the polymer. Thus, homopolymers of VDC are highly crystalline, i.e., they contain between 50 and 80% of crystalline material, the actual figure depending on the polymerization conditions. For this reason, they are normally unsuitable for further processing.

The symmetry of VDC polymer chains is disturbed by the incorporation of comonomers such as methyl acrylate. The crystallinity decreases steadily with decreasing mole fraction of VDC until it is completely suppressed at ca. 80 mol% VDC.

If the mole fraction of VDC in the copolymer is very high (93% VDC), the polymer particles of a PVDC dispersion may already crystallize in the aqueous phase. It is very difficult for such highly crystalline latex particles to fuse together, with the result that film formation on drying is hardly possible. For this reason, the VDC mole fraction in PVDC dispersions for general applications usually lies between 87 and 92 mol%.

The partially crystalline morphology of PVDC copolymers can best be described by a network of continuously interpenetrating crystalline and amorphous zones.

Studies on crystallization of coatings have revealed that if the mole fraction of VDC in the copolymer is ca. 88%, the amorphous state is retained for a long time (200–300 d under normal conditions) and that the crystalline phase is formed very slowly.

If the coatings contain a high proportion of VDC (91–92%), crystallization already commences after 1 d and attains a maximum within 5–20 d, depending on the product. This stage is referred to as primary crystallization. Further, secondary crystallization is slight and proceeds slowly.

Table 2 reviews the effect of increasing the VDC content in copolymers and the crystallinity on the properties of coatings and the processability of PVDC.

Permeability [39]. The most water vapor-resistant polymers are the most oxygen permeable and vice versa, with the exception of PVDC, which acts as a very good barrier to both (see → Films for comparison of permeability data). Table 3 lists the permeability of three PVDC grades.

Aromaproofness is closely related to the impermeability to water vapor or gases. It is important in practice that the contents of a pack should not lose their aroma as a result of diffusion from the inside to the outside. Likewise, their aroma must not be impaired by the diffusion of odoriferous substances from the outside to the inside.

The very good aromaproofness derives from its high resistance to diffusion and low solubility, particularly that of the crystalline sections of the polymers.

Figure 7 illustrates the good aroma barrier of PVDC-coated BOPP (biaxially oriented polypropylene) films (26 μm) in comparison with coextruded OPP and OPP coated on both sides with acrylic for limonene and menthol.

Table 2. Demands imposed on the properties of PVDC in relation to the mole fraction of VDC in the copolymers and the crystallinity

Demands on properties of PVDC	Effect of*	
	Increasing VDC mole fraction	Increasing crystallinity
Specific properties of PVDC impermeability to:		
water and water vapor	+	+
gases especially oxygen	+	+
aroma	+	+
resistance to solvents and chemicals	+	+
resistance to blocking	+	+
slip	+	+
flexibility	–	–
heat sealability	–	–
clarity	+	+
PVDC processability		
solubility (soluble grades)	–	–
film forming (aqueous dispersions)	–	–
schemal stability (extrudable)	–	–
film blowing aptitude (extrudable)	–	–

* + = improvement, – = deterioration.

Table 3. Permeability of PVDC

PVDC grade	Permeability		
	to oxygen (20–25°C)*	to carbon dioxide (20–25°C)*	to water vapor (38°C, 90% RH)**
Coating from PVDC lacquer	15–25	45–80	15–25
	10–15	30–45	10–15
Coating from PVDC dispersion	40–80	90–115	15–25
	15–40	35–90	8–15
PVDC film: plasticised slightly or unplasticised	300–1000	650–2200	50–100
	40–80	135–265	15–25

* Permeability in cm^3 μm m^{-2} d^{-1} bar^{-1} (dry gas).
** Permeability in g μm m^{-2} d^{-1}.

Resistance to Oils, Fats, and Chemicals. Pinhole-free films or coatings of PVDC offer high resistance to animal and vegetable fats and oils. They are not swollen by oil or grease, nor do they permit their diffusion. Exceptions are strongly unsaturated vegetable oils, which may cause amorphous grades of PVDC to swell somewhat.

Poly(vinylidene chloride) exhibits excellent chemical resistance. The crystallinity, the large volume proportion of chlorine, as well as the high density are responsible for the high resistance to numerous solvents and chemicals.

4. Processing and Uses

4.1. Extrusion

The commercial extrusion grades of PVDC are copolymers of vinylidene chloride with comonomers such as vinyl chloride, acrylic or methacrylic acid esters, and others. They are polymerized in emulsion and coagulated, or directly polymerized in suspension; they are generally available in powder form.

Normal processing formulations of those copolymers require a plasticizer and/or a stabilizer; some include, if necessary, a lubricant for the extrusion process, a slip agent if requested by the final properties of the extrudate, pigments, light stabilizers, and impact modifiers.

A typical PVDC film formulation, for instance, contains 0–10% plasticizer (e.g., dibutyl sebacate, tributyl acetylcitrate), 0.5–5% stabilizer (e.g., epoxidized soybean oil, sodium pyrophosphate), 0–1% lubricant (e.g., fatty acids and fatty acid amines, montan wax). The dry blend (formulated PVDC) is extruded in single-screw extruders at a compression ratio from 1/3.5 to 1/4.5. A ratio of screw length to screw diameter of 10–24 has proven to be satisfactory.

Since PVDC, even stabilized, does not tolerate long periods at high temperature, which causes the release of hydrogen chloride and leads to carbonization, all metal parts of the

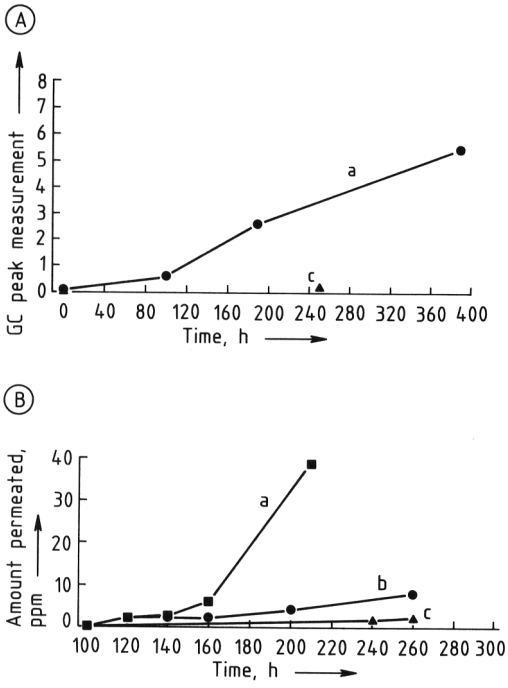


Figure 7. Aroma barrier properties of 25 μm plastic films
A) Menthol permeation at 0.2 ppm concentration (GC measurements); B) Limonene permeation at 2.5 ppm
a) Coextruded OPP film without barrier; b) OPP film coated with acrylic; c) OPP film coated with PVDC

extruder and dies in contact with hot molten polymer must be made of corrosion-resistant, noncatalytic metals. Recommended materials are chromium (particularly for the screw) and nickel alloys.

4.2. Films and Sheets

One of the major outputs for PVDC resins is the manufacture of films.

It is possible to process PVDC as monolayer film or as part of a coextruded sandwich, both techniques allowing the preparation of shrink or nonshrink materials.

Shrinkage can be obtained by applying tension before cooling (orientation) or by crosslinking.

Monofilm Biorientation. Usual film process for monolayer PVDC film requires the extrusion of a molten tube; the temperature of the PVDC melt is normally 150–160°C, depending on the selected additives formulation.

The shrink film bubble process can be applied to both mona and coextruded film. Immediately after the die, the molten tube passes into a cooling bath (2–10°C) which keeps the quenched cooled material in an amorphous state. The quenched, nontacky material is then slightly rewarmed in an oven and blown into a bubble. As the tube of amorphous polymer is oriented, crystallization takes place rapidly.

If a heat-stabilized film is desired, a further annealing step is applied by re-inflating the film and passing it through an infrared heating tunnel.

Coextruded Film. Since PVDC monofilm does not meet all requirements of film packaging, although formulations already allow great versatility, PVDC films are being increasingly coextruded with other materials. This technique is used to optimize the film properties by combining materials in such a way, so as to add their own advantageous properties, while minimizing their drawbacks. Furthermore, it provides better PVDC barrier properties. Since the PVDC is no longer a self-supporting material, it is possible to reduce the amount of liquid additives that adversely affect barrier properties but are necessary in monolayer extrusion to insure mechanical properties. Also, it allows lower thickness of the PVDC film to be used if required.

Two coextrusion techniques have reached a high level of development: multimanifold die coextrusion and feedblock coextrusion.

The common feature of both techniques is the ability to process the materials that will be used in the final complex, on different extruders, the difference being how the different melts are joined.

In *multimanifold coextrusion*, each molten material is brought into the die through its own flow and distribution channel.

In the *feedblock system* the materials are combined before they enter the die.

Limitations of the feedblock system are that relative viscosities and extrusion temperatures of the different melts must be similar.

Permeability data for extruded and coextruded PVDC films are summarized in Table 4.

Coextruded sheets are produced with feedblock systems in the same way as for coextruded films. The more common structures are PP–TIE–PVDC–TIE–PP or PE; PS–TIE–PVDC–TIE–PS or PE; and PVC–PVDC–PVC, where TIE denotes an adhesive (tie) layer.

4.3. Lacquering and Coating [40–43]

PVDC lacquer resins (powder form) are vinylidene chloride copolymers modified to give solvent solubility; vinylidene chloride homopolymer is almost insoluble in usual solvents. The usual comonomers are acrylonitrile, vinyl chloride, acrylates, and methacrylate esters.

Copolymers with very high vinylidene chloride contents (> 90%) are generally only soluble in THF mixtures.

Resins containing between 80 and 90% VDC are less crystalline and therefore are also soluble in methyl ethyl ketone (MEK) mixtures.

Materials with lower VDC content are soluble in common organic solvents at room temperature, such as esters, ketones, and cyclohexanone.

Coating of Regenerated Cellulose (Cellophane). A major field of application for PVDC lacquers with a high VDC content in the copolymer is the coating of cellulose film.

These tailor-made PVDC resins develop high crystallinity and are therefore soluble only in aggressive solvents such as mixtures

Table 4. Permeability of various PVDC structures

PVDC grade	Structure	Permeability to water vapor, g m^{-2} d^{-1}	Permeability to oxygen, cm^3 m^{-2} d^{-1} bar^{-1}
Aqueous dispersions	CBK + 15 g/m^2 PVDC	2.8–3.6	11–15
	CBK + LDPE + 20 g/m^2 PVDC	2–2.2	3.5–6.5
	PET (12 μm) + primer + 3–5 g/m^2 PVDC	6–10	10–15
	PA 6 (30 μm) + primer + 5–6 g/m^2 PVDC	6–11	7–10
	PVC (200 μm) + primer + 40 g/m^2 PVDC	0.6–1.1	2.6–3.3
	Cellulose film (37–48 g/m^2) + primer + 3 g/m^2 PVDC per side	5–8	3–6
Lacquer resins	Cellulose film (28–50 g/m^2) + primer + 1.5 g/m^2 PVDC per side	6–15	4–10
	PET (15 μm) + 1.5 g/m^2 PVDC per side	9–10	12–14
	BOPP (20 μm) + 3–5 g/m^2 PVDC	3–5	5–11
Extrusion grades	EVA (20 μm)/PVDC (10 μm)/EVA (20 μm) nonoriented films		
	unplasticized PDVC	1–8	5–22
	2% plasticizer	3–10	10–40
	4% plasticizer	10–28	40–140
	PVDC monolayer (30–70 μm), 6–9% plasticizer, heat shrinkable	8–15	30–200
	PVDC monolayer (15–25 μm), 4–6% plasticizer, slightly heat shrinkable	5–15	15–60

CBK = calendered bleached kraft. PET = poly(ethylene terephthalate). PA = Polyamide. BOPP = biaxially oriented polypropylene. EVA = ethylene-vinyl acetate.

of THF/toluene or MEK/toluene. These solvent mixtures (for instance, THF/toluene 70/30 to 55/45) generally allow 10–20% PVDC lacquers to be prepared. The required solution temperature is ca. 50°C; the MEK/toluene mixtures must be heated to 70–75°C to ensure complete dissolution.

Coating of cellulose film with PVDC is carried out by dipping on machines equipped with a vertical drying oven (Fig. 8).

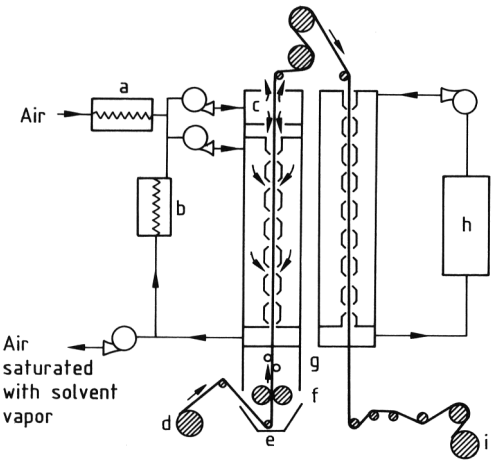


Figure 8. Cellulose film coating machine
a) Air preheater; b) Air heater; c) High-pressure chamber; d) Supply roll; e) Coating bath; f) Calibrating rolls; g) Smoothing roll; h) Rehumidifier; i) Receiving roll

To avoid blocking or sticking to the jaws of sealing machines, and to obtain the required slip properties, the following additives must be incorporated in the lacquer:

1. An additive to reduce sticking to the jaws of the sealing machine, such as fatty acids (behenic or stearic acid, for instance)
2. A natural wax (candellila, carnauba, etc.) or a synthetic wax (ketone or fatty amide) to improve blocking resistance
3. A mineral charge that roughens the surface to improve slip properties (silica, bentonite, talc, etc.)

Stabilizers are also incorporated in the solution in some cases to lower the corrosivity of the PVDC solution to metal parts of the machine.

As long as its moisture content is low, cellulose film constitutes a good barrier against gases; PVDC is thus applied to lower the water vapor permeability.

Barrier properties of cellulose film PVDC coated materials depend on the following factors:

1. Cellulose film composition
2. PVDC composition
3. PVDC coating thickness
4. Additives in the coating formula
5. Degree of crystallinity of the coating

Permeability data are listed in Table 4.

Lacquering of Paper, Foil, and Plastic Films. Some copolymers of vinylidene chloride are tailor polymerized to obtain good solubility at room temperature in a wide range of common organic solvents such as ketones and esters.

The interest of this family of product is:

1. Easier solubility
2. Heat sealability
3. Transparency and brilliance
4. Adhesion to a wide range of substrates
5. Good barrier properties and chemical resistance

These products, although less impermeable than the PVDC for cellulose film, are used for coating paper, plastic films, foils, and cardboards to lower their permeability (see Table 4) and make them heat sealable. They are also used as protective coatings. Coatings can be made by:

1. Coating on roll machines (reverse roll coating, squeeze coating, kiss coating, gravure roll coating, etc.)
2. Dip coating
3. Spray coating
4. Use of manual rollers or brushes

Depending on the final use, plasticizers, waxes, fillers, pigments, and dyes may be added to the solution.

Vinylidene chloride copolymers for coating are aqueous dispersions of copolymers with a high content of vinylidene chloride, in the form of a milky white liquid of low viscosity.

The usual comonomers are acrylic esters, unsaturated carboxylic acids, and vinyl chloride.

The PVDC aqueous dispersions are produced by emulsion polymerization. The dry solid content is 40–60%.

They can be applied to papers and boards; plastics, films, and sheets; and aluminum. The nature and quantity of the comonomer is adjusted according to the substrate leading to the following coating grades of PVDC:

1. Grades for the production of nonblocking, sealable top coatings for paper, board, or paper-based laminates (paper–PE, paper–aluminum, etc.); these substrates may be pretreated, if necessary, with a grade of PVDC giving more flexible coatings and/or with a primer.
2. Grades for the production of sealable or nonsealable, nonblocking top coatings for plastic films (oriented poly(ethylene terephthalate), OPET, biaxially oriented polypropylene, BOPP, poly ethylene, PE, rigid PVC, polyamide 6, PA 6, oriented polyamide, OPA, etc.). The films are coated with a primer or a first layer of PVDC (flexible grade) before coating with the nonblocking top coat.
3. Grades giving coatings that are more flexible, but also slightly more blocking and more permeable, than those made from the above grades. They are used mainly to coat paper, board, and paper-based laminates (with primer if necessary), and occasionally heavy-gauge plastic films with a primer.
4. Grades giving special coatings that adhere directly to certain plastic films without a primer. Their principal application is as an undercoat for subsequent coatings of another PVDC or PE applied by extrusion coating.
5. Grades for special coating or impregnation applications.

Although PVDC dispersions are in most cases supplied ready for use, under certain circumstances the user may need to introduce one or more additives to the aqueous dispersions prior to processing to modify the properties of the coating (surface characteristics, opacity, pigmentation, etc.) or the behavior of the product when applied by a coating or impregnation machine (corrosiveness, foaming, adjustment of coating weight, etc.).

PVDC dispersions are applied in roll-to-roll operations (web coating) in widths usually not exceeding 2500 mm. Processing speed has increased considerably in the last few years to 100–400 m/min.

The barrier properties of PVDC coatings depend on

1. Nature of PVDC (comonomers)
2. Quality of the substrate (porosity)
3. Coating weight and number of layers
4. Flexibility of PVDC and the substrate
5. Drying conditions
6. Crystallinity

Permeability data are listed in Table 4.

4.4. Uses

Extrudable grades are used for:

1. Monofilaments for the production of military combat boots and insoles, draperies and curtains, and filter applications
2. Medical applications, e.g., colostomy bags are made of monolayer or multilayer structures (EVA–PVDC–EVA)
3. Food packaging:
   a. Cling films, which are very thin films, slightly adhesive, used for wrapping foodstuffs, are monolayer films
   b. Shrink multilayer films (EVA–PVDC–EVA) are used to transport and store fresh cuts of meat between the slaughterhouse and the point of sale
   c. Some synthetic sausage skins are made of monolayer PVDC
   d. Rigid sheets (PP–PVDC–PP) are stable towards sterilization process and give shelf-stable storage

Aqueous dispersions are used for:

1. Pharmaceutical packaging blister packs for drugs which are very sensitive to water are made of PVC coated with PVDC.
2. Plastic food packaging:
   Biscuits are often packed in PVDC-coated OPP. Delicate chips or peanuts are packed in PVDC-coated PET laminated with LDPE. Cellulose casing for sausages is often coated with PVDC.
3. PVDC-coated paper is often used for biscuits, cereals, and dried food.
4. Technical applications:
   PVDC is generally used for its water-resistance, fireproof or binder properties in applications such as coating carpet backings, wood chip panels, and cork coating.

Soluble grades are generally used for coating cellophane, and in some cases for plastic films (e.g., PET).

5. Economic Aspects

Poly(vinylidene chloride) copolymers, as they arise from the polymerization, are marketed by the raw material manufacturer as dispersions or powders under various names.

Known trade names and producers are:

Daran, Owensboro Specialty Polymers (aqueous dispersions)

Diofan, SolVin (aqueous dispersions)

Ixan, SolVin (extrusion and lacquer resins)

Sara; The Dow Chemical Company (extrusion resins, PVDC films)

Serfene, The Dow Chemical Company (aqueous dispersions)

Krehalon, Kureha Corporation (extrusion resins, PVDC films)

Asahi Kasei Chemicals Corporation (aqueous dispersions, lacquer resins, Barrialon PVDC films and Saran fibers)

JV Henan Shuanghui Investment & Development Co, Kureha Corp. and Toyota Tsusho Corp. (extrusion resins for PVDC casings and films)

Hainan Shiner Industrial Co. (aqueous dispersions, PVDC coated films)

Zhejiang Wildwind Plastic Co. (aqueous dispersions, PVDC coated films)

Zhejiang Juhua Co. (aqueous dispersions, extrusion resins)

Nantong Repair-Air Chemistry Bioengineering Co. (aqueous dispersions)

The PVDC world market (2004) is estimated at 160 000 t [45]:

By grades:	
Aqueous dispersions	18%
Lacquer resins	9%
Extrusion grades	73%

6. Toxicology and Occupational Health [46, 47]

Monomeric VDC. VDC is a clear, colorless, volatile liquid with a sweet odor [48]. The substance is extremely flammable. In the presence of air or oxygen, 1,1-dichloroethylene can form peroxides which can be violently explosive at temperatures as low as 40°C [49]. VDC is readily absorbed following oral or inhalation exposures. VDC can be metabolized and excretion occurs via exhalation as unchanged VDC or

as CO_2 or via feces or urine [50, 51]. Also dermal absorption is likely, albeit that the high volatility is probably a limiting factor [52].The substance shows no bioaccumulation potential [53]. 1,1-dichloroethylene is irritating to the eyes, but the substance is not a skin sensitizer. A single but high uptake of the substance via the oral or inhalation route can be harmful. Chronic exposure to VDC can cause liver and kidney damage. Although effects were seen in tests with cell systems, more relevant studies in living animals did not reveal a genotoxic activity of VDC [53]. A substantial number of valid carcinogenicity studies were performed which did not detect a carcinogenic potential of 1,1-dichloroethylene [54]. Nevertheless, due to its similarity to other molecules with a confirmed carcinogenic activity, a carcinogenic potential in humans by VCD can not be excluded [55]. No specific effects on the male or female fertility or on the unborn child have been detected [53].

The solubility in water is 2.5 g/L [49]. VDC is stable in water, i.e., hydrolysis is negligible, but due to its high volatility it quickly evaporates. VDC degrades rapidly by reacting with hydroxyl radicals in the atmosphere with a half-life between 11 h and 57 h. The substance does not tend to accumulate in animals or humans. It is not readily biodegradable [54]. Based on the available short-term ecotoxicology data [56], VDC should be considered as toxic towards aquatic life.

PVDC is mainly used for packaging foodstuffs or pharmaceutical products, involving both direct and indirect contact with the contents. Such packaging is governed by highly stringent regulations at an international level.

These regulations are generally based on positive lists with specific migration limits. PVDC satisfies all of these regulations.

Residual VDC monomer in commercial polymers generally ranges from indetectable up to a few ppm since all modern producers have now adapted processes to outgas PVDC. These quantities are even lower when measured on coated or extruded materials.

In the United Kingdom, information on the content of VDC in food sold in retail outlets was collected by the MAFF [57]. Of the foods analyzed, only snack foods and foods contained in VDC–VC copolymer coated packs were found to contain measurable amounts of VDC. In most other cases of food packed in barrier-coated materials (polymer films and paper), the VDC content was below the detection limit of 0.03–0.05 ppm. From all the information available, the maximum possible intake of VDC per person, when averaged over the entire U.K. population, would be no more than 1 μg/d, in the worst-case assumption that all the residual VDC in food packaging was in fact ingested [57].

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Polymer Blends

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ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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1. Introduction

A continuous need for new materials is created by the increasing complexity of products that result from technological breakthroughs and the desire to obtain improved, cheaper materials for existing applications. Alongside the development of new improved base polymers and their copolymers, blend technology is one of the most widely used routes to satisfy this need. Polymer blends (also known as alloys) are combinations of two polymers with one or more distinctive properties that contribute to or are required for the proper functioning of a specific application. Their enhanced, especially adapted property profiles provide advantages to the processor and end user such as extra ease of processing, better low-temperature impact performance, higher strength, higher or lower gloss, reduced flammability, and higher transparency, often in combination with a lower price.

The first generation of blends was developed in the 1950s to improve impact performance. This impact modification normally requires the utilization of rubbery components (materials with a low glass transition temperature, T_g, and generally based on polybutadiene structures) that need a stabilization package. The first impact-modified grades were either made by special polymerization techniques (e.g., copolymerization, block and graft polymerization) or by compounding techniques. Their properties are based upon those of the main matrix polymer and are consequently limited in their scope of application. Although impact properties were improved, a number of undesirable properties were introduced (e.g., delamination, poor surface quality, and inconsistent property profiles). Better materials were made by introducing core – shell impact modifiers. A polymer with a property profile that fulfills market requirements in all areas does not exist.

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Table 1. Thermoplastics

Type of plastic	Abbreviation	Name
Commodity	PE	polyethylene
	PP	polypropylene
	PS	polystyrene
	PVC	poly(vinyl chloride)
Transitional	ABS	acrylonitrile – butadiene – styrene copolymer
	SAN	styrene – acrylonitrile copolymer
	SMA copolymer	styrene – maleic anhydride copolymer acrylics
Engineering	PA	polyamide
	PBT	poly(butylene terephthalate)
	PC	polycarbonate
	PETP	poly(ethylene terephthalate)
	POM	polyoxymethylene
	PPE	poly(2,6-dimethyl-1,4-phenylene ether)
	SMA terpolymer	styrene – maleic anhydride terpolymer
High-performance	PEI	polyetherimide
	PPS	poly(phenylene sulfide)
	PSU	polysulfone

Introduced in the early 1960s, engineering polymers such as PC and PPE (Table 1) became available as new basic resins for further blend developments. These second-generation blends offer improved heat resistance and higher continuous use temperatures compared to the older generation materials.

Thermoplastics can be classified into commodity, transitional, engineering, and high-performance plastics (Table 1). Commodity or bulk plastics are made in large volumes, and generally have a low continuous use temperature. High-performance thermoplastics have a high temperature resistance but a low production volume and high price.

Engineering polymer blends are a special group of plastics, whose applications are related to and depend on their specially designed property profile. They all offer dimensional stability over a wide range of maximum temperatures in combination with a minimum continuous use temperature of 85 °C. In addition, they usually possess high impact resistance over a wide range of temperatures down to as low as – 40 °C. Their dimensional stability is determined by the component with the highest glass transition temperature or by the combination of a high crystallinity and high melting point of the highestmelting component. The latter case can be exploited

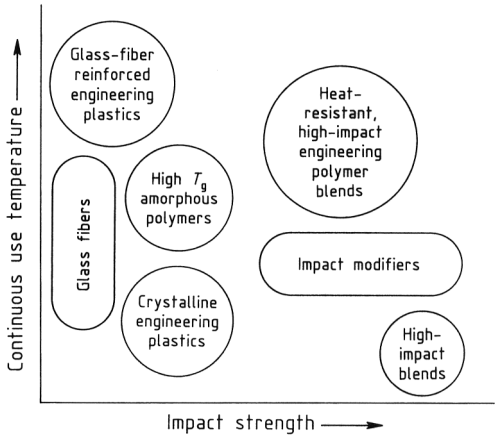


Figure 1. Second-generation polymer blends of engineering plastics

best by reinforcement with inorganic fillers or fibers. The use of a polymer with a high glass transition temperature as a functional filler yields even more interesting systems because they are not restricted to a limiting volume fraction and orientation of the reinforcement. Figures 1 and 2 compare engineering blends with thermoplastics and composites in terms of continuous use temperatures and impact strengths.

In 1990 blends accounted for 10 % of total thermoplastics production [1–7]. Annual growth figures of 6 – 8 % are predicted versus 2 –3 % for other plastics. Upgrading products based on commodity plastics by reinforcing or blending with engineering polymers creates a

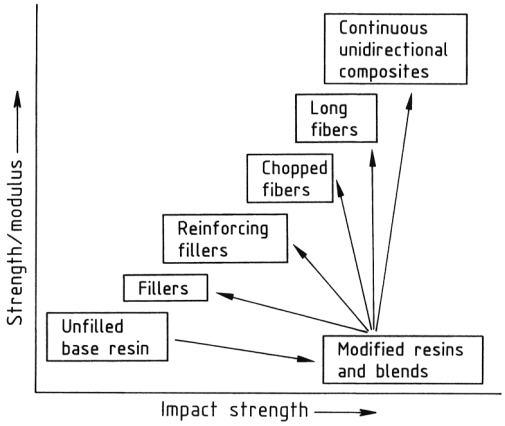


Figure 2. Relationship between mechanical properties and impact strength for various thermoplastic materials

very competitive situation for engineering plastics. It has been estimated that the U.S. market for speciality polymeric blends was $\$ 900 \times 10^6$ in 1990, and was growing at an annual rate of 7 % [7]. Growth rates for individual engineering blends depend on:

1. Growth rate of major application area (e.g., automotive appliance) [8]
2. Continent of interest (U.S., Europe, Japan)
3. Position in product life cycle: e.g., PPE – HIPS blends are considered a mature blend compared with PC – ABS, and will therefore experience lower growth figure.

Companies that offer blends usually manufacture one or more of the blend components [9]. More polymer manufacturers and compounders are entering this business now because most basic patents for the production of thermoplastics have expired (e.g., PPE, PC) and blends allow facile expansion of the product range [4], [9–11].

From a technical point of view, it is important to translate the demands of a given application to the key physical and mechanical properties of the engineering plastics blends. Target values for heat and chemical resistance, high- and low-temperature impact strength, and stiffness should be assessed. The rationale used for choosing two (or more) polymers (the blend) for a specific application is important (Fig. 3). The dominant factor that determines whether a specific polymer blend is suitable for a certain application is the requirement profile (Chap. 2). The requirement can either be one demanded by the customer or end user, or one imposed by the standards of the specific industry segment (e.g., flammability standards in the aircraft industry).

Two polymers may be miscible, partially miscible, immiscible, or compatible. Consequently, the property profile resulting from blending two polymers is not a simple combination of the two individual property profiles. The relation between different blend classifications in terms of properties and morphology are discussed in Chapter 3. Techniques used to influence blend thermodynamics and ultimate property profile are also considered.

The general guidelines for the identification of a blend property profile are outlined in Chapter 4, and are subsequently applied to the most important blends. Once a blend of two polymers has been selected, qualification of the resin for a certain application depends on processing and design considerations (Chap. 5). Chapter 6 focusses on new developments in polymer blends.

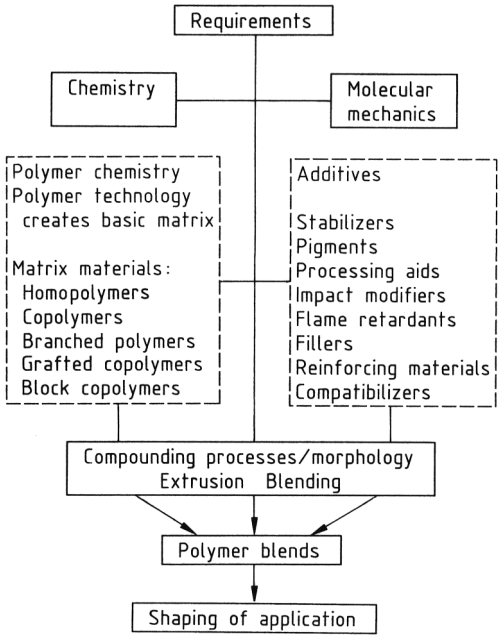


Figure 3. Schematic representation of blend development

2. Market Requirements

Specification of material requirements is determined by the needs of the end user and by the standards within an industry segment. All materials have to fulfill the requirements specified by industrial standards or mandated by law. These standards are controlled by standardized test methods and vary for different countries and industrial segments.

Blend development starts from the combination of a required property profile and an existing technology. The main industrial application areas for polymer blends are the automotive market, followed by the packaging industry, electronic and electrical industry, business equipment, and appliance sectors. Smaller

application segments are construction, consumer goods, sheet manufacturers, and aerospace industries.

Automotive Applications. A number of different application areas can be discerned in an automible. Horizontal exterior body parts demand a higher temperature resistance than vertical exterior body parts since they absorb more radiation from the sun. Both types require high surface quality and facile paintability, the coating technique being determined by the temperature resistance of the material. Mechanical properties are very important for structural body parts, but nonstructural body parts also require a high dimensional stability as characterized by a low coefficient of thermal expansion.

Bumper, or better bumper systems, have a crash-absorbing and an aesthetic function. The crash-absorbing function of bumper systems can be fulfilled by incorporating appropriate failure mechanisms. Decorative functions demand easy paintability, high UV resistance, and resistance to small impact loads. The trend is towards a separation of both functions. Facile dismantling is becoming important for recycling.

Wheel covers should have a good dimensional stability and be able to withstand the high temperatures caused by braking. Chemical resistance is usually provided by a coating.

Lighting systems consist of a light-reflecting component and a housing. The latter requires an extremely high dimensional stability and related mechanical properties. The reflector must be temperature resistant and possess sufficient reflecting capacity (surface quality and gloss).

The *passenger compartment* contains a high number of decorative applications designed for comfort. Resistance to low continuous loads (e.g., instruments in instrument panel) and glossy/nonglossy appearance are general considerations. The temperature requirement is related to exposure to the sun, but a heat distortion temperature of 120 °C is generally accepted. Key requirements for the dashboard material include a minimum heat distortion temperature of 120 °C, excellent accoustic properties (reduction of outside and engine noise), high impact resistance, and good scratch resistance. Paintability and compatibility with soft-touch overlay films are additional requirements.

Structural parts (e.g., chassis) demand such high mechanical properties that composites are the only feasible solution. *Under-the-hood applications* include cable and wiring, which demand electrical, chemical, and high-temperature resistance.

Fuel tanks place high demands on the barrier properties of the resin, in addition to its chemical resistance. PE in fuel tanks has been subjected to (sulfo)fluorination to increase surface polarity and improve barrier properties. Other techniques are employed in utilizing PA – PE or PA – PVAL and PVAL – PA blends [PVA = poly(vinyl alcohol)] for fuel tanks where a special layered morphology ensures impenetrability.

Applications in the *motor compartment* have to withstand harsh environmental conditions, and thus require a high-temperature and environmental (including chemical) resistance. The most suitable products are semicrystalline polymers.

Electronic and Electrical Applications. The dominating requirements in this industry are high heat and chemical resistance and high dimensional stability. A key requirement is a low, preferably temperature-independent, conductivity. The trend towards miniaturization demands better flowing resins coupled with a high heat resistance. Higher heat materials are also required for the introduction of the surface-mount circuitboard assembly [11] in which thermoplastics are combined with metals. The materials must be able to withstand chemical cleaning baths and temperatures over 260 °C for more than 1 min resulting from high-temperature soldering via wave, vapor-phase, IR, or laser methods. Dimensional stability should be maintained during these operations and under operating conditions. Electrical (office) equipment must fulfill stringent flammability requirements, particularly when used in restricted areas.

Appliance Sector. Basic requirements for household appliances are water resistance, chemical resistance, appearance (glossy etc.),

and temperature resistance. Electrical properties (e.g., conductivity) and absence of toxicity risks must conform to consumer and government standards.

Building and Construction Applications. Material requirements differ from country to country. Public buildings are subject to the most severe rulings. The greatest drawback of plastics is their intrinsic flammability resulting from their organic nature. The fire tests mandated for plastics are thus difficult to pass. To reduce the risk of fire, only relatively small amounts of plastics can be used in low-risk areas (e.g., outside sidings). The most important flammability characteristics are ignition and flame propagation behavior. Materials may have horizontal, vertical, or no fire propagation. Assessment of flammability characteristics is extremely complex, since the behavior of materials under fire conditions depends not only on the nature of the material, but also on its thickness and the configuration of the part.

Mechanical requirements are much easier to fulfill and depend largely upon the temperature resistance of the material.

Packaging Applications and Pipes. Basic requirements for packaging materials are barrier properties for water, oxygen, and carbon dioxide as well as excellent extrudability resulting from a high melt strength. Permeability requirements are usually satisfied by multilayer systems in which polymers are alternated with tie layers. Properties can be optimized by bidirectional orientation. These multilayer systems can be substituted by a single, special two-phase blend material.

Pipes for water distribution should have a long guaranteed life time (> 100 years), and prevent migration of low molecular mass compounds into the water.

3. Blend Technologies

From a thermodynamic perspective, polymer blends may be completely miscible, partially miscible, or immiscible (Fig. 4). An almost fluid transition is possible between these systems; by modifying the base polymers each blend can be optimally positioned for the foreseen application.

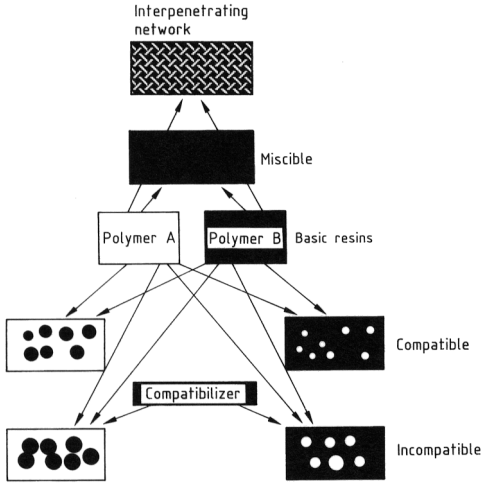


Figure 4. Possibilities of blend morphology

3.1. Thermodynamics

The thermodynamic blend requirements have been reviewed elsewhere [12–15]. Blend polymers interact with each other in their amorphous state, either in a melt or dissolved in a common solvent. A thermodynamically stable mixture of two polymers is obtained if the free energy of the mixture is lower than the combined values of the individual components, i.e., the energy of mixing ΔG_{mix} should be negative. The free energy of mixing is composed of an enthalpy and entropy term [12–15]

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \quad (1)$$

A homogeneous blend over the complete composition range of two components 1 and 2 is only obtained if

$$(\partial^2 G/\partial x^2) > 0 \quad (2)$$

in which x denotes the volume fraction of component 2. The entropy contribution to the overall free energy of the system is usually negligible, and is only important in special cases (e.g., blending with relatively low molecular mass components such as plasticizers).

The enthalpy resulting from the interaction energy between the two polymers determines whether they are completely or partially

miscible. Complete mutual solubility results in a single-phase system. Partial solubility provides a two-phase system with a very low interfacial energy allowing the production of very finely dispersed blend systems without the need for a third component such as a compatibilizing block copolymer. Normally, even when very similar components, such as polyolefins are blended, the enthalpy term is positive and leads to nonmiscibility. Phase separation can only be prevented if interaction between the different chemical groups in the two polymers is possible (e.g., dipole – dipole interaction, charge transfer complex formation, hydrogen bonding). A negative enthalpy value leads to a completely or partially miscible blend system. The miscibility of a two- component system can be improved by increasing the interaction energy between the two components or reducing the interaction energy within each component. The latter effect is achieved by using random copolymers made from monomers that, by themselves, form immiscible homopolymers. The internal repulsion energy in these copolymers can thus improve miscibility [16]. The interaction energy between two polymers is the main factor that determines the final blend result.

The morphology of incompletely miscible systems can be structured. In a two-phase system with a dispersed phase and a continuous phase, the polymer constituting the more important continuous phase can be selected. The second possibility consists of an interpenetrating, co- continuous network formed from both polymers (Fig. 4). Morphological control depends on chemical interaction and rheological factors such as the melt viscosity ratio of the two polymers and the dependence of melt viscosity on shear rate. The compounding conditions used during melt blending are therefore of major importance for the final blend property profile (see Section 3.2 and Fig. 3).

The influence of temperature on blend thermodynamics is important because it determines phase separation behavior and morphology (see Section 5.1). A typical example is shown in Figure 5. Three regions can be discerned: (1) a thermodynamically stable region (miscibility), (2) a metastable region where the system is stable only towards small concentration fluctuations, and (3) a region where spinodal decomposition yields a two-phase system. The binodal

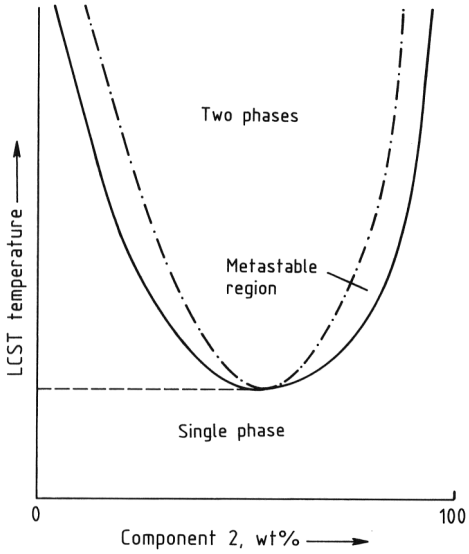


Figure 5. A schematic phase diagram for a polymer – polymer blend with a lower critical solution temperature (LCST)

(solid line) corresponds to $\Delta G_{\text{mix}} = 0$, the spinodal (dashed-dotted line) is defined by $(\partial^2 G/\partial x^2) = 0$.

3.2. Compatibility

The term compatibility describes all useful (scientific) means of producing stable blend microstructures that provide technologically important properties for the performance of the part. In the absence of interactions between two blend components, the blend morphology is largely determined by the interfacial tension. The interface between two polymers in the melt is characterized by the interfacial tension and the domain adhesion [17]. The interfacial tension γ_{12} between polymers 1 and 2 is defined as the work required to increase the interface

$$\gamma_{12} = (\delta G/\delta A)_{P,T,n} \tag{3}$$

where A is the surface area between polymers 1 and 2. The magnitude of the interfacial tension is determined primarily by the polarity difference between the two phases [17]. It is also related to the surface tensions of the constituent polymers which are defined as the work

required to increase the surface of a polymer by 1 cm^2. Increase in the surface area of a polymer involves the transport of polymer segments from the bulk to the surface which deprives them of the small forces acting in the bulk (e.g., van der Waals forces). In total,

$$\gamma_{12} = \gamma_1 + \gamma_2 - W_a \quad (4)$$

where γ_1 and γ_2 are the surface tensions of polymers 1 and 2, and W_a is the work of adhesion (equal to the decrease in Gibbs free energy on forming an interface between polymers 1 and 2). In practical terms this means that the work of adhesion increases as the interfacial attraction increases, corresponding to a decrease in interfacial tension. If two immiscible polymers are mixed, more interface is created and the free energy of the system increases. The system is thermodynamically unstable and strives toward a reduction of the total interface surface. Consequently, if two individually dispersed polymer droplets encounter each other, they agglomerate immediately. This leads to coarsening of the phase morphology which can only be prevented by the use of compatibilizers. A compatibilizer reduces the interfacial tension, improves the interfacial adhesion, permits finer dispersion during mixing, and stabilizes morphology during processing.

The most common types of compatibilizers are AB block copolymers for a blend of polymers A and B (Fig. 6) that are added prior to compounding or synthesized in situ [18], [19]. The block copolymer decreases the interfacial tension by dissolution of the copolymer block segments within their respective homopolymer phases, leading to covalent bonds being positioned across the interface. Physical anchoring of both phases contributes to the stability of the resulting morphology and mechanical strength. In commercial blends, 5 – 15 wt % compatibilizer is used.

Several other routes are available for compatibilizing phases in commercial multicomponent polymer blends. Large-scale phase separation can be prevented by promoting cocrystallization, by cross-linking the dispersed phase, or by the formation of interpenetrating networks. Ionic attraction between blend components can also be used to stabilize the phase structure. High stress shearing conditions may be applied to mechanically interlock both phases, but this technique is seldom practised.

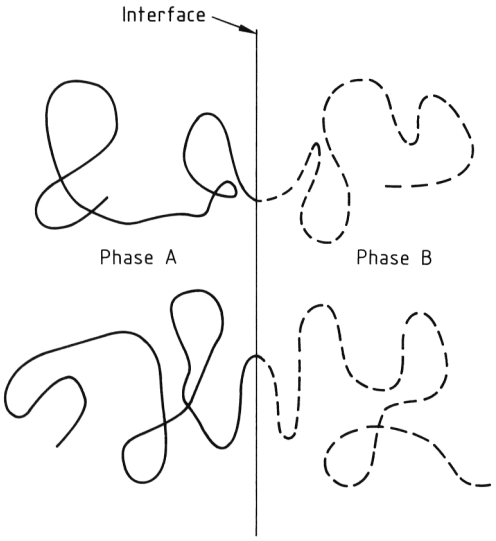


Figure 6. Ideal configuration of block copolymer at the interface between polymer phases A and B

3.3. Compounding

For scientific and screening purposes, limited amounts of blends are prepared by combining solutions of the blend components from the same solvent or mutually miscible solvents. Blends of miscible polymers can then be obtained by sol-vent evaporation or coprecipitation. Care must be taken not to heat a blend beyond a potential LCST temperature in a subsequent melt processing step. In dealing with partially miscible or compatible systems, coprecipitation followed by a melt cycle is usually employed [20], [21].

The main method of blend production is batch or continuous melt blending in kneaders or compounding extruders [20], [21]. The machines used are corotating twin-screw compounders with a mixing section based on the Erdmenger principle, Busch co-kneaders, and Banbury kneaders.

The technology involved in this method of manufacturing polymer blends is determined by the thermodynamics of the blend system (Section 3.1) and by the rheological conditions

during melt blending. The final morphology of the blend in the compounding step is of prime importance for its resulting property profile.

Compounding machines are not simple extruders which merely melt and transport the resin [15], [22], [23]. Intensive mixing of the melt is achieved by the dispersive or distributive action of the screw element. Depending on the thermodynamics of the mixture of molten components, a dispersion of component 1 in 2 or 2 in 1 is obtained. The criteria determining the continuous phase are the volume fractions used in the melt-blending process, the ratio of the individual melt viscosities, and the surface tension (the polymer with the lowest surface tension usually becomes the continuous phase).

Two basic microrheological processes can be discerned in the blending of polymers: distributive and dispersive mixing. Distributive mixing determines the homogeneous distribution of the second phase throughout the matrix, whereas dispersive mixing causes large particles to break up into smaller ones. During actual mixing both processes occur simultaneously.

Distributive Mixing. At the start of the blending process, the droplet size of the second phase is relatively large. Two counteracting stresses are in effect: the deforming shear stress τ and the interfacial stress σ/R. Their ratio is usually called the capillary number Ca.

$$C_a = \tau R/\sigma = \eta_m \gamma R/\sigma \tag{5}$$

where

γ = shear rate (s^{-1})
η_m = viscosity of matrix (Pa · s)
σ = interfacial tension (N/m)
R = radius of particle (m)

Typical shear stresses in polymer melts are in the order of 10^4 N/m^2. The local radius of a dispersed droplet is approximately 10^{-3} m in the early stages of the mixing process, and σ is typically 10^{-2} N/m. An affine deformation is the result.

The total interface is a measure of the effect of distributive mixing and, in the absence of reorientation, is directly proportional to the total shear γ.

$$A = A_0 \gamma \tag{6}$$

where A is the interfacial area and A_0 the initial interfacial area.

If the layers are oriented along the shearing direction, such as in corotating twin-screw extruders, distributive mixing becomes more efficient.

When two polymers dissolve in each other, they do so by diffusion. The time required for complete dissolution is greatly reduced by decreasing the droplet size of the starting dispersion; this is facilitated by minimal surface tension between the two initially molten phases. The distributive mixing action is produced by the shearing and elongating forces that act upon the continuous phase and are transferred to the dispersed phase [15], [22], [23]. Under stagnant conditions, the dispersed phase consists of molten droplets which are deformed into threadlike structures. The length – diameter ratio of these structures depends on the interfacial tension constraints of the dispersed phase, and on the effectiveness of the transfer of the deformation forces from the continuous phase to the dispersed phase. The latter is maximized when the ratio of the apparent melt viscosities of the continuous and dispersed phases is close to one. Equation (7) describes the equilibrium conditions for droplet formation [24], [25]:

$$\eta_1/\eta_2 = \Phi_1/\Phi_2 \tag{7}$$

where η is the melt viscosity and Φ the partial volume.

Dispersive Mixing. The dispersed phase deforms affinely with the fluid motion, resulting in elongated droplets. This process continues until the capillary number approaches unity. This limit is reached if the local radii are in the order of 10^{-6} m, resulting in $\sigma/R = 10^4$ N/m^2. The elongated droplets become unstable due to interfacial tension driven Rayleigh distortions, and droplets are formed, which are again subjected to shear stress.

This process of elongating and breaking up repeats itself until the droplet size reaches an equilibrium dimension determined by the above-mentioned factors. These process steps are shown in Figure 7.

Figure 8 illustrates the difference between the effect of shear and elongational flow on particle size. For high viscosity ratios (η_1/

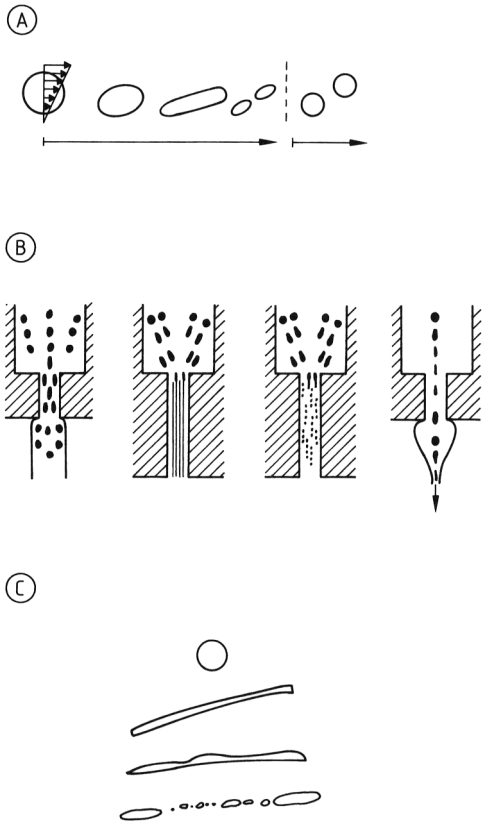


Figure 7. Droplet deformation A) Deformation caused by shear flow; B) Deformation caused by elongational flow; C) Actual droplet formation (combination of A and B)

η_2>4), dispersed particles do not break up in shear flow because they rotate around themselves. Elongational flows are irrotational, and dispersive mixing is possible. The final quality of the blend dispersion depends entirely on this process. The interfacial tension has to be very low(< 5 mN/m) to obtain a dispersed phase with dimensions smaller than 1 μm. In cases when the two blended polymers have a higher interfacial tension, compatibilizers are necessary to obtain the necessary dispersion quality. These compatibilizers are generally block copolymers consisting of monomeric units that are (preferably) miscible or at least highly compatible with the two phases of the blend system. During the melt-mixing process, they position themselves at the interface between the two miscible components, and thus overcome the repulsive effects of interfacial tension by forming chemical bonds between the two blocks. In this way, addition of a compatibilizer leads to a decrease in interfacial tension, yielding smaller particle sizes at the same viscosity ratio and shear stresses. It also provides the necessary morphological stability in this thermodynamically unstable system. Furthermore, mechanical properties are optimized if compatibilizer blocks of sufficient molecular mass are entangled in the relevant polymer phase.

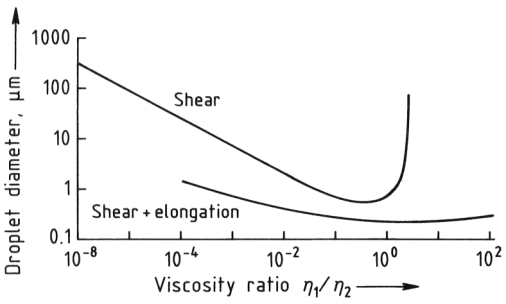


Figure 8. Influence of deformation forces on droplet diameter as a function of viscosity ratio η_1/η_2 with η_1 the dispersed and η_2 the matrix viscosity

The basic blend of two polymers described above can be regarded as the base matrix, which has to be further adjusted to the needs of the application by addition of additives (e.g., impact modifiers). The location of the impact modifier can be predetermined by chemical bonding with the desired phase or by specific surface interfacial effects.

Predicting Morphology. Why does one of the dispersed resin phases encapsulate the other? Under equilibrium conditions such effects are probably due to interfacial energy differences between the blend components. The tendency of a liquid to spontaneously spread across a solid or liquid substrate can be expressed in terms of the surface and interfacial tensions of the components using Harkin's equation

$$\lambda_{ij} = \gamma_j - \gamma_i - \gamma_{ji} \tag{8}$$

where γ_j, γ_i, and γ_{ji} are the surface and interfacial tensions of the solid, liquid, and solid/liquid respectively, and λ_{ij} is defined as the spreading coefficient. Equation (8) can be approximated by

$$\lambda_{12} = \gamma_1 - \gamma_2 - \frac{4\gamma_1^d\gamma_2^d}{\gamma_1^d + \gamma_2^d} - \frac{4\gamma_1^p\gamma_2^p}{\gamma_1^p + \gamma_2^p} \tag{9}$$

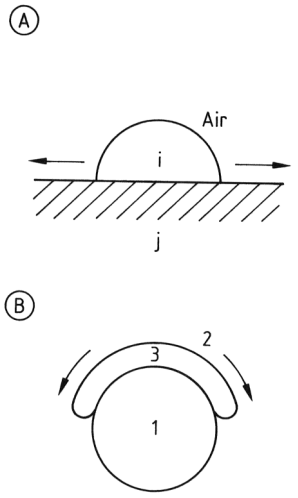


Figure 9. Schematic diagram showing spreading behavior of liquid on solid substrate (A) and one polymer phase on another within a third (B)

where γ^d and γ^p constitute the distributions of the contribution to the surface tension caused by dispersive and dipole interactions, respectively.

Spreading is predicted to occur only for positive values of λ_{12}. Melt blending is usually carried out at elevated temperature, interfacial tensions should therefore be known at processing temperatures but variation in surface tension with temperature is comparable for most polymers (0.06 – 0.08 dyne · cm/ °C).

With three or more different components a number of interfacial tension combinations result. This can create a competitive situation leading to a number of options. If the spreading coefficient λ_{12} is positive, component 1 will encapsulate component 2 and as such will be dispersed in 3 (Fig. 9) [26]. A three-phase system develops in those cases where none of the possible three-phase combinations has a positive spreading coefficient. All these morphologies are thermodynamically controlled.

One of the most severe problems encountered in blends of two immiscible components with an insufficiently low interfacial tension is loss of morphology or dispersion through agglomerization. This leads to uncontrollable thermodynamically driven, phase separation and delamination with total loss of mechanical properties.

3.4. Reactive Compounding

Reactive compounding is used in those cases where the above-mentioned agglomeration problem has to be overcome by creating chemical bonds across the interface [27]. This technique can be applied with a single-phase matrix and a two-phase blend matrix. An example is phase-selective impact modification where the modifier is chemically bonded to one phase component of the blend matrix. This is possible through the use of specially functionalized components containing reactive groups. One component may be functionalized with a group that can react with an existing reactive site in the second component. Alternatively, both components may be functionalized with mutually reactive sites.

The most commonly used chemical reactions are those between carboxylic acids or anhydrides with amines or epoxy groups, and between amino and epoxy groups. Reactive extrusion involves the introduction of these reactive groups into a nonreactive polymer by means of radically induced graft reactions with unsaturated monomers or by replacing available reactive groups with more or different reactive groups.

The term in situ compatilization denotes those cases where a functional group is introduced to establish chemical bonds between the two phases or to generate a compatibilizer in situ. An example of this technology is found in the manufacture of the completely immiscible blend of PPE and PA with the assistance the addition of, for example, maleic anhydride (see Section 4.5, PPE – PA blends).

3.5. 3.5Mechanical Properties [28]

Nearly all thermoplastics are subjected to mechanical loading during their lifetime. Mechanical properties are therefore often used as the basis for material selection. Engineering data sheets supplied by the manufacturer contain information on mechanical properties, thermal properties, electrical properties, flammability behavior, and chemical resistance. These properties are measured by standardized test procedures (e.g., ASTM, DIN, ISO), see → Plastics, Properties and

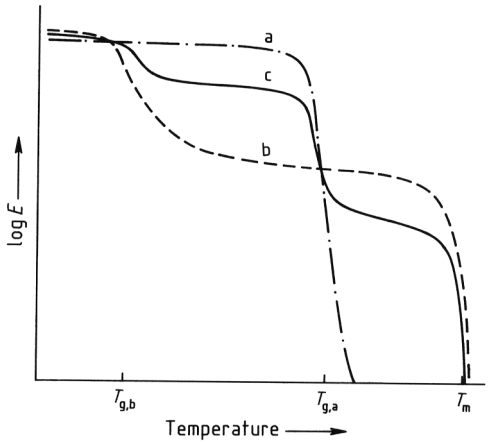


Figure 10. Generalized modulus – temperature diagram for two polymers and their blend a) Amorphous polymer with high T_g; b) Crystalline polymer (e.g., polyamide, polyester) with low T_g; c) Blend of a and b

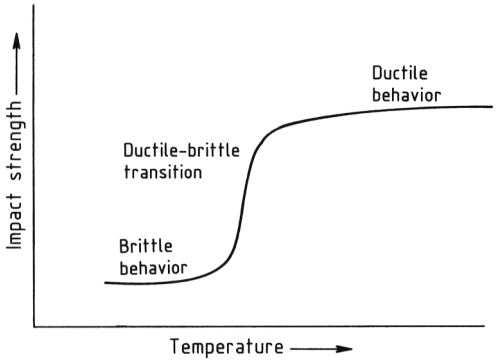


Figure 11. Typical impact behavior as a function of temperature

Testing. Important mechanical properties for engineering blends are discussed briefly in this section [28].

Characterization of a thermoplastic (blend) usually starts with a curve of tensile modulus (E) plotted against temperature (Fig. 10).

The *glass transition temperature* T_g (1 Hz) is the temperature at which the larger chain segments either gain or lose rotational freedom. Its location shifts with the frequency of the test method, i.e., the performance of a material is difficult to predict based on merely T_g values. Secondary transitions also play an important role in determining impact resistance, especially if the T_g (1 Hz) lies close to the use (or room) temperature.

Impact strength is the ability of a material to withstand impulsive loadings. Tests are performed using notched and unnotched samples. The material fracture mode is important, being either ductile or brittle and depends on temperature (Fig. 11). The location of the ductile – brittle transition is usually reported.

The *toughness* (ability to absorb mechanical energy without fracture) is measured as the area under standard (tensile) stress – strain curves. For many (engineering) thermoplastics it is usually improved by the incorporation of a low-modulus component (rubber) as a separate phase [29], [30]. When highly dispersed the rubber acts as an effective stress concentrator and initiates both crazing and shear-yielding phenomena in the matrix. Since both these processes can absorb large amounts of energy, impact-modified materials exhibit superior resistance towards crack propagation under impact conditions. The low-modulus phase may be incorporated by grafting, copolymerization, or melt blending. High stress concentration is reached when the ratio of the moduli of the rubber phase and the matrix is high. This value is increased when the rubber particle cavitates under the onset of the three-dimensional stress in the part.

Enhancement of the intrinsic toughness of the blend system increases impact resistance. The most important factor in optimizing the impact performance of a polymer resin is identifying the preferred deformation mechanism of the matrix polymer — crazing or shear band formation — because each mechanism requires a specific type of impact modification. In all cases the predominant deformation mechanism depends not only on the modified matrix system and its morphology, but also on variations in test conditions.

Two important phenomena are usually considered in *long-term behavior: creep* (the increase in strain for a material subjected to a constant load) and *stress relaxation* (reduction of stress induced in a material subjected to constant strain). Both processes provide estimates of the materials long-term dimensional stability and are important in selecting resins

and design parameters for a certain application (see Section 5.2).

The *ultimate use temperature* is the maximum allowed temperature at which the material will provide the required dimensional stability under the foreseen conditions. The *continuous use temperature* is related to the oxidative stability or intrinsic stability of the blend system. This is usually determined by the weakest blend component, whereas the ultimate use temperature of the most thermally stable blend component determines the thermal resistance.

The two most commonly employed ultimate use temperatures are the Vicat softening temperature (Vicat A or B) and the heat distortion (deflection) temperature (HDT). Typical HDT values for completely amorphous polymers are 20 °C lower than the T_g values. The Vicat values are somewhere inbetween. For typical semicrystalline polymers, large differences are found between the high- and low-load HDT values. The Vicat values are usually close to the low-load HDT values.

3.6. Additives

The role of additives in modifying polymer properties should not be underestimated. See also, → Plastics, Additives.

The distribution of stabilizers between the various blend components (including impact modifiers) is important. Redistribution of stabilizers initially present in the weakest component, may yield surprising effects. For instance the UV resistance of PC – ABS blends is markedly higher than expected for an ABS system due to the presence of UV stabilizers in the continuous PC phase. Redistribution processes can be prevented by using chemically bonded additives.

Oxidation at moderate temperatures (thermal oxidation) and under the influence of UV radiation (photo-oxidation) can lead to cross-linking, lowering of molecular mass, and deterioration of mechanical properties. Unsaturated rubbery polymers, such as those used for impact modification, are particularly sensitive to attack by oxygen and heat. *Heat stabilizers* and *antioxidants* are added to suppress these reactions.

Flame retardants are applied to allow a polymer to conform to flammability requirements. A large variety of compounds (e.g., aluminum trihydrate, organic phosphates, antimony oxide in combination with various halogen compounds) are used for this purpose. They increase the amount of solid (nonvolatile) material by carbonization or cross-linking, and/or interfere in the oxidation processes taking place in the flame (flame poisoning).

Plasticizers are used to reduce the modulus of the resin (i.e., to increase flexibility) over the expected use temperature range. They are also effective as flow-improving additives and modify the continuous phase. They have to be selected on the basis of compatibility parameters. They are sometimes moderate molecular mass polymers with a low T_g, but more commonly oligomers with a molecular mass of 3000 – 1000. The use of polymeric plasticizers versus the traditional organic materials is growing due to environmental concerns (nonvolatile and less migrating) and also due to practical performance reasons.

Release agents used to provide easy mold release are selected according to their volatility and thermal stability in relation to the processing temperatures.

A number of types of *fillers* exist. Mica and lime are used to increase volume and reduce the material price. Other particulate fillers such as graphite, carbon black, and aluminum flakes are used to enhance the material's conductivity for a variety of purposes. Reinforcing fillers (e.g., glass fibers, continuous glass mats, or glass fabrics) are used chiefly to improve mechanical properties such as modulus and strength and increase the heat distortion temperature (Fig. 2).

Transesterification catalysts in blends of two polyesters may catalyze copolymer forming transesterification reactions during (melt) processing.

Catalyst complexing agents are added to prevent these unwanted side reactions. Compatibilizers have been discussed in Section 3.2. The role of *impact modifiers* has been discussed in Section 3.5.

4. Property and Application Profiles of Selected Blends

Thermoplastics are crystalline or amorphous. Crystalline resins (PA, POM, PP, PSU,

Table 2. Property profile of engineering thermoplastics

Resin	Advantages	Disadvantages
ABS	impact strength, processibility, surface appearance	HDT, flammability
ASA	weathering performance, ductility	HDT
HIPS	processibility, impact strength	chemical resistance, HDT
PA	processibility, impact strength if saturated with water, toughness, chemical resistance (crystalline PA)	water adsorption leads to general change in mechanical properties and dimensional stability, HDT
PBT	chemical and solvent resistance	processibility, shrinkage
PC	low-temperature toughness, HDT, constant modulus, high T_g	stress-crack sensitivity, solvent/chemical resistance, impact strength under certain conditions
PETP	chemical and solvent resistance	shrinkage, low-temperature toughness, crystallization speed
POM	tensile strength, modulus	impact strength
PP	chemical resistance, low price, high flammability	HDT, oxidation sensitive, brittle
PPE	HDT, rigidity, flame retardancy, impact strength	processibility, oxidative stability (UV)
PS	processibility	brittleness
PSU	excellent thermal and oxidative stability	expensive, notch sensitive

polyesters) have superior resistance to organic solvents, a low melt viscosity, and are often not transparent. They also exhibit considerable mold shrinkage and warpage. High dimensional stability is only achieved below the glass transition temperature. Above this temperature, reinforcing fillers (e.g., glass fibers) are required to provide the desired dimensional stability and strength; they also enhance the tensile modulus. Furthermore, the crystallization rate and the history determine whether a material acts according to the characteristics described in Table 2.

Blending with engineering polymers is needed to improve their intrinsic property profile and expand their application range [31]. The amorphous polymers (ABS, PC) have excellent dimensional stability up to 20 °C below their T_g; maintain their properties at elevated temperature; and show good impact behavior, high transparency, and low warpage. Amorphous polymers with a very high T_g are very difficult to process and/or very brittle. Also their application area is limited due to lack of chemical resistance. These issues had to be addressed before they were accepted by the market. Semicrystalline engineering polymers frequently exhibit a too slow or too rapid crystallization with a poorly controlled crystalline phase morphology. This causes a processing-dependent property profile, leading to unpredictable impact behavior. Furthermore their mechanical properties vary widely depending whether they are used below or above their glass transition temperature.

The advantages and disadvantages of the most important thermoplastics are listed in Table 2. The key to the development of a successful blend is to maintain the strengths of both polymers while removing their disadvantages. The heat distortion temperatures of these polymers and some engineering blends follow:

ABS	80 – 100
PBT	70
PC	135
PEI	170 – 240
PP	70
PPE	200
PS	80
SMA	105
ABS – PC	110
ABS – SMA	95
PA – PPE	170 – 190
PC – ABS	100 – 125
PC – PBT	120 – 140
PC – SMA	115
PEI – PC	170
PPE – HIPS	80 – 175

In the following sections selected commercially important blends and engineering blends are discussed. The treatment of the blends is based upon the main component (defined as being present in an amount of more than 50 wt %), and not the (for mechanical properties very important) continuous phase. Each section is concluded with a short list of applications that may be similar because different blends are targeted for the same application.

4.1. Polyolefins

Polyethylene. Polyethylene [9002-88-4] (PE) is classified according to density which is controlled by the attainable degree of crystallization and the density of the amorphous phase [32]. Densities range from 0.8 to 0.95 g/cm^3 and are primarily determined by their underlaying molecular structure which results from the way these polymers are synthesized. See also → Polyolefins, Chap. 1..

High-density PE (HDPE) is produced by comparatively low-pressure polymerization with Ziegler or complex oxide catalysts; density 0.95 g/cm^3, melting temperature 130 – 135 °C.

Low-density PE (LDPE) is traditionally made by a high-pressure route; density 0.92 g/cm^3, melting temperature 115 °C, but lower crystallinity than HDPE due to presence of branching structures.

Linear low-density PE (LLDPE) is comparable in structure and general properties with LDPE but lacks long-chain branching. It is produced by copolymerizing ethylene with butene, hexene, octene, or 4-methylpentene at low pressure.

Very low-density PE (VLDPE) is an extreme version of LLDPE; density may be as low as 0.88 g/cm^3.

Ethylene copolymers are typically polymers of ethylene with polar monomers such as acrylates.

Ultimate rheological properties can be adjusted by blending to suit the processing techniques used. Density can also be adjusted by blending because it simply follows linear additivity of the components used. From a practical point of view the polyolefin systems are completely compatible due to their very low interfacial tension.

Vinyl, acrylic, and even carbon monoxide comonomers are used to modify polyethylene. The possibilities of these modifications are, however, restricted because crystallinity and melt temperature rapidly decrease with comonomer content, resulting in products with a very low modulus of elasticity. Rubbery materials are produced in this way and are frequently used as impact modifiers for blends. Although chemical modification of polymers is preferred (primarily due to cost reasons) some property profiles can only be obtained through blending.

Polyethylenes are widely used as blend components because they improve a number of important properties such as flow, impact resistance, chemical resistance, and environmental stress cracking sensitivity. Cost – price reductions and volume – price improvements are an additional advantage.

One of the most important application areas of PE blends is the packaging industry. They display barrier properties in particular toward oxygen and water vapor, and chemical resistance toward aqueous systems, edible fats, and oils. In blends of polyamides with slightly functionalized PE, the desired blend morphology is best described by the term controlled delamination (i.e., agglomeration of the dispersed PE phase leads to a two-phase layer structure but does not reach an undesirably high level that would cause delamination). This can only be achieved through extrusion shaping [33]. The inherent incompatibility in PE – PA blends is overcome by chemical bond formation between carboxylic or maleic anhydride groups of the modified PE phase and amine end groups of the PA phase. The following types of compatibilizers have been used: maleic-anhydride or chlorine-modified polyolefins [34], ethylene – methacrylic acid copolymers, ionomers (maleic-anhydride-grafted PE), and epoxy compounds. Increasing the degree of PE modification with polar groups improves the adhesion of these intrinsically nonadhering polymers to more polar polymer blend components to give extremely tough materials [33], [36], [36]. Applications include automotive parts (mainly injection-molded compounds), power tools, farm and garden equipment, as well as sport and recreational markets.

PE – isobutene films have improved properties and toughness compared to HDPE films. Typical applications are single-layer extrusion films, and heavy-duty bags. HDPE, LDPE, and LLDPE polymers are blended in different ratios to obtain films in a customer-preferred density. Uses include films for bags.

Polypropylene. Polypropylene (PP) [9003-07-0] (→ Polyolefins, Chap. 2.) is used as homopolymers, random copolymers and block

copolymers. Polypropylene is one of the most widely used commodity plastics. It has a good chemical resistance, excellent thermal stability, a low price, and high flowability. The polymer has three drawbacks: (1) it is sensitive to oxidation during processing and use, (2) it has a poor resistance to UV-induced degradation, and (3) it is rather brittle even though its glass transition temperature (– 10 °C) is below room temperature.

Thermal oxidation problems have been solved by use of specially developed additive packages. Impact performance can be improved by chemical modification (copolymerization) or blending. Comonomers are mainly ethylene and higher olefins. Cheap rubbers such as EPDM (ethylene – propylene – diene rubber) are frequently used for blending [37]. The miscibility between polyolefins is extremely limited in spite of their great chemical similarity (Fig. 7). However, due to the small interfacial tension the dispersibility is acceptable. Nevertheless, when blends of PP and other polyolefins are being made, they often require a compatibilizing block copolymer to provide the necessary degree of dispersion and to maintain morphological control during processing. The latter is essential for obtaining the desired mechanical properties of the product. Morphological stability can be further enhanced by in situ cross-linking of the dispersed phase (dynamic vulcanization) [38]. The main applications of PP and its blends are in bumper systems and dashboards.

Blending with incompatible polymers can be achieved via utilization of a functionalized PP (e.g., by grafting with maleic anhydride). The inherent interfacial tension differences are thus overcome by means of chemical bonds instead of physical adhesion. Blends of PP and PA based on this technique are becoming available [37].

4.2. Poly(Vinyl Chloride)

Poly(vinyl chloride) [9002-86-2] (PVC) is the oldest and one of the most important plastics, see → Poly(Vinyl Chloride). Worldwide sales of PVC-based plastics were expected to exceed 13×10^6 t/a in 1991 [39].

PVC has a number of important properties. Its amorphous character and T_g of 75 °C provide an excellent basis for good dimensional stability under load up to 60 °C. Its high polarity gives chemical resistance towards a broad range of solvents and an excellent flame retardancy. However, pure PVC is rather brittle under notched impact conditions and has a limited thermal stability. This last property has successfully been addressed by stabilization techniques. In combination with extensive utilization of blend technology, all conventional processing techniques are now possible for PVC. The abundant presence of strong polar C – Cl bonds make PVC highly suitable for blending. Depending on the concentration of strongly interacting dipoles in the blend components, completely miscible or compatible blends can easily be created. The resulting two-phase morphologies either have a particulate or a controlled delaminated character which controls the final deformation mechanism and its performance in blends of PVC.

Chlorinated polyethylene (CPE) is being used as a blend component to improve the impact and flow behavior of PVC [40]. Compatibilizers are not necessary because the chlorine content can be adjusted to the required compatibility level (35 wt %).

Similar effects are obtained for copolymers of ethylene and vinyl acetate (EVA) and/or ethylene and ethyl acrylate (EEA) [40]. The ester groups interact with the H – C – Cl groups of the PVC and provide the required compatibility if the comonomer content is in the range 30 –40 wt %. Afterchlorination of PVC yields CPVC which has a higher heat distortion than PVC. The T_g increase is directly related to the chlorine content. CPVC can be used directly or in completely miscible blends with PVC to obtain products having higher T_g s.

Heat-resistant blends can also be obtained by blending PVC with α-methylstyrene – acrylonitrile copolymer (see Section 4.3) which is completely miscible with PVC. Blends are also available with a low T_g. An important example is the blend of PVC with NBR rubber; depending on the nitrile content (critical level, 32 wt % acrylonitrile) a single-phase soft blend or a two-phase impact-modified PVC can be made.

Impact performance can be improved by blending with two-phase impact-modified

materials such as ABS and ASA (acrylonitrile – styrene grafted onto acrylic rubber). ASA does not impair weatherability as is the case for ABS. Blends with poly(methyl methacrylate) (PMMA) also show good weatherability performance. Blends of PVC with ABS, ASA, SMA, and PMMA are mainly applied as structural panels in the building industry. The blends are extruded in sheets which are shaped by vacuum forming and press molding. The PVC provides mechanical strength and flame resistance. The second component should provide the required heat distortion temperature and surface properties. The impact modification of PVC and its blends has been increased by using shell – core impact modifiers [41]. These modifiers consist of a very small rubber core, usually a butadiene homo- or copolymer or a poly(butyl acrylate) copolymer, and a "hard shell" made of PMMA or SAN. The shell polymers should have optimal interaction with the matrix PVC. These impact modifiers are not only very effective but also allow high shear processing without deterioration of surface appearance.

Since 1980, PVC and its blends have been able to penetrate the injection-molding market. This was made possible by (1) improving the flowability of PVC by an order of magnitude via reduction of its molecular mass, (2) a greatly improved stabilization package, and (3) improved thermal control in modern molding machines to prevent overheating.

The construction and pipe markets are supplied by PVC – chlorinated polyethylene blends (preferred in the United States) and PVC/EVA blends (preferred in Europe). Both blends have better impact properties than PVC. EVA blends have a slightly better UV stability.

PVC – polyurethane blends are typically used in shoe soles, boots, oil-resistant articles, and calendered coatings by virtue of their UV stability, better thermal stability, and low temperature flexibility.

The additions of small amounts of methyl methacrylate (MMA) copolymers to PVC improves its hot melt strength and reduces melt fracture during processing. Toughness and impact performance can be further improved by blending with MMA-containing impact modifiers. Applications include clear films and window profiles.

4.3. Styrene Polymers and Copolymers

See also → Polystyrene and Styrene Copolymers.

Polystyrene. Polystyrene [9003-53-6] (PS) is a very brittle polymer (T_g 100 °C) due to a low entanglement density and lack of secondary transitions. Its usefulness has therefore been limited severely. Poor impact performance has been a major concern and was originally addressed by blending PS with styrene – butadiene (SBR) rubber and subsequently by the now generally established chemical processes for making high-impact PS (HIPS). The block copolymer styrene – butadiene (SB) and terpolymer styrene – butadiene – styrene (SBS) as well as their hydrogenated derivatives, are used as blend components to improve impact properties [36]. The resulting deterioration of the continuous use temperature (T_g reduction by at least 10 °C) can be solved by either making copolymers of styrene with stiffer or more polar comonomers such as α-methylstyrene, maleic anhydride, acrylonitrile, or by blending with a miscible high-T_g polymer such as poly(tetramethylbisphenol A carbonate) or PPE (see Section 4.5). Blending relatively small percentages of PPE (< 30 %) with PS can be important because it increases the heat distortion temperature by about 1 °C per percent PPE. The mechanical deformation behavior of the blends is also greatly improved by the strong increase in the overall entanglement density. The overall property profile of pure PS is not good enough to make it an interesting blend component for a two-phase system.

PS – polyolefin blends have been developed for packaging purposes bringing the combination of printability, fat resistance, and barrier properties. They again have a controlled delaminated morphology and are typically extrusion materials. However, the more polar and functionalized PS copolymers offer far better blend possibilities and are widely used and discussed below.

ABS. See also → Polystyrene and Styrene Copolymers. Most commercial acrylonitrile – styrene – butadiene polymers [9003-56-9] (ABS) are blends of rubber-impact-modified styrene – acrylonitrile (SAN) copolymer with

SAN or other SAN-miscible copolymers. Blending can take place in a suspension or emulsion by coagulation or melt blending during the compounding phase. ABS can be produced by three different techniques: emulsion, suspension, and mass (bulk) polymerization [43], [43]. Each technique delivers ABS with slightly different properties.

The main properties of ABS resins are their good to very high impact strength and low price, coupled with very acceptable mechanical (engineering) properties up to 90 °C. They have an excellent surface appearance and good chemical resistance. In addition, they possess the excellent injection-molding behavior of PS, good melt flow, low mold shrinkage, and an excellent surface finish. Their main disadvantage is their poor resistance toward prolonged exposure to light and heat due to the unsaturated bonds in the butadiene rubber impact modifier systems. UV resistance can be improved by incorporation of acrylic rubbers (ASA). Principal advantages of ASA (SAN grafted onto acrylic rubber) over ABS are high outdoor stability, high resistance to yellowing on exposure to UV light, and good resistance to environmental stress cracking [43]. Other essentials of ABS are its composition-dependent T_g (100 – 120 °C) and a continuous use temperature between 80 and 100 °C. The actual use temperatures for ABS can be enhanced up to 118 °C through the incorporation of α-methylstyrene. Its high flammability can be improved by addition of 10 – 15 % bromine-containing compounds and 3 – 5 % antimony trioxide. This results in a higher density, reduced color intensity, lower surface properties, reduced impact performance and processibility, and corrosivity. Blending is a preferred method used to increase the heat distortion temperature, to improve weatherability (unsaturated impact modifiers), and overcome flammability concerns.

ABS – PC and ASA – PC Blends. These blends offer a somewhat higher heat distortion temperature than ABS and good processing characteristics [43–45]. The Vicat softening temperature of 100 °C for ABS can be raised to 130 °C by blending with PC. The carbonate group of the PC and the nitrile group of the SAN matrix interact [46], providing just enough compatability for a useful blend. Optimum interaction between the polymers is obtained for a SAN containing 30 wt % acrylonitrile [46]. Intrinsic compatibility can be enhanced through addition of a third component containing ester groups (e.g., PMMA or PBT) [47], an effect that can be explained in terms of mutual miscibility.

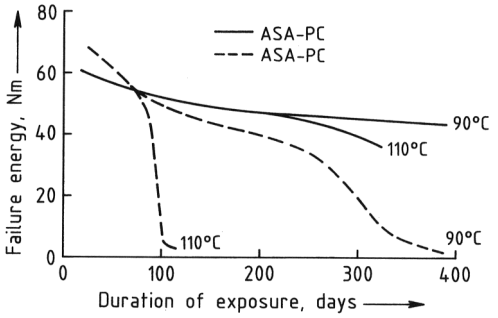


Figure 12. Failure energy of ASA – PC and ABS – PC as a function of the duration of exposure to heat

ASA – PC blends offer a better resistance towards UV light and heat aging compared to ABS/PC (Fig. 12). Applications include instrument panels, distribution boxes, and kitchen exhaust hoods [48].

ABS – PVC Blends. ABS has excellent surface properties with high gloss, but burns readily and completely. PVC (T_g 85 – 95 °C) on the other hand lacks the good impact behavior and processibility of the styrenics. An excellent interaction exists between PVC and ABS, removing the need for compatibilizers. ABS – PVC blends are used in low-cost electrical panels such as covers and enclosures [7].

SMA – ABS Blends. Copolymers of styrene and maleic anhydride (SMA) have glass transition temperatures ranging from 100 to 140 °C, depending on the maleic anhydride content. The materials are rather brittle, but impact-modified resins are known. Impact performance can be improved by blending with ABS. Both resins are compatible and have a good processibility (styrenics). The miscibility window is remarkably small considering the similarity in structures [49]. Instrument panel frames is a large automotive application.

ABS – PA Blends. Both chemical resistance and heat distortion temperature can be improved by blending ABS with semicrystalline

polyamides. Typical applications are automotive body panels, connectors, and under-the-hood components [7], [48]. See also Section 4.4.

4.4. Polyamides

Polyamides (PA) are either semicrystalline or amorphous. The polymer chain can consist of aliphatic, cycloaliphatic, and aromatic components. More than 60 different commercial polyamides are known. For further details, see → Polyamides.

Examples are included of the two most important general-purpose polyamides: (1) PA 6 [25038-54-4] made by ring opening polymerization of ϵ-caprolactam, and (2) PA 66 [32131-17-2] made from hexamethylenediamine and adipic acid. These aliphatic PAs are mostly used for their combination of wear resistance strength, chemical resistance, creep resistance, and low coefficient of friction. Good dimensional stability can only be obtained for (glass) filled materials which have the disadvantages of warpage and machine wear. Polyamides have a good strength and fatigue resistance. Tensile modulus values of the matrix can be increased by incorporation of aromatic monomers in the main chain. The fully aromatic PAs have a high intrinsic flame retardance. Decomposition temperatures for most aliphatic and aliphatic – aromatic PAs, are 280 – 300 °C, limiting the processing temperature.

The properties of PAs are highly dependent on the interactions of the polar amide linkage. Higher-melting PAs can be obtained by increasing the frequency of amide linkages [50]. The amide linkage interaction between the polymer chains in the crystal structure via hydrogen bonding is particularly strong in the amorphous phase. It also causes water absorption which is related to the methylene – amide ratio. Water absorption decreases the dimensional stability of the polymer, reduces the T_g (plasticizing effect), but increases the toughness. The magnitude of the T_g reduction with respect to relative humidity changes depends on the amount of amide linkages and stiffness of the chain. A major drop in tensile modulus at room temperature results when the T_g drops from 50 to below 0 °C. Other physical properties (e.g., dielectric constant, water permeability) also change considerably.

There are three major reasons for blending PAs:

1. To increase their heat distortion temperature (in a conditioned state)
2. To reduce their moisture sensitivity and thus enhance dimensional stability
3. To improve their dry impact strength (at low temperatures)

Polyamides are very suitable for in situ compatibilization techniques (reactive extrusion) due to the presence of reactive amine or carboxyl end groups. Carbonamide groups are also available for hydrogen bonding.

PA – PA Blends. Melting points of semicrystalline PAs are sometimes very close to their degradation temperatures, creating either a very small or no processing window. Blending aromatic semicrystalline PAs with aliphatic PAs improves their processibility. Aliphatic PAs generally have lower T_gs, but a higher water absorption value which can lower the T_g in the dry state significantly. Aromatic PAs possess more free volume, and have a lower dimensional growth with the same water absorption.

Blends of amorphous transparent PAs have been reported [51]. Predictions of miscibility windows between PAs using binary interaction and intramolecular repulsion models proved that the amide concentration was more important than compositional differences [52–54].

PA – ABS Blends. Blends of PA 6 and PA 66 with ABS combine chemical and abrasion resistance with high impact resistance. The ABS phase provides good dimensional stability up to 90 °C that can be further improved by substitution of styrene in the ABS with α-methylstyrene [55]. These blends are also more warp resistant due to the reduced (semi)crystalline volume fraction. Compatibilization is achieved through hydrogen bonding between amide NH and nitrile CN groups. Anhydride-containing polymers such as SMA have been used to improve compatibilization by covalent bonding and to obtain a smaller particle size [56].

Triax 1000, (Monsanto) is an example of a PA – ABS blend. It is used for a variety of

markets such as functional (mainly under-the-hood) automotive components, power tools, appliances, and sports goods. PA – ABS blends have excellent chemical resistance, stress resistance, and toughness due to their co- continuous network.

PA – PC Blends. Blends of PA 6 and PC have been investigated over the full range of compositions, and proven to be immiscible [57]. Chemical reactions are claimed to produce low molecular mass compounds that both plasticize and slightly compatibilize the blend. No commercial PA – PC blends have yet been developed.

PA – PP Blends. Blending PAs with PP raises impact strength, solvent and moisture resistance, and improves strength [34]. The addition of compatibilizers and/or glass fibers is required to obtain a blend with a stable morphology. Compatibilizers are formed in situ by using maleic anhydride-functionalized styrene – ethylene – butadiene – styrene (SEBS) triblock copolymers [58], [59], ethylene – propene copolymers, PP, HDPE, or glycidyl methacrylate copolymers [60] in concentrations of 1 – 30 wt %. Maleic-anhydride-modified compatibilizer intermediates yield a better dispersion (with particle diameters in the range 0.1 – 0.3 μm) and high impact values. Interestingly, material toughness is not enhanced by using smaller rubber particles [59].

PP is usually processed at 200 °C, but PA – PP blends are processed at 250 °C — the presence of PP leads to a readily flowing resin. These resins are used for decorative applications where dimensional stability is much more important than mechanical properties. Examples include automotive applications, sprinkler housings, and housings for industrial tools.

Impact-Modified PA. The notch sensitivity of most PAs can be reduced by blending with 20 – 30 % functionalized impact modifier such as maleic-anhydride-functionalized HDPE [61], [62], or maleic-acid-modified EPDM rubber. PA 66 has an intermediate level of ductility, characteristic of a semicrystalline resin. Chain mobility is reduced by the presence of crystalline regions and relaxation times of polymers are increased. Impact modifiers are used to create overlapping stress fields (optimum conditions at 30 vol % impact modifiers) which enhance ductility [61]. Good adhesion is provided by the maleic anhydride functionalities on the impact modifiers.

The materials are used for all applications where ordinary PAs fall short of required impact strength and toughness: oil pans, fan blades, connectors, and power tool housings.

4.5. Poly(2,6-Dimethyl-1,4-phenylene Ether)

Poly(2,6-dimethyl-1,4-phenylene ether) [25134-*01–4*] (PPE) and its blends have been extensively reviewed elsewhere, → Poly(Phenylene Oxides), but will be briefly summarized. PPE is an amorphous resin (T_g 215 °C) with a number of attractive properties [63]. It has a serious drawback however: its (melt) processing temperature is higher than temperatures at which severe side reactions take place, thus altering the polymer property profile.

PPE – HIPS Blends. The full miscibility of PPE with PS, discovered in the early 1960s [64], [65], led to the development of blends with lower (and thus acceptable) processing temperatures. Polystyrene has a low T_g and good melt processibility.

PPE – PS blends are fully miscible over the complete composition range as illustrated by a single T_g for each composition. This provides the end user with a tremendous flexibility in achieving required maximum use temperatures. Resulting heat distortion and Vicat B temperatures are discussed in [63], → Poly(Phenylene Oxides).

The miscibility of PPE with styrene copolymers and polymers of styrene derivatives, e.g., poly(α-methylstyrene) [64–66] has been studied. Many of these blends also demonstrate full miscibility, probably due to the interaction of the electron-deficient methyl groups of PPE with the electron-rich phenyl rings of PS [63], [67]. The reduction of impact performance of the ductile PPE by blending with brittle PS (Fig. 13) can be attributed to a reduction of the entanglement density and some loss of free volume [63], [67]. Impact performance is

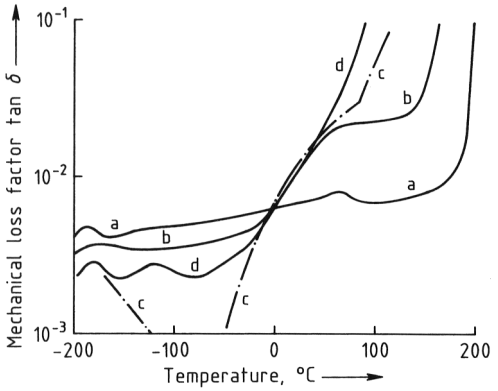


Figure 13. Impact strength of PPE – PS blends as a function of temperature a) PPE; b) PPE – PS (70 : 30); c) PPE – PS (30 : 70); d) PS

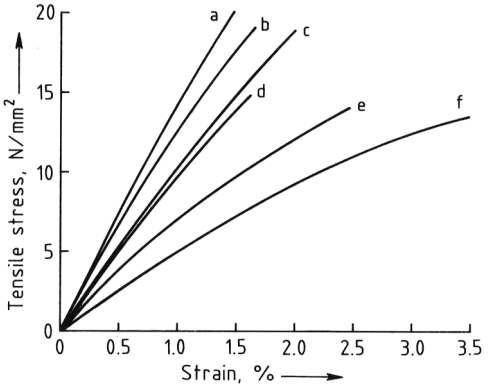


Figure 14. Creep behavior of PPE – PA 66 (Noryl GTX 900) at 23 °C and 50 % RH a) PPE – PA 66, 1 h; b) 100 h; c) 5000 h; d) PA 66 1 h; e) 100 h; f) 5000 h

greatly improved by incorporation of impact modifiers. Thermograms of commercial blends have two glass transition temperatures, with one of them being attributable to the rubber impact modifier [68].

Impact strength increases with PPE molecular mass. Commercial PPEs have weight-average molecular masses in the range 30 000 – 40 000. The rubber particle size is also important. Since their commercial introduction in 1964 by General Electric, PPE – HIPS blends have become the engineering polymer blends with the largest annual sales. They are used for applications ranging from automotive interior parts including dashboards and instrument panels, to business machine housings and chassis; from electrical conduits and lighting covers to gears and sprockets.

PPE – PA Blends. PPE – PA 6 and PPE – PA 66 blends have been extensively discussed elsewhere, see → Poly(Phenylene Oxides). In these blends, the finely dispersed PPE phase raises the continuous use temperature. The tensile modulus is maintained up to almost 205 °C with only a minor drop over the temperature range from 0 – 50 °C due to the T_g of the amorphous PA phase. The moisture sensitivity of the system is also reduced. The PA 6 and PA 66 phases provide easy processibility and chemical resistance. These PAs can be easily replaced by PAs with higher glass transition and melting temperatures [69–71]. Rubbery impact modifiers have been added to improve low-temperature impact performance [69–71]. These blends exhibit mechanical properties which are less moisture-sensitive than PA 66 as shown by the stress – strain curves (Fig. 14). At a stress level of 7 MPa, PA 66 exhibits three times as much creep as the PPE – PA 66 blend.

Blends of PPE and PA have been specifically developed for exterior automotive parts with a Class A surface quality (e.g., fenders of the Renault Clio 16 S). Other applications are rear quarter panels, and hood materials for lawn and garden tractors.

PPE – Polyolefin Blends. The usefulness of unmodified PPE is limited by its notch sensitivity and difficult melt processibility. Addition of polyolefins improves flow by modifying the melt rheology of the system but sometimes lowers the heat distortion temperature. New blends have been developed in which PPE is combined with special rubbers (e.g., high molecular mass polyoctanomer [72], [73]) that have a high impact strength, a high softening temperature up to 205 °C, and facile processibility. These PPE – polyolefin blends have a high gloss and are used in metallizable head lamp reflectors. Other application areas are dimensionally stable exterior automotive body panels, and major appliances.

The intrinsic flame retardancy of PPE has been enhanced with additives resulting in a new, halogen-free, flame-retardant material that

meets the most stringent low smoke [73], low toxicity, and low corrosivity standards. The key factor is increased char formation under fire conditions which reduces the amount of volatiles [73]. Potential applications of this material (Noryl Xtra LS) are in office buildings, trains, and tunnels.

4.6. Polycarbonates

The polycarbonate of bisphenol A [25037-45-0] (PC) is a linear polymer with a low rate of crystallization. See also → Polycarbonates. Thus, it is regarded as an amorphous polymer (T_g ca. 145 °C). Its maximum use temperature is approximately 130 °C and, because of its excellent thermal oxidative stability, this almost coincides with its continuous use temperature (125 °C). PC is noted for its high impact resistance, especially at low temperature. This is due to the high segmental mobility of the polymer chain (gamma transition at − 100 °C [74]). Polycarbonate suffers from stress – crack sensitivity coupled with poor chemical resistance. The latter prevents PC from being used in automotive applications where frequent contact with gasoline and oils would ruin its material properties. Chemical resistance can be improved by blending with semicrystalline polyester resins. The stress cracking sensitivity of PC can be overcome by blending with ABS or ASA.

PC – Polyester Blends. The advantages resulting from blends between PC and PBT are summarized in Figure 15. Blends of PC with polyesters are based on a partial miscibility of both components in the amorphous phase

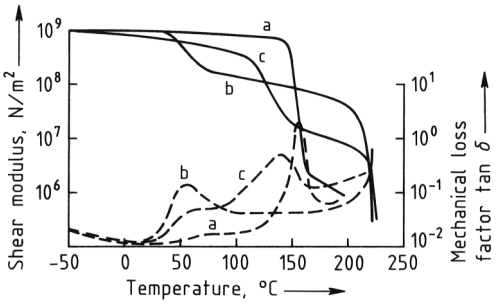


Figure 16. Dynamic mechanical properties of PC, PBT, and PC – PBT blends : shear modulus (————) and mechanical loss factor (– – –) as a function of temperature a) PC; b) PBT; c) PC – PBT (55 : 45)

[75–77]. Thermal and dynamic mechanical analysis shows a sharp T_g transition for PC at 150 °C (Fig. 16), and a sharp melting point at 225 °C with a broad glass transition for PBT due to the spectrum of relaxation times of the crystal – amorphous polymer interphase. Partial miscibility of PC and PBT is indicated by a shift of the PC T_g to 141 °C in a PC – PBT blend.

Blending both resins results in a complex co-continuous morphology. Resistance towards chemicals (e.g., oils and lubricants) is strongly enhanced as compared to PC. However, the impact properties of these blends are still insufficient for automotive applications. Impact modification with a rubber compound (frequently core – shell impact modifiers) solves this problem [78], [79].

The key to morphology control and thus mechanical properties is control of transesterification. Care should be taken to prevent these reactions (Figs. 17 and 18) catalyzed by residual

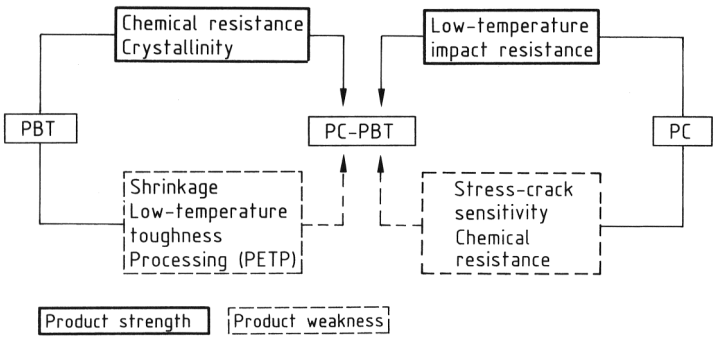


Figure 15. Blend motives for PC and PBT

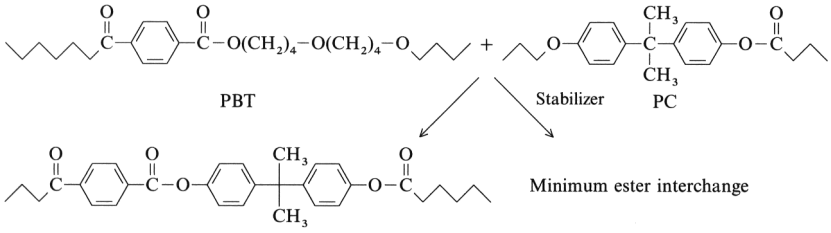


Figure 17. Ester interchange between PC and PBT

polycondensation catalysts present in the PBT [79–81]. Addition of proprietary additive packages is commonly practised. In addition, processing temperatures of 270 – 290 °C should not be exceeded.

One of the most successful applications of the blend of PC, PBT, and impact modifier (Xenoy, GE Plastics) is a car bumper, developed for the Ford Sierra in Europe, and transferred to the Ford Escort in the United States. This bumper withstands 5 km/h impact at high and low temperature.

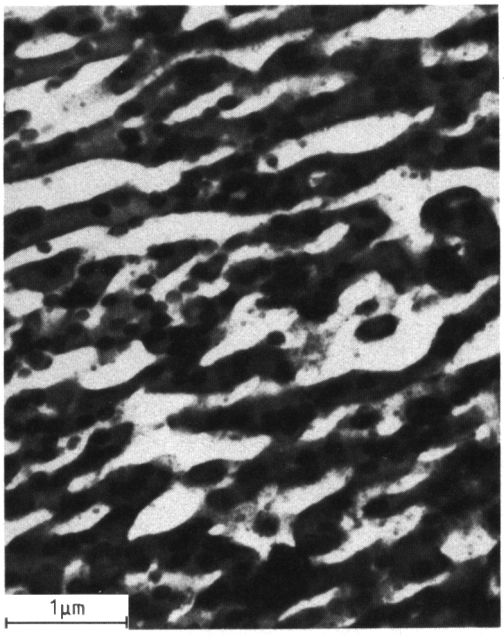


Figure 18. Morphology of impact-modified PC – PBT blend (Xenoy, GE Plastics)
The darker areas are PC, the black dots are impacted modifiers, the remainder is PBT.

PC – PETP blends have similar properties to their PBT analogs [7], [82], [83]. The lower crystallization rate of PETP allows the development of transparent materials for use in medical applications by virtue of their good dimensional stability, clarity, and low water absorption. The products have a better chemical resistance than PC and are impact modified to give acceptable low-temperature impact performance. PC –PETP blends flow better than PC, and are injection-moldable. Unreinforced PETP cannot be injection molded due to its low rate of crystallization.

PC – Polyolefin Blends. Despite its good toughness, PC has a distinct ductile to brittle transition which is dependent on temperature, thickness, test speed, stress configuration, and molecular mass. The dependency is reduced if PC is blended with low levels (4 – 8 %) of LDPE. This shifts the ductile – brittle transition of PC from about 0 °C to below − 20 °C. Moreover, the effect of part thickness on notch Izod impact strength is reduced [84].

PC – ABS Blends. Polycarbonate blends with ABS resins have been successfully used in automotive interior and exterior applications [85], [85]. The acrylonitrile content of the ABS plays a key role in determining the miscibility of the SAN phase with the PC phase. ABS has no low-temperature impact performance, whereas PC does through its gamma transition at − 100 °C and ample free volume [74]. The impact values of PC – ABS blends are directly correlated with their heat distortion temperatures. The presence of the rubbery impact modifier slightly reduces the tensile modulus. The HDT values are hardly affected at modulus values above 3 GPa. These are important values

because they are required for high-speed impact tests for automotive applications. In addition, PC – ABS blends provide paintability and better UV stability if PC is the continuous phase [86–89]. The addition of UV absorbers to the (transparent) PC phase improves the protection of ABS against the damaging effects of UV light (see Section 4.3). PC –ASA blends have superior weather resistance, however.

PC – ABS swells in aromatics, ketones, esters, and hydrocarbons. It has good electrical insulating capability. Major applications are instrument panels [7] and business equipment housings [90].

4.7. Polyesters

Thermoplastic polyesters have a low moisture absorption and are chemically resistant apart from being susceptible to hydrolysis at high temperature in alkaline environments. They have a low dimensional stability due to their low T_g; glass-filled materials are required to achieve acceptable use temperatures. Impact performance for these highly filled materials is poor, but can be improved by blending with impact modifiers. The most important polyesters are poly(ethylene terephthalate) [25038-59-9] (PETP) and poly(butylene terephthalate) [24968-12-5] (PBT). See also, → Polyesters PBT crystallizes within 1 – 3 s whereas PETP crystallizes within 15 – 20 s. PBT's higher melt flow and faster crystallization lead to a shorter cycle time. Special processing conditions are required if (partially) crystalline PETP is to be obtained: high mold temperature (120 – 140 °C) and long cycle times (2 min). The advantages of PETP over PBT are its higher melt temperature (256 vs. 226 °C) and strength.

PBT – PETP blends have enhanced surface quality and reduced warpage when reinforced with glass fibers. Both qualities are attributable to the lower rate of PBT crystallization caused by the addition of PETP. The weight ratios used in PBT – PETP blends are usually 85 : 15 to 75 : 25. HDT values are not affected, but costs are reduced due to the lower price of PETP. Typical ap-plications include hot-appliance housings (e.g., toasters, irons, and frying pans).

PBT – PC Blends. Addition of PC to glass-filled PBT grades increases impact strength values and improves thermal expansion, flow, and flatness (reduced warpage). The chemical resistance of these blends is slightly lower than that of a PBT compound. Core – shell impact modifiers are used for toughening [78], [79], [91]. The importance of interfacial adhesion with the matrix has been proven [91], [92]. Applications include grill doors, air cleaners, and appliance components where improved dimensional stability over PBT is required.

Miscelleneous Polyester Blends. Noteworthy are blends of PBT with copolyester elastomers containing short crystallizable PBT blocks [93]. The tensile strength and modulus of these compounds are increased upon blending with PBT while retaining its flexibility. Excellent surface quality and improved paint adhesion qualify these resins for bumper fascias. Similar uses hold for PETP – acrylic and PBT – acrylic materials. Toughened PBT and PETP blends are used to extend existing product lines by varying the amount and type of impact modifier. Ignition compounds, housings, and windshield wipers are typical automotive applications; flame-retardant grades are used for connectors and switches.

4.8. Polyetherimides

Polyimides are condensation polymers derived from bifunctional carboxylic anhydrides and primary diamines. Polyetherimides [61128-24-3] (PEI) contain an ether group in either or both the aromatic dianhydride or aromatic diamine building block. Ultem polyetherimide (GE Plastics) produced from bisphenol A bisether dianhydride is the only commercially available thermoplastic polyetherimide [94] (see also → Polymers, High-Temperature). It has a glass transition temperature of 217 °C, and can be subjected to conventional melt-processing techniques. Its thermal stability is maintained up to ca. 500 °C under nitrogen [95].

In commercial PEI grades, additives (e.g., reinforcing fibers) and modified base resins are used to increase the glass transition temperature and chemical resistance. Primary reasons for blending are therefore to improve processibility,

impact strength, and chemical resistance. PEI is used mainly in under-the-hood automotive applications, head-lamp reflectors, injection-molded printed circuit boards, trays for microwave ovens, and high-performance composite sheets with PEI as the matrix.

PEI – PC Blends. PEI – PC blends combine the high temperature resistance and intrinsic flame retardance of PEI with the good impact performance and ease of processing of PC. Interactions are strong enough to form an excellent blend without using compatibilizers. The high continuous use temperature of PEI is not decreased because PC is stable to thermal oxidation up to ca. 175 °C. Blending with PC reduces the price of the material and its notch sensitivity.

Two grades of PEI – PC thermoformable sheets exist, one is targeted to household applications (e.g., Tupperware microwave cookware), the other to aircraft interior components where the material satisfies all regulations pertaining to flammability, smoke, and toxicity. PEI – PC is used for aircraft window housings and seat backs.

Thermoformable PEI – PC products are also used as high-temperature paint masks in the automotive industry to prevent overspray. The high heat resistance and excellent dimensional stability enable the material to withstand the temperature conditions in the painting operation.

PEI – PEEK Blends. PEI is an amorphous resin. Its chemical resistance can therefore be improved by blending with a semicrystalline resin. PEI is miscible with the amorphous phases of polyetherketone [27380-27-4] (PEK) and polyetheretherketone [31694-16-3] (PEEK) over the entire composition range. Crystallinity and crystallization are not affected by incorporation of up to 40 wt % PEI [96]. The product range of these materials can be further enlarged by copolymerization of the PEI structure leading to enhanced inherent properties.

Markets for PEI – PEK and PEI – PEEK blends have not yet been fully exploited [97]. A 70 : 30 PEI – PEEK grade developed by Amoco Performance Polymers was not commercialized due to competition with the liquid crystalline polymer Xydar [7].

4.9. Polysulfones

Polysulfones [25135-51-7] (PSU) and polyethersulfones [25667-42-9] (PES) are amorphous high-T_g polymers with excellent thermal and oxidative stability (see also, → Polymers, High-Temperature). Their environmental stress-cracking resistance against most liquids encountered in the food and automotive industries is good because of the polar sulfone group.

Polysulfones are, however, expensive, demonstrate a severe notch sensitivity, and have a limited chemical resistance resulting in stress cracking sensitivity under certain conditions. Both problems can be overcome by blending with ABS (Fig. 19), PAs, PETP, and PBT.

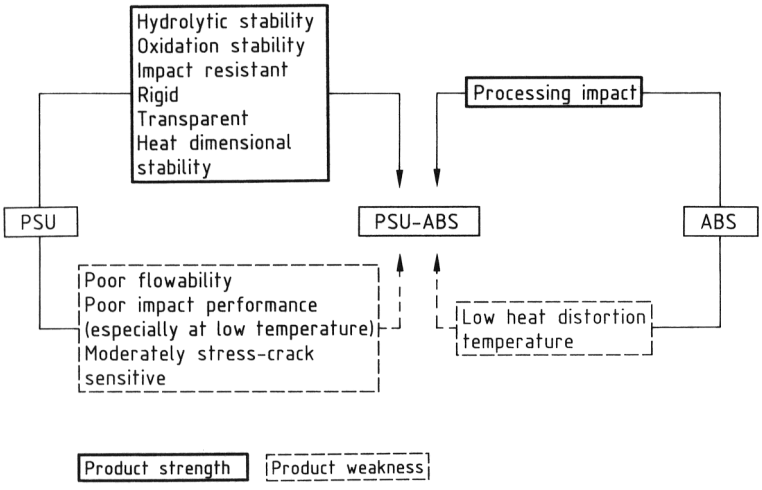


Figure 19. Blend motives for PSU and ABS

Chemical resistance is strongly improved if the semicrystalline resin constitutes the continuous phase. The principles and objectives followed for developing these blends are the same as those for PC – ABS, PC – PETP, and PPE – PA blends. Polar interactions are possible between the carboxyl groups of PSU and the nitrile groups of ABS.

Applications include household water faucets, electric, and electronic applications. PSU – PBT replaces PBT in selected connectors and switches due to its higher strength [7], [48].

4.10. Polyoxymethylenes

Polyoxymethylene [9002-81-7] homo- and copolymers are highly crystalline materials well known for their hardness, low friction coefficient, chemical stability, and relative brittleness; see also → Polyoxymethylenes. They are highly flammable (LOI 16) and their thermal stability is limited to 210 °C. In view of their melting temperature of 182 °C (homopolymer), careful processing is required.

Blends of polyoxymethylene homo- and copolymers are known. Silicone oils and polytetrafluoroethylene have been added to POM to enhance the high slip characteristics. Impact-resistant grades of POM use polybutadiene, acrylic rubber, grafted synthetic rubber, polyolefins, and polyurethane [98].

Impact-resistant POMs, comparable to super-tough nylon, have been produced by blending with compatible linear thermoplastic polyurethanes. They demonstrate a special morphology since the polyurethane phase forms an interpenetrating network structure in the POM matrix.

Applications are hinges and connectors that demand improved low-temperature flexibility and impact strength.

4.11. Polyarylates and Copolyarylate – Carbonate Blends

In principle the polyarylates (PAr) comprise all fully aromatic polyesters. In practice this term denotes polyesters derived from bisphenol A and mixtures of isophthalic and terephthalic acids in ratios between 70 : 30 and 30 : 70, but most frequently 50 : 50 [99], [100]. Due to their fully aromatic structure, the PArs are amorphous, transparent, practically colorless, and heat resistant. The T_g of the commonly used PAr containing bisphenol A and isophthalic/terephthalic acid in a weight ratio of 50 : 50 is 184 °C. This polymer is soluble in chlorinated hydrocarbon solvents, has a reasonable hydrolytic stability, good mechanical properties, strength, modulus, impact resistance, and excellent weatherability (despite yellowing). The polyarylates are intrinsically self extinguishing in flammability tests [101], [102]. Processibility is, however, marginal in view of the high processing temperatures (320 – 360 °C) required. Copolyester carbonates (PPCs) have therefore been developed with T_g's between those of PC (145 °C) and PAr (184 °C). PPCs are aromatic copolyesters in which part of the ester groups are substituted with carbonates. This group of polymers fills the T_g gap which existed between PC and the polysulfones [103].

Polyarylates are mainly used in applications demanding high heat stability and transparency such as lenses and medical equipment (high-pressure steam and radiation resistance needed for sterilization). Since the ultimate thermal dimensional stability of polymers under loading conditions is determined by the T_g of the matrix polymer, polyarylates and copolyarylates contribute significantly to the engineering property profile of blends.

Many PAr blends, especially those with semicrystalline aliphatic – aromatic polyesters such as PETP, PBT, and poly(cyclohexane terephthalate) (PCHT) have been made but very few have been successful. These polyester – PAr blends show the same features as the polyester – PC blends. PETP and PBT blends are partly miscible with PAr, whereas PCHT is completely miscible over the whole composition range. Furthermore, under melt-processing conditions, transesterification reactions catalyzed by polymerization catalysts rapidly transform the physical blend into a homogeneous copolymer with an averaged T_g value. Only by adding phosphites can the catalytic system be deactivated, yielding a usable blend with different characteristics from the existing PPCs. This holds particularly for the PETP and PBT blends. The ester interchange reaction does not need to be stopped in PAr – PCHT blends due to its complete miscibility [104–107].

PETP – PAr blends are used in the automotive industry for their improved chemical resistance and heat distortion temperature over PC and PC – PETP blends. They are also used in the lighting industry for reflectors. PCHT – PAr blends are used in medical applications because they have a very good resistance to yellowing when exposed to high-energy radiation for sterilization [103].

4.12. Poly(Phenylene Sulfide)

Poly(phenylene sulfide) [9016-75-5] (PPS) is a versatile thermoplastic engineering resin (see → Polymers, High-Temperature, Chap. 5.). It possesses high temperature resistance, inherent flame resistance, good mechanical properties, and high chemical resistance. The mechanical properties and dimensional stability of parts are determined by the crystallinity and orientation of the polymer during processing. Unfortunately, PPS is very brittle resulting from stiff spherulites and weak interspherulitic boundaries. Research is therefore directed at improving ductility while maintaining overall crystallinity levels.

Two types of PPS are commercially available: (glass) filled grades and blends with polytetrafluoroethylene (to improve moldability and crack resistance). A large number of other blends have been reported (e.g., PPS – PEI [108] and PPS – PETP [109]) but have not been introduced commercially.

5. General Application Technology

5.1. Processing of Blends

The utilization of thermoplastics, including blends, involves processing and adjustment of the bulk rheological properties of each commercial plastic grade to the requirements of the processing technique (e.g., injection molding, extrusion, blow molding). Adjustment is only possible if an acceptable processing window exists within the molecular mass constraints of the polymers which are needed to obtain the desired mechanical properties. The processing window is determined by the thermal stability and the processibility (viscosity) of the melt. In blends, the maximum melt temperature is determined by the stability of the least stable component.

The rheology of a blend system is determined by its components. Blend processibility can only be predicted to a limited extent. The rule of logarithmic additivity only applies to completely miscible systems of homologous polymers such as mixtures of the same polymer with different molecular masses (Eqs. 10 and 11), all functions having a molecular mass > entanglement molecular mass.

$$log\eta_b = \Phi_1 log\eta_1 + \Phi_2 log\eta_2 \tag{10}$$

$$\eta_b^{1/3.4} = \Phi_1 \eta_1^{1/3.4} + \Phi_2 \eta_2^{1/3.4} \tag{11}$$

where η is the viscosity, Φ is the partial volume, and the subscripts b, 1, and 2 denote the blend, component 1, and component 2, respectively.

Even for a completely miscible blend system (e.g., PPE – PS), corrections have to be made for the "positive deviation" which is associated with the mixing enthalpy (Eq. 12):

$$log\eta_b = \Phi_1 log\eta_1 + \Phi_2 log\eta_2 - \frac{\Phi_1 \Phi_2 \Delta H_{mixing}}{2.45RT} \tag{12}$$

This enthalpy factor depends on the temperature (LCST behavior, Section 3.1). In miscible or partly miscible blends with processing temperatures close to the LCST temperature this can have extremely important effects, such as shear-induced phase separation (temperature rises due to the introduction of mechanical energy via the processing equipment) leading to complete loss of morphology and mechanical properties. Furthermore, the elastic and viscous parameters that depend on temperature and shear rate also contribute to the rheology characteristics of a polymer, and are different for each polymer.

In impact-modified multiphase blend systems, the prediction of the rheology characteristics by means of (empirical) rules becomes highly unsatisfactory. Simple approaches based on the Einstein relation for dispersions of solid particles in a liquid are followed by assuming that two-phase systems behave as a dispersion of fixed particles of different deformability (from solid to rubbery). In more complex two-phase blends where the morphology of

the dispersed phase is not fixed and delamination is possible, a combination of parallel and series model of rheological effects is used with an interfacial layer correction.

The impact modifiers interact strongly with the matrix to create a thixotropic melt behavior in which the viscosity value at zero shear rate is much higher than in the unmodified systems. These characteristics can be very useful in creating the higher melt strength needed for extrusion and blow molding. Their presence may, however, also lead to poor surface appearance and knitline problems under excessive shearing forces.

In conclusion, the rheology of polymer blends is extremely complicated to predict, but commercial products are tuned to the requirements of most standard processing methods. The tolerance level for deviation from the recommended processing conditions is not unlimited.

5.2. Design Technology

The design considerations of a thermoplastic part involves functional factors related to production and assembly, and material factors related to the performance of a material in service.

Design procedure can be subdivided into the selection of the production process (e.g., injection molding, extrusion), resin characteristics (mechanical and electrical properties), flow analysis, stress analysis, long-term considerations (creep, fatigue, stress relaxation), appearance of a part, its assembly (including automation), and recycling. Computer programs aid the designer in developing a part capable of meeting all the mechanical requirements, while maintaining its production feasibility [28], [110].

The current emphasis on recycling demands that produced parts can be easily disassembled from final applications. In the case of cars, routes for facile dismantling and separation should be conceived in the designing step (see Section 6.1). Product designers and engineers must therefore consider all aspects of the primary and secondary life cycles.

Blends require special consideration of flow (viscosity), weld lines, processing temperature versus phase behavior (see Section 3.1), flow versus continuous phase, and high shear conditions. Thermodynamically controlled, shear-induced phase separation is possible leading to delamination and morphology changes (Section 5.1). Care should be taken to avoid high shear conditions.

The dependence of viscosity and shear rate on temperature is also very important for blends because the ratios between the blend components influence blend morphology and determination of the continuous phase (see Section 5.1). Prediction of rheology and flow behavior is more complicated than for single thermoplastic resins. Weld lines are an issue at positions where two flows encounter each other [111]. Design should result in placing weld lines in nonstressed regions.

6. Future Developments

6.1. Recycling

Recycling of plastics and polymer blends has drawn public attention, see also → Plastics, Recycling. Concern regarding plastic waste has risen because of the large volume of plastics (20 – 30 %) in municipal waste. It corresponds, however, to a weight fraction of only 8 % for which packaging materials are mainly responsible. The volume of waste must be reduced, particularly in densely populated areas. Thermoplastic blend producers and end users are faced with finding commercially effective recycling strategies. This is particularly acute for the automotive industry in Germany, where recycling laws demand the recycleability of 25 % of plastic car parts by the end of 1994.

The use of smaller quantities of better, more durable blend products may or may not have a positive overall environmental effect. One of the solutions to the waste problem practised in Japan is energy recycling by burning (70 %) and deposition of solid waste (30 %). This simple solution will soon disappear in the western world for political and economic reasons — waste disposal will become very expensive due to increasing tariffs. Other options (i.e., reuse of plastics in other applications) must therefore be considered.

The most important factor in plastic recycling is the purity and compatibility of the waste. Minimum waste is generated in plastic manufacturing and compounding facilities due to economic reasons; reworking of plastic waste is a standard procedure. Separation of the different plastics used facilitates backfeed and rework programs. Multilayer coathanger extrusion and two-component molding facilitate the usage of off-color and slightly off-grade materials.

The real problem starts with postconsumer plastic waste where purity and compatibility requirements are no longer fulfilled. Separation, sorting, and cleaning of the plastic waste from the bulk waste are necessary. This is very expensive and only economically feasible for a small number of cases. Any recycled material derived from plastics with different colors and grades therefore represents a downgrade product. In addition, this approach will only succeed if the recycle concept is economically viable, e.g., in the case of high-value engineering plastics.

Reusing the chemicals from which the polymers were made is another route. Thermal, pyrolytic, hydrolytic, or glycolytic processes are used to degrade the polymers [112]. This approach is only applicable in a few cases and has been proven technically feasible with PETP bottles [112]. However, the process economics are very limited.

Finally, the fuel value of the plastics should be considered. Polymers have a considerable caloric value being (mainly) organic materials. The energy in the material can be reclaimed by burning and then converted to electrical energy or steam.

Already 20 % of all plastics used can be considered blends. Blend thermodynamics, morphology, and careful processing are critical for obtaining the required/desired mechanical properties (Chap. 3). Lower-grade applications should be found for recycled blends. Typical examples are blends of postconsumer PE with PA 6 [113], scrap rubber [114], and recycled PETP with PE [115], [116] and PC [117].

Two important principles govern the role of engineering blends in recycling strategies:

1. Designing and developing better, more durable products via blend technology.
2. Combining compatible resin systems (i.e., minimization of the number of different resins in a module for various applications). The target is to obtain materials from one product family which are mutually compatible (Section 3.2). Only these compatible materials can be combined to yield economically viable, useful materials (Fig. 20).

An example of a module is a dashboard structure made of a glass-filled, injection-molded PPE – HIPS blend, which could include, for example, a large proportion of recycle material from dashboards. The air ducting is made of compatible, blow-molded PPE – HIPS and is mounted on the carrier unit by means of PPE – HIPS clip fasteners. The complete unit is overmolded in PPE – PS foam to form the outer surfaces and to provide sound insulation. A soft-feel foil is used to give a "luxury" look.

This principle influences the material selection step of the design process. Functionality (i.e., good performance) and cost are no longer the most important selection criteria because they may lead to a combination of incompatible materials. Instead compatibility considerations dominate. The flexibility of blend technology allows the creation of materials that satisfy compatibility and use criteria. It is conceivable that concessions may be made regarding functionality, i.e., although not all requirements are met, certain materials are chosen to give the cheapest module costs.

Recycling materials after their life cycle involves several steps [118]: dismantling, transportation of parts to general assembly, cleaning, processing of reground material into an application. The most important issues are identification of the numerous blends in similar applications, definition of separation procedures in which contaminants are removed, and facile disassembly steps during designing. Costs involved with collection, separation, cleaning, and reprocessing materials mean that this is only a viable concept for blends of engineering plastics with their high property level and high profit margin.

The cascade model (GE Plastics) envisages a cycle of applications for a material in keeping

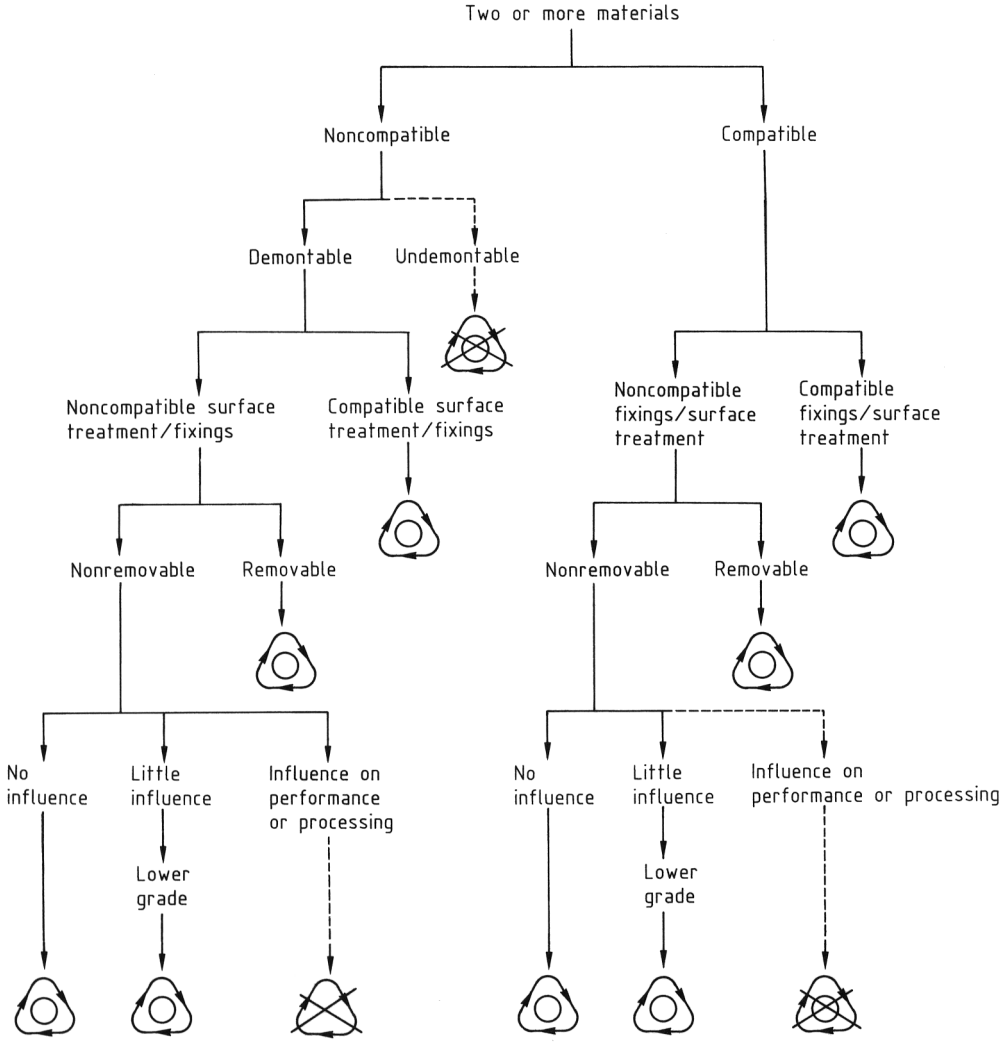


Figure 20. Generalized scheme illustrating the importance of resin compatibility in recycling

with the deterioration of mechanical and other properties.

Developments are under way to compatibilize the coatings, paints, and other materials used for aesthetic purposes with the main component.

Examples of cascade models for thermoplastics employed by Opel combine PP from battery cases and bumpers to make new fender liners, bumper carriers, and air-filter housings, and convert PC – PBT from old painted bumpers into new spoiler supports [119].

6.2. New Developments

Several promising new developments can be mentioned. PPE – PS blends are used to make expandable beads, which give strong low-density (down to 20 g/dm^3) foams with a heat distortion temperature > 100 °C, i.e., a sterilizable, re-usable material [120].

The use of PPE as an organic, heat-resistant, flame-retardant filter that does not affect mechanical properties at high filling ratios has been demonstrated for PA – PPE blends, and

can be applied to other blend systems. These new blends include a PPE – PBT blend under development (trade name Gemax, GE Plastics), which has an even lower moisture absorption and thus higher dimensional stability than PA – PPE [121]. The material is targeted for automotive and appliance markets. Blends of chemically modified PPEs will also find increasing use.

Hybrid systems are related blends and consist of thermoset networks filled with heat-resistant engineering thermoplastics [122]. High-performance thermoset materials are used in structural applications where dimensional stability is of the utmost importance. Their temperature stability is determined by the glass transition temperature, whereas their mechanical stability above this temperature is controlled by the network density. Stiffer, more heat-resistant materials can be obtained by using stiffer building blocks or increasing the network density. However, this also increases the brittleness.

Incorporation of heat-resistant engineering thermoplastics improves impact behavior while maintaining dimensional stability at high temperatures. Dissolution of these resins in epoxy systems allows easy processing. The thermodynamically controlled phase separation that takes place during the curing of the epoxy resin leads to a high flexibility in controlling the ultimate network density and thus mechanical properties. Commercially available materials include PEI – epoxy systems (Brochier, France) [123–125] intended for metal-laminating structures in the aircraft industry, and PPE – epoxy systems (General Electric, USA) [126], [127]. The latter systems provides another solution to the poor melt processibility of PPE (Section 4.5); it combines the low viscosity and easy processibility of thermosets with the toughness of thermoplastics. A commercial product (Getek, GE Electromaterials) is used as a circuit board material, the presence of PPE allows compliance with highly demanding techniques used for surface mounting and impedance control. A commercially available PPE has been functionalized with head and tail groups to provide optimal adhesion between the PPE phase and final cured epoxy resin. The PPE volume fraction determines whether the product is an epoxy-filled PPE matrix or a continuous epoxy matrix with a highly dispersed PPE phase.

A new reactive polymer system is based on oxazolines. Copolymers of styrene with a functional oxazoline monomer can react with carboxyl-, amino-, or anhydride-functional polymers to produce graft copolymers [128]. This reactive PS has been used to compatibilize the combination of PPE and an ethylene – acrylic acid copolymer, producing a high-impact engineering blend with excellent strength and processing properties.

Also new are blends of thermoplastics with 5 – 25 % liquid crystalline polymers. The resulting "molecular composite" can be regarded as a material in which the rigid crystalline polymers are reinforced at a molecular level. Liquid crystalline polymer blends have been reported for PC [129], [130]; PEI [129]; PP [131]; PBT [132]; PPE – PS [133]; ABS [134]; PSU [135]; PETP [136], [137]; and PA 6 [138]. These blends can be processed by conventional techniques such as extrusion, injection molding, and fiber spinning. Nearly all combinations of liquid crystalline polymers lead to an immiscible polymer blend. Consequently the mechanical properties of the blends are determined by the morphology of the liquid crystalline polymer domains in the thermoplastics. This morphology depends on composition, processing conditions, viscosity ratio of the component polymers, and the rheological characteristics.

Efforts are being made to use more biodegradable plastics for packaging. Commercial blends of PE with starch have been introduced by Feruzzi. The biodegradability of blends of polycaprolactone and LDPE or PP with cornstarch has been reported [139].

The development of thermoplastic blends for high-temperature composites (at > 200 °C) to be used in structural applications is described in [140]. Polymers with high temperature stability tend to be intractable or brittle, whereas easily processible polymers usually fall short of the projected temperature requirement. Luckily, many high-temperature, aromatic and heterocyclic polymers form miscible blends with each other which permits balancing of thermal response and processibility. Poly(2,2′-metaphenylene-5,5′-bibenzimidazole) (PBI), for example, is miscible with

PEI and with PAr; PEI is miscible with PEEK and PEKK.

Blending is also applied to improve the processibility of conductive polymers. Examples are Versicon (Zipperling) intended for transparent electrostatic coatings and corrosion prevention; electrically conductive blend or polyaniline and PVC with EMI properties; and conductive blends of poly(*p*-phenylene vinylene) and polyacrylamide [141]. Blends of (conductive) polyaniline in a matrix of elongated/stretched ultrahigh molecular mass PE are being commercialized by Neste.

6.3. Outlook

Blend technology will accelerate penetration of thermoplastics in markets where its presence is still limited [142]. Designers will have to be made aware of the advantages of working with thermoplastics instead of conventional materials such as wood and metal: their superior performance in a large number of applications, their versatile property profiles, the design freedom, and recycle options. The construction industry is an area with enormous potential for thermoplastic blends and composites. Short-term growth will be driven by applications such as windows, electrical systems, and skylights, followed by the replacement of wood, steel, and concrete. Advantages are lighter constructions, labor savings, and low maintenance costs. A number of possibilities are demonstrated in GE Plastics "Living Environment" concept house and a similar principle developed by Neste. They show the possibilities of thermoplastics and their blends, as well as the use of recycle materials in novel design concepts.

A breakthrough in the automotive market would be large exterior parts and structural components [143]. Two factors limit the use of thermoplastics in body panels. Firstly, cars will continue to feature steel – plastic body construction throughout the 1990s, requiring plastics to withstand vehicle assembly processes designed for steel. Secondly, car makers must compare the overall cost of plastics to steel including tooling, assembly, and customer value rather than on a raw material basis.

Miniaturization is the main driving force for the electronics expanded use of synthetic polymers in the electronics industry. With the development of new molding techniques for high-temperature resins such as polyarylsulfones and poly(phenyletheretherketone), new applications can be realized.

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Polymers, Biodegradable

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1. Glossary and Abbreviations

Glossary: Terms for Carbon Origin and Degradation

Biobased	Refers to the origin of the raw materials. Only significant if the carbon content of annually renewable raw materials is given as the share of the total carbon content.
Renewable	Refers to renewable (annually or otherwise renewable) raw materials such as corn, wheat, paper, wood, etc.
Fossil (nonrenewable) or fossil-based	Refers to raw materials not considered to be renewable, such as gas, crude oil, coal, which are organic in origin.

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Fragmentable (degradable)	Certain materials containing special metal additives as decomposition aids to obtain fragments under the effect of time, heat, and stress. Not fully biodegradable according to current scientific standards.
Biodegradable	Microorganisms such as bacteria, fungi, or algae metabolize these materials completely, giving off CO_2, water, energy, and biomass (aerobic process). In anaerobic biodegradation, also methane is produced.
Compostable	Fully biodegradable under composting conditions, as defined by current standards, i.e., ISO 17088, EN 13432, ASTM D 6400, Japanese GreenPla.

2. Introduction

Biodegradable polymers have been around on an industrial scale since the end of the 1990s. In contrast to biopolymers which are by definition made partially or completely of renewable raw materials, biodegradable polymers are not defined in terms of their raw material basis. After all, biodegradability means that a given substance can be completely converted into water, CO_2, and biomass through the action of microorganisms such as fungi and bacteria. This property is not dependent on the origin of the raw materials, but only on the chemical composition of the polymers. As will be shown, biodegradable polymers can be made either of renewable or of fossil raw materials [1].

Biodegradability is primarily a specific functionality which, like other properties, gives a product additional value and thus optimizes it for certain areas of application. Biodegradability is the possibility of disposing packaging material along with organic waste or of tilling agricultural films into the ground, with all the advantages this entails from the standpoint of hygiene, disposal logistics, and system costs.

A distinction has to be made between degradability (mechanical disintegration) and *bio*degradability (metabolism): not every polymer that can no longer be seen after a few weeks because it has disintegrated into small pieces has actually been biologically degraded. Biodegradability is a certified performance characteristic (ISO 17088, EN 13432 in EU, ASTM D 6400 in North America, GreenPla in Japan). To fulfill, e.g., the EN 13432 norm, the polymer has to be converted to CO_2 by over 90 % within 180 d under defined conditions of humidity, temperature, and oxygen level.

The following chapters will describe in more detail the key prerequisite for biodegradability followed by a description of the synthesis properties and processing of the various biodegradable polymers. The value of biodegradability including life-cycle assessment (LCA) will be addressed in Chapter 6. The significant growth of the market, the various market applications and the corresponding development of production capacities are reviewed in Chapter 5.

3. Biodegradability and Toxicology

The property of biodegradability is not dependent on the origin of the raw materials but only on the chemical composition of the polymers. A polymer is biodegradable if it is metabolized by microorganisms (bacteria, yeasts, algae, fungi) in their natural environment (e.g., surface or sea water, soil or compost) to energy, biomass, water, and carbon dioxide or methane within a given time period (e.g., in composting standards: six months).

Biodegradation is related to either aerobic or anaerobic processes. In an aerobic process, organic matter is transformed to carbon dioxide, water, energy, and biomass by microorganisms in the presence of oxygen. Aerobic biodegradation of polymers occurs in soil or in compost with a variety of microorganisms [2]. In anaerobic biodegradation, organic matter is metabolized by microorganisms in the absence of oxygen. In this process, organic matter is converted to methane, carbon dioxide, water, energy, and biomass.

3.1. Mechanism of Biodegradation

Most of the biodegradable polymers are insoluble in water. They are too big to pass the cellular membrane of microorganisms. Therefore, biodegradation of these polymers begins with chain cleavage by enzymes (e.g., lipases and esterases) secreted by the microorganism in the natural environment [3]. The polymer chains are cleaved to oligomers which can be absorbed and metabolized by microorganisms. The cells of the microorganism gain energy from the mineralization process producing water, biomass, carbon dioxide, or methane. Biodegradation is a surface erosion process because enzymes are too large to diffuse into

the biodegradable polymer in bulk [4]. The biodegradation process is influenced by humidity, oxygen level, light, and temperature.

The enzymatic degradation of a polymer chain depends on the following factors:

- Within the semicrystalline polymer, amorphous regions with flexible chains are present
- These polymer chains are flexible enough to enter the catalytic center of the enzyme
- Chemical bonds (e.g., ester bonds) can be cleaved by the enzyme

The process of biodegradation of polymers not only depends on the activity of enzymes but also on the temperature, humidity, nutrients, and gases (e.g., oxygen in aerobic biodegradation). Therefore, it is important to test the combination of the different factors to define the biodegradability of a specific polymer in a natural environment (e.g., as mulch film). Detailed biodegradation processes of the individual polymers are described in Chapter 4.

As an example for the class of biodegradable polymers, the aliphatic aromatic polyester poly [(butylene adipate)-*co*-(butylene terephtalate)] (PBAT, Ecoflex), will be used to describe the different test procedures and standards. Laboratory tests have been performed with PBAT to monitor the biodegradation of polymers with respect to the formation of intermediates. It has been shown by interrupting the biodegradation process that Ecoflex was degraded to oligomers and to the monomers used to synthesize the polymer. The residual polymer, oligomers, and monomers could at any stage be metabolized by > 99 % in an inoculum prepared from compost (Table 1) [5]. No accumulation of residues has been found.

3.2. Toxicity of Biodegradable Polymers

To prevent any negative impact of polymers which are designed for applications ending up in the environment, it is important to provide adequate information for comprehensive assessment of the environmental and toxicological safety of such a plastic. In general, this may be achieved by characterizing the raw materials, e.g., the polymer itself, and potentially resistant residues after biodegradation with respect to ecotoxicological and toxicological properties. As an example, results from laboratory tests are summarized in the following, which have been conducted with the polyester Ecoflex in order to identify toxic effects (see also → Ecotoxicology).

Water-Soluble Intermediates—Daphnia Test. In the toxicity tests, the toxicity of the water-soluble intermediates is particularly important because they can easily enter groundwater or be more readily absorbed by the organism.

Testing was carried out in accordance with DIN 38412 Part 30. In this test, the pollutant-dependent immobilization of the daphnia in solution of different concentrations (series of dilutions) is used. The control solution contains microorganisms that biodegrade Ecoflex enzymatically. The stock solution at the end of the test also contains the degradation intermediates of Ecoflex.

Table 1. Fragments of Ecoflex after degradation with isolated pure strain or pure strain and mixed cultures from compost (x = detected; n.d. = not detected)

	Monomers*			Aliphatic oligomers*		Aromatic oligomers*	
	B	**A**	**T**	**BA**	**ABA**	**BT**	**BTB**
Test 1	x	x	x	x	x	x	x
Test 2	x	x	x	x	x	n.d.	n.d.
Test 3	x	x	x	n.d.	n.d.	n.d.	n.d.
Test 4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

* A = adipic acid; B = 1,4-butanediol; T = terephthalic acid; BA and ABA = co-monomers of butane diol and adipic acid; BT and BTB = co-monomers of butane diol and terephthalic acid. Test 1: 1750 mg polyester in 80 mL media. Intermediates from isolated pure culture after 21 d. Enzyme activity stopped by pH shift (in situ building of high amounts of acids during degradation). Test 2: 350 mg polyester in 80 mL media. Intermediates from isolated pure culture after 7 d. Test 3: 350 mg polyester in 80 mL media. Intermediates from isolated pure culture after 21 d. Test 4: Residues after a 7-d inoculation by isolated pure culture and a 14-d inoculation with compost eluate. No intermediates were detected by GC analysis.

The polymer was successively diluted and for each concentration 10 daphnia were placed in the test solution (20 °C, pH 7.0). After 24 h, the number of daphnia still swimming was counted. Even with a low dilution (Stage 2) as in the control solution, there were still nine daphnia swimming. The test was therefore passed.

Plant Growth Test. The ecotoxicity of composted biodegradable polyester (Ecoflex) was studied in a plant growth test following the EN 13432, Annex E, which is based on the OECD guideline 208. In this test, effects on seedling emergence and early plant growth are investigated with different higher plant species exposed to treated compost. Seeds are placed in contact with treated and control soil. Four plant species covering the three categories outlined in OECD guidance 208 were introduced in the test, namely wheat (*Triticum sativum*), summer barley (*Hordeum vulgare*), mustard (*Sinapis alba*/*Brassica alba*), and the mung bean (*Phaseolus aureus*).

The following samples were prepared and used for testing:

- Mixture of reference soil and 25 % compost with addition of Ecoflex after 12 weeks composting
- Mixture of reference soil and 50 % compost with addition of Ecoflex after 12 weeks composting.

The evaluation of the test results on seedling emergence and biomass showed no significant effects when treated soil was compared to control soil (Fig. 1). With all four plant species, both parameters reached at least 90 % of the control level regardless of the test concentration.

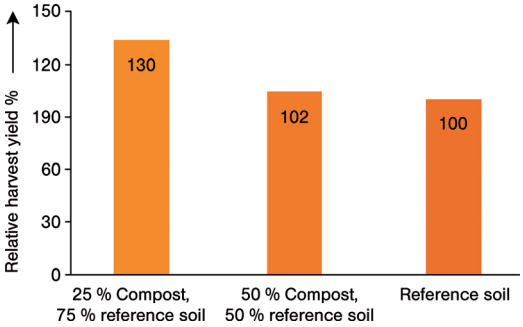


Figure 1. Result of plant growth test for PBAT (Ecoflex) according to OECD 208

An overview of the described and other tests is shown in Table 2 [6]. Biodegradation of PBAT (Ecoflex) causes no accumulation of environmentally dangerous compounds either in organisms or in the ecosystem.

3.3. Standards for Biodegradable Polymers

3.3.1. Controlled Composting Test

Biodegradability of polymers is appropriately described by test and assessment methods in international standards. Industrial composting is today a well-established disposal process for organic waste materials. In order to adapt this industrial composting process, laboratory tests have been developed and certified in standards.

The most important proof of aerobic biodegradability is the controlled composting test according to ISO 14855, which is a central part of every standard for biodegradable polymers. In a composting vessel, the test polymer is

Table 2. Ecotoxicological tests of PBAT (Ecoflex)

Test	Result
Acute toxicity to daphnia DIN 38412 Part 30, fishes	passed
Terrestrial plant toxicity OECD 208	no effects at the highest concentration
Earth worm toxicity OECD 207	no effects at the highest concentration
Primary skin irritation rabbit OECD 404	nonirritant
Primary irritations of the mucus membrane rabbit OECD 405	nonirritant
Guinea pig OECD 406 (modified Buehler test)	nonsensitizing
LD_{50} rat (oral) OECD 423	> 4000 mg/kg, virtually nontoxic after a single ingestion
Ames test OECD 471	substance was not mutagenic

incubated in a batch process—mixed with a defined, mature compost quality. The vessel is aerated continuously with carbon dioxide free air at 58 °C and at defined humidity. Thus, the composting process runs under optimum moisture and oxygen conditions. Simultaneously, a blank compost inoculum without additional carbon source is tested under the same conditions. The carbon dioxide content of the exhaust air of both vessels is compared. After subtracting the carbon dioxide evolution of the blank inoculum, the carbon dioxide evolution related to the test polymer is monitored as the biodegradation curve. Figure 2 shows that in a controlled composting test of Ecoflex more than 90 % of the polymer was converted to carbon dioxide after 80 d.

The biodegradation curve shows the relative carbon dioxide evolution of the test inoculum with test polymer related to the theoretical carbon dioxide evolution of the test polymer. According to the ISO standard compostable polymers, ISO 17088, 90 % of the theoretical carbon dioxide evolution of the test polymer has to be detected after 180 days. The activity of the compost inoculum in the controlled composting test is validated using a cellulose reference instead of the polymer. The strict requirements on the test result ensure that only compost with a defined degree of maturity is used to test the polymer.

3.3.2. Standard Assessment of Biodegradable Polymers

Like the ISO 17088, the European standard 13432 and the American standard ASTM D 6400 define basic requirements for packaging

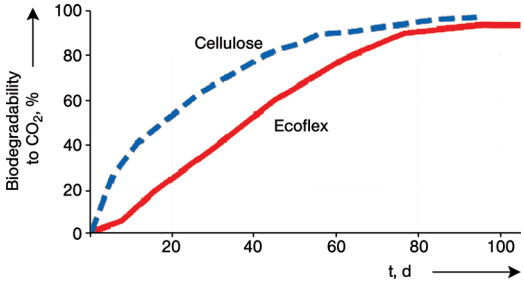


Figure 2. Controlled composting test of PBAT (Ecoflex) and cellulose

and packaging materials to be considered as biodegradable and compostable in industrial composting facilities by addressing the scheme summarized in Table 3. The test results have to be certified by registered test institutes (e.g., DIN-Certco, D; Vincotte, B, Biodegradable Products Institute, USA).

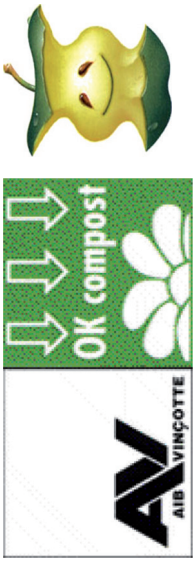
The new ISO standard 17088 became effective in 2008 and is mainly based on EN 13432 and ASTM D 6400. This standard can be used worldwide. Additional tests may be necessary to obtain the product registration according to ISO 17088 based on a regional standard.

Registered biodegradable polymers are used to produce biodegradable finished products, e.g., bags, packaging, cutlery, plates, which have to be certified in the next step. This procedure at a certified test institute shall prevent the use of nonconforming additives, colors, and packaged goods. The certificate entitles the holder to use the regional symbol for biodegradable plastics on his packaging or article in combination with his certification number (Table 4):

Table 3. Registration scheme for biodegradable polymers

Test	Assessment
Declaration of polymer composition	volatile solids > 50 %; heavy metal content < limits in EN 13432
Laboratory test of biodegradability (ISO 14855, controlled composting test or equivalent)	EN 13432: > 90 % of theoretical CO_2 evolution after 180 d ASTM D 6400-04 (homopolymers): > 60 % of theoretical CO_2 evolution after 180 d ASTM D 6400-04 (heteropolymers): > 90 % of theoretical CO_2 evolution after 180 d
Disintegration in pilot-scale composting test using specimen of maximal thickness	< 10 % of the weight of the specimen shall fail to pass through a > 2 mm fraction sieve
Analysis of compost quality	density; dry solids; volatile solids; salt content; pH; content of elemental N, P, Mg, Ca
Ecotoxicity of compost using minimum 2 species of plants	rate of germination and biomass > 90 % of blind value of compost without polymer

Table 4. Logos of biodegradable polymers according to the standards [7]

Organisation	DIN-Certco	Vincotte	Jätelaito-syhdistys	BPI/USCC	BPS
Location	Germany	Belgium	Finland	North America	Japan
Logo					
Standard	EN 13432 ASTM D 6400	EN 13432	EN 13432	ASTM D 6400	GreenPLA certification scheme

4. Biodegradable Polymers: Synthesis, Properties, and Suppliers

4.1. Raw Materials

Biodegradability is a functional performance characteristic of the polymer backbone, which can be achieved with renewable as well as fossil-based raw materials.

Fossil-Based Raw Materials. Major fossil-based monomers are butanediol (BDO) and the dicarboxylic acids adipic acid, terephthalic acid, and succinic acid. BDO is produced in world-scale plants with different processes and feedstocks (acetylene by Reppe process, butane, butadiene). Compared to BDO, succinic acid is produced in smaller scale based on maleic acid anhydride (MSA). Adipic acid is based on cyclohexane derived from benzene, and terephthalic acid is based on *p*-xylol.

Renewable raw materials are used as

- feedstock for monomer production (e.g., lactic acid) or polymer production (polyhydroxyalkanoates, PHA)
- structural material (e.g., cellulose) and as a compound ingredient (e.g., starch) for biodegradable polyesters

Feedstocks for Monomer or Polymer Production. Starch (from corn, wheat, etc.) → Starch, is transformed to glucose, which is further used as fermentation feedstock for monomers (e.g., lactic acid) or PHA production. Other feedstocks for fermentative monomer production are sucrose, glycerol, or plant oils [8]. Intensive work is underway to use cellulose raw materials (C_6 and C_5 sugars) not only for bioethanol production but as well for different chemical intermediates and monomers like lactic and succinic acid [9].

Besides the indirect use of feedstocks for monomer production via fermentation, the direct access to monomers via extraction and processing of renewable feedstocks (e.g., sebacic acid, biorefinery) → Biorefineries – Industrial Processes and Products is intensively elaborated and being commercialized. For example, Novamont plans to install a biorefinery process for the production of biodegradable polyesters using local feedstocks [10].

The most established monomer production via fermentation for biodegradable polymers is the production of lactic acid [11] whereas commercial succinic acid production is underway [12].

Structural Materials and Compound Ingredients. Cellulose can be used as a basic material for coating and/or lamination with biodegradable polyesters. Starch (from corn, wheat, potato) is used as a compound ingredient for biodegradable polyesters to produce film materials (see Section 4.2). The biodegradable polyester is needed as an "enabler" to improve the properties and processability of the starch. Furthermore, starch is used as loose fill material (not further described in this article).

4.2. Starch

→ Starch

Native starch occurs in the organs of plants as discrete particles (starch granules). Starch molecules are polysaccharide compounds composed of anhydroglucose units. Starch serves as a food reserve and energy source of plants.

Starch granules consist of a multilayer structure from two polymers: amylose and amylopectin. Amylose is a predominantly linear 1,4-α-D-anhydroglucose polymer. Potato starch contains about 21 % of amylose at an average degree of polymerization M_n of 4900 (Fig. 3). Corn starch contains about 29 % of amylose at a much lower M_n of about 900 [13].

Amylopectin forms 70 – 85 % of regular starches at a very high M_n of approximately 2 000 000. Amylopectin consists of anhydroglucose units connected by 1,4-α-linkages. Branch points are generated by 1,6-α-linkages at selected sites (Fig. 4). Amylopectin and amylose together form grain structures which are partially crystalline because of hydrogen bonds.

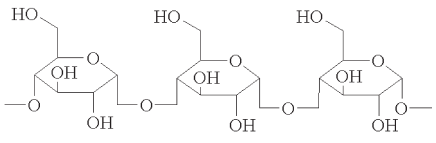


Figure 3. Representative structure of linear amylose

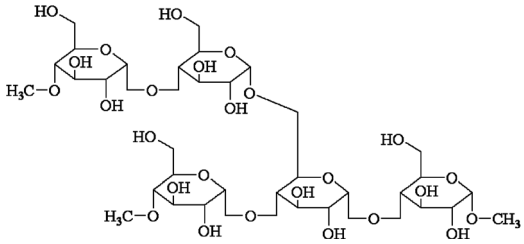


Figure 4. Representative structure of amylopectin including 1,6-α-D branch point

The particle size distribution depends on the type of plant (Table 5). The size of the potato starch granules is considerably higher than the size of corn and tapioca starch granules. Also the moisture absorption of potato starch is much higher than for corn and tapioca starch. Thus, processing of tapioca starch in technical processes like compounding is similar to that of corn starch [14].

Pure starch can be successfully formulated only for a limited number of plastic applications such as foam, e.g., for loose fill. Pure starch films and sheets are brittle and moisture-sensitive. They even disintegrate in the presence of water. Additionally, the temperature window for processing is very small because of the limited temperature stability of natural starch of about 170 – 180 °C. Chemical modification of starch by partial substitution of hydroxyl groups (e.g., with esters or ethers) can significantly improve hydrophobicity and the rheological properties. Cross-linking of the starch chains improves stability against acids, heat treatment, and shear forces [15]. However, the high requirements of film applications are not fulfilled by modified starch alone. Compounds with biodegradable polyesters as "enablers" are the appropriate

Table 5. Particle size distribution and moisture of starch from different plants

	Potato starch	Corn starch	Tapioca starch
Diameter (average), μm	5 – 100 (23)	2 – 30 (10)	4 – 35 (10)
Number of granules per gram	100×10^6	1300×10^6	500×10^6
Moisture absorption at 65 % relative humidity, 20, °C %	19	13	13

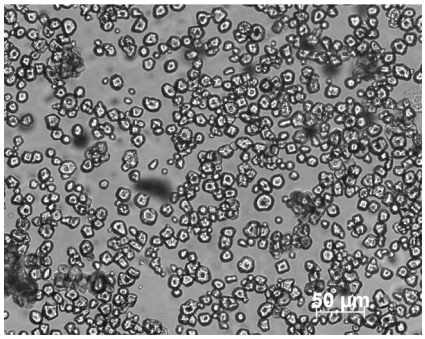


Figure 5. Light micrograph of granular corn starch dispersed in PBAT as continuous phase

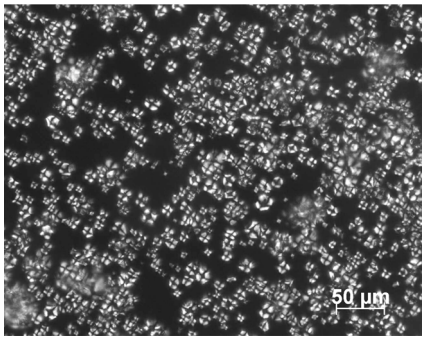


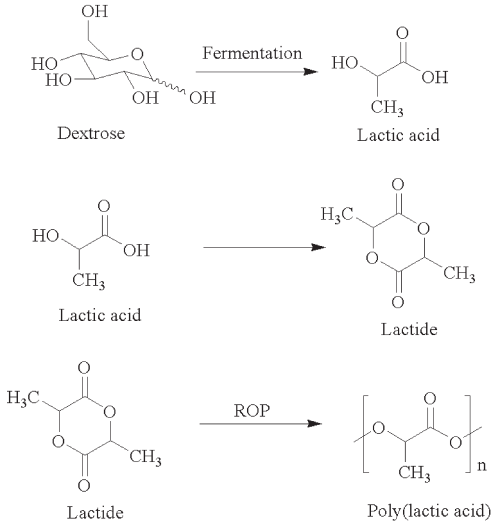
Figure 6. Light micrograph of granular corn starch dispersed in PBAT in polarized light to demonstrate cristallinity

solution (see Section 4.7). Figures 5 and 6 show microscopic pictures of starch compounds.

4.3. Poly(lactic acid) (Polylactide, PLA)

→ Lactic Acid

Synthesis. PLA is a melt-processible thermoplastic polymer completely based on renewable resources. The manufacture of PLA includes one fermentative step followed by several chemical transformations. The typical annually renewable raw material source is corn starch which is broken down to unrefined dextrose. This sugar is then subjected to a fermentative transformation to lactic acid (LA). Direct polycondensation of LA is possible but usually LA is first chemically converted to lactide, a cyclic dimer of LA, via a PLA prepolymer. Finally, after purification, lactide is converted via a ring-opening polymerization (ROP) to PLA [16–20]:



Properties and Applications. Due to its stereogenic center, lactic acid exists in two enantiomeric forms (D- and L-lactic acid) leading to three different lactide stereoisomers (D-, L-, and *meso*-lactide, Fig. 7). Depending on the relative amounts of the different stereoisomers in the final polyester, the crystallinity of the resulting PLA is heavily influenced and in this way the properties of the polymer can be adjusted to satisfy the needs of different applications [17, 21, 22].

PLA shows properties similar to polystyrene. Its high stiffness and transparency makes it a suitable material for applications such as plastic bottles, cups for cold drinks, stiff packages like clamshells as well as degradable films. PLA is completely nontoxic and classified in the USA as generally recognized as safe (GRAS) [23].

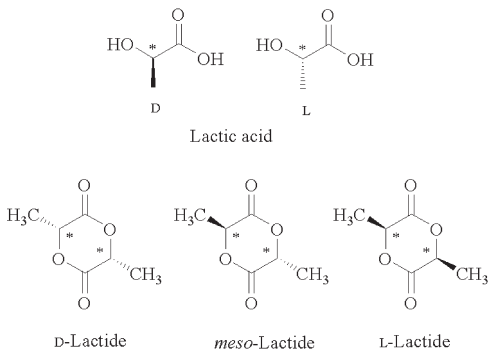


Figure 7. Lactic acid and lactides

PLA can be processed on standard equipment and used in injection molding, injection stretch blow molding, and for the production of blown and cast films, biaxially oriented films, or transformed to extrusion paper-coating compounds, etc. Although PLA is a compostable material, it is also more and more used in durable applications because of its biogenic origin and its sustainable image.

Limitations and Technical Developments Underway. Nevertheless, PLA still suffers from several drawbacks like its low impact strength, its poor barrier properties and especially its low heat resistance. A lot of research activities are currently in process to overcome these drawbacks. More and more companies offer solutions to the problems based on masterbatches of PLA copolymers or compounds.

Biodegradation. Chemical hydrolysis is considered to be the main degradation route for PLA [17]. This hydrolysis process takes place at high humidity and at elevated temperatures, which, for example, are found in industrial composting facilities. The fragments that result from the hydrolysis process, i.e., short oligomers and monomers, can then be consumed by microorganisms. Therefore, PLA articles can be certified to be compostable under these conditions but will not degrade in home composting piles because of the fact that temperatures are typically much lower. Apart from composting (or incineration), PLA can be chemically recycled by conversion of the used polymer back to the monomers followed by repolymerization.

Producers. The leading producer of PLA is NatureWorks LLC, a joint venture of Cargill Dow LLC and Teijin, with a nominal production capacity of about 140 000 t/a (see Chap. 9) [24]. NatureWorks LLC sells PLA resins for packaging and fiber applications under the trade name Ingeo. In Japan, NatureWorks PLA polymer is sold by Mitsui Chemicals under the trade name Lacea [25].

4.4. Polyhydroxyalkanoates (PHA)

Introduction. Structurally related to PLA are the polyhydroxyalkanoates (PHA), a class of polyesters derived from hydroxyalkanoic acids which can differ in chain lengths and in the positions of their hydroxyl groups (Fig. 8). The most common representatives among this class of biodegradable polymers, which are available so far in pilot-scale amounts, are poly(3-hydroxybutyrate) (P(3-HB)), poly(4-hydroxybutyrate) (P(4-HB)), poly(hydroxybutyrate-*co*-valerate) (PHBV), and poly(hydroxybutyrate-*co*-hexanoate) (PHBH).

Synthesis. Like PLA, PHAs are derived from annually renewable resources like sugars, starch, or fatty acids. Moreover, hydrocarbons like methane have recently been described to be used for the fermentative synthesis of PHB by

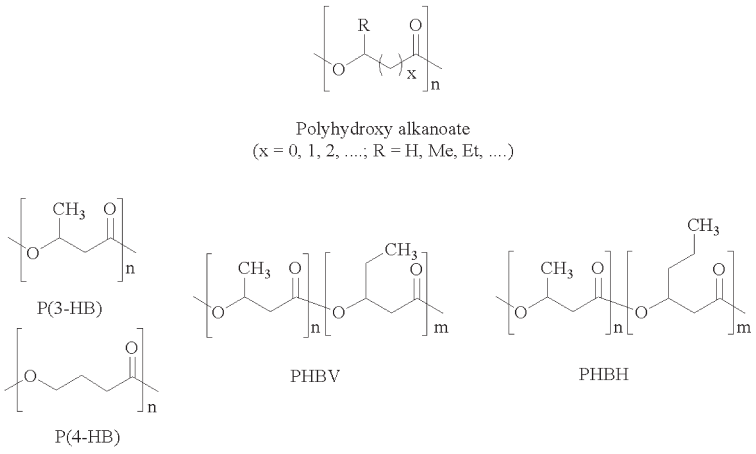


Figure 8. Polyhydroxyalkanoates, general structure and most important derivatives

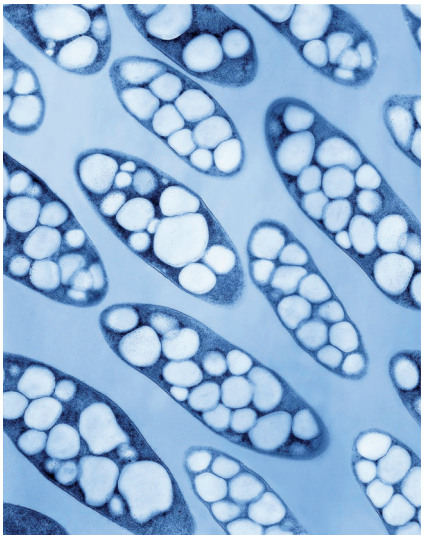


Figure 9. Polyhydroxyalkanoate particles in microorganism (photograph provided by Telles, USA)

methanotrophic bacteria [26]. In contrast to the PLA production, for PHAs is no chemical transformation needed. The polymer itself is made by various microorganisms as a carbon- and energy-storing substance (Fig. 9) [27]. The mass of the polymer in the microorganism can reach up to 90 % of the dry weight of the cell mass. The chemical structure of the resulting PHA depends on the bacterial species and the composition of the carbon source on which the microorganisms are grown [28]. After fermentation and cell lysis, high-purity PHA can be isolated by chemical extraction. Companies are currently working on the optimization process by designing genetically modified microorganisms, and recently transgenic plants that produce PHAs in their cell membranes have become objects of research [27, 29]. However, bacterial fermentation is still the most commercially viable way to produce PHAs in industrial scale [30].

Properties and Applications. The great structural variety of PHAs (see Fig. 8) gives rise to a multitude of different property profiles and different possible applications including injection-molded articles for bioresorbable medical and nonmedical applications such as fishing nets, degradable films, etc. [27, 31, 32].

Biodegradation. As PHAs are direct metabolites of microorganisms found in natural environments, they are accepted as food sources by many abundant microbe species which break the polymer down by extracellular poly(hydroxyalkanoic acid) depolymerases [33]. This is the reason why PHAs are quickly biodegraded both under aerobic conditions (e.g., composting) and in environments where anaerobic degradation takes place (e.g., marine environments, landfills).

Producers Although fermentative PHB has been known since 1926, commercial interest occurred not earlier than in the fourth quarter of the 20th century [34]. The major player today is Telles (joint venture of Metabolix and ADM) with the trade names Mirel, Biopol. Other companies active in the area of PHAs are Kaneka (Nodax), Mitsubishi Gas Chemicals (Biogreen), PHB Industrial (Biocycle) and Tianan (Enmat). The production capacities of PHAs are still modest and only pilot-scale quantities are found in the market today. But it can be expected that the capacities will be increasing significantly in the next years: Telles plans to produce Mirel in a capacity of 50 000 t/a by the end of the second quarter of 2009 [35] (see Chap. 9).

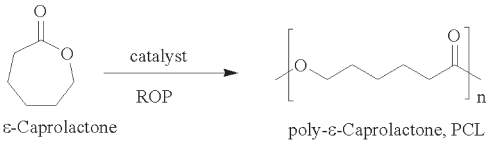
4.5. Synthetic Polyesters

4.5.1. Aliphatic Polyesters

Introduction. It is not the origin of the raw materials used in the manufacture of a polymeric material that renders it biodegradable: It is the chemical structure which allows enzymatic attack and enzymatic hydrolysis of the polymer chain followed by complete digestion of the fragments by microorganisms (see Chap. 3) [36]. With this knowledge, polymers can be specifically designed and produced from existing fossil-based monomeric building blocks in existing production plants. These polymers are then not only biodegradable but also exhibit beneficial mechanical properties. Aliphatic polyesters were the first completely fossil-based polymers which combined both the biodegradability of polymers found in nature as well as the useful mechanical properties of modern plastics.

Structure and Synthesis. There are two fundamentally different structures of synthetic polyesters. One of them is closely related to fermentative PHAs (Section 4.4) and is derived

from hydroxyalkanoic acids or their intramolecular, cyclic condensates, lactones. The most common derivative is poly--caprolactone and, as the name suggests, this polyester is produced in a ROP from -caprolactone [37, 38]:



The other type of polyester is based on a direct condensation reaction of aliphatic dicarboxylic acids and aliphatic glycols [39]. The most important derivatives are polycondensates from 1,2-ethylene glycol or 1,4-butanediol with succinic acid, adipic acid, or combinations of both (PES, PBS, and PBSA,respectively, Fig. 10).

Properties and Applications. Due to the broad spectrum of different monomers that can be used for the synthesis of these polymers, the properties can be adjusted to a certain degree. While PBS is a relatively stiff polyester, other combinations with longer dicarboxylic acids lead to more flexible materials. Generally, aliphatic polyesters are low-melting, flexible plastic materials which are best suited for and usually found in film applications like organic waste bags or mulch films and monofilament fibers. However, they are also found in foams and injection-molded parts. Processing on conventional polyolefin equipment is typically possible [39]. A drawback of aliphatic polyesters is the fact that they are prone to chemical hydrolysis leading to limitations in shelf life and transportation.

Biodegradation. In microbially active environments like soil and compost, aliphatic polyesters are degraded in a combination of chemical and enzymatic hydrolysis and the fragments are ultimately degraded to carbon dioxide and water [39].

Producers. PCL and biodegradable derivatives are sold by Solvay (Capa), Daicel (CellGreen), and by Dow under the trade name Tone. Due to the low melting point and low modulus of PCL, this biodegradable polymer is mostly used as a component in blends with biopolymers (see below). The Japanese company Showa Highpolymers produces aliphatic polyesters of the latter type in amounts of several thousand tons per year and sells them under the tradename Bionolle [39]. IRE Chemicals, a Korean company, sells polyesters of the same structure under the tradename EnPol, and Mitsubishi

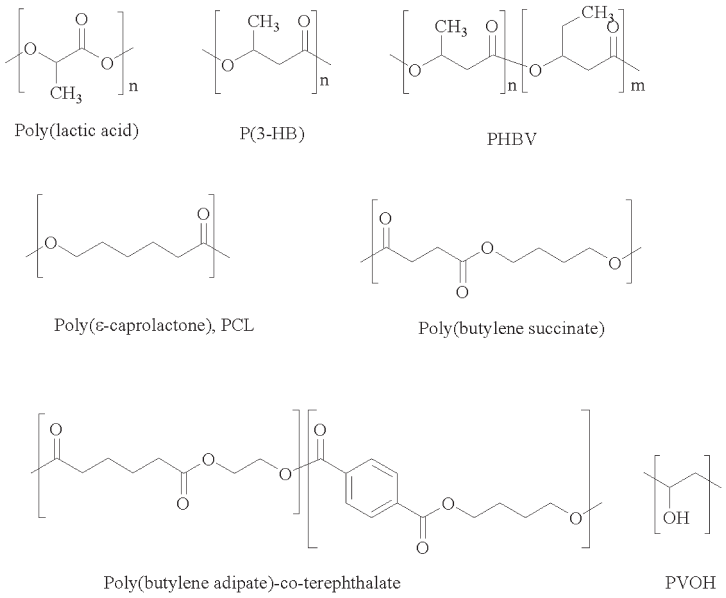


Figure 10. Commercially available biodegradable polymers

Chemicals has a biodegradable, aliphatic copolyester with a small amount of PLA (GS-PLA) in its portfolio.

4.5.2. Aliphatic/Aromatic Polyesters

Synthesis. The good biodegradability of aliphatic polyesters can be combined with the good mechanical properties of aromatic polyesters to some extent by copolyesterification of aliphatic and aromatic monomers [40]. Aliphatic/aromatic polyesters are synthesized in melt polycondensation processes from aliphatic acids (typically adipic acid) as well as aromatic dicarboxylic acids (typically terephthalic acid) with aliphatic glycols (typically 1,4-butanediol). The best known aliphatic/aromatic polyester is Ecoflex by BASF (Fig. 11).

Properties and Applications. Ecoflex is designed to be a strong and flexible material with mechanical properties similar to PE [41]. Therefore, Ecoflex can be melt-processed on standard polyolefin equipment and is mainly used in film applications like organic waste bags, mulch films, shopping bags, cling films, etc. Ecoflex is also used as a replacement for PE in paperboard coating, e.g., to yield completely biodegradable paper cups (see Chap. 9).

Due to its beneficial properties and its complete biodegradability as well as to a clear trend to renewable raw materials, Ecoflex is used as an "enabler" for renewable biopolymers like starch, PLA, PHAs, lignin, and cellulose. Ecoflex/starch as well as Ecoflex/PLA blends (e.g., Ecovio by BASF) are the most common renewable and biodegradable plastic materials for film applications in the market.

Biodegradation. Although pure aromatic polyesters like poly(butylene terephthalate) (PBT) are not prone to microbial attack, copolyesters of aliphatic and aromatic monomers are completely biodegradable if the aromatic content does not exceed a certain limit [40–43]. Similar to aliphatic polyesters, these mixed structures also degrade in microbially active environments mainly by enzymatic hydrolysis followed by complete mineralization of the fragments [5].

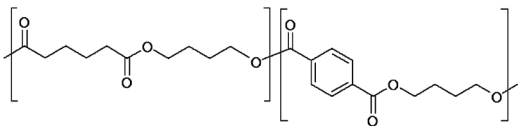


Figure 11. Aliphatic/aromatic polyester, Ecoflex

Producers. Ecoflex is the most important aliphatic/aromatic polyester in the market. Ecoflex is a product by BASF and current production capacities amount to 14 000 t. Recently, BASF announced to increase capacities by another 60 000 t by the end of 2010. Another supplier of aliphatic aromatic polyesters is DuPont (Biomax).

4.6. Other Synthetic Polymers

Another class of synthetic polycondensates produced in industrial scale are polyamides. Due to their ability to hydrogen bonding, polyamides generally show high melting points and have a highly suppressed mobility of the polymeric chains. This is the reason why polyamides have a good profile of mechanical properties but are—apart from naturally occurring homopolyamides and some materials of academic interest (e.g., PA4)—not biodegradable [44, 45]. The homopeptide polyaspartate → Polyaspartates and Polysuccinimide is a synthetic analogue to naturally occurring peptides. It is synthesized in a polycondensation reaction of aspartic acid via polysuccinimide, which is hydrolyzed to polyaspartate. This water-soluble and biodegradable polyamide (not discussed here in detail) is commercialized by Lanxess under the tradename Baypure and used, e.g., as an additive for detergents [46].

Poly(ethylene glycol) (PEG) is a water-soluble polyether mainly used in detergents and shampoos. PEG is both aerobically and anaerobically biodegradable if the molecular weight is not too high [47–50].

The only existing biodegradable polymer with an all-carbon backbone is poly(vinyl alcohol) (PVOH). Poly(vinyl alcohol) is synthesized by (partial) hydrolysis of poly(vinyl acetate) and shows a solubility in water which depends on the degree of hydrolysis. PVOH can be processed into films by solution casting or by thermoplastic melt processing [51]. The films are biodegraded in wastewater treatment or in composting facilities. Main application of PVOH as biodegradable polymer is in flushable items.

The mechanism of biodegradation is different from the ones discussed for polycondensates: it includes oxidation of the alcohol functionalities followed by enzymatic chain scission to smaller fragments which can finally be mineralized [52]. Major suppliers of PVOH are Kuraray (Poval, Mowiol), Nippon Gosei (Hi-Selon) and Indroplast (Hydrolene).

4.7. Compounds

Biodegradable polymers have defined property profiles (Table 6) as explained in the previous chapters, which limit their application range to a certain extent. If the market demands biodegradable polymer solutions using renewable resources, a compound can be developed by using a combination of rigid polymers like PLA or PHA and soft and impact-resistant synthetic biodegradable polymers like PBAT. Such a material responds precisely to the application requirements (Fig. 12). One example is the PBAT/PLA compound (Ecovio L BX 8145), which enables the production of film products similar to PE-HD.

4.7.1. Compounds of Starch and Biodegradable Polyesters

Based on the experience in extruder cooking of starch for products like peanut flips and dry pet food, compounding equipment for compounds of biodegradable plastics has been developed. Corotating, intermeshing, and self-cleaning twin-screw extruder concepts are available from machinery suppliers like Coperion, Clextral, Extricom, Leistritz, Krauss Maffei Berstorff, and others. These extruder concepts prevent caking and charring of the dew during starch cooking.

Starch compounds with polyesters are used to enhance hydrophobicity as well as mechanical and thermal properties of compounded products. The crystalline structure of starch granules has to be disintegrated prior to its use in applications (e.g., production of thin films and bags) because starch granules as large as the film thickness reduce the mechanical properties. High shear forces, heat, and/or plasticizers (e.g., moisture, glycerol) are used in a separate compounding step to turn granular starch into thermoplastic starch.

Compounding of starch and biodegradable polyesters can be efficiently performed in a four-stage process:

1. Starch is destructurized by temperature, pressure, and plasticizer (e.g., water, glycerol).
2. The biodegradable polyester (e.g., PCL, PBAT, PVOH) is added.
3. The melt has to be degassed by an effective vacuum, leaving only a few percent of moisture in the compound.
4. The compound is granulated under water or air and subsequently dried in a vacuum drier.

Film products with good mechanical characteristics are only obtained if thermoplastic, plasticized starch has been used. Another

Table 6. Properties of biodegradable polyesters and reference polymers*

Test	Standard	PET	PLA	PHB	PBAT	PBS	PE-LD
Transparency		transparent	transparent	opaque	translucent	translucent	transparent
Density, g/cm^3	ISO 1183	1.35	1.25	1.25	1.25	1.26	0.92
Melting point, °C	DSC	245	140–175	175	115–120	115	105–115
Glass transition temp. T_g, °C	DSC	75	58	−4	−33	−32	−100
Vicat A, °C	ISO 306	75	56	96	91	93	90
Mechanics MD/CD**							
Module of elasticity, MPa	ISO 527	3100	3600	1900	80	645	250
Tensile stress, MPa	ISO 527	58	70	27	23	35	20
Ultimate elongation, %	ISO 527	50	3	8	470	47	500
Barrier properties							
Oxygen, mL m^{-2} d^{-1} bar^{-1}	ASTM D 3985	15		45	600	100	1500
Water absorption, %		0.15	0.3	0.5	0.5	0.4	
Food contact	2002/72/EC	o.k.	o.k.	o.k.	o.k.	no	o.k.
Biodegradability	EN 13432	no	yes	yes	yes	yes	no

* Injection-molded specimen, 4 mm, barrier values: blown film: 100 μm.
** MD = machine direction = direction of extrusion of blown film, CD = cross direction = perpendicular to direction of extrusion of blown film.

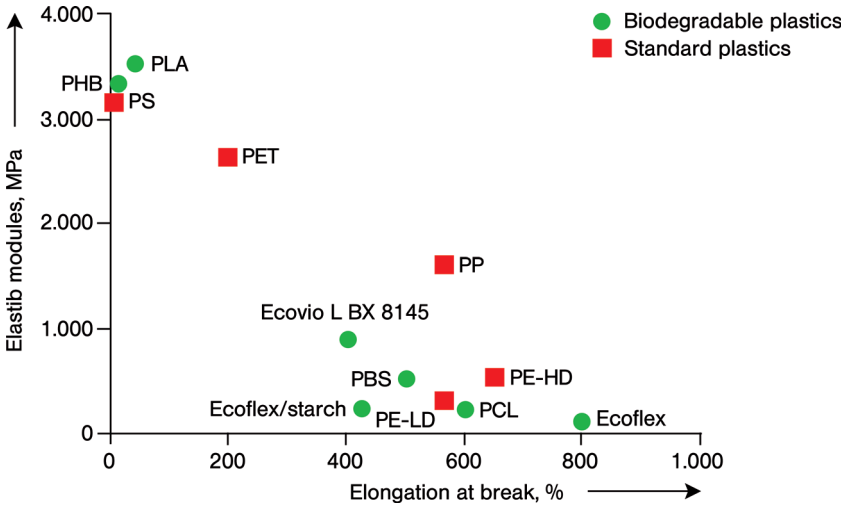


Figure 12. Stiffness versus flexibility for typical standard and biodegradable plastics, ISO 527
Ecoflex = PBAT; Ecovio LBX 8145 = compound containing 45 % PLA, about 55 % Ecoflex, and compatibilizers

condition is that the biodegradable "enabling polyester" forms the coherent phase [53]. If no plasticizer is used, biodegradable polymers with merely limited mechanical properties will be obtained. In this case, coextrusion with the base polyester or another polymer is the way to upgrade mechanical and/or moisture barrier properties.

In Table 7, most of the mechanical properties of average PE-LD carrier bags from blown film, 30 µm, are close to the PBAT/starch compounds containing thermoplastic starch. The reduction in stiffness by 20 – 25 % compared to that of PE-LD is lower than for PBAT/starch compounds with granular starch, which amounts to 50 – 55 %. The reduction in tensile strength is similar for both starch compounds: 10 – 35 %. If granular starch is used, the film samples exhibit a rough surface. Thus printability and mechanical properties (stiffness and puncture resistance) of PBAT compounds with granular starch are inferior to PBAT/starch compounds with thermoplastic starch by about 30 – 55 %.

In comparison to PE-LD, compounds of PBAT/thermoplastic starch are stiffer than pure PBAT. PBAT/thermoplastic starch compounds are used because they combine biodegradability and renewable resources.

Table 7. Examples for blown films, 30 µm

Test	Standard	PE-LD carrier bags (mean)	PBAT	PBAT+granular starch compound	PBAT+thermoplastic starch compound
Transparency		opaque	translucent	opaque	opaque
Printability		8 colors flexoprint	8 colors flexoprint	poor printability	8 colors flexoprint
Mechanics MD/CD*					
Modul. of elasticity, MPa	ISO 527	330/270	110/100	150/140	270/205
Tensile stress, MPa	ISO 527	32/25	35/40	23/22	21/20
Ultimate elongation, %	ISO 527	460/640	640/750	390/590	490/540
Puncture resistance, J/mm	DIN 53373	17	26	9	19
Barrier properties					
Oxygen, mL m^{-2} d^{-1} bar^{-1}	ASTM D 3985	4800	2000		
Water vapor, g m^{-2} d^{-1}	ASTM F 1249	3	240		
Food contact	2002/72/EC	not limited	not limited	dry food	dry food
Biodegradability	EN 13432	no	yes	yes	yes

* MD = machine direction = direction of extrusion of blown film, CD = cross direction = perpendicular to direction of extrusion of blown film.

4.7.2. Compounds of PLA and Biodegradable Polyesters

Polylactic acid is a transparent, stiff polyester (see Section 4.3). It can also be transformed into transparent flexible films with properties close to cellophane using biaxial orientation technology and into fibers using standard production process of fiber spinning and subsequent orientation and fixation. However, for most of the flexible-film applications the stiffness of PLA (3600 MPa) is too high. Therefore, compounds of PLA and soft biodegradable polyesters like PBAT are used to reduce the stiffness efficiently [54].

The addition of 20 % PBAT (e.g., Ecoflex) in PLA already reduces the stiffness of PLA by 25 % (Fig. 13), keeping the impact strength (e.g., Charpy, unnotched, according to ISO 179/1eU at −20 °C) at 22 kJ/m^2, which is above the level of high-impact polystyrene. Containers produced from this compound are resistant even to sudden impact—they deform without brittle failure at room temperature (23 °C).

Flexible-film applications are much more demanding regarding the stiffness/toughness ratio of the PBAT/PLA compound. Usually, PP with a stiffness of 1600 MPa is the stiffest product to be used in blown-film extrusion. But most blown-film lines for stiff products can only handle conventional PE-HD with a stiffness of 600 – 1200 MPa. Moreover, high requirements have to be fulfilled concerning the bubble stability at lower film thicknesses, e.g., at 10 – 15 μm or below.

Corotating, intermeshing, and self-cleaning twin-screw extruder concepts (e.g., from machinery suppliers like Coperion, Clextral, Leistritz, Kraus Maffei Berstdorf, Extricom as being employed for starch compounds can be modified for the compounding of PBAT and PLA. The volume elements for deaeration of starch powder have to be changed to elements for conveying and melting of granulates. Adapted shear mixing devices are used to blend the melts at low shear energy to avoid high temperatures causing pronounced hydrolysis of the PLA phase. A thorough venting in one or two steps as needed for starch compounds is not necessary for PBAT/PLA compounds. It is frequently possible to achieve higher output rates with PBAT/PLA compounds than with PE-LD.

Good performance characteristics are obtained for PBAT/PLA compounds with PBAT as the continuous phase and PLA as the discontinuous phase. Examples are given in Table 8 for a blend with 45 % PLA (PLA as discontinuous phase, PBAT as continuous phase) and a blend with 60 % PLA (PLA as continuous phase, PBAT as discontinuous phase), compared to PE-HD.

Table 8 shows that a compound with 45 % PLA and PBAT can achieve about 70 – 75 % of the mechanical properties of an average PE-HD carrier bag at 30 μm thickness. The values of a PE-LD compound (see Table 7) are reached or exceeded. The 45 % PLA compound (Ecovio L BX 8145) yields a biodegradable film that comes closest to the properties of PE-HD films on the market.

The flexibility of PBAT/PLA compounds with PBAT as continuous phase can always be enhanced by using PBAT in the dryblend.

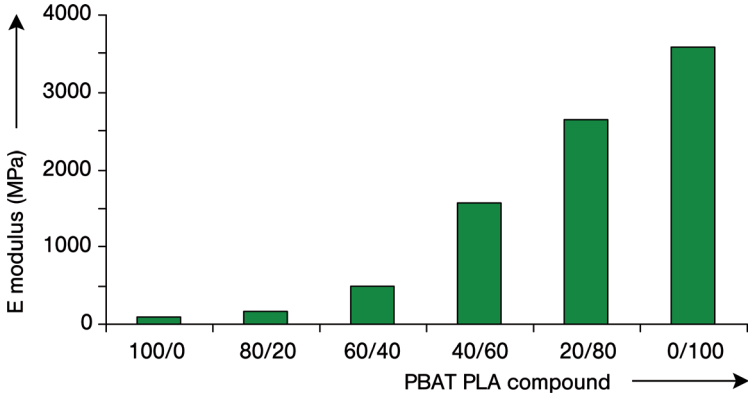


Figure 13. Stiffness of injection-molded specimen from PBAT/PLA compounds with varying PLA content according to ISO 527

Table 8. Characteristics of blown films, 30 μm, from PE-HD and compounds with PBAT

Test	Standard	PE-HD[a]	PBAT+PLA 55/45 dryblend[b]	PBAT+PLA 55/45 compound[c]	PBAT+PLA 40/60 compound[d]
Transparency		opaque	opaque	opaque	translucent
Printability		8 colors flexoprint	8 colors flexoprint	8 colors flexoprint	8 colors flexoprint
Mechanics MD/CD[e]					
Modul. of elasticity, MPa	ISO 527	650/630	1180/490	1020/440	1560/1080
Tensile stress, MPa	ISO 527	45/42	39/21	50/32	47/30
Ultimate elongation, %	ISO 527	640/520	360/170	430/360	160/160
Puncture resistance, J/mm	DIN 53373	42	19	31	31
Barrier properties					
Oxygen, mL m^{-2} d^{-1} bar^{-1}	ASTM D 3985	2000		1400	
Water vapor, g m^{-2} d^{-1}	ASTM F 1249	1.3		160	
Food contact	2002/72/EC	not limited	not limited	not limited	not limited
Biodegradability	EN 13432	no	yes	yes	yes

[a]Average values for carrier bags.
[b]Dryblend of 55 % PBAT and 45 % PLA.
[c]Compound of approx. 55 % PBAT and 45 % PLA.
[d]Compound approx. 40 % PBAT and 60 % PLA.
[e]MD = machine direction = direction of extrusion of blown film, CD = cross direction = perpendicular to direction of extrusion of blown film.

Thus, PE-HD-like or PE-LD-like properties can be achieved by using an appropriate combination of PBAT and PBAT/PLA compound [55].

Another important aspect of biodegradable PBAT/PLA blends is their shelf life under regular storage conditions. Because standard climate is used to condition plastic specimens prior to test, standard room climate (23 °C, 50 % relative humidity) has been used to store film samples from PBAT and PBAT/PLA compounds. After three years of storage under these conditions, biodegradable films from PBAT (Ecoflex F BX 7011) achieve or exceed the mechanical properties of PE-LD carrier bags except for stiffness. Films from PBAT/PLA compounds (e.g., Ecovio L BX 8145) maintain the property level of PE-LD carrier bags during two years of storage for stiffness, tensile strength, and puncture resistance. The ultimate elongation can be adjusted by using PBAT (e.g., Ecoflex F BX 7011) [55].

4.8. Cellulose Derivatives

Cellulose esters (e.g., with acetic acid or propanoic acid) are well-known amorphous plastics which are used for injection molding of transparent articles. Thus, there are compounds for injection-molded products on the market, e.g., for candle housings in cemeteries or as disposable cutlery. However, only cellulose acetate with a degree of substitution of not more than 2.5 is biodegradable. Biodegradability certificates according to EN 13432 are difficult to achieve because the biodegradation of cellulose derivates is a very slow process.

Cellulose films (e.g., cellophane) are very transparent and exhibit an excellent barrier against oxygen and aroma if the moisture level is kept below 50 % relative humidity. When a coating based on natural waxes is used, a high water-vapor barrier can be achieved, which makes these films applicable for packaging of food, e.g., cereals, pasta, cheese, fruit, and vegetables.

5. Processing and Additives

(→ Plastics, Processing; → Films, Section 6.10.)

5.1. Introduction

Biodegradable polyesters are designed for processing on regular equipment for standard polymers. Nevertheless, the equipment has been originally designed according to the property profiles of standard polymers. Therefore, the following limitations have to be taken into account if a conversion process is selected for a biodegradable polyester.

1. Limited compatibility to standard polymers. Biodegradable polyesters are incompatible to standard polymers like polyolefins, PS, and PVC, forming large domains in blends with standard polymers.

Table 9. Sensitivity of polymers to moisture, thermal melt instability, and crystallization rate

Polymer	Moisture tolerance	Thermal melt instability	Crystallization rate
Polyolefins	no	> 320 °C	low – high
PVC	no	> 180 °C	no
PET	< 100 ppm	> 300 °C	low
PS	no	> 270 °C	no
PLA	< 200 ppm	> 270 °C	no – high
PBAT	< 1000 ppm	> 270 °C	low
PBS	< 200 ppm	> 270 °C	high
PHA	low	< 190 °C	high

2. Sensitivity to moisture. Chain cleavage caused by hydrolysis depends on the type of polyester, the moisture level, and the processing temperature and time [56–58].
3. Reduced thermostability at higher melt temperatures. Natural polymers like starch or cellulose become instable at processing temperatures above 170-180 °C, depending on the processing time. Decomposition and charring occur under these conditions. Synthetic biopolymers like PBAT, PCL, and PBS are stable without significant change of viscosity until 200 °C. A significant change in melt viscosity is observed at a melt temperature above 230 °C for PBAT [59].
4. Low crystallization rate. Biodegradability is related to a low degree of crystallinity [58, 60]. Thus a low crystallization rate enables the converter to control crystallinity. This is important because a high degree of crystallinity correlates to high mechanical properties.

The sensitivity of biodegradable polyesters to these limitations depends on their chemical composition (Table 9).

5.2. Extrusion

Extrusion is a continuous conversion process by melting and subsequent transformation of granules or powders of biodegradable polymers and additives into semifinished or finished articles like sheet, profiles, tubes, bottles, films, tapes, or monofilaments (e.g., lines, yarns). The term "extrusion" also refers to compounding processes, because the same definition applies to the production of granules by either cutting strands or directly by underwater pelletizing.

Single-screw extrusion is the most common conversion process for biodegradable plastics. Only injection-molded and injection stretch blow molded rigid containers like closures and bottles are not produced by a continuous extrusion process.

The common element of extrusion processes is the extruder itself. Thermoplastic biopolymer granules are introduced into the hopper by means of automatic dosing equipment. The granules enter the screw at the cooled barrel inlet. In the screw the material is conveyed, densified, deaerated, and eventually melted by means of energy dissipation and external barrel heating. Shear and mixing elements on the screw allow for a good and even temperature distribution in the screw channel. At the end of the screw, the back pressure from the die needs to be generated for proper flow control [61].

Basically, biodegradable polyesters are designed to run on existing extruders for polyolefins, PS, PVC, or PET. The limitations of biodegradable polyesters have to be addressed by the selection of an appropriate extruder.

Because of the incompatibility of standard polymers to biodegradable polyesters, an appropriate purging procedure has to be developed.

Because of their sensitivity to moisture, biodegradable polymers need to be processed either in a dried form or on extruders which extract volatile components [62].

Usually high shear forces and stagnation zones should be avoided when processing biodegradable polyesters, e.g., starch compounds because they are sensitive to thermal degradation [63].

5.3. Blown-Film Extrusion

In general, mechanical properties of polymers are improved by orientation processes [54, 56, 58]. Because of the biaxial orientation, films from blown-film lines exhibit a high puncture resistance. Blown-film lines are designed to produce flexible PE-LD or PE-HD films ranging from 5 – 200 μm.

The extrusion process requires the following steps:

1. The biodegradable polyester is first processed by the extruder forming a melt stream with constant melt temperature and output

rate. The melt is transformed into a tube in the die head using spiral mandrel-type dies.
2. The tube leaves the die at or close to melt temperature. It is cooled down quickly by the air ring and in some cases the internal bubble cooling.
3. The sizing unit allows for an even cooling process of the film as well as a fixation of the film bubble. The ratio of the maximum bubble diameter to the diameter of the die exit yields the blow-up ratio — an important measure for the biaxial orientation of the film.
4. After the sizing basket, the film thickness is determined by the thickness measuring unit.
5. The film bubble is collapsed to a flat tube in the collapsing frame, which is typically equipped with aluminum rolls, wooden boards called slats, or an airboard.
6. A reversing unit changes the position of the film in the cross direction by turning the film continuously.
7. The web is split and wound in two flat film rolls.
8. The production process can be controlled by automatically keeping constant meter weight, thickness distribution, and film width. This device enables an automatic quality control of the production process.

Specific requirements for biodegradable polyesters are:

- Biodegradable polyesters like PBAT and their compounds, PBS, PBSA, and PCL run well on extrusion lines for PE-LD. Branching and chain extension, e.g., of PBAT lead to a good bubble stability even at low thickness of ≤ 15 μm.
- Low melt temperatures, e.g., 140 – 170 °C for PBAT and PBAT/starch compounds and 165 – 190 °C for PBAT/PLA compounds can be achieved, which are beneficial for blown-film stability and thermal stability of biodegradable polymers.

Welding. PCL, PBAT, and its compounds are weldable on existing bag-making machines for PE-LD und PE-HD—but at lower welding temperatures of, e.g., 90 – 100 °C for PBAT. As the crystallization process is slower than with PE-LD, the welding line can stick to the surface, if direct surface contact is possible. Therefore, the welding machine has to allow for extra cooling of the weld lines.

5.4. Cast-Film Extrusion

Cast-film extrusion of polyolefins has been developed to obtain flexible films with a high level of transparency by freezing the amorphous polymer structure of the melt on a chill roll. Cast films are mono-oriented in the extrusion direction.

The process is divided into the following steps:

1. The biodegradable polyester is first processed by the extruder, which forms a melt stream with constant melt temperature and output rate.
2. In the forming section, the melt streams of several extruders can be merged into one using an adapter feed block. This device controls the flow of each stream to obtain an even layer distribution [64].
3. Then, the melt stream is transformed into a flat film in the film die. The thickness distribution is controlled automatically by means of expansion bolts. The melt film leaves the die in a defined angle to obtain a tangential contact with the chill roll, maximizing the contact angle with the chill roll and thus the cooling capacity. Between die exit and the contact line on the chill roll, the film is stretched by a factor of 10 – 50 within a fraction of a second. The film is positioned on the chill roll by static discharge units. After the subsequent chill rolls, the film thickness distribution is determined by a thickness measuring unit. The film can be corona-treated using an electrical discharge process to increase surface tension and thus facilitate printing. In most cases, this procedure is not mandatory for biodegradable polymers because their surface tension is > 38 dyn without corona treatment.
4. The film is wound into rolls using a contact/surface winder with an option for automatic roll change.
5. The production process can be controlled automatically, keeping meter weight and thickness distribution constant. This device enables an automatic quality control in the production process.

Specific requirements for biodegradable polyesters are:

- Biodegradable polymers are processed at low melt temperatures, e.g., 170 °C for PBAT and 170 – 190 °C for PBAT/PLA compounds.
- A mat chill roll with a high surface roughness should be used to minimize sticking problems of biodegradable polyesters. The chill-roll temperature should be kept at about 30 – 40 °C for PBAT/PLA compounds. Pure PBAT can be run at lower chill-roll temperatures.
- Because of the limited thermal stability of, e.g., PBAT/starch compounds, dead spots in the feed block adapter or the film die have to be avoided. Thus, a reduction of the film width by closing the die gap with metal bars (deckling) is not recommended for PBAT/starch compounds.

5.5. Modification of Biodegradable Polyester Films

5.5.1. Additives

To improve processing and performance of films made of biodegradable polyesters, film qualities can be modified by using additives in the form of masterbatches:

- Slip agents are used to reduce the coefficient of friction of the final film as well as the adhesion of the film to metal parts or to itself during processing. Biodegradable amides of fatty acids, e.g., oleamide, erucamide, ethylene-*bis*-stearylamide, fatty acid esters like glycerol oleates or glycerol stearates, as well as saponified fatty acids, e.g., stearates are typically used as slip agents for biodegradable polyesters.
- Antiblock agents like talc, chalk, or silica can be used in form of masterbatches, e.g., based on PBAT [59, 67].
- Pigment masterbatches can be used to achieve specific colors in film applications. The use of pigment masterbatches is limited by the requirements on heavy metal content by the standards for biodegradability, e.g., EN 13432 [65]. Examples for heavy metal free pigments are carbon black and titanium dioxide. Carbon black pigment is used to make black films, which are applied as mulch film to increase the soil temperature in spring. Coated titanium dioxide pigments allow the production of white films, e.g., for carrier bags or for white mulch films, which reflect infrared radiation to reduce the soil temperature. The maximum loading with titanium dioxide is limited by the standards that have to be met.
- Inorganic nucleation agents like talc or calcium carbonate and organic nucleation agents can be used to improve the clarity of pure biodegradable polyesters: With their help, PBAT, PHA, or PLA films of thicknesses > 20 μm achieve the clarity level of PE-LD.
- Antifog agents like fatty acid esters are used to avoid the formation of water droplets on the film under condensation conditions, e.g., in cling film applications at the transition from room temperature to a refrigerated warehouse. The antifog agent is hydrophilic. It reduces the surface tension of droplets so that a uniform water film does not impair the clarity of the cling film [67].

5.5.2. Printing

In general, PBAT and PBAT/PLA compounds can be printed and welded on standard equipment for PE-LD. Both alcohol-based or water-based inks can be used after testing. Prior to printing, the material has to be corona-treated if the surface tension is < 38 dyn. The drying temperatures should be kept below PE-LD conditions, depending on the content of PLA in the PBAT/PLA compound. As drying conditions depend very much on the machine design, they should be determined during production trials [67].

5.5.3. Metallization

Depositing of a thin metal layer under a high vacuum using a plasma process is one of the most efficient production processes for high-barrier films. Slip and antiblock agents in the

film have to be avoided, because surface defects reduce the barrier properties of the coating. Biodegradable polyesters like PLA, PBAT/PLA compounds, and cellulose derivates like cellophane can be metallized on standard equipment [66].

5.5.4. Multilayer Films

Film properties of different polymers can also be combined to meet the requirements of specific applications.

In the lamination process, films of different materials are bonded using heat and/or biodegradable adhesives [68]. A metallized film, e.g., from PLA with high barrier and stiffness can also be laminated onto a PBAT/starch compound with good welding performance to produce a stand-up pouch for detergents.

A reason for the use of multilayer films is to minimize the use of additives. Surface active additives like slip, antiblock, or antifog agents are used only in the outer layers of a multilayer film. The migration of the organic additives and their solubility in the polymers has to be considered.

5.6. Extrusion Coating

→ Plastics, Processing, 1. Processing of Thermoplastics

Extrusion coating has been developed to form thin polymer layers on flexible substrates like paper, paper board, and metal foils in a high-speed process [68–70]. In combination with paper and paper board, the polymer protects the substrate from moisture, oil and fat. The polymer provides the welding properties to transform, e.g., the paper board/polyethylene substrate into a paper cup, a liquid carton or a box for frozen food.

Biodegradable polyesters like PBAT and PBAT compounds have a good adhesion to paper and cardboard. PBAT compounds can be processed on existing extrusion coating lines designed for PE.

5.7. Sheet Extrusion and Thermoforming

Sheet extrusion lines produce foils and sheet from 200 μm to > 10 mm. Packaging applications usually require thicknesses < 2.5 mm, which can be provided in rolls for the subsequent thermoforming process. Sheet extrusion lines have originally been designed for PP, PS, PS copolymers, PET, and PC [70, 71].

The extruder provides a continuous, thermally homogeneous melt stream which is transformed into a sheet by a die. The sheet thickness is controlled by the die and the line pressure distribution in the roll stack. The sheet has to cool down slowly to avoid the build up of high internal stresses which influence the subsequent thermoforming process.

During the thermoforming process the sheet is heated above the glass transition temperature and below the melting point of the crystalline phase. Afterwards, the hot sheet is formed into a chilled mold using vacuum, pressure, and/or mechanical force. After a cooling step, the thermoformed containers are trimmed and ejected. The skeleton — some 30 – 70 % of the total volume — is recycled in the same application [72].

Inline extrusion/thermoforming machines integrate the processes of sheet extrusion and thermoforming. After sheet extrusion, the hot sheet is transferred and processed in the thermoforming unit.

Biodegradable polyesters have to be dried before sheet extrusion. Melt temperatures of 180 – 220 °C can be used for PLA and PLA/PBAT compounds. Reprocessing of about 30 – 70 % of regrind from the subsequent thermoforming process requires an acceptable processing stability of the biodegradable polyester for 5 – 10 processing cycles. Inline extrusion/thermoforming machines provide the best recycling performance because the contact of the scrap to air moisture is minimized.

5.8. Injection Molding

The advantage of the injection molding process is the accurate reproduction of complex three-dimensional shapes [73, 74].

The melt is plastified into a reservoir in front of the screw using an extruder unit as described in Section 4.2. In contrast to this extruder, the screw of the plastification unit of an injection-molding machine is pushed back while the melt for the next shot is produced. The next shot starts with the injection of the melt through a melt distribution system of runners and sprues which provide an even filling of the mold.

Injection pressure is maintained on the injected part to refill the loss of volume of the polymer during the cooling phase until the sprues are frozen. After the cooling period, the part is ejected. Hot runner sprue systems are constantly kept at melt temperature to avoid scrap from sprues in cold runner systems.

Biodegradable polyesters can be injection-molded as well. But because of the slow crystallization of most biodegradable polyesters the cooling times have to be prolonged, thus increasing production costs. In the production of injection-molded packaging like dairy cups, lids or caps, and closures, hot-runner systems are standard to enable a scrap-free production. To be used in these hot-runner systems, the thermostability of the biodegradable polyester must be at a high level. Currently, only a few applications have been realized using PLA, PBS, and cellulose acetates in injection-molding processes.

5.9. Blow Molding

Blow molding is the main process for the production of hollow articles like bottles, jerry cans, drums, vats, fuel tanks, and integrated bulk containers. Originally the process has been designed for PE-HD, but today a variety of different plastics can be used in blow molding [75, 77]. Blow molding can be performed in a continuous process (extrusion blow molding) and in a discontinuous process (injection stretch blow molding).

Extrusion Blow Molding. In order to achieve a high melt strength, a parison is extruded at low melt temperature (e.g., PBAT/PLA compound: 170 °C; PE-HD: 180 – 220 °C) using an extruder as described in Section 4.1 and 4.2. The parison is clamped between the two parts of a mold and inflated into the mold. After a cooling step, the hollow article is ejected. Scrap (30 – 70 %) is trimmed off and recycled into the same application [75, 76].

In extrusion blow molding, biodegradable polyesters have to fulfill basically the same requirements as for the sheet extrusion/thermoforming process.

Injection Stretch Blow Molding. The injection stretch blow molding (ISBM) process has been designed to improve the performance of PET bottles by using a biaxial stretching process at temperatures above glass transition temperature to maximize crystallization, clarity, barrier, and mechanical properties without scrap. Thus, less material is needed than in extrusion blow molding. The process can also be used well with PP or PS [78]:

A preform of the shape of a test tube with a defined thickness distribution is injection-molded in one unit (Section 5.8). The preform is transferred to the stretch-blowing unit and heated above glass transition temperature. Then, it is stretched by using a metal device and inflated by pressure. After cooling, the hollow article is ejected.

Biodegradable polyesters like PLA and PBAT/PLA are suitable for ISBM because they can be oriented sufficiently without failure in the biaxial stretching process.

The advantage of the ISBM is the scrap-free production, thus one is free from the thermostability requirements due to the recycling process. For hollow biodegradable articles, it is a challenge to keep the balance between good mechanical properties—requiring a high level of crystallinity—and good biodegradability—requiring a low level of crystallinity.

6. Market Overview and Growth Drivers

Compared to the global market for PE film applications (approx. $30\,000 \times 10^3$ t in 2007), the market for biodegradable polymers (65×10^3 t in 2007; excl. loose fill) represents a small niche segment, which has been established over the last decade. The competitive advantages and market drivers of biodegradable polymers in specific applications are based on

- superior life-cycle eco-efficiency (e.g., for garden waste bags)
- changing consumer behavior based on higher sensitivity for environmental issues and an increased interest in environmentally friendly products
- increased interest of retailers to differentiate in the market
- support by municipal authorities (providing a composting infrastructure)
- legislative frameworks to enhance the use of biodegradable products (e.g., in France, Spain, Italy)

- technology progress including access to new applications
- larger production plants and increasing production capacities

The authors expect the market for biodegradable polymers to grow from 65×10^3 t (2007) to 400×10^3 t (2015), which means an average annual growth rate of 25 %. As this forecast takes into account not only the potential but also the risks of new technologies/markets, it is quite conservative compared to other market studies ranging from 480×10^3 t to 6350×10^3 t in 2015 [79]. Depending on the development of the above-mentioned factors and technology progress, the market growth for biodegradable polymers may be influenced significantly.

Biodegradable Polymers versus Feeding the World. In contrast to fuels and energy, the much lower amount of renewable resources needed for the production of biodegradable polymers does not lead to a competition to global food production. As mentioned, according to the authors, the market for biodegradable polymers will grow to 400×10^3 t in 2015. The volume of corn needed for the production of this amount of biodegradable polymers would equal approx. 0.1 % of the total $700\,000 \times 10^3$ t of annual global corn harvest [80]. This amount does not influence the overall volume balance of corn, especially when considering that other raw materials like sucrose (from sugar cane or beet) or potato starch, etc. can be used, too. With the long-term perspective of making cellulosic materials available for monomers (e.g., lactic acid) and biodegradable polymers (e.g., PLA, PHA), no correlation to food production is going to exist.

7. Value of Biodegradability — Life-Cycle Assessment (LCA)

Biodegradable plastics are developed for special applications where a possibility for a safe release into the environment is required. They are particularly attractive when economic and/or ecological benefits can be gained by leaving plastic products in the soil or organic waste stream.

To define the value of biodegradable polymers, the overall system costs and the environmental impact of individual products in their respective target applications have to be considered. To this end, comprehensive life-cycle assessments (LCA) are an appropriate tool, especially when accompanied by costs evaluations that cover all phases from the cradle to the grave.

When looking at the life cycle of biodegradable plastics, two aspects are of particular importance: the end-of-life options and the use of renewable resources in the material production (the major part of the currently available biodegradable plastic products are made of blends of fossil-based polymers and polymers derived from biomass).

By using renewable carbon from biomass, an improvement in the CO_2 balance can be achieved. However, significant effects beyond the impacts on greenhouse gas emissions are possible, e.g., soil modification, eutrophication, impact on biodiversity, land requirements, and water consumption. These aspects depend on different factors like feedstock type, scale of production, cultivation and land-management practices, location, and downstream processing routes. Especially the environmental implications of agriculture are sometimes difficult to assess by the LCA methodology and require further research.

With regard to the end-of-life phase, there are different disposal routes for biodegradable plastics.

Organic Waste. The waste in the EU contains approx. 30 – 40 % of organic waste. For the disposal of this organic waste, different end-of-life options are possible: landfilling, incineration, and biological treatment.

Landfilling. This traditional way is still the one disposal method used most widely in the EU. In landfills, biodegradable waste decomposes to produce landfill gas and leachate. The landfill gas consists mainly of methane and, if not captured, it contributes considerably to the greenhouse effect. For this reason, the diversion from landfill is an important part of the European Waste Framework Directive.

This directive (amended in 2008) stimulates a more intensive utilization of organics waste, the diversion from landfill, separate collection of organic waste, and treatment in a way that fulfills a high level of environmental protection. It supports the use of environmentally safe

materials produced from organic waste. The member states are requested to amend their national waste laws within two years after its coming into force.

Incineration. Organics waste is usually incinerated as part of mixed municipal waste stream. Depending on the facility and the energy use, this process can be regarded as energy recovery or as disposal. As the moisture content in organics waste is mostly very high (about 60 %), the efficiency of such processes is quite poor.

Biological Treatment. Composting is the most common biological treatment option. It may be considered as a recycling option when the resulting compost is used as fertilizer or soil improver. Effects like increased water retention capacity and improved soil structure are ecological benefits which are of particular importance when soil erosion is a serious problem (for example in some Southern European countries).

Anaerobic digestion is a method of producing biogas from organic waste for energy purposes and, thus, could be seen as energy recovery. This waste management option is especially suitable for treating wet organics waste. In addition, the processes of digestion and composting are usually combined as successive steps at one facility.

Direct Release in Agricultural Applications. A nonbiodegradable agricultural film has to be recollected after use (labor costs) and disposed (or recycled), which generates additional costs within the system. In contrast to PE film, the biodegradable agricultural film can be simply tilled into the ground.

8. Applications

The following paragraphs describe the major applications today and to come (loose-fill applications excluded). An overview of applications and volumes for 2007 and 2015 is shown in Table 10. Volumes are expected to grow from 65×10^3 t in 2007 to 400×10^3 t in 2015. Compounded annual growth rate (CAGR) is 25 % Table 11 shows an overview of the material properties with respect to the applications and the standard polymers.

8.1. Organic Waste Bags

As described above, composting is the most favored method of recovery of post consumer organic waste. Composting is already well-established in some European countries, and is being established in others. The Netherlands and Germany are the leading counties in the development of a composting infrastructure. In these two countries, 95 % and 60 % of all households, respectively, have access to industrial composting plants. In the EU, organic matter accounts for 30 – 40 % of total domestic refuse. With the expectation of continuous expansion of the composting infrastructure, a significant growth of organic waste bags is expected.

From a technical point of view, compost bags have to be biodegradable according to EN 13432. Beyond the mechanical properties, it is necessary to down-gage the bags at 15 – 30 μm to achieve a good LCA. The temperature resistance should allow transport and storage at 60 °C. Breathability, i.e., low-barrier properties for water and gases are an advantage. The proposed biodegradable polymers fulfill these basic requirements for compost bags. Only the moderate stiffness of PBAT and the low heat resistance of PCL (40 °C) limit the use of these materials for compost bags.

Paper is a biodegradable alternative to plastics. Compost bags made of paper are rather heavy. Pure Kraft paper exhibits a limited resistance to oil and fat and the rough surface limits the printability. But the acceptance on customer level is high because paper is perceived as an environmentally friendly material.

Table 10. Development of applications for biodegradable polymers

Application	Volume 2007, 10^3 t	Volume 2015, 10^3 t	Comment
Organic waste bags and shopping/carrier bags	16	131	most established segment
Packaging including foam	42	248	food and nonfood packaging
Mulch film and horticulture	7	21	
Sum	65	400	

Table 11. Applications of biodegradable polymers and compounds

Application	Reference polymers	PLA	Starch+ PBAT	PLA+ PBAT	PHB	PBS/ PBSA	PCL	Biodegradable alternative	Comment
Basic: flexible film Compost bags	PE	○	●	●	○	●	◔	paper	material selection depends on desired property profile, e.g., PE-LD- or PE-HD-like
Mulch film	PE	○	◔	◔	○	◔	◑	paper	biodegradability depending on local climate is key issue
Development flexible film Carrier bags	PE	○	●	●	○	●	◔	paper, cotton	material selection depends on desired property profile, e.g., PE-LD- or PE-HD-like; political application
Shrink film	PE	○	◑	●	?	?	?		development status
Hygiene film	PE	○	●	●	○	◑	◑		development status
Knitted nets	PE-HD	◑	◔	●	◑	◔	◑	cotton	development status, biodegradability depends on stress induced crystallization.
Rigid container Extrusion + thermoforming	PET, PP, PS, PVC	◔	○	◔	◑	◑	◑	cardboard	extrusion-coated cardbord is an alternative for nontransparent market
Injection molding, ISBM	PP, PS, PET	◑	◑	◑	◔	◑	●		development status, biodegradability of bottles to be enhanced

● Application requirements fulfilled as described

◔ 1 Property < 70 %

◑ 2-3 Properties < 70 %

○ > 3 Properties < 70 %

8.2. Shopping (Carrier) Bags

Changing consumer behavior based on higher sensitivity for environmental issues and an increased interest in environmental friendly products accompanied by an increased interest of retailers to differentiate in the market are the major drivers for the market growth of biodegradable shopping bags. After shopping, these bags can be applied for the disposal of organic waste resulting in a double use of the material.

Thin biodegradable carrier bags have a property profile which is similar to that of compost bags:

- Good mechanical properties for loads of about 1000 times of their own weight
- Good puncture resistance, e.g., for liquid beverage cartons
- Down-gaging to 10 – 20 μm
- Good printability (8 color flexo printing) for superior presentation
- Good welding performance for high-speed bag making
- Usefulness as compost bags after several services as a carrier bag

Except for the optical presentation and the resulting need for printability, biodegradable carrier bags have to fulfill the same requirements as biodegradable compost bags. Thus the material options are also the same.

Because of the higher prices of high-end carrier and shopping bags, paper bags are more often used as shopping than as compost bags. However, paper bags with high-quality printing and coatings are generally not biodegradable because of the coating materials applied.

8.3. Mulch Film

Agricultural films are a well-established application in Japan and the EU. This application is very cost-sensitive because of the subsidy structure of the agricultural sector of the EU. However, the regulations for waste disposal of mulch film require either recycling or adequate treatment (e.g., incineration). If thin mulch films are concerned, the recovery of the film in the field is crop-dependent and difficult. Cleaning of the soil residues is cost intensive. In this case it can be more cost-effective to use biodegradable mulch film, which is adapted to the climate and the fruit application.

Cucumber, e.g., is harvested up to 25 times per growing season using heavy machinery. At the end of the season, the mulch film is difficult to recover. For this application the use of biodegradable mulch film is of interest.

Because of the limited UV resistance of PBAT, it is difficult to use this polymer and its compounds for mulch-film applications: In Europe, more than eight weeks of intact performance of the mulch film is required. PCL does not exhibit the necessary temperature resistance for this application. PBS and PCL biodegrade too quickly for most mulch-film applications—they need to be formulated with a plastic of slower biodegradability like PBAT.

Since the most important property of mulch film is the appropriate biodegradability, extensive experiments in each region are indispensable.

8.4. Horticulture

Different horticultural items made of biodegradable polymers such as plant pots, seed/fertilizer tape and binding materials, foams, and nets for erosion control offer reduction of system complexity by reducing the number of work steps.

8.5. Packaging

The packaging market, especially the food packaging market, offers large opportunities for biodegradable polymers. In the following section, the focus will be on flexible food packaging, rigid food packaging, and paper coating (see also → Foods, 4. Food Packaging). For nonfood packaging, the example of hygiene film applications will be described in more detail.

8.5.1. Food Packaging

Shrink films are used to combine several sales items in one packaging — e.g., six bottles in a six-pack. The bottles are packed in a piece of film which is heated and shrunk in a heating tunnel above the melting point of the film for a short time. The shrink forces after relaxation

have to stay high enough to store and carry the packaged goods along the logistic chain: Thus the requirements are:

- High shrink values in extrusion direction MD > 60 %
- Low shrink values in cross direction CD < 20 %
- High shrink rate during heating in the oven
- Welding of the loose end during shrink process
- High shrink forces after relaxation

Although the market is large, biodegradable shrink films are still under development. PBAT/PLA compounds have a good strength and an adequate heat resistance. Films thereof exhibit the necessary shrink values. These prerequisites are promising—but still the materials need to be tested in more detail.

Knitted nets are produced from blown film or specialized extrusion lines with corotating dies. The film rolls are slit into small tapes of 2–5 mm width. Then the tapes are stretched on heated rolls (galettes) in several steps to achieve and maintain a high level of orientation. Typical stretching factors are 3–5 times. Thus, the materiel undergoes a strain-induced crystallization which maximizes the crystallinity level in the tape.

Based on the processing, polymers like PCL, PBS, and PHA obtain a high crystallinity. High crystallinity levels correlate to low biodegradability speed. Therefore, amorphous polymers like PBAT compounds are more suitable. However, pure PBAT is too soft and elastic for orientation.

Rigid Packaging Containers. Transparent rigid containers account for about 60 % of the European market for rigid packaging. They are best produced using PLA in an extrusion/thermoforming, blow-molding or injection blow-molding process. If biodegradability is an issue for the application, it needs to be checked under composting conditions.

Nontransparent containers (e.g., dairy cups) account for the remaining 40 % of the European market. If toughness requirements are not met by PLA, PBAT/PLA blends can be used for the extrusion of rigid containers. They have an adequate viscosity and they can be recycled if the moisture problem is solved by drying the recycled material (like virgin PLA: to a moisture level below 200 ppm).

PBAT/PHA compounds have a high temperature resistance and a good stiffness/toughness ratio. However, up to now they are too sensitive to thermal decomposition in processing. PBS and PCL are too soft for rigid containers. Moreover, PCL shows a limited thermal stability and PBS still has to prove its suitability for food contact in the EU.

Paper Coating. Coated or laminated paper products represent another potential market for biodegradable polymers. At present, paper packaging such as disposable cups are extrusion coated with PE-LD, which restricts the biodegradation of the paper substrate since it acts as an impervious barrier. By using biodegradable polymers, the synergies with the biodegradable paper can be fully explored. Synthetic biodegradable polymers, such as PBAT or PBAT compounds, thus take over the function of the PE-LD and are used to toughen and to protect against fat, moisture, and temperature variations.

8.5.2. Nonfood Packaging

Hygiene films have to be soft, permeable, strong and thin:

- Soft films comply with the haptics of, e.g., diapers
- Only water-vapor-permeable films are comfortable to wear
- Strong films fulfill the requirements for high-speed processing during assembly of hygiene products
- Thin films comply with the requirements of the LCA as well as reduce cost
- The film has to comply with various regulations concerning skin contact.

Currently only PBAT compounds fulfill all the requirements, because the ratio of stiffness/flexibility can be adjusted by the PBAT content. Pure PBAT is too soft, PBS is too stiff and PCL too temperature-sensitive for hygiene applications. The materials still have to pass the relevant tests for skin contact.

Foam. For loose-fill applications, foamed biodegradable polymers based on starch have been

Table 12. Expected development of production capacities of biodegradable polyesters and compounds

	Manufacturers	Product	Capacity 2007, t/a	Capacity 2010, t/a	Country
PLA	Cargill	NatureWorks	70 000	140 000	USA
	Pyramid Bioplastics Guben GmbH	PLA	0	60 000	Germany
Starch-based compounds					
	Novamont	Mater-Bi	20 000	60 000	Italy
	Biotec	Bioflex	10 000	20 000	Germany
PHA					
	Tianan	Enmat	1000	10 000	China
	Metabolix/ADM	Mirel	5000	50 000	USA
Aliphatic/aromatic polyesters					
	BASF	Ecoflex	14 000	74 000	Germany
Aliphatic polyesters					
	Showa H.P.	Bionolle	3000	3000	Japan
	Daicel	Celgreen	1000	1000	Japan
	IRE Chemicals	EnPol	3000	3000	Korea
	Mitsubishi Chemicals	GS-PLA	6000	6000	Japan

used for more than one decade (not addressed in detail in the text and excluded in Table 10). A new generation of biodegradable foams for food packaging applications has been introduced to the market (e.g., by NatureWorks) or is under development (BASF, consortium PURAC/Synbra/Sulzer). The foams have the potential to replace PS foams currently used for food and protective packaging.

Others: Medical Applications. Historically, one of the first applications has been the use of biodegradable polymers for medical purposes. Quantitatively, these applications play a minor role in market size, but a major role in health and safety of medical procedures.

Nonbiodegradable Applications — Durable Use. In the last years, biodegradable polymers like PLA have been established in different nonbiodegradable applications. PLA is processed into fibers (e.g., for textiles) and is used for durable parts in electronics. The driver for these applications is the content of renewable materials and not the polymer's biodegradability.

9. Production Capacity

After one decade of market development, production capacities will be increased significantly in the next years. Next to a planned increase of the NatureWorks PLA capacity to 140 000 t/a, further suppliers of PLA will enter the market. In 2009, Telles (Metabolix/ADM joint venture) will start up its 50 000 t/a PHA capacity plant and BASF has announced the increase of its Ecoflex capacity by 60 000 t/a in 2010. A summary of existing and planned capacities is shown in Table 12.

10. Outlook

Biodegradable polymers are specialty plastics for selected applications where biodegradability adds value. The market for biodegradable polymers (65×10^3 t in 2007; excl. loose fill) represents a small niche segment compared to the global market for PE film (approx. $30\,000 \times 10^3$ t in 2007) or to the global polymer market (approx. $250\,000 \times 10^3$ t in 2007). Based on different market drivers (changing consumer behavior, improved composting infrastructure, technology, application, and capacity development), the expected growth rate of approximately 25 % p.a. can be influenced significantly. Biodegradable polymers combine different chemical and biotechnological steps in their synthesis and degradation and thus are an excellent example of a symbiosis between these disciplines.

Abbreviations

BDO	butanediol
LA	lactic acid
LCA	Life-cycle assessment
MSA	maleic acid anhydride
PBAT	poly[(butylene adipate)-*co*-(butylene terephthalate)]
PBS	poly(butylene succinate)

PBSA	poly[(butylene succinate)-*co*-(butylene adipate)]
PBT	poly(butylene terephthalate)
PC	polycarbonate
PCL	polycaprolactone
PE	polyethylene
PE-HD	high-density polyethylene
PE-LD	low-density polyethylene
PEG	poly(ethylene glycol) (also poly(ethylene oxide), PEO)
PES	poly(ethylene succinate)
PET	poly(ethylene terephthalate)
PHA	poly(hydroxyalkanoate)
PHB	poly(hydroxybutyrate)
PHBH	poly(hydroxybutyrate-*co*-hexanoate)
PHBV	poly(hydroxybutyrate-*co*-valerate)
P(3-HB)	poly(3-hydroxybutyrate)
P(4-HB)	poly(4-hydroxybutyrate)
PLA	poly(lactic acid)
ROP	ring-opening polymerization
PP	polypropylene
PS	polystyrene
PVC	poly(vinyl chloride)
PVOH	poly(vinyl alcohol)

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Polymers, Electrically Conducting

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1. Introduction

Electrically conducting polymers (ECPs) are materials with an extended system of C=C conjugated bonds. They are obtained by reduction or oxidation reactions (called doping), giving materials with electrical conductivities up to 10^5 S/cm. These materials differ from polymers filled with carbon black or metals because the latter are only conductive if the individual conductive particles are mutually in contact and form a coherent phase.

This review concerns the synthesis routes, polymerization techniques, doping, orientation, and development of well-defined, highly conducting polymeric materials. Their wide range of potential uses from electrodes in rechargeable batteries to organic transistors is limited by their vulnerability to air and moisture due to their highly conjugated structures and the doping agents. Electrically conducting materials are compiled, their specific properties and potential applications are described.

Numerous attempts have been made to synthesize "conductive organic materials". The first was the synthesis of polyaniline by F. Goppelsroeder in 1891 [1]. After decades interest grew in organic polymers as insulators, but not as electrical conductors.

In the late 1950s organic semiconductors became the focus of investigations. Preliminary studies in this field up until the mid 1960s are reviewed in [2]. The semiconducting polymers were termed "covalent organic polymers", "charge-transfer complexes", "organometallic polymers", "hydrogen-bonded polymers", and "mixed polymers". Highest conductivity values reached about 10^{-3} S/cm. In 1964 Little theoretically evaluated the possibility of superconductivity in polymers and suggested a model, consisting of a polyene chain with cyanine, dyelike substituents [3]. In the same year systematic studies were presented based on aromatic and heterocyclic compounds exhibiting electrical conductivities of 0.5 S/cm [4], followed by studies correlating doping, pressure, irradiation, and chain length to conductivity, with values up to 100 S/cm [5].

Interest heightened and became acute from 1975 when IBM scientists showed that poly (sulfur nitride), $(SN)_n$, was superconductive [6] and MacDiarmid's group reported [7] the doping of polyacetylene films prepared by Shirakava [8] reaching conductivity values of 38 S/cm. Since then many expectations have been raised, but scientific progress and practical

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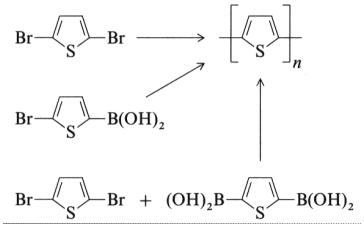
applications have been limited; they depend on the reproducible production of well-defined specimens, the determination of synthesis conditions, and the laws relating these conditions to product properties. Synthetic methods are improving; more easily processible, soluble, flexible materials are now being produced.

2. Synthetic Routes

The synthesis of electrically conducting polymers with conjugated –HC=CH– bonds requires the controlled coupling of a large number of monomers (unsaturated compounds or compounds with difunctional groups). Alternatively, pendant groups attached to existing polymers can be cyclized to give conjugated systems.

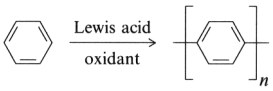
Polymerization of unsaturated monomers gives polymers with long chains that are often branched and cross-linked and therefore insoluble. Alkynes polymerize as follows:

1. n HC≡CH → CH=CH$_n$ insoluble polyacetylenes [9]
2. n HC≡C–CH=CH$_2$ → CH=CH–CH=CH$_n$ insoluble polyacetylenes [9]
3. n RC≡CH → CR=CH$_n$ soluble polyacetylenes where R denotes alkyl or aryl groups [10]
4. Alkyne or allene → 460 °C thermal polymerization, insoluble polyenes and aromatics [11]

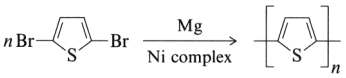


Stepwise coupling of monomers with difunctional groups runs in a more controlled fashion than polymerization of unsaturated monomers but problems are caused by low conversion rates and purification of the starting monomers. This method includes Wittig, MacMurry, retro Diels – Alder, and elimination reactions. It is accessible to a wide variety of soluble precursors and produces defined polymers. Examples follow:

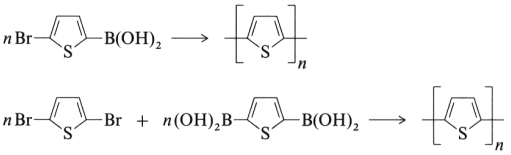
1. Oxidative coupling [12] can be applied to pyrrole, thiophene, aromatic, and heteroaromatic systems (0 – 350 °C)



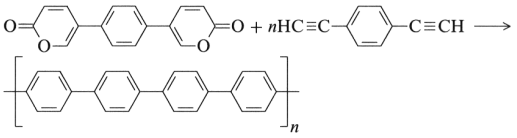
2. Grignard coupling [13]:



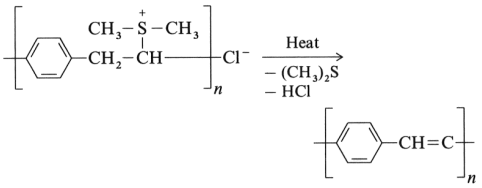
3. Boronic acid coupling [14]:



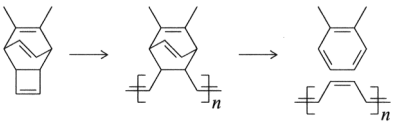
4. Stille reaction [15]:



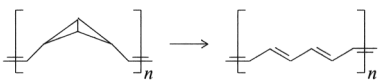
5. Elimination reactions [16]:



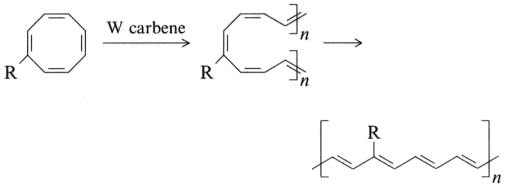
6. Feast reaction (retro- cycloaddition) [17]:



7. Grubb's method: polybenzvalene is isomerized to polyacetylene in the presence of $HgCl_2$ [18]:

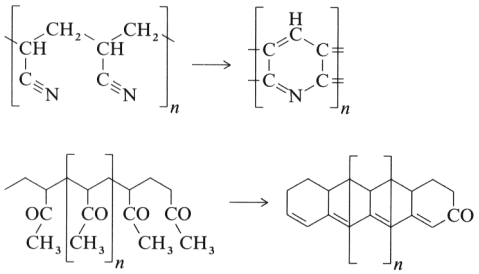


Cyclooctatetraene is also polymerized to give soluble polyenes [19]:



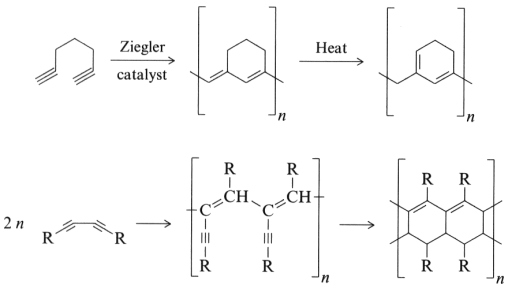
Polycyclization starts with polymers whose pendant side groups are cyclized to give condensed systems, often under pyrolytic conditions. Defects cannot be excluded.

These methods lead to the basic structures of electrically conducting organic materials (ECOMs) and are reviewed in [9]. Examples follow [12]:



Analogous reactions occur with $-CH{=}CH_2$ pendant groups.

Monomers may also be cyclized [10], [20]:



3. Principles of Electrical Conduction

The electrical properties of materials are determined by their electronic structure (Fig. 1). The band theory accounts for the different behaviors of metals, semiconductors, and insulators.

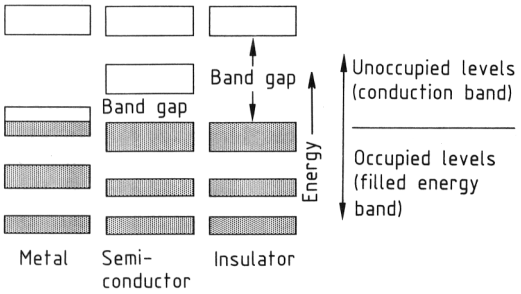


Figure 1. Model of band structure

The band gap is the energy spacing between the highest occupied energy level (valence band) and the lowest unoccupied energy level (conduction band). Metals have a zero band gap which means that they have a high electron mobility, i.e., conductivity. Semiconductors have a narrow band gap (ca. 2.5 – 1.5 eV), conductivity only occurs on excitation of electrons from the valence band to the conduction band (e.g., by heating). If the band gap is larger (> 3 eV), electron excitation is difficult; electrons are unable to cross the gap and the material is an insulator [21].
Electrically conducting organic materials such as polyphenylene, polyacetylene, or polypyrrole are, however, peculiar in that the band theory cannot explain why the charge-carrying species (electrons or holes) are spinless. Conduction by polarons and bipolarons is now thought to be the dominant mechanism of charge transport in organic materials [22]. This concept also explains the drastic deepening of color changes produced by doping. A polaron (a term used in solid-state physics) is a radical cation that is partially delocalized over several monomer units (e.g., in a polymer segment). The bipolaron is a diradical dication. Low doping levels give rise to polarons, whereas higher doping levels produce bipolarons. Both polarons and bipolarons are mobile and can move along the polymer chain. See also, → Plastics, General Survey.

Doping. The process that transforms insulating polymers (e.g., polyacetylene, conductivity 0.1 S/cm) to excellent conductors (Fig. 2) is the formation of change-transfer complexes by electron donors such as sodium or potassium (*n* doping, reduction) or by electron acceptors such as I_2, AsF_5, or $FeCl_3$ (*p* doping, oxidation). The doped polymer backbone becomes

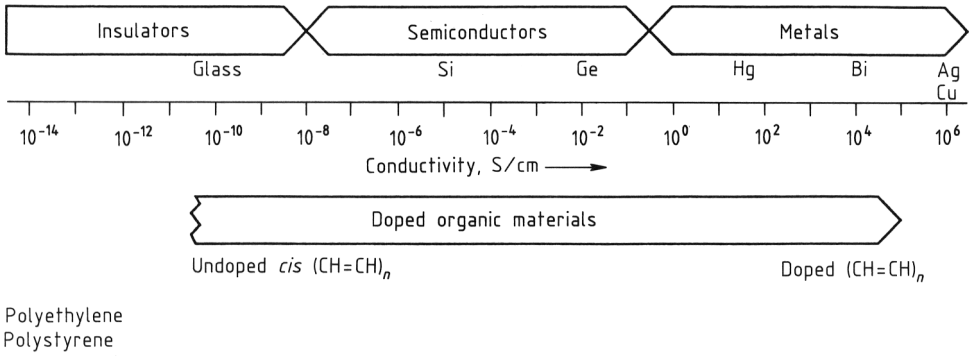


Figure 2. Comparison of the electrical conductivity (300 K) of organic and inorganic materials and the effect of doping

positively or negatively charged [23] with the dopant forming oppositely charged ions (Na^+, K^+, I_3^-, I_5^-, AsF_6^-, $FeCl_4^-$). The polymer can be switched between the doped, conductive state and the undoped, insulating state by applying an electric potential that makes the counterions move in and out. This switching corresponds to charging and discharging when these materials are used as electrodes in rechargeable batteries.

Measurement. Electrical conductance is a measure of the flow of current through a material for a given applied voltage [24].

The electrical conductivity σ in reciprocal ohms or siemens per centimeter (Ω^{-1} cm^{-1} or S/cm) denotes the current flow through a body of length 1 cm and with a cross-sectional area of 1 cm^2. The conductance σ is usually measured via its inverse, the electrical resistance R ($\sigma = 1/R$).

The resistivity is the inverse of the conductivity

$$\sigma = \frac{d}{F}\frac{1}{R}$$

(R in Ω, σ in Ω^{-1} cm^{-1}, d is the thickness of the specimen in cm, and F its surface area in cm^2).

Ohm's law ($R = V/I$) is valid for electrical conductors (metals) and semiconductors and allows R to be determined by measuring the applied voltage V in volts and the current I in amperes with a simple measuring system (Fig. 3) or with a Wheatstone bridge.

With high resistances (i.e., $\sigma = 10^{-4}$ to 10^{-14} S/cm), two-point measurement is enough. Higher conductivities, as in electrically conducting polymers, require four-point measurements because the contact resistances in the circuit are frequently as great or greater than that of the material under investigation.

Contactless measurements of the conductivity are possible in a microwave field [24].

4. Orientation Processes

Orientation processes are powerful methods that are used to improve conductivity and other material properties (e.g., transparency, anisotropy). Orientation can be achieved in several ways, including stretching.

Mechanical stretching can be performed after polymerization, e.g., in noncross-linked polymers [25]. In the case of polyacetylenes prepared with aged Ziegler – Natta catalysts [26], [27], stretching increases conductivity from 2500 S/cm to values as high as 10^5 S/cm.

Continuous electrochemical polymerization (e.g., of polypyrrole) on the surface of a rotating drum permits simultaneous peeling off,

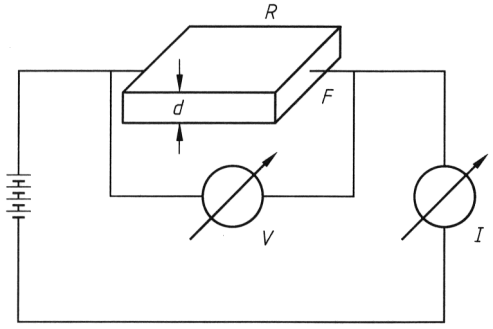


Figure 3. Conductivity measurement equipment

mechanical stretching, and orientation $\sigma \leq 200$ S/cm [25]. Greater stretching rates and therefore greater conductivities are reported in poly(pyrrole perchlorate) films (σ up to 10^3 S/cm) [28]. Biaxially stretched films yielded conductivities of 800 S/cm parallel to the stretching direction and 290 S/cm in the cross direction. Stretched poly(phenyl vinylenes) and poly(thienyl vinylenes) yielded conductivities of ca. 10^3 S/cm [29].

Orientation can also occur during polymerization or by performing polymerization in an oriented matrix consisting of liquid crystals and using magnetic fields [30]. Variants are the use of liquid crystal matrices during the electro chemical synthesis of polyheterocycles [31] and the synthesis of polymers (e.g., substituted thiophenes) with liquid crystal side chains that contain sulfonate groups [32]. The sulfonate groups act as "self dopants" and the liquid crystal side chains are responsible for orientation.

Polymerization of extremely thin polyacetylene films (< 1 μm) on crystal surfaces by epitaxial growth (e.g., on frozen benzene) [33] also induces orientation in the deposited polymer layer. Substituted polypyrrole films with a high anisotropy can be produced by the Langmuir – Blodgett technique [34–36].

5. Types of Electrically Conducting Organic Materials

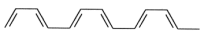
Electrically conducting organic materials can be divided into three main groups: polyenes, polyheterocycles, and polyaminoaromatic compounds. Polyacetylene, polypyrrole, and polyaniline are the most intensively studied polymers.

5.1. Polyacetylene

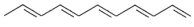
Polyacetylene (PAC) exists in various isomeric forms:



cis-transoid (*cis*-polyacetylene)
[*25786-70-1*], [*74373-36-7*]



trans-cisoid
[*73589-68-1*]



trans-transoid (*trans*-polyacetylene)
[*25768-71-2*]

cis-Polyacetylene is relatively unstable and reverts to the thermodynamically stable *trans*-polyacetylene via the metastable *trans*-cisoid form. *cis*-cisoid PAC has not yet been prepared in pure form, it has a cyclic, helical structure [37].

The term "polyacetylene" was first mentioned in 1866 [38]. In 1898, E. ERDMANN and P. KÖTHNER [39] described a "high-molecular-weight copper acetylene" that was formed when acetylene gas was passed over copper powder below 250 °C. In 1948 REPPE [40] prepared Cuprene film with a metallic luster. In 1961 HATANO reported the polymerization of acetylene with a $AlEt_3/Ti(OBu)_4$ catalyst to give polymers with conductivities up to 0.001 S/cm [41]. Since then intensive work has been carried out on the various polymer types, reviews are given in [42]. Some important syntheses are listed in Table 1. Table 2 shows the conductivities of various types

The polyacetylenes grow primarily in the form of fibrils with an internal surface area of up to 200 m^2/g [45]. The fibrils are insoluble and can be rendered electrically conductive by incorporation of *n*-type or *p*-type dopants.

The polyacetylenes are chemically unstable and react, for example, with atmospheric oxygen to form epoxy, carbonyl, or carboxyl groups. $N-(CH=CH)_n$ compounds are more stable, probably due to the absence of defect sites at high crystallinity. Conductivity increases as a function of crystallinity and decreases as a function of defects (sp^3-bonded carbon atoms, $-CH_2CH_2-$) [46].

Figure 4 illustrates two types of polyacetylene. The standard Shirakawa type (Fig. 4 A) is cross-linked and contains ca. 2 % sp^3 fractions. The new BASF technique involves polymerization at room temperature (instead of − 76 °C) and the use of a tempered catalyst. The stretched polyacetylene product has parallel fibrils (Fig. 4 B). It is linear (no sp^3 fractions), is highly orientable (can be stretched by up to 660 %), and has a conductivity exceeding 10^5 S/cm. A convincing demonstration of the high anisotropy (1: 100) in the stretched samples is the fact that when strips of such a stretched polymer are laid across each other, polarized light (sunlight) is extinguished in the region of overlap [47].

Substituted Polyacetylenes. The synthesis of polymers from substituted acetylene monomers

Table 1. Preparation and properties of polyacetylenes

Name of method	Catalyst	Polymerization-temperature, °C	*cis/trans* ratio	Defects (sp^3 fraction), %	Conductivity, S/cm (iodine doped)	References
Reppe	Ni acetylacetonate	100	5/95	15	10^{-3}	[43] (Table 1, no. 2)
Luttinger – Green	$NaBH_4$/CO (II)/Ni (II)	– 76	50/50	8	10^{-3}	[43] (Table 1, no. 6)
Hatano	$AlEt_3/Ti(OBu)_4$	100	20/80	10	10^{-5}	[43] (Table 2, no. 8)
Shirakawa	$AlEt_3/Ti(OBu)_4$ in toluene	– 76	90/10	3	520	[43] (Table 1, no. 16)
Naarmann (BASF)	1) $AlEt_3/Ti(OBu)_4$ in silicone oil	20	85/15	0	500	[44]
	2) as 1), but with an aged (> 100 °C) catalyst	20	85/15	0	2 000	[44]
	3) as 2) but oriented	20	85/15	0	$> 10^5$	[44], [45]
Feast	thermal cleavage of tetracyclobis (trifluoromethyl) decatriene	80	75/25		100	[17]
Grubbs	isomerization of polybenzvalene,	20	40/60		1	[18]
	cyclooctatetraene ring opening by carbenes	20	40/60		350	[19]

is directed toward the preparation of substituted, conjugated chains which ameliorate the negative properties of polyacetylenes (e.g., sensitivity to air, insolubility, and infusibility) while maintaining the desired electrical properties of acetylene's conjugated backbone [10], [48]. Alkyl- and aryl-substituted polymers result. They are soluble (e.g., in toluene and cyclohexane) and processible, but have low conductivities (< 0.1 S/cm) compared with the unsubstituted polyacetylene.

Modification of Polyacetylenes. The controlled modification of the polyene chain by radical reactions and Diels – Alder addition leads to functionalized systems with slightly improved atmospheric stability but diminished conjugation length and electrical conductivity. Examples

Table 2. Conductivities of some metals and different types of polyacetylene

Metal or polyacetylene	Conductivity (volume), S/cm	Density[d], g/cm^3	Conductivity (weight), S cm^{-2} g^{-1}
Hg	10 365	13.54	767
Pt	101 522	21.45	4 733
Cr	77 519	7.19	10 781
Fe	102 986	7.87	13 085
Au	470 588	19.3	24 382
Ag	671 140	10.49	63 972
Cu	645 000	8.94	72 147
Shirakawa polyacetylene [8]	897 [a]		813
	30 [b]	1.23 (0.40)	22
Shirakawa polyacetylene, oriented in liquid-crystal matrix [30]	1 600 [b]	1.10 (0.50)	1 750
BASF polyacetylene, oriented [44]	23 000 [c]	1.12 (0.85)	20 000
BASF polyacetylene with additional reducing agent, oriented [44]	120 000 [c]	1.15 (0.90)	104 347

[a] Doped with $FeCl_3$.
[b] Doped with I_2 vapor.
[c] Doped with a saturated solution of I_2 in CCl_4.
[d] Densities for polymers denote values after doping; values before doping are given in parentheses.of polyacetylenes and compares them with those of metals.

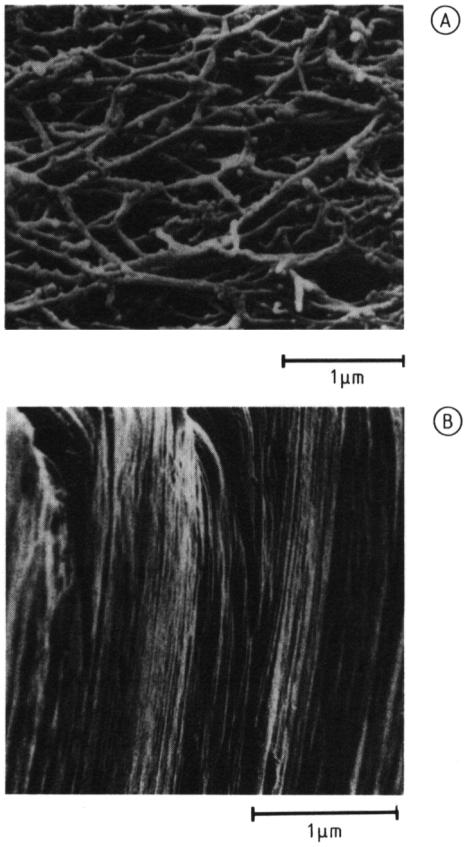


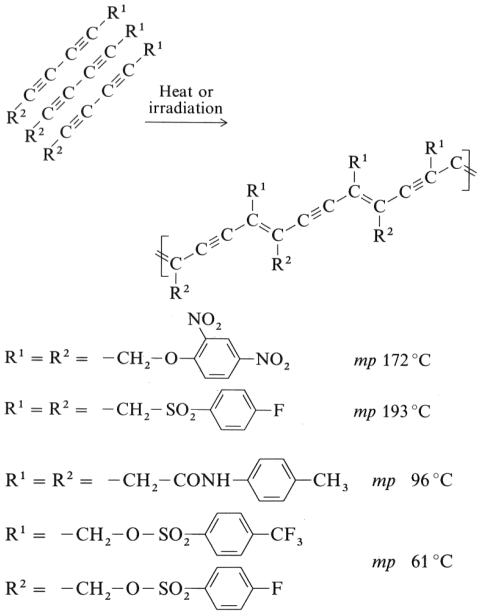
Figure 4. Scanning electron micrographs of iodine-doped polyacetylene a) Standard, cross-linked polyacetylene (conductivity ca. 500 S/cm); B) Stretched polyacetylene (conductivity > 100 000 S/cm)

include reaction with tosylmethyl isocyanide ($TosCH_2-N{=}C$) to give polyenes with pyrrole units [49], with nitrogen-substituted spin-labeled compounds to give spin labels (e.g., maleimido peroxyl groups) [50], with chlorosulfonyl isocyanate to give $-SO_3$ and $-COO^-$ groups [47], with tetrachloromethane to give $-Cl$ and $-CCl_3$ groups [27], and with 3-chloroperbenzoic acid to give epoxy groups [27]. Cycloaddition with 3,4-dichloromaleic anhydride leads to a fusible polyacetylene (165 – 180 °C) [47].

5.2. Polydiacetylenes

In contrast to polyacetylene, polydiacetylenes [27987-87-7] have limited electrical conductivity (≤ 0.1 S/cm), but can be obtained as large, single crystals.

The polymerization of diacetylene



is an example of a topochemical polymerization in which 1,4-addition of 1,3-diyne units takes place in the crystalline state. The reaction does not require a catalyst and is performed by irradiation of the diacetylene crystals with visible or UV light, X-rays, or γ-rays, or by annealing the crystals below their melting point. The unreacted monomer is then extracted with a suitable solvent (e.g., hexane, toluene), leaving a single, dark red crystal of polydiacetylene. This unique polymerization process was already observed in 1882 [51] and has now been intensively studied [52]. A correct interpretation of the phenomena was first provided in the early 1970s [53].

5.3. Polypyrrole

Polypyrrole [30604-81-0] is a polysalt that can be produced in the form of powders, coatings, or films; it is intrinsically conductive.

Synthesis. The preparation of polypyrrole (pyrrole red and pyrrole black) by oxidation of pyrrole dates back to 1888 [54] and by electrochemical polymerization to 1957 [55]. A fairly

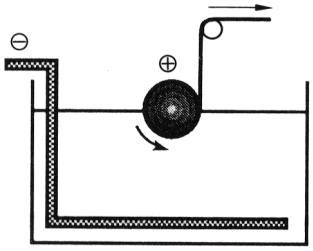


Figure 5. Continuous electrochemical process (BASF) for producing polypyrrole on a rotating drum electrode

long period elapsed before this organic π-system attracted general interest and was found to be electrically conductive [4].

Conductive polypyrrole films are obtained directly by anodic polymerization of pyrrole in aqueous or organic electrolytes (acetonitrile) [56]. They are black and, under suitable reaction conditions, can be detached from the anode in the form of self-supporting films (minimum thickness ca. 30 μm). Some of the conducting salt used in the electrolyte solution is incorporated in the film as a counterion.

In contrast to polyacetylene, polypyrrole has a high mechanical and chemical stability and can be produced continuously as flexible film (thickness 80 μm; trade name: Lutamer, BASF) by electrochemical techniques (Fig. 5) [57].

Other electrochemically polymerizable heterocycles are thiophene, furan, and their substituted and oligomeric derivatives.

The polymerization reaction is very complex. The main reaction steps are shown in Figure 6 [58]. A radical cation is formed in

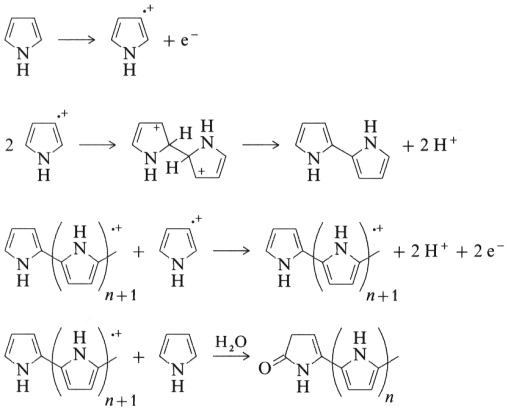


Figure 6. The oxidative coupling of pyrrole [58]

the initial oxidation step. This is followed by a coupling reaction, deprotonation, and a one-electron oxidation which regenerates the radical cation system. Also important is the reaction introducing oxygen with formation of a labile −CONH group in the ring system.

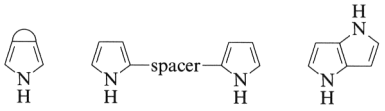
The quality of the polymers is greatly influenced by many factors, e.g., impurities, electrode material, pressure, concentrations, temperature, and comonomers. The most decisive, however, are the current density and the electrolyte, particularly the conducting anion X^- [59] because it is incorporated into the polymer as a counterion.

The properties of the counterion (e.g., its size, geometry, charge) influence the properties of the polymer. The amount of counterion (anion) incorporated depends on the reaction conditions. In general, one anion is incorporated for every three pyrrole units. Exceptions are pyrrole- or thiophenesulfonic acids where the counterion is coupled directly to the monomer (self doping) [60]. Some typical conducting anions are fluoroborate, perchlorate, aromatic sulfonic acids, penicillin, *n*-dodecyl sulfate [59], [61], phthalocyanine sulfonic acid, poly(styrene sulfonic acid), camphor sulfonic acid, styrene sulfonic acid, and heparin [52].

By changing reaction conditions, polymers with different surface morphologies, (e.g., an open porous structure) can be obtained.

The anion X^- can also be released, e.g., by applying a negative potential. Release can be specifically controlled, offering interesting possibilities for active counterions of medical interest (e.g., heparin and monobactam) that are incorporated into polypyrrole.

Variation of the monomers and their substituents yields polymers with conductivities between 10^2 and 10^{-4} S/cm [59]. Alkyl substituents also increase the solubility of the polymers with the result that electrically conducting polymers can be applied as coatings from solutions. This also applies to polymers bridged pyrroles. Examples follow [62]:



An interesting variant is the chemical oxidation of heterocycles (e.g., thiophene or pyrrole

[58]) dissolved in an organic solvent (e.g., ethanol) on the surface of various materials. Conductive coatings (thickness 0.01 μm) can be produced on films of poly(phenylene sulfone), block copolymers of butadiene and styrene (Ultrason, Styrolux), poly(vinyl chloride), or other polymer films to give transparent, antistatic films with conductivities of about 0.001 S/cm. Ceramics and glass can also be coated in this way. Porous material (e.g., wood, fabrics, and open-celled foams) or fibers (e.g., polyamide, glass, or carbon fibers) can also be modified and rendered antistatic by this method.

Conductive powders (e.g., polypyrrole) with particle sizes of about 0.1 μm and conductivities of up to 10 S/cm can also be produced by chemical oxidation and can be incorporated as fillers in thermoplastics. These materials can be used for chip carriers.

Potential Uses. The conductivity of polypyrrole film suggests applications such as flexible conductive paths in printed circuits, heating films, and film keyboards.

Polypyrrole films show good electromagnetic shielding effects of about 40 dB over a wide range of frequencies (0 – 1500 MHz).

Although the new systems appear to be promising, stability problems may be encountered. High mechanical stability and/or stable conductivity are required under a variety of conditions (e.g., presence of air and moisture, temperature, and duration of exposure). Polypyrroles in which the counterion is 4-hydroxyphenyl sulfonic acid do not undergo any change in conductivity if they are exposed to nitrogen for two months at 140 °C. No change in conductivity was observed when these polymers were stored in the laboratory for three years at room temperature and 55 % R. H. Polypyrrole is sensitive to moisture because this leads to leaching of the counterion and thus to a decrease in conductivity. This can be avoided by use of appropriate hydrophobic or polymeric counterions [e.g., camphor sulfonic acid or poly(styrene sulfonic acid)] or by incorporating hydrophilic compounds. Polypyrroles obtained by synthesis in aqueous electrolytes maintain their conductivity at a level of about 20 S/cm. Polypyrroles with perchlorate as a counterion are unstable under atmospheric conditions but can be used as electrodes in rechargeable batteries [63].

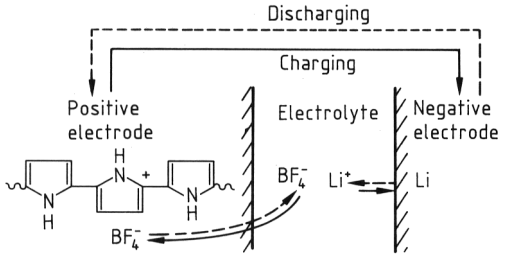


Figure 7. Electron reactions of a rechargeable polypyrrole – lithium battery
During discharge electrons flow from the negative electrode to the positive electrode and reduce the polypyrrole from the doped to the neutral state. During recharging an opposite potential is applied to the electrodes. The polymer takes up BF_4^- ions from the electrolyte and is oxidized. Lithium ions are also deposited at the other electrode.

The redox character of polypyrrole was first studied in 1975 [64]. It is a suitable electrode material for rechargeable electrochemical cells. The advantage of polymer electrodes is that they can be easily shaped, allowing novel battery designs (e.g., for the electronics sector) and less expensive production methods. Polymer cells with polypyrrole and lithium electrodes have been developed (Fig. 7) [63]. In the flat cell, the polypyrrole and lithium films are sandwiched together; in the cylindrical cell, the two films are wound concentrically. Their energy per unit mass and their discharge characteristics are similar to those of the nickel – cadmium cells now on the market. More than 500 charging and recharging cycles have been achieved with laboratory cells. Applications include dictaphones and pocket radios [63].

5.4. Polythiophene

Since the first report of thiophene polymerization in 1883 [65] decades passed until thiophene was considered to be an attractive monomer for conducting polymers [66]. Interest is still growing because thiophene is easier to handle than pyrrole (less sensitive to oxygen) and allows the simple preparation of substituted monomers leading to soluble polymers. Three methods have been used to produce polythiophene [25233-34-5]: chemical oxidation (Lewis acid), coupling with organometallic agents or by the Grignard reaction, and electrochemical

oxidation (anodic). The preparation techniques for films, powders, and coatings are similar to those of pyrroles but thiophene needs stronger oxidants for its polymerization than pyrrole or other heterocycles. Standard oxidation potentials follow:

Pyrrole	+0.8 V
Indole	+0.9 V
Azulene	+0.9 V
Thiophene	+1.6 V
Furan	+1.85 V

The oxidation potential of the monomers correlates to the ease of polymerization.

Figure 8 illustrates the correlation between UV – VIS absorption and the oxidation potential of thiophene oligomers [67]. The oxidation potential of the series $(thiophene)_n$: $n = 1 - 6$ decreases with the increasing number of thiophene units.

Substituted Polythiophenes. Alkyl-substituted thiophenes with alkyl chains up to C_{18} yield polymers that are soluble in common organic solvents with electrical conductivities up to 100 S/cm. Due to their good processibility [68] and high chemical and electrochemical stabilities in air and moisture, polythiophene and its derivatives are excellent candidates for practical applications (e.g., display devices, electrochromic devices [69], energy storage, field transistors [70], solar energy cells, and overchargeable batteries [66].

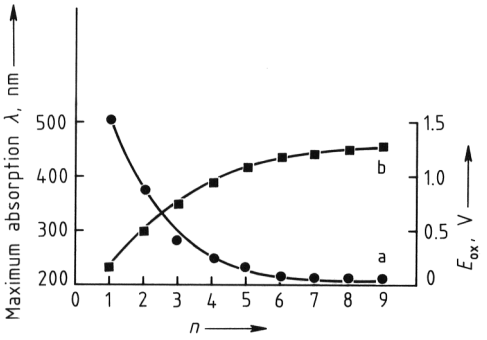
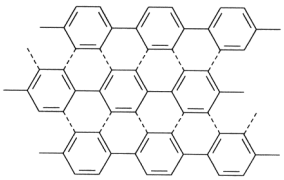


Figure 8. Correlation between maximum absorption wavelength (a) and oxidation potential (b) of thiophene oligomers Oxidation potential measured in 0.5 mol/L Et_4NBF_4 in acetonitrile versus saturated calomel electrode.

5.5. Polyphenylene

Synthesis. First attempts to prepare polyphenylene [9033-83-4], [24991-24-0], [25190-62-9], [26499-97-8] date back to 1842 [71]. RIESE describes a process in which polyphenylene (n=13) is synthesized from 1,4-dibromobenzene and sodium. Further methods are the Ullmann reaction, thermal decomposition of diazonium salts, coupling of phenylene dihalogenide – Grignard compounds [72], and the oxidative coupling of benzene with $AlCl_3$ and $CuCl_2$ (Kovacic method [73]). In 1963 the Kovacic method was systematically extended by varying reaction conditions (temperature, catalysts, Lewis acid, and oxidants) and starting materials [4]. Many side reactions occur leading to cross-linked graphite-like lattices.

Other aromatic compounds, substitution products, condensed systems (e.g., diphenylene, terphenylene, pyrene, anthracene, chrysene), unsaturated



cyclic compounds (e.g., cyclopentadiene, cyclooctatetraene), heterocyclic compounds (e.g., thiophene, pyrrole, quinoline), and metal complexes (e.g., phthalocyanines, ferrocene) were investigated.

All Friedel – Crafts catalysts and the usual dehydrogenation agents can be used for oxidative coupling. Oxidizing Friedel – Crafts agents, such as $FeCl_3$, assume both functions. The degree of suitability has been tested on benzene/$CuCl_2$ (Eq. 1) and on benzene/$AlCl_3$ (Eq. 2).

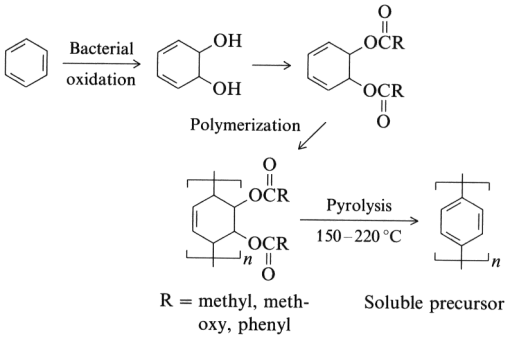
$$AlBr_3 > AlCl_3 > FeCl_3 > MoCl_6 > NbCl_5 > TiCl_4 > SnCl_4 > BF_3 > ZnCl_2 \quad (1)$$

$$Pd(II) > Co(III) > Mn(III) > Cu(II) > Fe(III) > chloranil > V(III) > I_2 \quad (2)$$

The oligomeric and polymeric reaction products were also characterized in terms of thermoelectric power, dark conductivity, and photoconductivity. They showed electrical

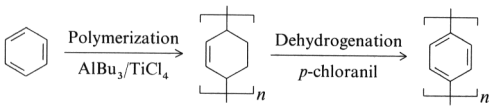
conductivities up to 0.1 S/cm, the highest value obtained at that time [4]. The polymers were obtained as powders and were processed by press sintering. Later synthesis by Diels – Alder [74] or boronic acid coupling [75] lead to soluble or meltable materials.

A novel route to high molecular mass poly (*p*-phenylene) is based on the polymerization of derivatives of 5,6-dihydroxycyclo-1,3-hexadiene, a compound that is easily prepared by the bacterial oxidation of benzene [76].



The advantage of this process is that it involves a soluble precursor polymer, which means that films can first be cast, objects coated, or fibers spun from solution; poly(*p*-phenylene) is then formed on heating.

The Marvel method is similar to the Kovacic method [77]:



Properties. The properties of polyphenylenes depend mainly on their linkage (*m*-, *p*-), but also on the method used to prepare them. *o*-Polyphenylenes are unknown: *m*- and *p*-polyphenylenes are crystalline (> 50 %), intractable, and insoluble. *p*-Polyphenylenes are stable up to ca. 500 °C in air and up to 650 °C under nitrogen (10 % weight loss); the stability of *m*-polyphenylenes is approximately 200 °C lower [78]. Figure 9 demonstrates the drastic differences between *m*- and *p*-substituted poly- phenylenes. The *para* derivatives are soluble in toluene up to $n = 6$, the *meta* derivatives are soluble up to $n = 16$. Polymer powders can be processed by press sintering (400 °C, > 100 bar).

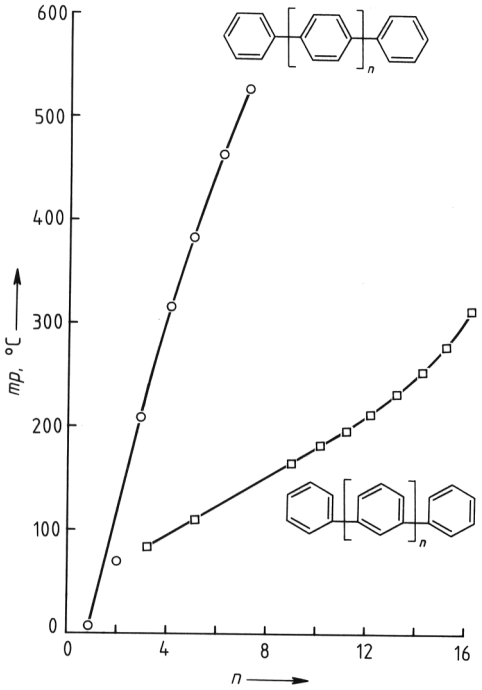


Figure 9. Correlation of the melting points and the degree of condensation (n) of *m*- and *p*-polyphenylenes

Poly(*p*-phenylene) can be *n*-doped with electron donors or *p*-doped with electron acceptors, electrical conductivities reach 10^2 S/cm. Donor doping is best accomplished with the aid of an electron-transfer agent (e.g., by adding naphthalene or α-methylstyrene in tetrahydrofuran) [79], [80]. Acceptor doping is usually done by exposing the powders to AsF_5 gas or heating with nitromethane solutions of SbF_5. Electrochemical doping (anodic oxidation or cathodic reduction) is performed in suitable electrolytes (e.g., acetonitrile), the electrodes being separated by diaphragms.

Anodic oxidation:

$$p\text{-PP} + AgBF_4 \rightarrow p\text{-PP}^+BF_4^- + Ag^+$$

Cathodic reduction:

$$p\text{-PP} + LiClO_4 \xrightarrow{+e^-} p\text{-PP}^-Li^+ + ClO_4^-$$

PP = polyphenylene

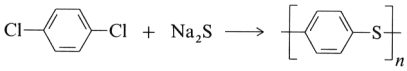
Oxidation potentials, conductivities, and spectra of polyphenylene are cited in [79].

Soluble, substituted polyphenylenes and polyaromatic systems are discussed in [81].

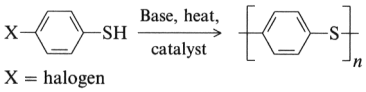
Potential Uses. Poly(*p*-phenylene) can be used as electrodes for rechargeable batteries.

5.6. Poly(Phenylene Sulfide)

Poly(*p*-phenylene sulfide) [9016-75-5], PPS, (white powder, T_g 92 °C, *mp* 270 – 290 °C, 65 % crystallinity) was the first melt-processible polymer to be doped with strong electron acceptors (e.g., AsF_5) to yield highly conductive products [82]. The first laboratory synthesis of PPS was reported by MACALLUM [83] and involved the melt reaction of 1,4-dichlorobenzene, sulfur, and sodium carbonate. A commercially product has been available as powder, film, or fiber since 1973 from Phillips Petroleum under the trade name Ryton; it is produced from 1,4-dichlorobenzene and sodium sulfide (high-pressure process) in a polar solvent (*N*-methylpyrrolidone) [84].

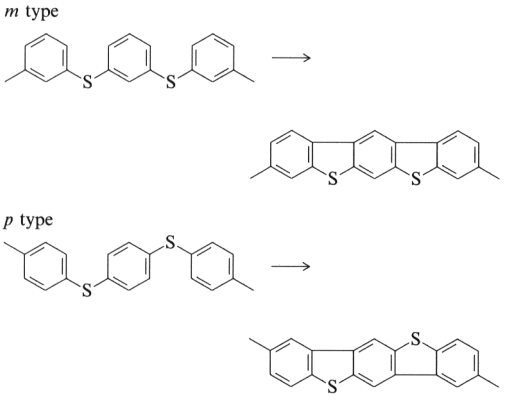


Another process involves self condensation of a halogenated thiophenol resulting in "head-to-tail" polymerization [85]:



Poly(*m*-phenylene sulfide) and substituted (methyl-, fluoro-) poly(*p*-phenylene sulfide) are prepared by analogous reactions from appropriate monomers.

Doping of PPS with AsF_5 produces conductivities up to 2×10^{-2} S/cm [86]. Attempts to make *n*-doped PPS have been unsuccessful. In addition to AsF_5, doping with $FeCl_3$, H_2SO_4, $HClO_4$, FSO_3H, CF_3SO_3H, $AlCl_3$, TaF_5 has been investigated [87]. Heavily doped PPS undergoes intramolecular cross-linking to form benzothiophene rings [79]:

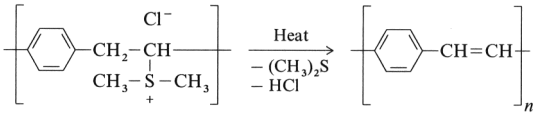


Poly(phenylene sulfides) are used where resistance to heat and chemicals is required, for example in the chemical process industry (pump housings, impellers, valves, metering devices, tanks, coil bobbins). See also, → Polymers, High-Temperature, Chap. 5..

Poly(*p*-phenylene selenide) [52410-66-9] and poly(*p*-phenylene telluride) [84174-18-5] have been prepared by techniques similar to those used to prepare PPS [79]. Conductivities of AsF_5-doped samples reach 0.01 S/cm.

5.7. Poly(Phenylene Vinylene)

Poly(*p*-phenylene vinylene) [88] [96638-49-2], [87092-55-5], [26009-24-5] was first synthesized by the Wittig condensation of terephthaldehyde and *p*-xylene bis(triphenylphosphonium) chloride. The method which is now mainly employed starts from a soluble polysulfonium salt [89], for example:



The polysulfonium salt is obtained by the reaction of α,α'-dichloro-*p*-xylene with excess dimethyl sulfide (50 °C, 20 h), and polymerization with sodium hydroxide (0 °C, 1 h). The first doped poly(phenylene vinylene) was reported by KARASZ using AsF_5 as dopant [90]; its conductivity was 3 S/cm. Stretching the precursor film at high temperature and doping with

AsF_5 and SO_3 yielded conductivities up to 2800 S/cm [36], [91].

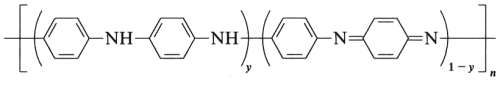
Substituted derivatives [92], copolymers [93], and blends [94] show better thermal stability. Highly conductive graphite films have been prepared by pyrolysis of poly(phenylene vinylene) (> 3000 °C), stretched samples doped with SO_3 had conductivities of 10^5 S/cm [95]. Poly(phenylene vinylene) can be used as tunable polymer diodes or luminescent electrodes [96].

5.8. Polyaniline

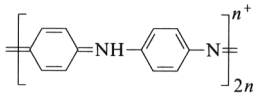
The synthesis of polyaniline [25233-30-1] is remarkably simple and is summarized in Figure 10 [97], [98]. Aniline can be chemically (1863, LIGHTFOOT) or electrochemically (1865, LETHEBY) oxidized and dehydrogenated to form a quinone diimine.

Oxidation of the primary aromatic amine usually does not stop at the monomeric quinone imines but gives rise to more complex quinone imine products. The type of product depends largely on the oxidants and the reaction conditions. 1,4-Benzoquinone-4-imino-1-phenylimine is an unstable intermediate which reacts with further aniline molecules and oligomerizes to give the final product, polyaniline.

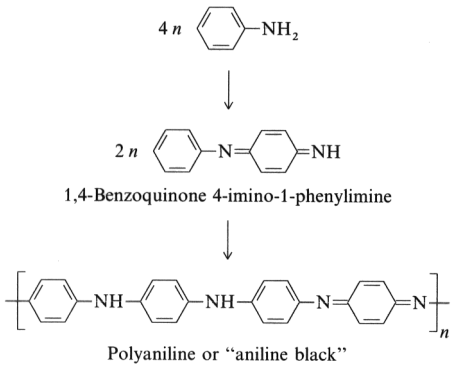
Studies on polyaniline suggest that the polymer can exist in a wide range of structures [99], which can be regarded as copolymers of reduced (amine) and oxidized (imine) units of the form:



When $0 < y < 1$ these structures are poly(*p*-phenylene amine imines), in which the oxidation state of the polymer increases with increasing content of the imine form. The fully reduced form ($y = 1$) is leucoemeraldine, the fully oxidized form ($y = 0$) is pernigraniline, and the 50 %-oxidized structure ($y = 0.5$) is emeraldine. Each structure can exist as the base or as its salt, formed by protonation. Four repeating units can therefore be envisaged in the polymer chain in amounts which depend on the degree of oxidation and protonation of the structure. The "metallic state" is



The reaction of aniline to "aniline black" proceeds through a number of intermediates [98]:



Emeraldine is very stable and can be directly prepared from aniline by oxidation with sodium perchlorate or V(III) chloride [100]. Nigraniline

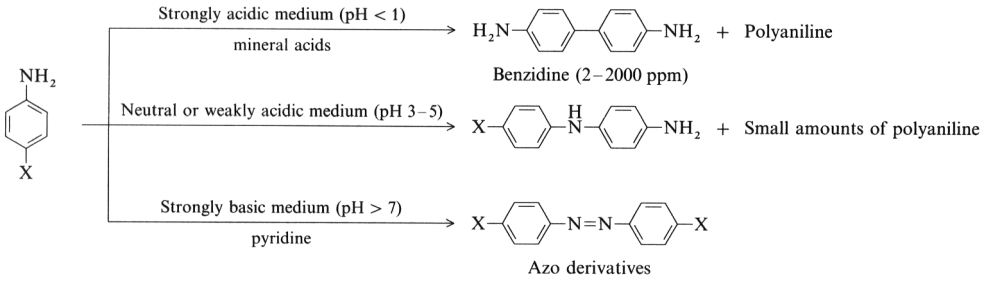


Figure 10. Products of aniline oxidation formed at different pH values

and pernigraniline are further oxidation products of emeraldine, both are very unstable. The structure of emeraldine and related molecules is described in [101].

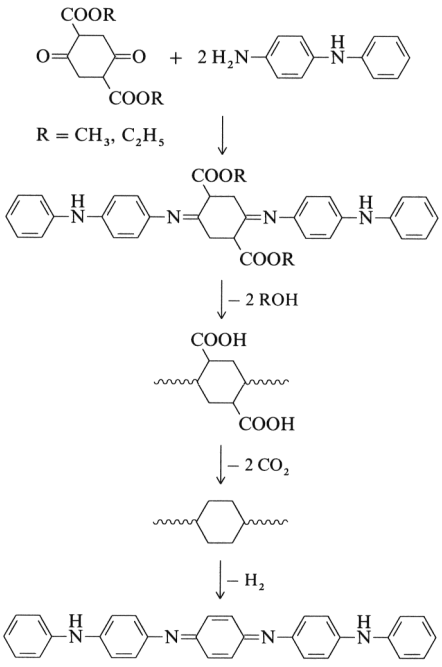
Nitrogen- or ring-substituted homologues of aniline can apparently be oxidized similarly, yielding corresponding "aniline blacks".

Oxidants used for preparing oligomers and polymers of aniline include $Cr_2O_7^{2-}$, $S_2O_8^{2-}$, Ce^{4+}, and Pb^{4+} ions. Aniline can also be polymerized by anodic oxidation.

The reaction conditions (temperature, duration, pH, oxidants, and catalysts) determine the yield and type of oxidation product [97].

A decisive handicap in the production of polyaniline is the formation of small quantities of carcinogenic benzidene (Fig. 10) [102].

HONZL synthesized benzidene-free polyanilines by avoiding the use of aniline as the starting monomer [103]:



Similar structures can be obtained by polycondensation of quinones and aromatic amines [104].

Properties. The conductivity of polyaniline is 10 S/cm up to pH 4, but decreases to 10^{-10} S/cm above pH 4. The polymers are stable up to 250 °C (undoped) and up to ca. 150 °C (doped). Conduction in polyaniline can be accounted for in terms of electrons hopping under the assistance of proton transfer, for which the presence of water plays an essential role [105].

In contrast to other electrically conducting polymers, polyanilines may be doped with protons. Polyaniline is available as powder, film, or fibrils (Versicon, Allied Signal) [106], [107].

The electrochemistry of polyanilines was first investigated at the end of the nineteenth century. In the mid 1960s, interest in this topic was renewed. The use of polyaniline as a battery electrode on account of its redox and proton transfer behavior was described in 1968 [108]. In 1986, polyaniline was presented as a "novel conducting polymer"; its preparation and redox behavior were described [109]. The phenomena of anodic oxidation and discharge by means of reversed polarity have been known since 1891 [1].

Uses. Polyaniline is primarily of interest as an electrode material. Its discharge capacity is greater than that of polypyrrole(+)/perchlorate (−), its self-discharge is higher than that of polythiophene or Ni/Cd battery systems [66]. GENIES has announced a rechargeable battery based on polyaniline (anode), propylene carbonate – $LiClO_4$ (electrolyte), and Li – Al (cathode) [110], [111]. This polyaniline is made by oxidizing aniline with ammonium persulfate in ammonia/2.3 mol/L hydrogen fluoride as solvent. The discharge capacity of the polymer is 100 A · h/kg at 25 °C and 140 A · h/kg at 40 °C for current densities of 0.5 mA/cm^2 and for an amount of material giving a capacity of 10 mA · h. The voltage in open circuit for the fully charged battery developed by GENIES is 3.6 V. The average utilizable potential is 2.8 – 3 V. The energy density for the polymer lies between 280 and 420 W · h/kg. Its behavior with regard to self-discharge and to constant applied voltage (floating life) is excellent [111]. Like polypyrroles, polyanilines show excellent antistatic behavior and have a high shielding efficiency for electromagnetic interference.

5.9. Miscellaneous Polymers

There has been a flood of literature concerning new electrically conducting polymers, examples are listed below.

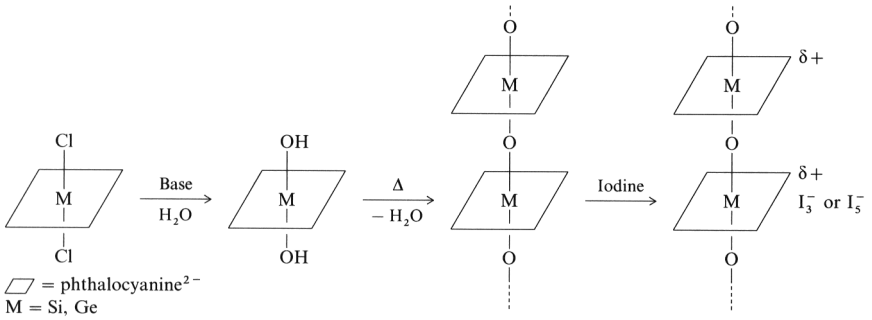
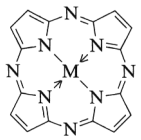
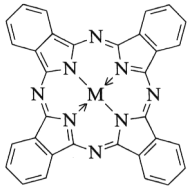


Figure 11. Synthesis and doping of bridged phthalocyanine polymers

Bridged macrocyclic complexes [81] are mainly derivatives of tetraazaporphyrin or phthalocyanine:



Tetraazaporphyrin (M = H_2)

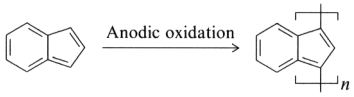


Phthalocyanine (M = H_2)

The synthesis and doping of bridged phthalocyanine polymers is illustrated in Figure 11. The bridging ligand can be linked by two σ bonds, by two coordinate bonds, or by one σ and one coordinate bond (Fig. 12).

After doping with iodine, conductivities up to 10.1 S/cm are obtained. Substituted phthalocyanines are soluble and can be cast as films or handled by the Langmuir – Blodgett technique to give ultrathin, well-defined molecular layers. The insoluble powders can only be processed by press sintering.

Polyazulene [82451-56-7] [112], [113] is synthesized by electrochemical polymerization with ClO_4^- as counterion (similar to that of polypyrrole) yielding amorphous polymer films which can be peeled from the anode. Conductivity is 0.01 S/cm. The films may be electrochemically and reversibly discharged to the nonconducting form.



Polycarbazole [51555-21-6] [113]. Solutions of carbazole in acetonitrile may be electrochemically oxidized (counterion ClO_4^- or

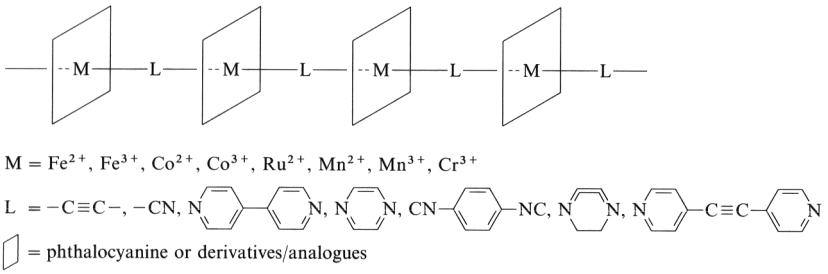
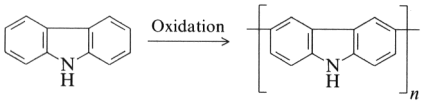
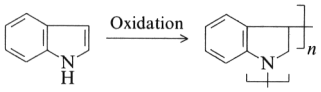


Figure 12. Construction of bridged macrocyclic transition-metal polymers

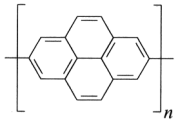
BF_4^-) at a platinum anode to give electrically conductive films with poor mechanical stability and conductivities up to 0.001 S/cm. Polycarbazole has also been obtained by vacuum evaporation of carbazole and by chemical condensation [114].



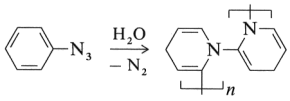
Polyindole [82451-55-6] [48]. Electrochemical oxidation of indole (counterion ClO_4^- or BF_4^-) yields brittle films with conductivities of ca. 0.01 S/cm. Polyindole has been employed as a polymer coating in a glucose sensor [113].



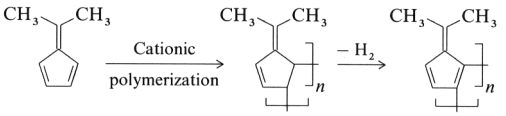
Polypyrene [41496-25-7] [113]. Electrochemical oxidation of pyrene (counterion BF_4^-, ClO_4^- or AsF_6^-) yields insoluble, brittle films with conductivities up to 1 S/cm.



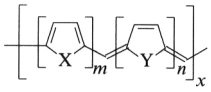
Polyazepine [115483-32-4] [115]. Phenyl azide can be photopolymerized in the gas phase to yield films of poly-1,2-azepine with a conductivity of 10^{-2} S/cm (after I_2 doping).



Polyfulvenes [107889-59-8] [116]. Polyfulvenes are formed by cationic polymerization of 6,6-dimethylfulvene followed by chemical or electrochemical dehydrogenation, conductivity 10^2 S/cm (after I_2 doping).

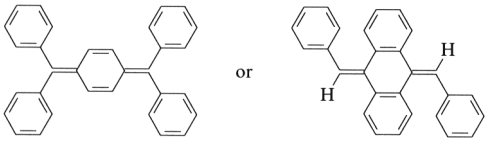


Low-band-gap aromatic polymers [117]. An important prerequisite for obtaining low-band-gap polymers is that the ground state of the polymer has a quinonoid contribution. These polymers have the general formula:



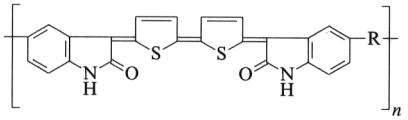
X, Y = SO_2, SO, S, N−R, CH=CH

Benzenoid and anthracenoid precursors are:



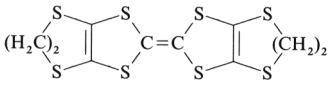
Low- or narrow-band-gap systems (gap < 0.5 eV) already contain a high proportion of thermally excited electrons at room temperature. These materials can be oxidized electrochemically at a low oxidation potential to give conducting polymers. Cross coupling with organometallic intermediates affords the undoped polymers. Conductivities up to 10 S/cm are reached (after iodine or electrochemical doping).

Polyindophenines [138309-48-5] [118] are prepared by reaction of isatin with thiophene and have conductivities up to 10^{-2} S/cm without additional dopant. The polymers are soluble in dimethyl sulfoxide and can be cast as films; the material is thermostable up to 230 °C.

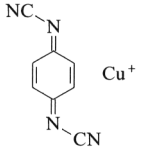


Charge-transfer complexes [119] are combinations of electron donor compounds with electron acceptor compounds. They are synthesized,

for example, by electrochemical charging of aromatic hydrocarbons with ClO_4^-. The charge-transfer complexes are assembled in defined stacks and have conductivities up to 10^3 S/cm, in some cases with superconductivity. Examples are given below [120], [121]:



Bisethylene dithiotetrathiofulvalene – I_3 complex
T_c 8.1 K



Dicyanodiimine quinone–copper complex
$\sigma = 10^3$ S/cm

Finally it should be remembered that all electrically conducting organic materials are due to the various dopant charge-transfer complexes [123].

Buckminsterfullerene [99685-96-8] [122] is an allotrope of carbon (Fig. 13). When doped with potassium, it reaches conductivities up to 500 S/cm; cooling to 18 K makes it superconducting.

6. Uses

Few of the organic materials discussed above have been demonstrated to be sufficiently stable for critical applications.

Stability is a relative property and is the "Achilles heel" of electrically conducting polymers. For example, polypyrroles with BF_4^- as counterion are unstable under atmospheric conditions but are as stable as Ni/Cd electrodes in rechargeable batteries. It was hoped that electrically conducting organic materials could combine conductivities comparable to those of metals with the processibility of plastics. Work over the last decades has gone a long way in this direction but there are still many obstacles to be mastered before these materials become widely used.

Polyene chains with extended double bond systems are unstable against oxygen, forming epoxy, carbonyl, and carboxyl groups. They also undergo cross-linking and substitution reactions (Diels – Alder and radical reactions). Aromatic and heterocyclic structures are much more stable against environmental conditions (e.g., temperature, irradiation).

Doped materials (*n* or *p* doped) are saltlike compounds and are therefore unstable against humidity, oxygen, and temperature. Conductivity is lost as a result of interruption of the conjugation system, this destroys the charge-transfer complexes within a few days.

Defect-free oriented polyacetylenes are more stable, they do not loose any conductivity for 3 months [24]. Polypyrroles and polythiophenes show unchanged conductivities over several years (Sections 5.3, 5.4). Polyindophenines are "intramolecularly doped", containing covalently bonded electron donor and acceptor groups within the same molecule (Section 5.9).

How many uses do conducting polymers have? The short answer is "scarcely any" [123], but they do have some applicability [80], [124], [125] for:

1. Rechargeable batteries [120], [126] (Sections 5.3 and 5.4)
2. Coatings for electromagnetic radiation shielding or electrochemical metallization [63], [127]
3. Semiconducting devices and photovoltaics [128]
4. Catalysis [129]
5. Sensors and electrochromic displays [130], e.g., for gas detection (NH_3, CO_2)
6. Solar energy conversion, e.g., electroluminescence [131]

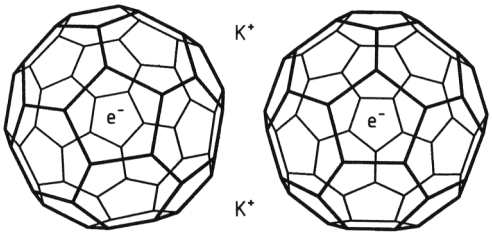


Figure 13. Potassium-doped C_{60} molecules

It seems that this class of electrically conducting materials will form the basis for a new generation of "intelligent" material systems [132].

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Polymers, High-Temperature

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1. Introduction

Definition. Any definition of a *high-temperature polymer* is necessarily arbitrary. Today's conventional engineering plastics [e.g., nylon, poly(ethylene terephthalate)] were yesterday's high-temperature polymers, and the quest for improved temperature performance is ongoing. In the context of this review, thermoplastic polymers exhibiting useful mechanical properties at temperatures in excess of 150 °C would seem an appropriate description.

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Various other synonyms such as *high-performance polymers* or *advanced engineering polymers* have been employed. These materials are characterized by relatively low-volume sales compared with conventional engineering polymers and a relatively high selling price. Thus the ratio of the sales price for nylon to the sales price for the high-temperature polymers considered here varies from about 1 : 3 to 1 : 20. However, these polymers enjoy applications in varying market sectors such as the electrical–electronic, automotive, aerospace, and chemical process industries because they offer good performance to cost ratio.

The fact that the polymers can be used at high temperatures should not disguise that they possess many other useful and interesting properties. The crystalline polymers, polyetheretherketone and poly(phenylene sulfide), for example, find many room-temperature applications as a result of their good environmental resistance, particularly to solvents.

Classification. As with all polymers, high-temperature polymers fall into two classes, amorphous and (semi)crystalline. Polysulfone (PSU), poly(ethersulfone) (PES), and polyetherimide (PEI) are amorphous whereas poly-(phenylene sulfide) (PPS), polyetheretherketone (PEEK), and polyetherketone (PEK) are semi-crystalline.

Despite the high linearity of the sulfone polymers (100% 4,4′-specificity), the differences in the conformations of the phenyls bordering the sulfone and ether links preclude close packing of chains whereas the regular conformations of the phenyls in chains of PPS, PEEK, and PEK lend themselves to crystal formation. Interestingly, the ether and carbonyl moieties in PEEK are crystallographically equivalent.

Crystalline polymers (particularly filled grades–glass, carbon, mineral) retain useful mechanical properties above their glass transition temperature (T_g). Thus, although PEEK has a T_g of 143 °C its continuous service temperature (CST) is 250 °C. A further advantage of the crystalline range is inertness to aggressive media: PEEK shows outstanding resistance to aqueous acids, alkali, and organic solvents.

History [1]. Two synthetic routes lend themselves to the production of high-temperature polyaromatics: polycondensation (nucleophilic) or electrophilic processes. All of the polymers considered here may be made by polycondensation, and are currently manufactured by this process. Initially, electrophilic routes to PES (ICI) and various polyketones were developed but were quickly superseded by the polycondensation process, largely due to the lack of selectivity for linear polymers and the corrosive reactants used in the electrophilic process.

Raychem in 1972 launched their version of PEK (Stilan) produced via electrophilic chemistry, but this material was short-lived in the marketplace. Development of electrophilic processes continues, with recent announcements of polyketones by Du Pont (PEKK), and BASF (Ultra PEK).

Routes to PPS (Philips), PES (ICI), and PSU (Union Carbide, now produced by Amoco) were developed during the 1960s with commercial launch in the early 1970s. Similarly, polycondensation routes to PEEK (ICI), PEK (ICI), and PEI (General Electric, GE) were developed in the 1970s with launches in the 1980s.

To put the timescale of one of these developments into perspective, ICI research for routes to polyketones started in 1972. The first 20 g sample of PEEK was made in ICI laboratories at Welwyn Garden City in 1977, followed quickly by scaleup to semitechnical quantities. PEEK manufacture moved to full production scale at Hillhouse in late 1978 and became commercially available in 1981. A dedicated plant for PEEK production was brought on-line at Hillhouse in 1987.

One of the keys for success for polymers made by polycondensation is the use of high-purity monomers to guarantee the high degree of reactivity required (> 99%) for useful molecular masses, and the high degree of stereospecificity for properties such as toughness. Indeed, the history of the development of high-temperature polymers is mirrored by the development of their component monomers.

Stability. High-temperature thermoplastic polymers which have found commercial application have done so because they can be processed using conventional techniques such as extrusion or injection molding. However, for these materials to stand the processing temperatures employed they must exhibit stability against degradation. Typically an amorphous polymer is processed at 130–150 °C above its

T_g and a crystalline polymer at 30–50 °C above its crystalline melting temperature (T_m). Thus, PES (T_g 225 °C) and PEI (T_g 217 °C) are processed at 350–370 °C while PEEK (T_m 343 °C) is processed at 370–390 °C. Filled and high-viscosity grades may require even higher temperatures.

High temperature stability is attributable to high melting or softening points, high bond dissociation energies, structures not susceptible to chain (unzipping) degradation reactions, lack of inter- or intrabond formation, and low chemical (particularly to oxygen) reactivity. Resistance to chain degradation is perhaps the most important and is most easily provided by replacing aliphatic with aromatic units. Thus although aliphatic polymers have high bond dissociation energies and the first step in degradation is a high-energy process, it yields highly reactive, free-radical species which "unzip" the chain. Unzipping is precluded in aromatic polymers because any free radicals generated are stabilized by delocalization via the π system. Furthermore, volatile fragments cannot be readily formed.

Clearly, the totally aromatic polyparaphenylene should therefore have optimum stability. It is indeed stable to above 500 °C. However, extreme chain stiffness results in an intractable material. In order to take advantage of aromatic stability but provide processibility, flexibilizing link units are incorporated into the chain [O,S,C$(CH_3)_2$]. Other, relatively inert moieties may be used to replace the aromatic ring (e.g., SO_2, CO). The balancing of these groupings gives the polymers their characteristic properties.

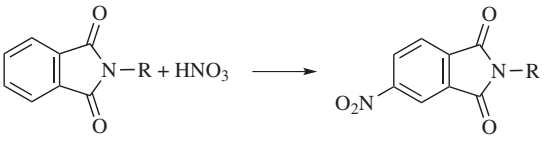
2. Polyetherimides

In 1982 General Electric Plastics introduced the first and still only thermally processible polyetherimide (PEI) resin under the trade name Ultem [61128-24-3]. It was the result of a ten-year development effort headed by J. Wirth of General Electric's Center of Research and Development in Schenectady (USA). The idea behind this development was to maintain the already known thermal and chemical stability associated with the aromatic ether and imide structures while building a polymer chain flexible enough to provide melt processability within the limits of the melt stability.

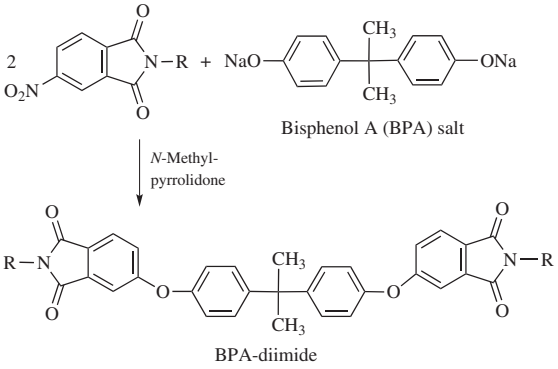
Polyimides are condensation polymers derived from bifunctional carboxylic anhydrides and primary diamines. Polyetherimides form a special class within these polyimides as they contain an ether group in either or both the aromatic dianhydride or aromatic diamine building block. A number of possible monomeric units are shown in Table 1. To date, Ultem produced from bisphenol A bisether dianhydride is the only commercially available thermoplastic polyetherimide. The synthesis thereof forms the basis for the development of these PEI resins [2, 3].

2.1. Production

Polyetherimides are synthesized by melt polycondensation of bisphenol A dianhydride with a diamine, usually *m*-phenylenediamine [4]. The starting dianhydride for PEI is produced as follows. First, an *N*-alkyl phthalimide is nitrated:

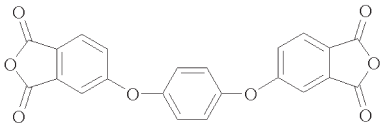
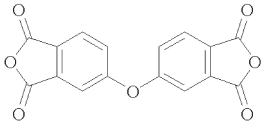
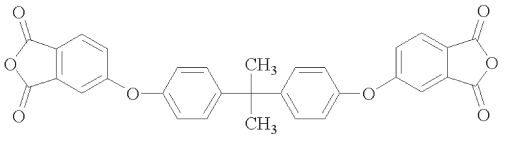
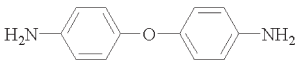
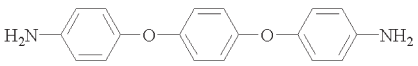
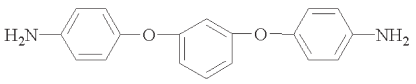


The NO_2 groups are then nucleophilically displaced by bisphenolate A (BPA) ions:

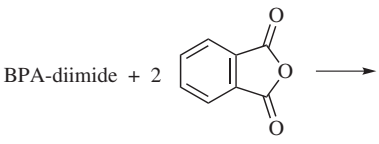


The resulting BPA diimide can be converted into the desired BPA dianhydride by an

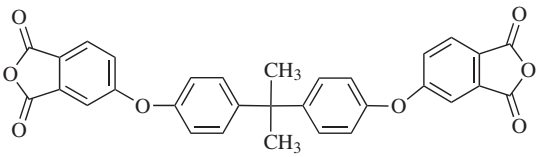
Table 1. Possible monomers in polyetherimides

Name	Structure
Dianhydrides	
Hydroquinone bis(3,4-dicarboxyphenyl)ether dianhydride	
Bis(3,4-dicarboxyphenyl)ether dianhydride	
Bisphenol A bis(3,4-dicarboxyphenyl)ether dianhydride	
Diamines	
4,4′Diaminodiphenyl ether	
1,4-Bis(4-aminophenoxy)benzene	
1,3-Bis(4-aminophenoxy)benzene	

exchange reaction with phthalic anhydride:

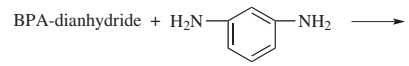


Phthalic anhydride

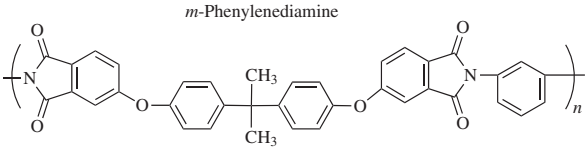


BPA-dianhydride

The final polycondensation of the BPA dianhydride with an aromatic diamine (e.g., *m*-phenylenediamine) can be performed in a number of ways, ultimately resulting in the formation of PEI:



m-Phenylenediamine



Polyetherimide

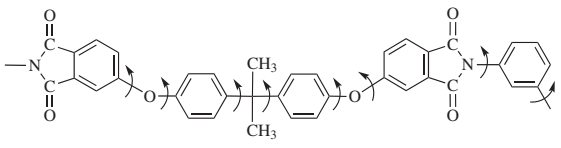
PEI resins with a number-average molecular mass of 15 000–17 000 are usually produced.

The number-average molecular mass can be adjusted with monofunctional phthalic anhydride [5, 6]. Commercial PEI grades are tuned to the specific needs of an application and are obtained in three ways:

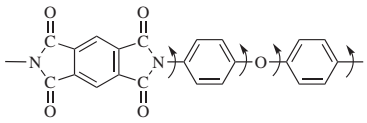
1. Use of additives, such as reinforcing fibers, mineral fillers, conductive fibers, pigments, polytetrafluoroethylene (to reduce frictional resistance), release agents, and flow improvers.
2. Modification of the base resin by copolycondensation with other monomers such as *p*-phenylenediamine and pyromellitic anhydride. This allows for higher glass transition temperatures and/or changes in chemical resistance.
3. Blending with other polymers (e.g., polycarbonate) improves processibility and impact resistance.

2.2. Properties

The structures of Ultem and Kapton, a polyetherimide produced by Du Pont (available as "Kapton polyimide film"), are shown in Figure 1 [7–9]. The segmental mainchain rotational freedom in Ultem (shown by arrows) provides this PEI molecule with many more configurational possibilities than the more symmetrical Kapton. Ultem therefore has a lower glass transition temperature (217 °C) than Kapton (360 °C) and can be more readily melt processed. The thermal stability of both polymers is almost the same (± 500 °C under nitrogen) [10]. Properties of some Ultem grades are listed in Table 2.



Ultem Polyetherimide
(GE Plastics)



Kapton (Du Point)

Figure 1. Polyetherimide (PEI) structures

Mechanical Properties. Ultem has a very high tensile strength of about 110 MPa compared to, for example, polycarbonate (60 MPa), as well as a long-term, high-load, high-temperature dimensional stability. This is the combined effect of a high glass transition temperature, a high tensile modulus, a low thermal expansion coefficient, low creep, and a low water absorption. Stress–strain behavior is shown in Figure 2.

The relatively constant mechanical property profile of the PEI grades as a function of glass fiber content over a wide temperature range (up to 175 °C) is a direct result of the high glass transition temperature (217 °C) of this amorphous resin (Fig. 3). The excellent adhesion of PEI resins to glass fibers gives a linear relationship between the flexural modulus or tensile strength and glass fiber content up to 30 wt% [11].

Fatigue properties are excellent. The endurance (stress) limit at 10^6–10^8 cycles for PEI reinforced with 30% glass fibers is 30 MPa. Isochronous stress–strain diagrams from which the creep performance up to 100 000 h can be extrapolated, indicates a good resistance of PEI against creep (Fig. 4).

Aging characteristics (UL 94 temperature index) indicate a continuous service life up to 100 000 h at 175 °C.

Impact Behavior. The unfilled resin has excellent ductility due to the large number of possible segmental rotations and the high entanglement density that results from the kinked structure of the macromolecular chain. Its rather high notch sensitivity can be overcome by making sure that parts made of PEI have wellrounded edges.

Chemical Resistance. Environmental stress crazing and cracking are typical problems of amorphous engineering plastics, including to a lesser extent also PEI resins. Contact and subsequent interaction between the polymer and a liquid may result in dissolution or swelling, depending on the strength of the molecular interaction forces between the polymer and the liquid molecules. These forces are

Table 2. Properties of Ultem PEI

Property	Standard	Ultem grade (x_1, x_2, x_3, x_4)*					
		1000	**1010**	**2100, 2110**	**2200, 2210**	**2300, 2310**	**2400, 2410**
Mechanical							
Tensile strength, yield, MPa	ISO 527	105	105	120			186
Tensile strength, break, MPa	ISO 527	90	90	115	140	160	
Tensile elongation, yield, %	ISO 527	8	8	5			
Tensile elongation, break, %	ISO 527	60	60	6	3	3	2
Tensile modulus, GPa	ISO 527	3.0	3.0	4.5	6.9	9.0	11.7
Flexural strength, yield, MPa	ISO 178	145	145				
Flexural strength, break, MPa	ISO 178			200	210	230	250
Flexural modulus, GPa	ISO 178	3.3	3.3	4.5	6.2	9.0	11.7
Hardness, Rockwell		M 109	M 109	M 109	M 114	M 114	M 125
Izod impact strength notched, J/m	ISO 180/1A	50	30	60	90	100	105
Thermal							
Vicat softening temperature, rate B, °C	ISO 306	219	219	223	226	228	234
Vicat VST/B/120, °C	ISO 306	215		222	224	226	
DTUL** (0.45 MPa), °C	ISO 75	210	207	210	210	212	216
DTUL** (1.82 MPa), °C	ISO 75	200	197	207	209	210	213
Thermal conductivity, $W\,m^{-1}\,°C^{-1}$	DIN 52 612	0.22	0.22				
Coefficient of linear expansion, flow, $mm^{-1}\,°C^{-1}$	DIN 53 752	5.6×10^{-5}	5.6×10^{-5}	3.2×10^{-5}	2.5×10^{-5}	2.0×10^{-5}	1.4×10^{-5}
Physical							
Density, g/cm^3	ISO 1183	1.27	1.27	1.34	1.42	1.51	1.61
Water absorption, 24 h, %	DIN 53 495	0.25	0.25	0.28	0.26	0.18	0.12
Water absorption, equilibrium, %	DIN 53 495	1.25	1.25	1.00	1.00	0.90	0.90
Mold shrinkage, flow, %	ASTM D955	0.7	0.7	0.5–0.6	0.3–0.6	0.2–0.4	0.1–0.3
Electrical							
Volume resistivity, Ω · m	IEC 93	6.7×10^{15}	6.7×10^{15}	1.0×10^{15}	7.0×10^{14}	3.0×10^{14}	
Dissipation factor (2450 MHz)	IEC 250	0.0025	0.0025	0.0046	0.0049	0.0053	
Comparative tracking index, V	IEC 112	100–175	100–175	100–175	100–175	100–175	100–175
Flame characteristics							
Oxygen index, %	ISO 4589	47	44	47	50	50	54
Flame retardancy (mm thickness)	UL 94	V-0 (1.60) 5 V (1.90)	V-0 (0.71)	V-0 (0.41)	V-0 (0.41)	V-0 (0.25)	V-0 (0.25)

* The first three digits (x_1, x_2, x_3) have the following meanings: x_1=1 unfilled resin; x_1=2 glass-fiber-reinforced resin; x_2=1, x_2=2, x_2=3, glass fiber content=10, 20, and 30%, respectively; x_3=0 standard resin; x_3=1 easy flow. Ultem is a registered trade mark of GE Plastics.

** DTUL=deformation temperature ultimate limit.

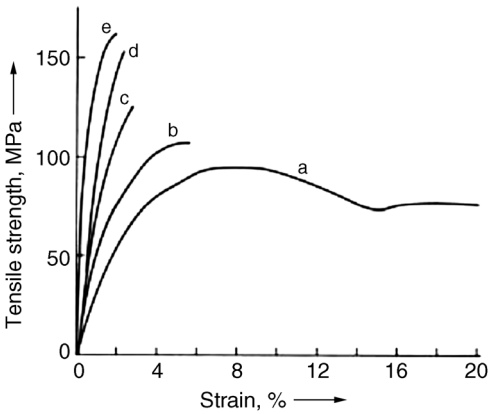


Figure 2. Stress–strain curves of unmodified PEI and glass reinforced PEI
a) Unmodified PEI; b) 10% glass-reinforced PEI; c) 20% glass-reinforced PEI; d) 30% glass-reinforced PEI; e) 40% glass-reinforced PEI

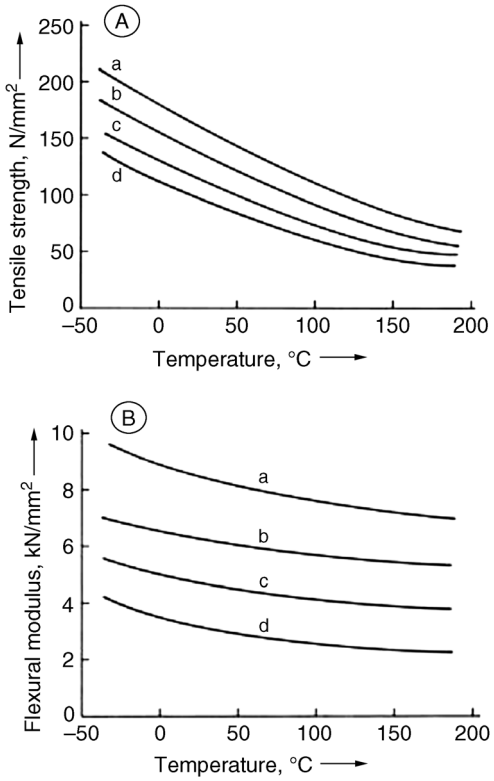


Figure 3. Tensile strength (A) and flexural modulus (B) of nonreinforced and glass-reinforced PEI
a) Ultem 2300 (30% glass-reinforced); b) Ultem 2200 (20% glass-reinforced); c) Ultem 2100 (10% glass-reinforced); d) Ultem 1000 (nonreinforced)

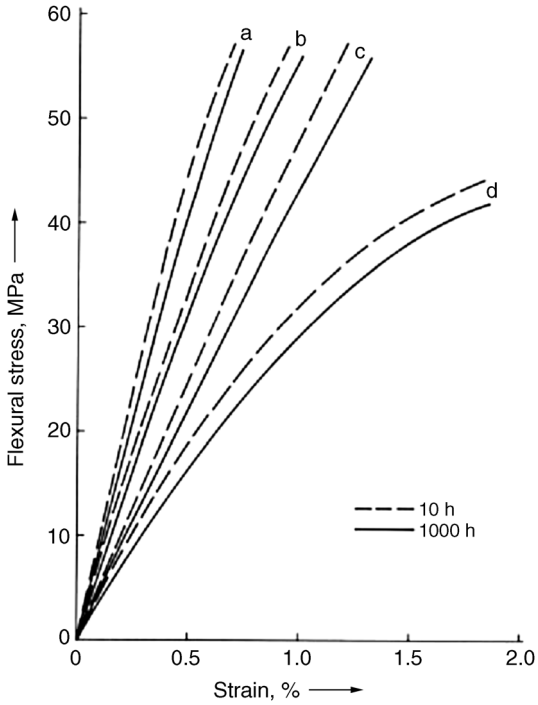


Figure 4. Isochronous stress–strain diagram of PEI (Ultem) at 23 °C
a) 30% glass-reinforced; b) 20% glass-reinforced; c) 10% glass-reinforced; d) Unfilled

characteristic for each combination of liquid and amorphous polymer and are determined by the differences in solubility parameter δ, defined as

$$\Delta = \sqrt{(\text{cohesive energy}/\text{molar volume})} = \sqrt{\text{cohesive energy density}}$$

For PEI δ is 9.3–11.7 $(\text{cal/cm}^3)^{0.5}$ [12]. Its behavior toward contact with liquids of different solubility parameters is shown in Figure 5. If the difference between the solubility parameters of PEI and the liquid is larger than 5, i.e. $|\delta_{PEI} - \delta_{liquid}| > 5$ $(\text{cal/cm}^3)^{0.5}$, then no stress cracking problems are to be expected. However, if $|\delta_{PEI} - \delta_{liquid}| < 5$ $(\text{cal/cm}^3)^{0.5}$, swelling of PEI is possible and stress cracking may result from load, leading to actual strain which in time may result in crack problems. Moreover, if $\delta_{PEI} \approx \delta_{liquid}$, the

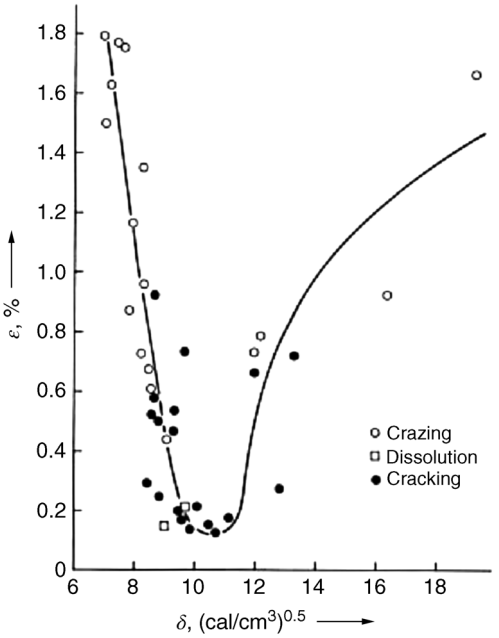


Figure 5. Dependence of critical strain ϵ_c for crazing, cracking, and dissolution of PEI versus liquid solubility parameter δ

polymer dissolves and the part disintegrates. The chemical resistance of PEI towards several solvents is summarized in Figure 6.

Flammability. The flammability behavior of Ultem as characterized by a high limiting oxygen index (LOI) of 47 results from the highly aromatic structure with a hydrogen/carbon molar ratio of 0.64. Selfsustained burning requires an oxygen rich atmosphere of over 45 vol%, making Ultem a selfextinguishing engineering plastic [13]. Therefore PEI resins fulfil the most severe flammability requirements stipulated by various countries for different industrial segments and part thicknesses:

1. Electrical and electronics industry: Rating V-0 at 0.64 mm wall thickness according to UL 94 Rating 5 V at 1.5 mm wall thickness according to UL 94
2. Building and construction industry: Class B-1 at 1.5 mm according to DIN 4102 (Germany) M 1 rating at 1.5 mm according to NFP 92–501 (France) Class 0 at 1.5 mm according to BS 476, parts 6 and 7 (UK)
3. Aircraft interior construction Passed FAR 25.853 at 1.5 mm (Federal Aviation Regulations, USA)

Requirements with respect to heat, smoke, and toxic gas generation during burning can also be met. Both the heat release rate criterion of ≤ 65 W at a 65 W radiation energy input and the NBS smoke density criteria (measured according to ASTM D 662) can easily be complied with.

Electrical properties of unfilled PEI and PEI reinforced with 30% glass fiber are presented in Table 3. The dielectric constant ϵ has a nearly constant value over the entire service temperature and frequency range. The temperature and frequency dependence of the dissipation factor (Fig. 7) are much lower for PEI than for other engineering resins. The values at 915 and 2450 MHz are of particular interest since these are the most well-developed microwave bands for power applications. The low value (in an

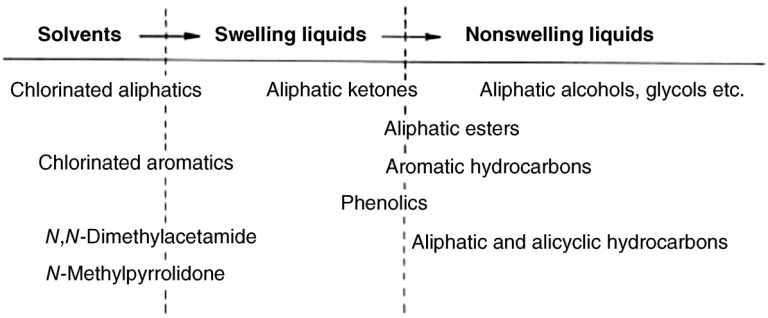


Figure 6. Chemical resistance of polyetherimides
Neutral basic, acidic and/or oxidative aqueous systems have no effect with the exception of aqueous amine and ammonia which cause hydrolytic breakdown of PEI resins.

Table 3. Electrical properties of PEI

Property	Test	Unfilled	30% reinforced with glass fiber
Dielectric strength, V/mm	D 149	2840	2520
Dielectric constant ϵ (1 Hz)	D 150	3.15	3.7
Dissipation factor (1 kHz, 50% R.H.)	D 150	0.0013	0.0015
Volume resistivity, $\Omega \cdot$ cm	D 257	6.7×10^{17}	3×10^{16}

absolute sense) ensures that dielectric losses are minimal, especially at high temperatures.

Weather and radiation resistance of PEI parts is excellent. A 1000-h weatherometer test had no effect on mechanical properties.

2.3. Processing

The rheological characteristics of PEI resins allow them to be subjected to all thermoplastic processing techniques, i.e., injection (blow) molding, extrusion, structural foam molding, and compression molding [14]. Processing should be based on guidelines applicable to amorphous engineering plastics, but with appropriate temperature adjustments. The high glass transition temperature (217 °C) requires a melt temperature typically in the range 360–425 °C. Clean, well-processed regrind can be recycled in the feed in amounts of 20–50%. PEI resins absorb water and have to be extensively predried before they are melt processed to prevent severe surface splay upon molding or extrusion.

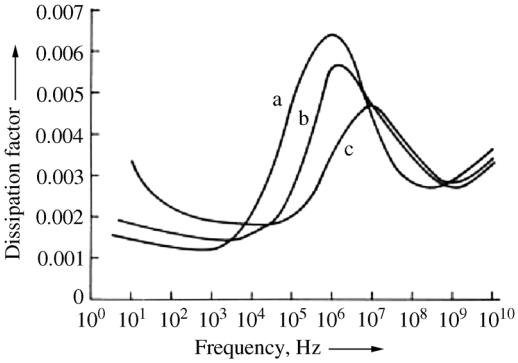


Figure 7. Dissipation factor of PEI unmodified resin versus frequency at 50% relative humidity (ASTM D 150)
a) 23 °C; b) 49 °C; c) 82 °C

Heating for at least 4 h at 150 °C is required to lower the water content to the desired level of 0.03%.

Although processing fumes are negligible, proper ventilation is advised. Purging of the processing equipment can be achieved with high molecular mass polyethylene in combination with a gradual lowering of the melt temperature from 400 to 200 °C.

2.4. Uses

Commercial PEI grades are used in several industrial segments, of which the most important are reviewed below [15].

The *automotive industry* uses PEI mainly in under-the-hood applications, where long-term mechanical strength and dimensional stability are required at high service temperatures in combination with resistance to oil, grease, brake- and cooling fluids. Examples are sensor housings, oil pump parts, ball bearing cages, and bearings.

PEI can easily be metallized and is therefore used in head-lamp reflectors, especially in combination with energy-intensive halogen lamps.

The *lighting industry* has similar requirements to those mentioned above for head-lamp reflectors. A special feature of PEI is its IR transparency. Thus unfilled, unpigmented PEI reflectors made by the recently developed dichroic layer technology can produce "cool" light. Heat is not concentrated by the reflector but diffuses through it. This principle is of importance in lighting systems employed in operating theaters, art exhibitions, etc. The dichroic coating technique uses the different refraction of various wavelengths at interfaces and its dependence on layer thickness to separate the IR and the visible part of the emitted light. The visible part of the spectrum is

reflected, whereas the IR part diffuses through the PEI.

The *electrical and electronic industries* make use of PEI's intrinsic flame resistance and its excellent dielectric properties. Notable is the development of two- and three-dimensional injection-molded, printed circuit board structures where the design allows integration of mechanical and circuitry functionality. A special, newly developed, metal-plating technique for PEI makes this even more interesting [16]. Other applications include circuit boards, connectors, switches, and controls. PEI's low tracking resistance (comparative tracking index=145 V, according to IEC standards) makes it unsuitable for high-voltage parts that carry direct current.

Polyetherimides are also used in the *food processing and beverage industries* on account of their high heat resistance, favorable mechanical properties, good chemical resistance to and cleanability (sterilization) of contact liquids, as well as lack of toxicity and disadvantageous effects in taste and odor. Specially developed PEI grades fulfil these requirements and have been formally approved by most European health agencies (e.g., Bundesgesundheitsamt in Germany) and the FDA in the United States. Polyetherimides are used in liquid-handling equipment, pumps, high-pressure dispensors, coffee makers, kitchen utensils, microwave trays, dishes and cups, cheese molds, and lightweight unbreakable baking forms. The food processing industry is becoming one of the most important volume markets for PEI.

PEI parts are also utilized in *household appliances*, e.g., water reservoirs for steam irons, hair dryers, doors of microwave ovens, and coffee-maker reservoirs.

Medical equipment often has to be sterilized and must be inert to body fluids. Here, parts made of PEI have a good performance and can be sterilized by all conventional methods (e.g., use of steam, irradiation, and chemicals). The intrinsic transparency of the material is also advantageous. Examples of applications in the medical equipment sector include surgical staplers and sterilization tanks.

The *aircraft industry* is also interested in materials that offer cost and weight savings without sacrificing safety (especially in relation to flammability issues). Components made of PEI with a high volume fraction of glass fibers or other high modulus fiber provide an excellent substitute for metal (especially aluminum) parts. The injection moldability of PEI resins allows the economic production of complex parts and multifunctional integration. High-performance composite sheets with PEI as the binding resin are used in monolithic and laminated structural parts, such as interior partition walls and floor elements. Ducts and casings are also made from PEI composites. The composites have a thermoplastic matrix and can easily be thermoformed into complex shapes.

2.5. Economic Aspects

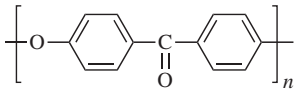
The commercial development of PEI has been very successful. Since the introduction of the first commercial Ultem grade in 1982, annual worldwide sales volume exceeded 5000 t in 1990. Future growth is expected to increase because applications are expanding and further market development activities are underway. Potential large-volume markets in composites and in household and industrial appliances are emerging. Extra market growth may be expected from developments in high-speed trains, where the same composite materials can be used as in the aircraft industry due to the emphasis on fire safety issues. Possible markets for the compatible PEI–polycarbonate blends and the completely miscible PEI–polyetherketone or PEI–polyetheretherketone blends have not yet been fully exploited [17]. Moreover, the product range of these materials will be further enlarged by simple modification of the PEI structure through copolymerization, leading to enhanced inherent properties. An example of the flexibility offered by chemical modification of the polymer main chain is siloxane–etherimide block copolymers (PSEI) [18]. Siloxane segments provide not only flexibility, toughness, and reduced moisture absorption, but also specific surface properties and lower dielectric constant. The length of the siloxane blocks is the key to these properties [18]. PSEI copolymers have recently been commercialized by GE Plastics under the trade name Siltem as high-performance coating materials for electrical wires. They are also used with Ultem in aircraft interior applications where they

improved the impact performance of PEI, while maintaining its flame retardancy and heat resistance. Applications of PEI do not pose any environmental issues. It is possible to recycle PEI, provided the material has been well processed and does not contain impurities.

3. Polyaryletherketones

The first reports of syntheses of polyaryletherketones (PAEKs) appeared in the early 1960s [19, 20], and the syntheses were based on electrophilic substitution reactions, essentially Friedel–Crafts acylations. The problem of limited solubility of the crystalline polymers was solved by conducting the polymerization in strongly acidic media, initially polyphosphoric acid [21] and later HF/BF_3 [22], which dissolved the polymers by protonation of their carbonyl groups. Despite the fact that high-molecular-mass polymers with useful mechanical properties could be produced, production problems associated with the highly aggressive reaction medium and problems of obtaining pure, stable polymers retarded the full commercialization of PAEKs.

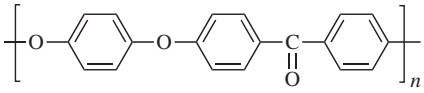
Poly(oxy-1,4-phenylenecarbonyl-1,4-phenylene) [27380-27-4] (polyetherketone, PEK), synthesized by polyacylation in HF/BF_3, was available on a limited scale from Raychem for a short period in the mid 1970s as "Stilan".



Polyetherketone PEK

The first synthesis of PAEKs by nucleophilic displacement was reported by Johnson et al. [23] (Union Carbide) in the late 1960s, but the molecular masses of the polymers were low because of crystallization resulting in premature precipitation; mechanical properties were consequently poor.

The key breakthrough in the synthesis of PAEKs by nucleophilic displacement was achieved when Rose et al. [24, 25] (ICI) identified diphenyl sulfone as a suitable solvent for the potentially highly crystalline, high-molecular-mass polymers. Nucleophilic displacement polymerization in this solvent formed the basis of the large-scale industrial route to poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene) [31694-16-3] (polyetheretherketone, PEEK), the first PAEK to be fully commercialized. PEEK has been commercially available from ICI since the early 1980s and PEK, synthesized by a similar nucleophilic route, since 1987.



Polyethetherketone PEEK

In the 1980s and 1990s, Hoechst tried to enter the PAEK market with poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylenecarbonyl-1,4-phenylene) (polyetheretherketone ketone, PEEKK, Hostatec) produced by the nucleophilic route, and BASF with polyetherketone ether ketone ketone (PEKEKK, Ultrapek) produced by the electrophilic route, but they failed to gain substantial market share and, therefore, left the field of PAEK.

In 1993, ICI sold its Victrex PEEK business to a management buyout group, which established Victrex plc. Since then, Victrex has become the major manufacturer of PAEK resins, producing Victrex PEEK, Victrex HT (PEK), and Victrex ST (PEKEKK).

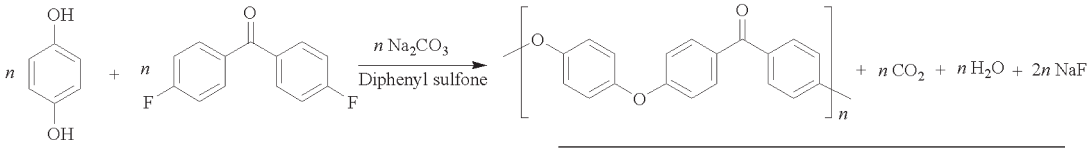
In 2005, Degussa (after 2007 Evonik Degussa) formed a joint venture with Jilin University in China for the production of PEEK (VESTAKEEP). Gharda Chemicals in India produced PEEK, based on a novel electrophilic route. This business was acquired by Solvay in 2005, which built a plant in India for the production of PEEK by the nucleophilic route (KetaSpire).

Rallis in India is currently (2010) the main manufacturer of PEKK and supplies material to Cytec for aerospace applications and thermoplastic composites. PEKK, being used for various industrial and medical applications, is sold by Oxford Performance Materials, which was acquired by Arkema in early 2009.

3.1. Production

The vast majority of PAEKs is produced by methods based on nucleophilic displacement reactions.

PEEK. The commercially significant PAEK, PEEK, is prepared by reacting 1,4-benzenediol (hydroquinone) with 4,4′-difluorobenzophenone in diphenyl sulfone in the presence of alkali-metal carbonates under an inert atmosphere at temperatures approaching the melting point of the polymer (> 300 °C) [26].



The hydroquinone is deprotonated in situ by the alkali-metal carbonate to give a hydroquinone salt. The hydroquinone anion then attacks the 4,4′-difluorobenzophenone in a nucleophilic manner, replacing the fluorine atom and leading to the formation of an ether bond.

The polymer is isolated from the diphenyl sulfone and inorganic impurities, which can destabilize the polymer melt, by solvent extraction (leaching). A slight excess of 4,4′-difluorobenzophenone is normally employed to prevent the formation of phenoxide chain ends, which can destabilize the polymer. The water formed as a result of polycondensation could potentially hydrolyze the fluoro groups and prevent formation of the high-molecular-mass polymer but is lost because of the high reaction temperatures and the hydrophobicity of the solvent.

The expensive difluoro monomer is employed in the reaction rather than the less expensive dichloro analog because the weakly electron-withdrawing carbonyl group does not strongly activate the halogen for a nucleophilic displacement reaction and, consequently, a good leaving group is necessary to make reaction efficient. Nevertheless, some attempts have been made to use the less expensive chloro monomers for the production of PEEK [27, 28] but a relevant industrial process using the chloro monomers has not been established so far.

An electrophilic route for the production of PEEK was developed by Gharda [29]. The process is based on the reaction of phenoxy phenoxy benzoic acid in alkane sulfonic acid (e.g., methane sulfonic acid) with a condensating agent like thionyl chloride.

PEK can be produced by two nucleophilic routes [25] which are essentially similar to the route to PEEK. The two-monomer route employs 4,4′-dihydroxybenzophenone in place of 1,4-benzenediol. The single-monomer route employs the potassium salt of 4-fluoro-4′-hydroxybenzophenone. The latter route has the greatest tendency to exhibit side reactions leading to branching (via carbanion formation due to abstraction of a proton *ortho* to the fluoro group of the monomer), which results in polymers with inferior mechanical properties. The two-monomer route is, therefore, usually preferred.

PEK has been produced by electrophilic acylation [30]. The most convenient synthesis involves the Friedel–Crafts polycondensation of 4-phenoxybenzoyl chloride. The preferred reaction medium of HF/BF_3 necessitates the use of special polytetrafluoroethylene reaction vessels. This electrophilic route employs relatively cheap nonfluoro substituted aromatic monomers. If the problems associated with the aggressive reaction medium can be solved, this route may prove to be the cheapest route to PEK.

Gharda Chemicals developed a route for production of PEK using the low-cost chloro monomer 4-chloro-4′-hydroxybenzophenone in the presence of potassium carbonate [31]. The monomer is prepared by reaction of 4-chlorobenzoylchloride with phenol in the presence of $AlCl_3$ as a catalyst.

PEKEKK is produced similar to PEEK and PEK (two-monomer route) by a nucleophilic displacement reaction of 1,4-bis(4-fluorobenzoyl)benzene with 4,4′-dihydroxybenzophenone.

PEKK is produced by the electrophilic route using diphenyl ether and terephthaloyl chloride and isophthaloyl chloride, and $AlCl_3$ as a

catalyst [32]; the incorporation of the isophthaloyl groups reduces the crystallinity.

Although the nucleophilic route is also possible here, it is not the preferred one because of the complexity of the required monomers, 1,4-bis(4-fluorobenzoyl)benzene and 1,4-bis(4-hydroxybenzoyl)benzene.

PAEKs with high glass-transition temperatures. Since the mid 2000s there has been increased interest in PAEKs with glass-transition temperatures (T_g) higher than those of PEKK due to the increasing challenges of oil and gas extraction. The exploitation of offshore oil and gas reserves requires the use of materials that have outstanding mechanical and chemical properties at high pressures (>150 MPa), high temperatures (>200 °C), and chemically aggressive environments (hydrogen sulfide, brine, crude oil).

The glass-transition temperature can be increased by the incorporation of sulfone groups into the backbone of the polymer chain. Various sulfone-containing monomers can be used, ranging from dichlorodiphenyl sulfone to monomers especially designed to maximize the increase in T_g while minimizing the effect on crystallinity [33].

The reaction of 4,4′-difluorobenzophenone with 4-(4-hydroxyphenyl)phthalazinone in a polar solvent in the presence of potassium carbonate yields an amorphous PAEK with a high T_g [34]. This attempt can be further extended by copolymerizing the aforementioned monomers with 4,4′-biphenol, which results in a melt-processible semicrystalline PAEK with T_g ranging from 180–240 °C and melting temperatures (T_m) ranging from 310–376 °C, depending on the monomer ratios [35].

3.2. Properties

Physicochemical Properties. Most wholly aromatic PAEKs are semicrystalline because of the strong interchain forces between the polar groups in the backbone and the crystallographic near-equivalence of the ether and carbonyl units [36]. Many of the desirable properties of commercial PAEKs are related to their tendency to develop a high degree of crystallinity under normal processing conditions.

The semicrystalline morphology of PAEKs is largely responsible for their excellent resistance to solvent attack. For example, PEEK is insoluble in all common solvents. It is soluble at room temperature only in strongly acidic media (e.g., concentrated sulfuric acid, hydrofluoric acid, and trifluoromethanesulfonic acid) that can protonate the carbonyl groups. At temperatures well above the glass-transition temperature the polymer is soluble in a few unusual media (e.g., diphenyl sulfone, some high-boiling-point esters, benzophenone, and 1-chloronaphthalene). PEEK absorbs small amounts of water [37] but can absorb significant amounts of dichloromethane and related solvents that contain a hydrogen atom activated by neighboring electronegative groups [37, 38].

The insolubility of PAEKs causes problems in the molecular-mass characterization of the polymers. Viscometry and light-scattering methods using concentrated sulfuric acid and a high-temperature gel-permeation-chromatography method have been developed [39]. The number-average molecular mass of commercial PEEK grades is typically in the order of tens of thousands.

The essentially linear aromatic backbone of PEEK results in excellent resistance to chemical attack and ionizing radiation. The only common reagents that degrade PEEK are chlorine, bromine, and concentrated nitric acid [40]. Dissolution of PAEKs in concentrated sulfuric acid results in monosulfonation of the aromatic rings substituted by two ether linkages [41].

PAEKs display limited resistance to degradation by UV light, as is the case for all linear polyaromatics, but the problem is only serious in high-insulation environments (i.e., prolonged exposure to intense sunlight) and is much reduced by incorporation of a suitable pigment (e.g., carbon black).

PAEKs exhibit excellent resistance to gamma radiation due to the delocalized bonding electrons in the aromatic rings.

Thermal Properties. Differential scanning calorimetry studies of quenched amorphous PEEK indicate a T_g at 143 °C and a melting endotherm with a maximum at 334 °C [42]. Increasing the ratio of carbonyl-to-ether linkages in polyarylether backbones increases both T_g and T_m; PEK, therefore, has a T_g at 154 °C and T_m at

367 °C, and PEKK has a T_g at 165 °C and T_m at 386 °C [43, 44].

Isothermal crystallization studies indicate that PEEK crystallizes very rapidly [42] and normal processing conditions generally result in degrees of crystallinity of 25–35%.

The thermal stability of PAEKs is excellent. PEEK melts are stable for > 1 h at 400 °C. Thermoxidative stability is lower with prolonged heating above 300 °C, which results in cross-linking. The presence of copper impurities significantly accelerates the thermal degradation of PEEK melts [45].

Mechanical Properties. The high crystallinity rapidly developed by PEEK and PEK results in very high flexural moduli and tensile strengths. These properties decrease substantially above the T_g but useful residual values are maintained up to temperatures over 250 °C, which is close to the melting temperature of the crystalline regions, this is reflected by the maximum service temperature of the polymers. PAEKs with higher T_g and T_m show improved high-temperature retention of their properties.

PAEKs are notch-sensitive like many thermoplastics, i.e., the presence of a stress-raising feature lowers the otherwise acceptable impact strength.

Selected mechanical properties of various PAEKs are given in Table 4.

Flammability. PAEKs have low hydrogen-to-carbon ratios and do not produce large amounts of combustible volatiles; therefore, they are difficult to ignite. Moreover, PAEKs have very low smoke emissions and burn in excess oxygen producing only nontoxic gases.

Electrical Properties. PAEKs have a high volume resistivity (i.e., they are good insulators) and a low dissipation factor for electromagnetic radiation. Both properties are stable over a wide temperature range up to the T_g.

Selected electrical properties of various PAEKs are listed in Table 4.

3.3. Processing

The thermal stability of commercial PAEKs allows melt processing in conventional equipment [50] capable of reaching the required processing temperatures (approx. 40–60 °C above T_m). This stability also allows reworking and recycling of PAEKs.

PAEKs can be injection- and compression-molded; extruded into amorphous or crystalline film, sheet, and mono- or multifilament fiber; powder- and dispersion-coated; blow-molded; used for thermoplastic composites; welded; metallized, adhesively bonded; and machined. A recent processing technology to PAEKs is laser sintering [51], in which a focused laser beam melts PAEK powder layer by layer to form a solid object. Starting from construction data (e.g., computer-aided design data), a highly accurate manufacturing of objects having very complex shapes can be achieved.

Table 4. Selected properties of various PAEKs [46–49]

Property*	PEEK (VESTAKEEP 4000G)	PEK (Victrex HT G45)	PEKEKK (Victrex ST G45)	PEKK (OXPEKK-C)*
Tensile modulus, GPa (ISO 527)	3.5	3.7	4.3	4.4
Tensile strength, MPa (ISO 527)	96	115	115	110
Tensile elongation,% (ISO 527)	30	30	20	12
Charpy notched impact strength, kJ/m^2 (ISO 179)	7		4	
Izod notched impact strength, kJ/m^2 (ISO 180)		7		7
Heat deflection temperature A, °C, (1.8 MPa, ISO 75)	155	163	172	175
Dielectric strength, kV/mm (IEC 60243-1)	16	17	21	23
Volume resistivity, Ω · cm (IEC 60093)	10^{15}	10^{16}	10^{16}	10^{16}
Dissipation factor (1 kHz, IEC 60250)	0.003			0.004

* ASTM data

3.4. Uses

PAEKs can be found in almost all industry segments and their use is generally connected with their outstanding high-temperature performance and chemical resistance.

Compounds and Blends. The properties of PAEKs can be modified by adding various high-temperature-stable additives or fillers (→ Plastics, Additives, Chap. 7). The most common fillers are glass fibers and carbon fibers for reinforcement. Other fillers such as graphite and polytetrafluoroethylene for lubrication, hard inorganic fillers for the improvement of the abrasion resistance, talc and mica for the reduction of shrinkage and warpage, and conductive fillers for the preparation of highly conductive grades or grades with electrostatic dissipation properties are used.

PEEK can be blended with various other polymers to improve some of the properties (→ Polymer Blends). Some common blend partners are polyarylethersulfones [52] for the reduction of warpage and cost, polyetherimide [53] for the increase of T_g and the reduction of the crystallization rate, polyphenylene sulfide [54] for cost reduction and the improvement of melt flow, and polybenzimidazoles [55] for the improvement of wear resistance at high temperatures.

Stock shapes (e.g., rods, sheets, tubes) are manufactured by extrusion or compression molding of powder and used in various industry segments for prototyping, small production runs, and large-volume applications.

Films (→ Films) can be produced by means of a conventional extruder; the crystallinity of the film is controlled by the temperature of the casting rolls.

PAEK films are used for different applications, e.g., seals, bearings, liners, heat exchangers, speakers, and membranes.

Fibers (→ High-Performance FibersI). PAEK monofilaments and hollow monofilaments, multifilaments, as well as staple fibers are available. The fibers are produced by extrusion and orientation and have high strength.

PAEK fibers are used for open-mesh conveyor systems, textile printing, food processing, aerospace components, thermoplastic composites, dry filtration, chemical separation, sports strings, braids, brushes, and cords.

Coatings. Cable coatings are obtained by extrusion of PAEK. Another coating process is the use of fine powders for powder coating applied by electrostatic powder spraying, flame spraying, or dispersion coating applied by dispersion spraying techniques.

PAEK coatings are applied where thin layers are sufficient, e.g., for the protection of other materials, especially metals.

Composites (→ Composite Materials). PAEK composites are mainly continuous carbon fiber reinforced and produced by proprietary impregnation processes. Fine powders with particle sizes down to 10 μm are available for the impregnation process.

PAEK composites are mainly used in the aerospace industry for bolts, brackets, fasteners, inserts, and nuts, as well as for structural objects.

Medical Applications (→ Surgical Materials). Medical devices like surgical instruments have been manufactured from PAEK for many years. In 1999 implantable PEEK grades were launched by Invibio Ltd.. Ten years later, PEEK has become one of the major polymers used for medical devices and implants, and implantable PEEK grades are available from all major PEEK producers.

Compared to metals used in implantology, PEEK offers various advantages: the tensile modulus is close to the one of bones (reduced stress shielding), metal ions are not released, artifacts in X-ray imaging do not occur, parts can be sterilized by gamma radiation, steam, and ethylene oxide, and complex shapes can be easily formed.

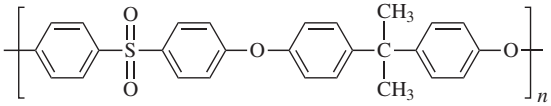
4. Polysulfones

Polysulfone is the generic term for all sulfone-containing polymers. Polysulfones are an important class of engineering thermoplastics. The polymer backbone consists of *para*-linked

aromatic groups connected by ether, sulfone, and in some cases alkyl groups.

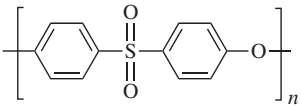
Development work on polysulfones was active by the early 1960s. Early syntheses were electrophilic, being in effect polysulfonylations [56]. This type of reaction did not generally produce a linear *para*-linked chain, and the introduction of *ortho* linkages and branchpoints resulted in polymers with poor mechanical properties [57].

An alternative strategy for the synthesis of polysulfones based on nucleophilic aromatic substitution reactions [58, 59] proved more successful for the production of *para*-linked, essentially linear polymers with good mechanical and thermal properties. This route was subsequently employed in all large-scale commercial routes to polysulfones. By the late 1960s the first commercial polysulfone, poly(oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylene(1-methylethylidene)-1,4-phenylene) or bisphenol A polysulfone [25135-51-7] (Udel, Union Carbide) was available.



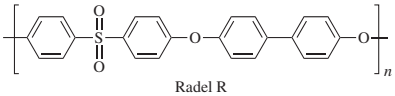
Udel

This was followed by the introduction in the early 1970s of the polyethersulfone poly(oxy-1,4-phenylenesulfonyl-1,4-phenylene) [25667-42-9] (Victrex, PES) by ICI and Astrel 360 by 3 M, a biphenyl containing polysulfone with a high glass transition temperature but poor processability.

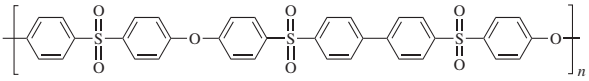


Victrex PES

More recent developments include the introduction of polysulfones containing biphenyl groups in the repeat unit (Radel R polyphenylsulfone [68518-59-2], Union Carbide; Victrex HTA [121763-41-5], ICI) which have higher T_g values but retain melt processibility.



Radel R



HTA

The major manufacturers of polysulfone resins are Amoco, which acquired the Union Carbide polysulfone business (Udel, Radel A and R), and ICI (Victrex PES and Victrex HTA). BASF have recently marketed comparable polysulfones to the ICI and Amoco polymers but on a smaller scale (Ultrason S Polysulfone, Ultrason E Polyethersulfone).

Since drafts were first submitted for publication, ICI has announced that it is to withdraw from the manufacture and sale of Victrex PES and HTA. BASF have announced a capacity increase for their Ultrason products.

4.1. Production

Bisphenol A polysulfone (Udel) is synthesized by nucleophilic substitution of 4,4′-dichlorodiphenyl sulfone (DCDPS) by 4,4′-(1-methylethylidene)bisphenol (bisphenol A) in a dipolar aprotic solvent such as dimethyl sulfoxide (DMSO) [60]. The reaction is carried out in two stages. Firstly addition of two equivalents of aqueous NaOH or KOH to a solution of the bisphenol in a mixture of DMSO and azeotroping solvent (e.g., chlorobenzene) generates the more nucleophilic bisphenate salt. Excess water is then removed by azeotropic distillation at 120–140 °C before the dichloro monomer, which could be hydrolyzed by water and lead to a low molecular mass product, is added and polymerization proceeds. Polymerization is carried out at 130–160 °C under an inert atmosphere to prevent oxidation of the bisphenate salt. The dipolar aprotic solvent promotes very rapid rates of nucleophilic substitution and the molecular mass of the polymer can become excessively high unless it is controlled by the addition of monofunctional halides or phenols.

Radel R and Radel A (structure not disclosed) are probably also synthesized by this type of route but employing the appropriate bisphenol monomers.

The synthesis of Victrex PES is similar to the synthetic route to Udel with 4,4′-sulfonylbisphenol (bisphenol S) being condensed with DCDPS [61]. The lower solubility and reactivity of the bisphenol (nucleophilicity reduced by electron-withdrawing sulfone group para to the hydroxy group) necessitates a significantly higher reaction temperature (up to 285 °C). Consequently, the dipolar aprotic solvent used is diphenyl sulfone, phenate salts being notionally generated "in situ" by the action of K_2CO_3 or Na_2CO_3. The high reaction temperature and the hydrophobicity of the solvent result in the efficient removal of water that might otherwise hydrolyze the dichloro monomer. Azeotropic distillation is not necessary.

Victrex HTA is produced by an analogous route but with the DCDPS being replaced by bis (4-chlorophenylsulfonyl)biphenyl.

4.2. Properties

Physicochemical Properties. Key properties of Udel polysulfone and Victrex PES are listed in Table 5.

All commercial polysulfones are essentially amorphous as utilized. The unfilled polymers display good clarity.

The polysulfones are relatively polar and their solubility characteristics reflect this. Polysulfones are soluble to some extent in a variety of dipolar aprotic solvents (e.g., dimethyl sulfoxide, dimethylformamide, *N*-methylpyrrolidone) and certain chlorinated hydrocarbons (e.g., dichloromethane, chlorobenzene). Udel polysulfone is significantly soluble in low molecular mass ketones and some aromatic hydrocarbons [62]. Victrex PES and biphenyl-containing polysulfones are more solvent resistant than Udel polysulfone [63]. The polysulfones are crazed but not dissolved by solvents with polarities similar to that of the polymer and this tendency increases with stressed samples.

Table 5. Properties of Udel polysulfone and PES

Properties*	Udel polysulfone P 1700	Victrex PES 4100 G
T_g, °C	185	223
Heat distortion temperature, °C (D 648)	174	203
Water absorption, % (D 570)	0.22	0.66
Tensile strength, MPa (D 638)	70	84
Flexural modulus, GPa (D 790)	2.7	2.6
Izod impact strength, J/m (D 256)		
Unnotched	no break	no break
Notched	69	83

* Appropriate ASTM test method given in parentheses.

Polysulfones can absorb small amounts of water but this has a minimal adverse effect on dimensions and mechanical properties. Polysulfones are very resistant to hydrolysis, even by hot water or steam. They are stable to dilute acid and caustic but are degraded by concentrated nitric and sulfuric acids. Chlorine and bromine also degrade polysulfones.

Polysulfones show limited stability to UV light and the materials must be filled for outdoor applications. Resistance of the wholly aromatic polysulfones to ionizing radiation is excellent, Udel polysulfone has a lower resistance due to the presence of aliphatic groups.

The ready solubility of polysulfones allows the determination of average molecular masses and distributions by a variety of common techniques including gel permeation chromatography. Number-average molecular masses of commercial polysulfones are typically of the order of tens of thousands.

Thermal Properties. Commercial polysulfones cannot be crystallized from the melt or by annealing and are amorphous as utilized. The T_g tends therefore to be responsible for short-term temperature ceilings (e.g., heat deflection temperature) for applications of the polymers. Aromatic rings and sulfone groups introduce chain rigidity whereas ether links increase flexibility. Hence increasing the ratio of sulfone to ether links in the repeat unit increases the T_g. The presence of biphenyl groups (e.g., HTA and Radel R) also increases chain rigidity and hence T_g.

The thermal stability of polysulfones is excellent due to the strong bonds in the backbone and results in stable melts during processing below 400 °C. The aliphatic isopropylidene groups in Udel polysulfone significantly reduce the thermooxidative stability relative to the

wholly aromatic polysulfones and prevent prolonged high-temperature use close to T_g. Melt processing on conventional equipment is still possible however.

Commercial polysulfones possess selfextinguishing behavior. Despite the presence of sulfur-containing groups, they exhibit relatively low levels of smoke and toxic gas emission.

Mechanical Properties. The polar groups in the polysulfone chain result in a very high flexural modulus. Modulus decreases rapidly as T_g is approached. The impact strength of the unnotched polymers is also high, but the presence of molded or accidental notches dramatically reduces the impact strength. The notched impact strength of the biphenyl-containing polysulfones is significantly higher than that of other polysulfones.

Filling of the polymers with glass or carbon fiber substantially increases the modulus of the polysulfones but generally only increases the heat deflection temperature slightly.

Electrical Properties. The polysulfones have high resistivities and low dielectric constants and dissipation factors for electromagnetic radiation which are substantially retained up to the T_g of the polymer.

4.3. Processing [62, 64]

Commercial polysulfones are all melt processible on conventional equipment, the required processing temperatures increasing with the T_g of the polymer. The polysulfones are dried before processing to prevent the evolution of adsorbed moisture from lowering the quality of moldings. Annealing at a temperature close to the T_g of the polymer is recommended to prevent stress cracking of moldings.

4.4. Uses

The mechanical properties of Udel polysulfone and Victrex PES are similar. If enhanced high-temperature performance or chemical resistance is required Victrex PES is preferred. The biphenyl-containing polysulfones are significantly more expensive than Udel and Victrex PES, their use is limited to situations where extreme heat or impact resistance is required. Their use as films and foamed plastics are described elsewhere, see → Films, Section 6.10., → Films, Section 6.11.,→ Films, Section 6.12.,→ Films, Section 6.13. and → Foamed Plastics.

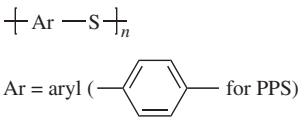
Udel and Victrex PES have been widely used to produce injection-molded articles, replacing metals in low- to medium-temperature applications where weight saving is important — particularly aerospace applications. Notch sensitivity limits the application of the polymers in critical load-bearing components.

The high-temperature hydrolytic stability of polysulfones has permitted widespread use in fluid-handling components and steam-sterilizable biomedical moldings. Chemical resistance enables a range of chemical process and automotive applications.

Good insulating properties up to high temperatures favor polysulfones as insulation for electrical cables and as a circuit board material (→ Insulation, Electric, → Insulation, Electric).

5. Poly(Phenylene Sulfide)

Poly(phenylene sulfide) [9016-75-5] (PPS), poly(thio-1,4-phenylene), is a high-temperature-stable, thermoplastic accessible from very cheap monomers. It has therefore seen continuously high growth rates since its commercialization in 1972. PPS consists of repeating aromatic monomer units joined by sulfur bridges:

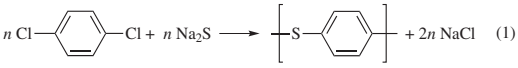


Reactions between sulfur and aromatic hydrocarbons carried out by Friedel and Crafts [66, 67] in 1888 and by Genvresse in 1897 [68, 69] resulted in cross-linked resins and low-molar-mass products but not well-defined linear polymers. In the late 1940s, Macallum developed a process for preparing poly(arylene sulfides), including PPS, by reacting dichlorinated

aromatic compounds with sulfur. He also obtained partially cross-linked products [70].

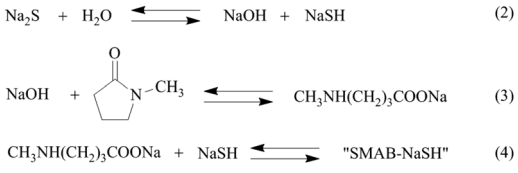
In the early 1960s a process was developed by Dow Chemicals which involved copper-induced self-condensation of aromatic halothiophenols and resulted in an experimental product [71, 72].

In 1963 EDMONDS and HILL developed a process, eventually commercialized in 1972 by Phillips Petroleum, in which PPS was prepared from *para*-dichlorobenzene (*p*-DCB) with sodium sulfide in *N*-methylpyrrolidone (NMP) as a suitable polar aprotic solvent [73].



(1)

It appears that all technical PPS polymerization processes make use of this polymerization reaction. Reaction kinetics investigations [74] demonstrated that NMP not only acts as a mere solvent but undergoes a ring-opening hydrolysis to sodium *N*-methyl-4-aminobutyrate (SMAB) before the polymerization starts:



SMAB forms a truly crystallizable stoichiometric 1:1 complex with NaSH, which is considered to be the nucleophile attacking the chloroaromatics. During the polymerization reaction, HCl is formally set free, which subsequently reacts with SMAB to regenerate NMP with NaCl and water as byproducts. Because of the reaction sequence (2)–(4), the monohydrate appears to be the optimum sodium sulfide form for PPS polymerization. Less water would not allow the SMAB-NaSH to be formed, more water would slow down the polymerization at least in the early phase.

Although Reaction resembles a step-growth polycondensation of the A–A plus B–B type following CAROTHER's law, the actual polymerization kinetics are different. Oligomers of higher molar masses are already formed early in the polymerization process, i.e., at a low conversion of $X \approx 20\%$. This observation has triggered a scientific discussion on the polymerization mechanism, including the proposal of a chain polymerization carried out by activated species [75, 76]. Researchers at Phillips Petroleum finally demonstrated [74] that the PPS reaction is a polycondensation reaction but with monomers (in particular, *p*-DCB) being about a factor of ten less reactive than growing-chain end groups. Because this low monomer reactivity would eventually lead to polydispersities of $D \approx 20$ or higher, a cleavage reaction of already formed polymer chains by Na_2S has been included in the polymerization model to explain the experimentally observed polydispersities of $D \approx 2$–5 [77].

5.1. Production

The key challenge in PPS polymerization engineering is the achievement of a sufficiently high polymerization degree. At high monomer conversions of $X > 0.9$ the polymerization degree P_n approximately follows CAROTHER's law:

$$P_n = \frac{1}{(1 - X)}$$

Therefore, an exact stoichiometric match between the monomers Na_2S and *p*-DCB is required to achieve sufficient molar masses. Typically the reaction is carried out with a slight excess (1–3 mol%) of *p*-DCB over Na_2S because

- *p*-DCB is much less reactive than chlorine-terminated polymer chains and, therefore, reacts only very slowly with sulfur-terminated polymer chains
- an excess of Na_2S, on the other hand, cleaves already formed polymer chains in a very fast reaction
- an excess of Na_2S undergoes complex side reactions to form bad smelling organosulfur compounds

Achievement of an exact stoichiometric match is further complicated by the fact that sulfur equivalents charged to the reactor might be lost from the reaction mixture as H_2S over the vapor phase or coprecipitate as NaSH with the byproduct NaCl [77].

In the initial process variant the reaction product is a suspension that contains comparatively low-molar-mass PPS and sodium chloride as the solid phase. The suspension can be freed

and *p*-DCB by processes such as flash evaporation. The resulting powder consists of polymer and salt. It is washed with water at various pressures and temperatures to remove the salt and then dried [78, 79].

The PPS powder is then cured to achieve the necessary molar mass. Curing means chain extension and branching through thermooxidation, in the simplest form with air [73, 80]. The melt flow index (MFI) can be reduced from about 6000 g/10 min to 50–700 g/10 min (ASTM D 1238–70, 316 °C, 5 kg). Similar products of increased melt viscosity but branched chain architecture may be obtained by adding small amounts of trifunctional aromatics to the reaction mixture [73, 81].

Because a branched PPS polymer cannot be processed into useful films or fibers, several processes were developed to obtain higher molar masses and linear PPS molecules. In general the processes are based on two concepts:

1. Phase separation
2. Molar mass build-up in a homogeneous reaction

Concept 1 involves the addition of "catalyst" substances such as sodium or lithium acetate to the reaction mixture [81, 82]. The reaction mixture then partially separates into a solvent- and water-rich phase of high ionic strength and a polymer-enriched phase where the further condensation of low-molar-mass chains continues at increased end-group population density. Phase separation has also been induced by adding water or low-volatile ethers to the reaction mixture to recover the polymer in granular form directly [83].

In a further development of the phase-separation concept, a well-defined amount of water is added to the reaction mixture at low conversions, i.e. the low-molar-mass, prepolymerized PPS solution. The reaction mixture then undergoes complete phase separation and linear PPS polymers of high molar masses are formed as fine granules in a separate molten phase. After cooling down the reaction mixture, the granules may be separated by mechanical screening from the liquid or fine-particle phase of the reaction mixture. They are subsequently washed, dried, and directly melt-processed into specific compounds. Under these reaction conditions, a low-molar-mass polymer fraction of up to 15% of the total PPS remains dissolved in the solvent phase, which is removed as a fine-particle fraction from the main product in the screening step [84]. This technology has been extended to a continuous work-up process [85].

In a process development following concept 2, lithium sulfide is added instead of sodium sulfide. Li_2S employed in the polymerization reaction leads to formation of LiCl as a byproduct, which, in contrast to NaCl, is soluble in NMP. Thus complications during the polymerization reaction due to reaction mixture inhomogeneity and salt byproduct precipitation can be avoided. As a result, high-molar-mass PPS is formed under well-defined, homogeneous-phase reaction conditions which may enable a continuous polymerization process [86]. However, the presence of lithium requires additional downstream separation and cleaning steps [87].

Almost homogeneous reaction conditions are also achieved in a two-step process using conventional Na_2S. In the first step, *p*-DCB is employed in stoichiometric excess to form easily crystallizable, chlorine-terminated prepolymers. A major part of NaCl is formed in this step and removed. Subsequent reaction of the prepolymers with further amounts of Na_2S produces only very little salt and proceeds in an essentially homogeneous reaction mixture [88]. A similar approach comprises firstly the preparation of cyclic oligo(phenylene sulfide) in dilute solution and, in a second step, a ring-opening polymerization, optionally in the presence of some linear polymer. This step might be carried out as a solvent-free process in the melt [89]. Though effective in providing linear, high-molar-mass PPS of narrow molar-mass distribution, such two-step process schemes add complexity to the overall process.

The PPS polymerization reaction approximately follows second-order reaction kinetics [74, 75, 77] and shows very low reaction rates at high conversions. Temperatures of up to 290 °C have been combined with cycle times of 10 h and beyond in PPS batch reactions [73, 78–84]. Moreover, the PPS formation reaction is strongly exothermic [75, 90], because the lattice energy of the insoluble NaCl is set free. A number of attempts have thus been undertaken to improve reaction control by employng

continuous or semibatch reactors. A cascade of continuously stirred tank reactors has been designed [91] for a fully continuous PPS reaction.

Semibatch reaction control schemes enable high polymer concentrations in the reaction mixture, because the immiscible monomers Na_2S and *p*-DCB do not have to be compatibilized at their respective maximum concentrations. In one of the semibatch reaction processes, the *p*-DCB is charged to the reactor and the sulfide component metered under reaction conditions. A eutectic mixture of Na_2S and NaSH is added as a melt. This approach is combined with the use of *N*-methyl--caprolactam as a solvent, which allows water to be removed in an azeotropic distillation near atmospheric pressure around 212 °C. The polymerization was thus carried out in a water-free mode [92]. In another semibatch reaction approach, the sulfur component is added as a SMAB-NaSH complex to the reactor already charged with some *p*-DCB. The two monomers are then added in parallel. An improved control of H_2S loss is achieved by counter-currently absorbing the H_2S in the highly alkaline sulfide stream and simultaneously distilling off the water [93].

Generally, the synthesis of PPS according to Reaction has a poor efficiency. For each equivalent of PPS (108 g) two equivalents of byproduct NaCl (117 g) are formed. A higher efficiency would be achieved by directly producing PPS from benzene and sulfur, which are even less costly compounds than Na_2S and *p*-DCB. Attempts using *p*-diiodobenzene (*p*-DIB) made from benzene as an intermediate, which subsequently reacts with elemental sulfur in the melt, have been published [94–96]. The key technical hurdles in this approach are the formation of di- or polysulfide bridges in the polymer chain, iodine recovery, and the iodine content in the polymer product.

5.2. Properties

5.2.1. Material Properties

The properties of PPS may vary to a limited extent, depending on the production process and workup.

Various methods have been described for characterizing the melt behavior and estimating the molecular mass of PPS. A commonly employed method is the measurement of a melt index: (melt flow index (MFI) in g/10 min, or melt volume index (MVI) in mL/10 min). In many publications the ASTM D 1238–70 standard with a modified application force (5 kg) and melt temperature (316 °C) is recommended [80–82]. The method determines only one parameter, however, as a single-point measurement on a shear-dependent melt curve. Furthermore, the standard does not permit measurement of higher values (i.e., high flowability). Measurement of the melt viscosity as a function of the shear force in a cone–plate or capillary viscosimeter is more useful [99].

Solution viscosity and light scattering measurements in combination with size-exclusion chromatography (gel permeation chromatography) have also been used to determine molecular masses [100]. Industrially produced poly (arylene sulfides) generally have broad distribution curves, which become wider after curing (see above). For further details of measurement of molecular mass, see → Plastics, Analysis.

PPS can be characterized by IR or nuclear magnetic resonance spectroscopy [101]. The thermal degradation of PPS has been investigated by direct pyrolysis in the ionization source with the aid of mass spectroscopy. In the presence of oxygen, aromatic ether bonds are formed by oxidation, and condensed aromatic compounds are produced by elimination of hydrogen sulfide. Sulfur dioxide is another inorganic gaseous product [102].

Surface oxidation produces sulfoxide and sulfone groups that can be detected by electron spectroscopy for chemical analysis (ESCA) methods [103]. Thermogravimetric measurements have shown that the high thermal stability of PPS compared to other plastics is due to cross-linking reactions [104].

Chloroaryl, thiol, or thiolate groups may be expected as end groups for poly(arylene sulfides) with a regular structure. The chlorine end group content can be determined by elemental trace analysis (e.g., Wickbold combustion) [105]. Determination of thiol groups is more difficult, a wet chemical method is described in [106].

The content of ionic impurities may be critical in certain applications, for example in the

Table 6. Mechanical properties of nonreinforced PPS

Property	Standard	Melt viscosity*, Pa · s		
		14	66	168
Impact strength, kJ/m^2	ISO 180/1 C	14	26	34
Tensile strength, MPa	DIN 53 455	40	67	59
Elongation at break, %	DIN 53 455	1.1	2.3	10.9
Modulus of elasticity (tension), MPa	DIN 53 457	3940	3560	3460

* Measured in a rotation viscosimeter at 306 °C and a shear rate of 100 s^{-1} (measurements made at Bayer).

electronics sector. The polymer must be brought into solution to release and determine its salt content [107]. A physical method for determining chloride ions has also been published [108].

5.2.2. Properties of Nonreinforced Moldings

PPS is a partially crystalline material. Moldings thus consist of an amorphous phase and a crystalline phase. The amorphous phase has a glass transition temperature of 90 °C. The thermodynamic melting point of the crystalline phase for "ideal" crystals is between 300 and 310 °C [109]. The platelet-shaped, orthorhombic crystals (length and width ≤ 1000 nm, thickness ≤ 10 nm) in moldings have a melting point between 280 and 285 °C. The PPS crystallites form spherical spherulites from still melts, and stacks with a hard-fiber morphology from flowing melts [110].

During injection molding or extrusion, PPS crystallizes when the melt is cooled. Differential scanning calorimetry (DSC) shows that crystallization begins at about 250 °C. The final degree of crystallinity depends on whether the melt is cooled above or below the crystallization temperature of ca. 127 °C, and how quickly this takes place.

It is often impossible to obtain the maximum degree of crystallization during injection molding. Such moldings may become distorted due to post-shrinkage during subsequent use under thermal stress. In order to ensure that PPS moldings are dimensionally stable during subsequent use, it may therefore be necessary to temper them beforehand (i.e., to store them at elevated temperature, e.g., 220 °C) to complete their crystallization under controlled conditions.

Injection moldings of nonreinforced PPS have high tensile and flexural strengths, as well as high moduli of elasticity (Table 6). They have a high rigidity and a low flexibility, with the result that they may fracture even under very small loads. The impact strength and notched impact strength are also extremely low. Whereas moldings of low-viscosity PPS exhibit brittle fracture even under slight deformation, moldings of high-viscosity PPS can be deformed before they fracture in a ductile manner [111].

Thermal and electrical properties of nonreinforced PPS are listed in Table 7. Moldings of nonreinforced PPS that are not mechanically stressed retain their shape up to the melting temperature. Under mechanical loads, however, they become deformed above ca. 90 °C, i.e., the glass transition temperature. For a partially crystalline thermoplastic the coefficient of linear thermal expansion is extremely low. The thermal conductivity of PPS is also very low [112].

On the basis of its dielectric values and resistance values PPS is a slightly polar insulator.

PPS is an inherently flame-resistant thermoplastics (oxygen index 0.44). It is classified as a

Table 7. Thermal and electrical properties of nonreinforced PPS (Ryton R 6)

	Standard	Value
Thermal properties		
Vicat softening temperature (VST/B_{120}), °C	DIN 53 660	≥ 240
Heat deflection temperature (HDTA), °C	DIN 53 641	117
Linear coefficient of expansion, K^{-1}	DIN 53 752	
at 20–90 °C		60×10^{-6}
at 100–180 °C		110×10^{-6}
Electrical properties		
Dielectric strength, kV/mm	ASTM D 149–64	15
Volume resistivity, Ω · cm	ASTM D 257–66	4.5×10^{16}
Dielectric constant	ASTM D 150–70	
at 1 kHz		3.1
at 1 MHz		3.1
Dissipation factor	ASTM D 150–70	
at 1 kHz		0.0005
at 1 MHz		0.0009

Table 8. Chemical resistance of PPS on storage at 93 °C

	Weight increase after 24 h, %	Tensile strength after 24 h, MPa	Tensile strength after 3 months, MPa
	0	74	74
Gasoline benzene	0.07	71	64
Trichloroethylene	6.5	51	
Butanol	0.05	72	74
Butanone	1.02	77	52
Dibutyl ether	0	79	74
Amyl acetate	0.14	92	74
Butylamine	1.52	49	0
Hydrochloric acid (37%)	0.57	75	41
Sulfuric acid (30%)	0.14	81	74
Nitric acid (10%)	0.32	83	23
Sodium hydroxide (30%)	0.07	69	74

V-0 material (UL 94) at a thickness of 0.8 mm (→ Flame Retardants, Chap. 3.) [112].

At low temperature PPS is resistant to all organic solvents and chemicals. PPS moldings swell, however, under the action of some organic compounds on heating, particularly after prolonged exposure (Table 8). PPS is extremely resistant to acids and alkalis but oxidizing agents, in particular nitric acid, attack PPS on heating and destroy the moldings. PPS is moderately permeable to diffusion of gases and water vapor [113].

5.2.3. Properties of Reinforced Moldings

Reinforcement of PPS with fibers and/or mineral fillers increases its mechanical strength and thereby compensates for its low impact strength, and also improves its dimensional stability at high temperature. Fibrous reinforcing materials are usually made of glass but carbon fibers and aramid fibers are also employed on a small scale. Mineral fillers are generally used in combination with glass fibers and include calcium carbonate, kaolin, calcium sulfate, mica, talc, and quartz. These fillers and reinforcing materials can be incorporated into PPS in high concentrations (up to about 70 wt%) by using conventional compounding equipment [113–116].

Injection moldings made of glass-fiber-reinforced PPS have a high hardness, ultimate tensile strength, flexural strength, and modulus of elasticity, but a very low formability and ductility and only moderate impact strength and notched impact strength. Such moldings can permanently withstand high vibrational stress. The slip properties and abrasion resistance of glass-fiber-reinforced PPS molding compounds are inferior to those of other partially crystalline thermoplastics reinforced with glass fibers [115].

Glass fiber–mineral-reinforced PPS injection molding compounds have relatively high hardness and rigidity, and relatively low impact strength and percentage elongation at break (Table 9). The properties may be altered within wide limits by varying the weight ratio of glass fibers to mineral fillers [113, 114].

Reinforcing PPS with mineral fillers also considerably improves its heat resistance, hardness, and rigidity (Table 10). It also results in moldings with very smooth surfaces and high dimensional stability. Omission of fibrous reinforcement means, however, that the flexural

Table 9. Mechanical properties of PPS molding compounds reinforced with 40 wt% glass fiber

Property	Standard	Craston XMB 3100 (Ciba-Geigy)	Fortron 1140 A 4 (Hoechst Celanese)	Ryton R 4 (Phillips Petroleum)	Supec G 401 (GE Plastics)	Tedur KU 1–9510–1 (Bayer)
Tensile strength, MPa	DIN 53 455	175	159	116	170	190
Elongation at break, %	DIN 53 455	1.6	1.4	0.9	1.0	1.6
Modulus of elasticity (tension), GPa	DIN 53 457	17.5	14.2		14.5	15.0
Flexural strength, MPa	DIN 53 452	250	240	190	240	300
Modulus of elasticity (bending), GPa	DIN 53 457	15.5	12.4	13.0	14.0	13.0
Impact strength (Charpy), kJ/m^2	DIN 53 453	20	29	11	25	35
Notched tensile impact strength (Charpy), kJ/m^2	DIN 53 453	8	9	6	8	9
Ball indentation hardness, MPa	DIN 53 456	300	305	300	300	300

Table 10. Mechanical properties of PPS molding compounds reinforced with glass fibers and mineral fillers

Property	Standard	Craston X MB 3110	Fortron 6165 B 4	Ryton R 10	Tedur KU 1–9521
Density, g/cm^3	ASTM D 1505–68	1.93	2.1	2.0	1.9
Glass fiber/mineral content, wt%		60	65	70	60
Tensile strength, MPa	DIN 53 455	110	111	86	110
Elongation, %	DIN 53 455	1	1	0.7	1
Modulus of elasticity (tension), GPa	DIN 53 457	21.5	18.2	18.0	20
Flexural strength, MPa	DIN 53 452	165	190	140	180
Modulus of elasticity (bending), GPa	DIN 53 453	20.0	16.7	15.0	19
Impact strength (Charpy), kJ/m^2	DIN 53 453	11	19	6	10
Notched tensile impact strength (Charpy), kJ/m^2	DIN 53 453	6	7	4	6
Ball indentation hardness, MPa	DIN 53 456	370	430	350	300

and tensile strengths of the moldings are very low: they can be deformed only very slightly before they fracture [113, 114].

Nonreinforced PPS exhibits partial softening at 90 °C and moldings cannot be mechanically stressed above this temperature. Reinforcement with glass fibers or minerals improves the strength to such an extent that moldings can withstand mechanical stress at elevated temperature. This is reflected in the heat resistance values according to ISO 75, i.e., the heat deflection temperature (HDT), which consistently lies between 260 and 270 °C [113, 114].

Maximum service temperature is characterized by relative temperature indices which are the temperatures at which 50% loss of initial mechanical properties occurs after an exposure of 25 000 h. The relative temperature indices of reinforced and filled PPS molding materials are 200–240 °C. The thermal conductivity of reinforced PPS injection molding compounds is primarily determined by their glass fiber content and the fiber orientation in the molding. In moldings fabricated from materials reinforced with glass fibers and mineral fillers, the anisotropy of the thermal expansion is less. Reinforced PPS injection molding compounds are recommended as excellent electrical insulators on account of their high volume resistivity and surface resistivity (Table 11) [113, 114].

Reinforced PPS molding materials are extremely flame-resistant, with a very low fume density. In addition they pass the Ohio State University (OSU) test [113, 114].

Moldings are extremely resistant to most organic compounds, even at elevated temperatures. However, on prolonged storage at elevated temperature in water or in water vapor they lose up to 60% of their initial strength [116]. Water absorption is extremely low, even in boiling water, and accordingly dimensional changes due to water absorption do not occur. Under prolonged storage in hot air, above ca. 120 °C PPS injection moldings turn brown. However, this is not associated with reduction of mechanical strength (maximum use temperature: 200–240 °C) [113, 114].

PPS undergoes photooxidation in the light, and prolonged weathering results in yellowing and moldings with a dull, rough surface. Their mechanical strength decreases only very slowly however. PPS is resistant to high-energy radiation [113, 114].

Repeated processing of PPS injection molding compounds does not result in degradation of the PPS macromolecules, as is confirmed by the constant melt viscosity. Recycling of regenerated material from sprues and defective parts is therefore acceptable [113, 114].

Table 11. Electrical properties of reinforced PPS molding compounds (measurements made at Bayer)

Property	KU 1–9511	KU 1–9521
Specific volume resistance, Ω · cm (VDE 0303, part 1)		
4 d, 23 °C, 50% R.H.	7.2×10^{15}	2.5×10^{15}
4 d, 23 °C, 92% R.H.	6.7×10^{14}	9.2×10^{14}
Surface resistivity, Ω · cm (VDE 0303, part 3)		
4 d, 23 °C, 50% R.H.	6.4×10^{15}	2.7×10^{15}
4 d, 23 °C, 92% R.H.	9.6×10^{13}	3.4×10^{13}

5.3. Processing

5.3.1. Injection Molding [117]

PPS injection molding materials containing glass fibers and/or minerals have an extremely good processibility on account of their low melt viscosity.

Injection Conditions. It has proved advantageous to store the molding powder for 3–6 h at ca. 150 °C prior to injection molding to remove any volatile constituents. Materials that contain hydrophilic fillers should always be dried beforehand under these conditions.

PPS injection molding compounds are processed at melt temperatures of 350–370 °C, the most common range is 320–340 °C. PPS only crystallizes extremely slowly and incompletely below 120–130 °C, the temperature of the molds must therefore be above 130 °C and, if possible, between 150 and 170 °C to obtain moldings with smooth, uniform surfaces.

Solidification during filling results in surface damage and weak spots on the moldings. The injection rate should therefore be as high as possible and is usually performed at 75–150 MPa. High injection pressures are advantageous since they ensure uniform moldings, good surfaces, and favorable mechanical properties. Overinjection can easily occur however, with the formation of mold marks. After-pressures of 50–70% of the injection pressure are normally employed.

PPS molding compounds can be processed in all conventional screw-injection molding devices, triple-zone screw arrangements with compression ratios of 1 : 2 to 1 : 3 are often used. PPS materials generally contain glass fibers or mineral fillers and thus, wear down screws and cylinders, particularly in the feed section. Reinforced (armor-plated) screws and cylinders are therefore recommended, with shutoff nozzles instead of open nozzles. Heated channel nozzles may also be used.

Molds. Since the PPS melt has a low viscosity, it may penetrate between the mold parting surfaces, and thus cause formation of burrs and marks. High clamping pressures are used to prevent this.

PPS moldings reinforced with glass fibers shrink anisotropically. Nonwarping moldings can, however, be obtained by modifying the mold shape, injection rate, mold temperature, and the temperature of the melt. Shrinkage is also lower in PPS materials that contain both mineral fillers and glass fibers. Such materials are consequently better suited to the production of nonwarping, dimensionally stable moldings.

The high content of glass fibers and fillers in most PPS injection molding compounds can lead to considerable abrasion of the molds, and wear-resistant mold steels are therefore used. Steels with Rockwell hardnesses of 59 HRC to 62 HRC are preferred.

The mold cavities should be vented sufficiently rapidly, normally through venting slits in the mold parting surfaces. The slits should not be wider than 0.01 mm to avoid the formation of burrs and marks on the moldings.

5.3.2. Other Molding Methods

PPS moldings can be produced not only by injection molding (Section), but also by compression or by sintering PPS powders or mixtures of PPS powders and glass fibers, fillers, and/or additives (e.g., molybdenum sulfide or polytetrafluoroethylene).

The property spectrum of PPS pressed moldings is substantially inferior to that of injection moldings. The mechanical strength of sintered parts roughly corresponds to that of pressed parts of the same composition. An advantage over compression molding is that hot (360 °C) molds do not need to be handled [118].

Low-viscosity PPS powders are used to coat metallic parts (coating from aqueous dispersions, electrostatic powder coating, fluidized-bed coating). Coatings of oxidatively cross-linked PPS are rigid, flexible, and wear-resistant, and can withstand high thermal stress over prolonged periods. The chemical resistance of PPS coatings is decisive for their use in protecting metal parts against corrosion [119].

5.3.3. Finishing of Shaped Articles

Most PPS materials contain a high concentration of glass fibers and mineral fillers. The use of hard-metal drills, milling machines, and saws to finish PPS moldings is therefore recommended.

PPS moldings can be strongly bonded to one another by ultrasonic welding, hot-plate

welding, and with two-component adhesives, in particular epoxy and polyurethane adhesives.

Coatings on PPS moldings can be obtained only if a polyurethane primer is applied.

5.3.4. Extrusion

Films [120]. See also → Films, Section 6.12.4..

Films, particularly biaxially stretched films, constitute one of the main uses of unfilled PPS, and are mainly used in capacitors. Biaxially stretched PPS films have good mechanical properties, their outstanding property being their high thermal resistance. If ignited, they rapidly cease burning after the flame has been removed. PPS films are resistant to bases, acids, solvents, and other chemicals. However they are rapidly destroyed by concentrated sulfuric or nitric acid at room temperature.

PPS films can be coated and printed after corona or plasma pretreatment. The very low polarity of the PPS molecules accounts for the low dielectric constant and the low dielectric loss factor.

To produce biaxially stretched PPS films the filtered PPS melt is extruded at ca. 320 °C onto cooled rollers. It has also proved advantageous to remove volatile constituents by degassing the melt before the extrusion, this is achieved by releasing the pressure and applying a vacuum. The amorphous film is then stretched at 90–120 °C successively or simultaneously in the longitudinal and transverse directions.

Fibers [121]. See also → High-Performance Fibers, Section 2.3.2.

Fibers constitute the second largest area of use of unfilled PPS, and are employed particularly in the form of fabrics and nonwovens for filtering hot and/or aggressive media.

PPS fibers have a high mechanical strength, and can be used for short periods up to about 230 °C, whereby they retain 40% of their tensile strength at 23 °C. The longterm service temperature is 190 °C. If fabrics made from PPS are ignited, they rapidly cease burning once the source of ignition is removed.

PPS fibers have a high resistance to acids, alkalis, and most organic solvents, even at elevated temperature. Oxidizing agents attack PPS fibers however. In boiling water PPS fibers may shrink by up to 10%.

Extrusion of the raw fibers is followed by two-stage stretching and heat setting, in which the fibers are heated under tension at 265–270 °C for 1 min to ensure satisfactory crystallization of the PPS.

5.3.5. Semifinished Products

Reinforced PPS materials are processed into continuous profiled sections, rods, pipes, etc. On account of its high resistance to heat and solvents, poly(phenylene sulfide) is also an excellent matrix for high-performance composite materials [122].

5.4. Uses

The high price of PPS injection molding materials limits their uses and applications. They are therefore mainly used where technical and economic requirements cannot be satisfied by other industrial thermoplastics.

The applications of PPS molding materials are determined by their unique combination of technical advantages, the most important being:

1. High dimensional stability even at high temperature
2. Very high rigidity and hardness
3. Very good long-term static and dynamic loadability
4. Low static and dynamic coefficients of friction
5. Extremely high resistance to almost all chemicals
6. Low flammability
7. Good processability by injection molding
8. Machinability and weldability
9. Inscribability of the moldings by printing or laser inscription

The main areas of use for PPS molding materials include the electrical/electronics, automotive, and lighting sectors. PPS moldings are also used in many other market sectors, for example in household appliances, chemical plant construction, and mechanical engineering.

In the *electronics sector*, special, highly filled PPS molding compounds with particularly low melt viscosities have to some extent replaced epoxy compositions in the housing of electronics components such as transistors, coils,

and capacitors. Glass fiber-reinforced PPS is also used for integrated circuit housings (chips). Connectors (e.g., high-density connectors) made of PPS reinforced with glass fibers (and minerals) are produced on a large scale in the United States. The high mechanical strength of moldings made from glass fiber-reinforced PPS accounts for its use in components of electric motors (e.g., brush holders and wound cores).

PPS molding compounds are also being used increasingly in the *automotive sector*. For example pumps in petrol tanks are fabricated from PPS reinforced with glass fiber and minerals. In pump impellers of vacuum pumps used in steering and braking systems, the PPS moldings have to satisfy extremely stringent requirements as regards dimensional accuracy, dimensional stability, mechanical strength, dynamic longterm stress, and abrasion resistance.

In the *lighting sector* the trend towards small automobile headlamps and high light intensities means that a great deal of heat is generated in a confined space. Housings are therefore made of special, highly-filled PPS molding compounds. Caps and holders of halogen lamps are also produced from glass fiber-reinforced PPS.

PPS molding compounds are employed in *chemical plant construction* (e.g., for valves, column packings, and distillation columns). In feed pumps the danger of spark formation as a result of buildup of electrostatic charge can be excluded by using PPS molding materials whose electrical conductivity has been increased by incorporating carbon black.

On account of its resistance to chemicals, PPS is suitable for *applications involving contact with food*. Certain PPS compounds have been approved by the BGA and FDA for use as a material for kitchen utensils [123].

5.5. Economic Aspects

Despite the fact that PPS has been commercially available since the mid 1970s, it is a very "young" product. On account of its outstanding property profile it has a broad, constantly increasing range of applications. Newly developed copolymers and poly(arylene sulfides) based on dihalogenated aromatics with tailor-made property profiles are reinforcing this development [124].

Table 12. PPS turnover forecast [65]

Region	Turnover, t		Average annual growth, %
	1989	1995	
North America	5 500	10 500	11.4
Far East (including Japan)	4 000	7 700	11.5
Western Europe	2 500	4 800	11.5
Total	12 000	23 000	11.5

PPS compounds are used in strongly expanding sectors. In parallel with growing awareness among customers, further processors are beginning to use PPS which provides a good precondition for high growth rates for PPS compounds. Average annual growth rates exceeding 11% are expected in North America, the Far East (including Japan), and Western Europe (see Table 12) [65, 125].

Trade Names. In the mid 1970s only Phillips Petroleum was represented on the market, with its Ryton types. Following the expiry of the basic patents other companies are becoming increasingly active both as regards resin production and compounding [125].

Trade names of companies with their own primary resin production include Ryton (Phillips); Tedur, Tregalon (Bayer); Fortron (Kureha); Tonen PPS (Tohpren); Susteel (Tosoh Susteel); Torelina (Toray); (Sung Yong)

Trade names of companies without their own primary resin production include Supec (General Electric, United States); Tedur (Miles, United States); OFL and OCL (LNP, United States); Fortron (Hoechst Celanese, United States, Western Europe); Craston (Ciba-Geigy, Western Europe); Primef (Solvay, Western Europe), Larton (Lati; Western Europe); DIC-PPS (Dainippon Ink, Japan); Sumicon (Sumitomo Bakelite, Japan); Nova PPS (Mitsubishi Kasei, Japan); Fortron (Polyplastics, Japan); Denka PPS (Denka, Japan); Toyobo PPS (Toyobo, Japan); PPS (Ube, Japan); Petchem Idemitsu PPS (Idemitsu, Japan).

6. Liquid Crystal Polymers

6.1. Introduction

After first approaches in the late 1960s, the development of liquid-crystalline polymers (LCPs) has accelerated as a direct result of

the increased knowledge of structure–property relationships. Highly oriented materials have been made by designing rodlike LCPs [126].

The family of LCPs can be divided into two main classes:

1. Thermotropic LCPs. The liquid crystalline phase is formed when the pure component is heated.
2. Lyotropic LCPs [127]. The liquid crystalline phase is formed when the polymer is mixed with a solvent. These polymers are mainly used in fiber application.

The liquid crystalline state is a highly ordered state where the thermal energy has exceeded the intermolecular forces (molten, liquid state) while still maintaining the ordered state of a crystal structure. Molecules that form liquid crystalline phases have either rigid, long lathlike shapes with a high aspect ratio (unidirectional) or disklike molecular structures (bidirectional) The behavior of LCPs is determined by the fact that parts of the polymer, or the whole material, cannot be bended or entangled, showing a high level of stiffness.

The stiff elements in the polymer chain are called mesogens. The mesogens can be connected in three different ways:

- Linking the mesogens to form a rigid main-chain LCP, e.g., by means of a polycondensation
- Attaching to or grafting the mesogens onto a flexible polymer backbone to form a side-chain LCP with a comblike structure
- Combination of both concepts [127]

The geometric arrangements of main-chain LCPs and side-chain LCPs are shown in Figure 8.

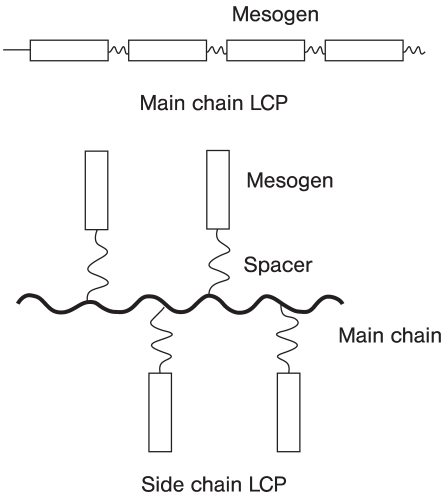


Figure 8. Schematic representation of the two geometric arrangements of main-chain and side-chain LCPs [128]

Processing the thermotropic LCPs yields highly oriented fiberlike materials with anisotropic properties. These materials show extraordinary stiffness and rigidity and typically low coefficients of linear thermal expansion in the direction of fiber orientation. Perpendicular to this direction, these properties are less pronounced. The anisotropic behavior can be reduced by implementing flexible segments into the polymer or using suitable fillers like, e.g., glass fibers that disturb the orientation of the material and its crystalline phases [129].

Liquid crystals exhibit phases of one- or two-dimensional order, which is between that of regular crystals (three-dimensional) and amorphous phases (no order). These phases are called mesophases. Figure 9 shows the orientation and order of molecules in smectic (sm), nematic (nem), and cholesteric (chol) mesophases. For detailed information on liquid crystal structure and phases, → Liquid Crystals.

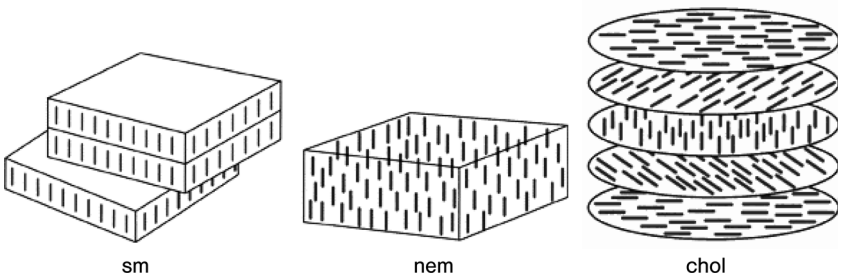


Figure 9. Schematic representation of the molecule ordering in smectic (sm), nematic (nem), and cholesteric (chol) mesophases [130]

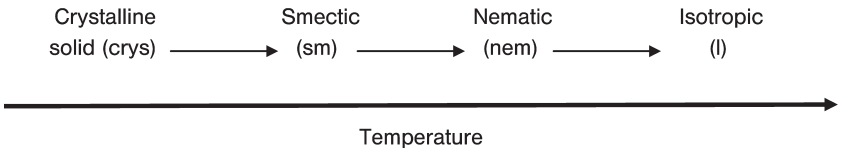


Figure 10. Sequence of the phases by heating crystalline LCP [126]

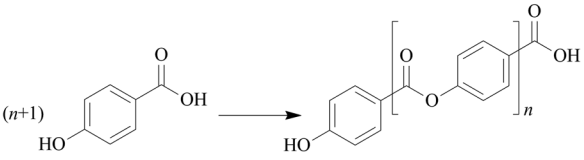
In smectic phases, the molecules are structured in layers. The axis of the molecules is perpendicular to the layers, i.e., parallel to the layer normal. In the nematic state, the molecules are oriented parallel to each other but they do not form distinguished layers. The cholesteric state lies in between the smectic and nematic state, i.e., the molecules are ordered in layers but the molecular axis is tilted with respect to the layer normal, and they are ordered in a spiral fashion [131].

For thermotropic LPCs, increasing the temperature leads to a transition from the crystalline solid state (crys) to the smectic (sm), nematic (nem), and, finally, to the isotropic state (i) (Fig. 10). Not all possible phases may appear, and many types of smectic crystals may be present simultaneously. Additionally, the liquid crystalline phases may appear rather upon cooling than upon heating [126].

In 1956, Flory predicted the behavior of rigid rodlike polymers. He postulated that this kind of material would form ordered structures in solution at some critical concentration. This lyotropic behavior was first reported in 1937 for solutions of tobacco mosaic virus. Flory offered an explanation for the lyotropicity, which was verified by systematic experiments on concentrated solutions of poly(γ-methyl glutamate) and poly(γ-benzyl glutamate) [126, 127, 132].

In the late 1960s, also thermotropic liquid crystalline polymers were synthesized, which opened a market for thermoplastic applications. Since then, this class of materials has seen a rapid development. Carborundum developed poly(*p*-hydroxybenzoic acid), a homopolyester based on *p*-oxybenzoyl repeating units that was first developed in 1955 by Aelony and Renfrey [133]. Poly(*p*-hydroxybenzoic acid) was the first commercial LCP and was commercialized under the trade name Ekonol. Saint-Gobain acquired the Ekonol business in the mid-1990s. Poly(*p*-hydroxybenzoic acid) is a rigid linear polymer with extremely high crystallinity but no melt transition up to 600 °C. Flow and creep are virtually nonexistent below the melting point. Because this melting point is significantly above the degradation temperature, thermoplastic processing is not realizable without damaging the polymer matrix. Additionally, the material is insoluble in all known solvents and does not allow any casting processing technologies, which makes analysis and characterization difficult. However, the extraordinary thermal stability of poly-(*p*-hydroxybenzoic acid) makes this material very interesting for high-temperature applications. Because of its insolubility and the lack of a melt transition, Ekonol has to be processed by hammering, plasma spraying, or sintering [126, 131, 134–136].

The structural principles of thermotropic LCPs are exemplified by poly-(*p*-hydroxybenzoic acid):



The high melting point of the polymer is a result of the high symmetry in the polymer chain. Breaking the molecular symmetry leads to a reduction of the melt transition temperature below the degradation temperature. This can be done by several methods [127] (Fig. 11):

- Copolymerization of mesogenes of different size or functionality
- Incorporation of flexible mesogene units
- Introduction of lateral substituents
- Synthesis of chains with kinks or branches

Changing the bridging group of the mesogens is one option to introduce either flexibility

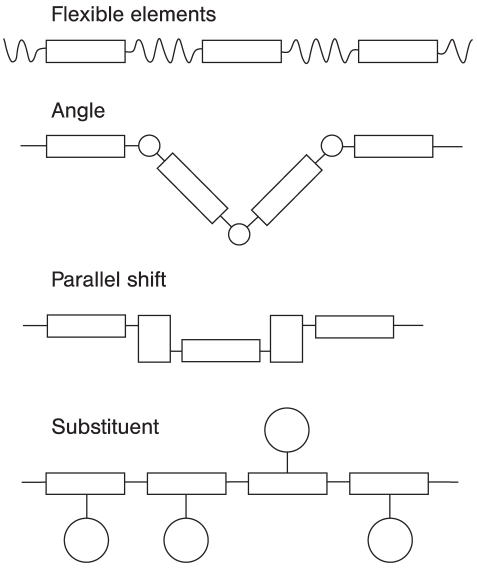


Figure 11. Various methods of breaking the symmetry of LCPs to control the transition temperature [128]

or stiffness. Table 13 gives examples of bridging groups which can be used alternatively to the ester function.

Both the nature and the orientation of the bridging groups influence the flexibility and the crystallization properties and, hence, the transition temperature of the LCP. For example, substitution of *p*-hydroxybenzoic acid (bridging group type A–B) by a hydroquinone (A–A) and terephthalic acid (B–B) lowers the crystallinity and reduces the flexibility of the chain. Although the ester groups cannot be oriented absolutely parallel, their conjugation leads to stiffening. On the other hand, addition of biphenylic groups to the backbone (no bridging group) introduces a twist at the C-C bond between the two non-conjugated aromatic groups. Linking groups and polymerization mechanism have to be selected in a way that the tacticity of the polymer will be maintained [127].

Another option for varying the mesogen is changing the aromatic structure that defines the major amount of stiffness of the backbone. For example, naphthalene derivatives can be used besides benzoic systems. Although higher conjugated systems are theoretically also possible, they are not commercially relevant. The position of the substituents on the aromatic systems defines the orientation of the polymer chain and influences crystallinity and flexibility of the chain significantly (Table 14) [127, 137–140].

Another approach is the introduction of aliphatic segments into the polymer chain. After the commercialization of poly(*p*-hydroxybenzoic acid) by Carborundum (Ekonol) and Dartco (Xydar), the next series of LCPs entered the market, Tennessee Eastman's X7G, a modification of poly(ethylene terephthalate) (PET). Here, the mesogenic units are implemented into regular PET by a transesterification of PET with *p*-acetoxybenzoic acid, which produces a thermotropic LCP composed of *p*-oxybenzoic (60%) and ethylene terephthalate units (40%). The use of this material is limited because of its reduced thermal stability, which is due to the content of aliphatic segments [126, 127, 141–143].

Table 13. Examples of bridging groups as building blocks in LCPs

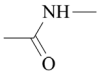
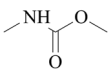
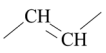
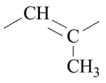
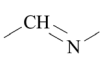
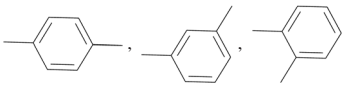
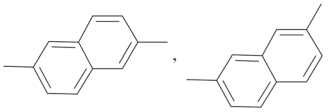
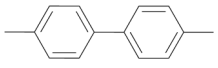
Esters	
Amides	
Ethers	
Urethanes	
Alkenes	
Substituted alkenes	
Azo compounds	
Aldimines	

Table 14. Examples of possible aromatic groups as building blocks in LCPs

Phenylidene	
Naphthylidene	
Biphenylidene	

Most of the commercial concepts for fully aromatic thermotropic LCPs use poly-(*p*-hydroxybenzoic acid) that employs chain-disrupting comonomers to obtain a better processability. Comonomers are, e.g., isophthalic acid, hydroxynaphthoic acid, hydroquinone, terephthalic acid, and *p*, *p*′-diphenyl ether groups.

In the early 1980s, Vectra LCP was introduced by Ticona, followed by the market entry of Polyplastics Co. as a second commercial manufacturer of Vectra LCP in 1996 and by other manufactures such as DuPont (Zenite), Sumitomo (SumikaSuper), Solvay (Xydar), and Toray (Siveras). The materials comprise a family of copolyesters and copolyesteramides, based on *p*-hydroxybenzoic acid copolymerized with hydroxynaphthoic acid and, optionally, a selection of other suitable monomers. These monomers provide the building blocks given in Table 13 and Table 14 [127, 139–142].

6.2. Physical Properties

Typically, LCPs exhibit a high mechanical strength even at high temperatures, inherent flame retardancy, and good weather resistance. LCPs have a high *z*-axis coefficient of thermal expansion. The polymers show extreme chemical resistance and resist stress cracking at elevated temperatures in the presence of most chemicals, including aromatic or halogenated hydrocarbons, strong acids, bases, ketones, and other aggressive industrial substances. The hydrolytic stability in boiling water is excellent. Environments that deteriorate the polymers are mainly high-temperature steam, concentrated sulfuric acid, and caustic materials [144].

6.2.1. Mechanical Properties

The properties of LCPs are influenced to a high degree by its liquid crystal structure. The rod-shaped molecules are highly oriented in the flow direction during injection molding or extrusion and remain rod-shaped even in the melt phase (Fig. 12).

Due to the highly ordered nature of LCPs, mechanical properties of its parts, shrinkage, and other characteristics depend on the flow pattern in the specific part. During mold filling, for example, the molecules are oriented in the flow direction. In the finished part, these molecules are ultimately aligned on the surface, where they form a skin that is highly oriented in the flow direction. The skin makes up to 15–30% of the total thickness of the part (Fig. 13).

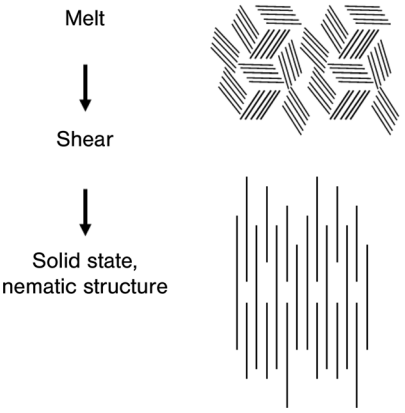


Figure 12. Orientation change of rod-shaped polymers due to the influence of shear [144]

This molecular orientation causes a self-reinforcement effect giving exceptional flexural and impact strength as well as good tensile performance. The increase in relative strength values is directly correlated to a decrease in wall thickness.

These properties depend primarily on the type of filler or reinforcement used. Glass fibers impart increased stiffness, tensile strength, and heat deflection temperature. Carbon fibers give the highest stiffness. Mineral fillers might also improve stiffness and provide increased toughness and a smoother surface compared to glass

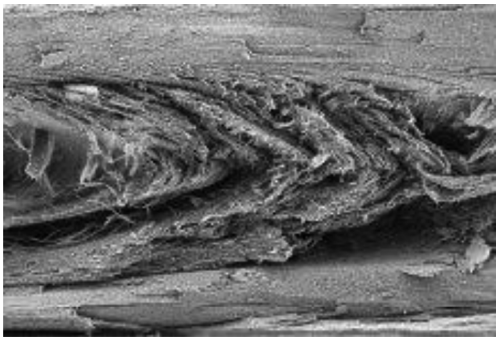


Figure 13. Layered structure of injection-molded LCP [144]

fiber reinforcement. Graphite improves elongation at break and adds lubricity. Polytetrafluoroethylene (PTFE)-modified grades have excellent sliding and wear properties. The impact strength of unfilled Vectra polymers is reduced by the addition of fillers and reinforcing materials but still remains high [144].

Anisotropy and Wall Thickness. LCPs are well known to have anisotropic properties when molded into parts. Unlike other engineering polymers, LCPs become significantly less anisotropic if formulated with mineral fillers or, to a lesser extent, with glass-fiber reinforcement. A comparison of the anisotropy of an LCP test specimen with that of a test specimen produced from a conventional engineering plastic, poly(butylene terephthalate) (PBT) with and without glass-fiber reinforcement is shown in Figure 14.

The anisotropy of 30% glass-fiber-reinforced Vectra and 30% glass-fiber-reinforced PBT is very similar. In grades with a high mineral filler loading, the anisotropy ratio can even be reduced to 1 (isotropic) [144]. One explanation for this effect is the orientation of the LCP fibrils in the specimen: Without solid fillers, the fibrils follow the shear profile within the flowing melt. If solid fillers are added, the polymer melt tends to flow faster and the fibrils flow around the fillers. This gives the fibrils a partial orientation in any direction of the part, even perpendicular to the flow direction. The total distribution of the fibril direction becomes more statistical and, consequently, the microscopic properties of the material become more isotropic.

Another factor causing anisotropy is the wall thickness of the part: as the wall, film, or sheet thickness decreases, the highly oriented outer layer accounts for a higher proportion of the total wall thickness. This higher percentage of oriented surface layer results in greater strength and modulus in the thinner sections [144].

Short-Term Mechanical Stress. Tensile stress–strain curves show that the ultimate stress of LCPs is nearly untouched by the addition of fillers or reinforcing additives [128]. The tensile stress–strain curves of Vectra with different reinforcements and fillers shown in Figure 15 are representative for other LCPs. The stress as break differs considerably with the base polymers as can be shown by the comparison of Vectra A130 with Vectra E130i (both 30% glass-fiber-reinforced). If differs less within the polymer series (compare Vectra S135 (35% glass-fiber-reinforced) to Vectra S540 (40% mineral-filled)).

As with any thermoplastic, the stiffness and strength of Vectra decreases with both increasing temperature and increasing wall thickness. The influence of the wall thickness on the

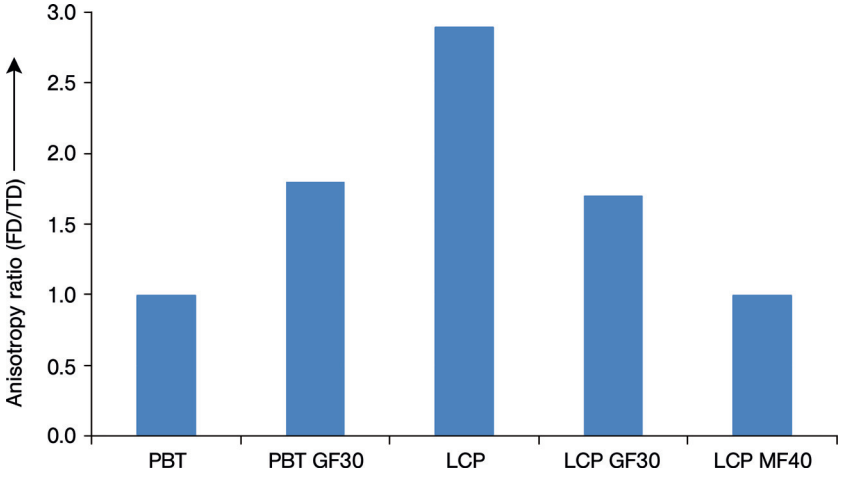


Figure 14. Comparison of the anisotropy ratios of LCP grades versus those of PBT grades (ISO test specimen) [144]
FD/TD = Tensile strength in flow direction/tensile strength in transverse direction
GF30 = 30% glass-fiber-reinforced
MF40 = 40% mineral filled

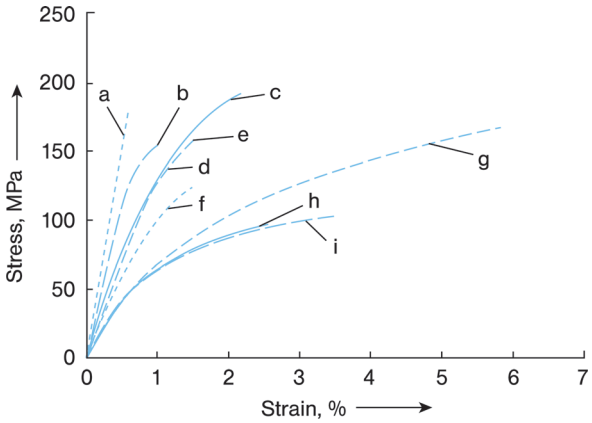


Figure 15. Stress–strain curves of Vectra with various fillers and reinforcements (tensile test at 23 °C) [144]
a) B230 (30% carbon-fiber-reinforced); b) A230D-3 (30% carbon-fiber-reinforced); c)A130 (30% glass-filled); d) S135 (35% glass-fiber-reinforced); e) E130i (30% glass-filled); f) S471 (45% glass/mineral-filled); g) A430 (25% PTFE filled); h) S540 (40% mineral-filled); i) E540i, (45% glass/mineral-filled)

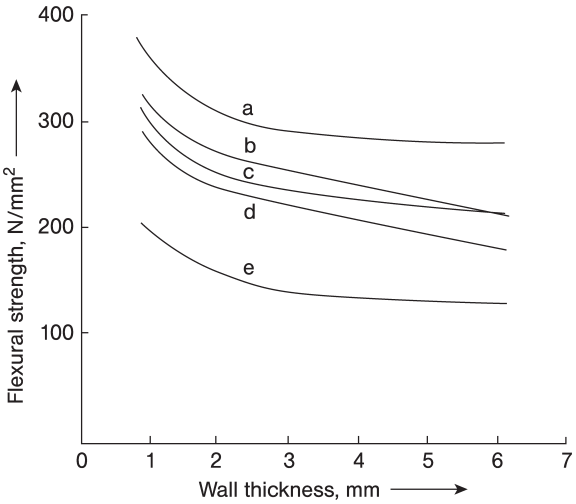


Figure 16. Flexural strength of Vectra with various fillers and reinforcements in relation to the wall thickness [128]
a) B130 (30% glass-filled); b) A130 (30% glass-filled); c) A230 (30% carbon-fiber-reinforced); d) C130 (30% glass-filled); e) A 625 (25% graphite-filled)

flexural strength is shown in Figure 16, that of the temperature in Figure 17 [128].

Long-Term Mechanical Stress. LCPs exhibit a good creep resistance. In particular, the creep resistance above 200 °C is remarkable compared to that of other thermoplastics. Figure 18 shows the flexural creep modulus of Vectra A130 between 23 °C and 220 °C for various stress levels. The maximum exposure time was 10 000 h. The stress levels were 30% of the short-term failure stress. Creep rupture was not observed at stress levels below 30% [128, 144].

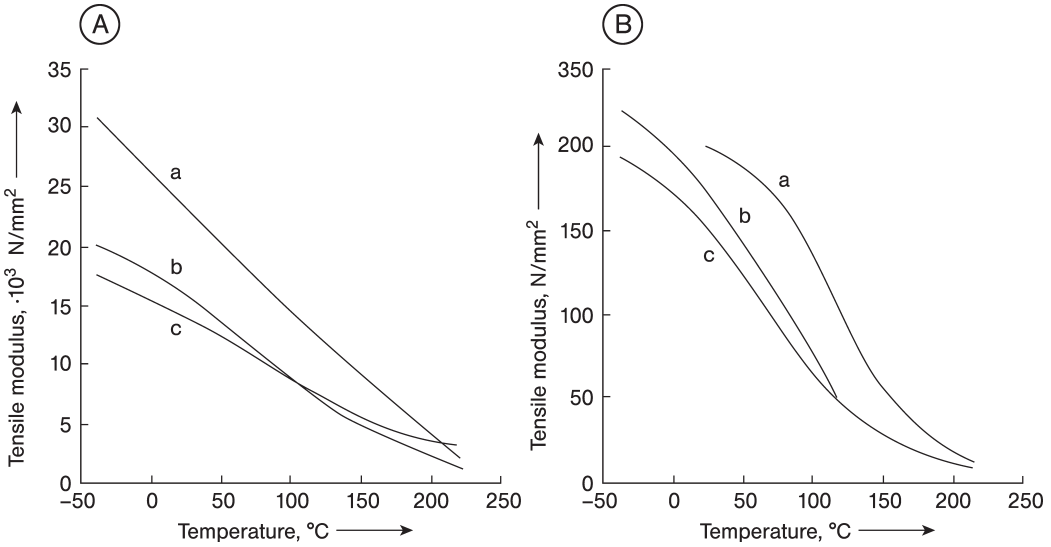


Figure 17. Tensile modulus (A) and strength (B) of Vectra types (all 30% glass-filled) in relation to the temperature [128]
a) B130; b) A130; c) C130

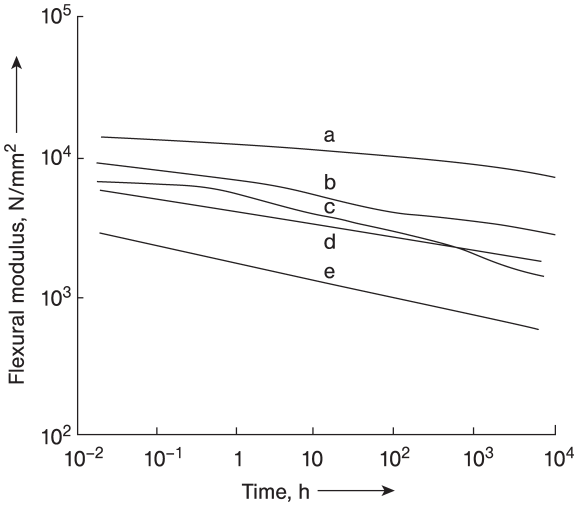


Figure 18. Flexural creep modulus of Vectra A130 (LCP GF30) at various temperatures and under loads from 4 to 80 N/mm^2 [128]
a) 23 °C, 80 N/mm^2; b) 80 °C, 40 N/mm^2; c) 120 °C, 20 N/mm^2; d) 180 °C, 8 N/mm^2; e) 220 °C, 4 N/mm^2

Impact Stress. LCPs have very high notched and unnotched impact strength because of their woodlike fibrous structure. The process-determined orientation of the fibers parallel to the surface and, hence, perpendicular to the impact results in a high level of impact resistance. Again, the high performance of LCPs at elevated temperatures is remarkable (Fig. 19).

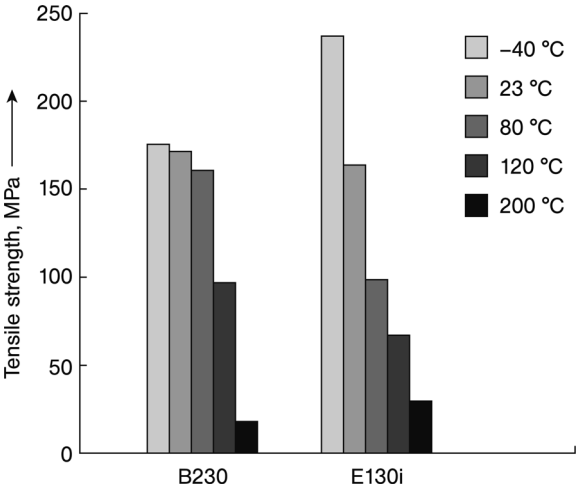


Figure 19. Influence of the temperature on the tensile strength of Vectra (B230, 30% carbon-fiber-filled; E130i, 30% glass-fiber-reinforced) [144]

If the fibrous structure is cut by notching, such as in a notched Izod or Charpy specimen, this resistance is significantly reduced. Although the energy to break drops, it remains still high compared to that of other glass-reinforced thermoplastics [128, 144].

Tribological Properties. In general, LCPs show good friction and wear properties under low loads. However, the friction and wear characteristics are very specific to the kind of application. Typical slip- and wear-modified grades contain PTFE, carbon fibers, graphite, or a combination of these with other fillers and reinforcing materials. Dynamic coefficients of friction, μ, typically range from 0.1 to 0.2 (also depending on the friction partner). More specific data are obtained from standardized tests (Table 15).

Figure 20 compares the dynamic coefficient of friction, μ, of a number of Vectra LCP grades with that of standard polyoxymethylene (POM). The test specimens were in unlubricated sliding contact with a rotating steel shaft under low load. Conditions were as follows: For friction testing, a polymer plate run against a steel ball (diameter = 13 mm, roughness height = 0.1 μm), load $F_N = 6$ N, sliding speed $v = 60$ cm/min. Wear testing was performed on a rotating shaft with a peripheral speed $v = 136$ m/min, load $F_N = 3$ N, for 60 h [144].

Although LCPs exhibit a moderate surface hardness, the wear tends to be low in the direction of the LCP and filler fibers. Perpendicular to this direction, the wear is significantly higher because the inner adhesion of the material is significantly lower in this direction than in the direction of fiber orientation. Again, LCPs exhibit a high performance at elevated temperatures, also in terms of low friction. This performance is used, for example, in

Table 15. Coefficient of friction of Vectra with various fillers (according to ASTM D1894) [144]

Description	Vectra LCP grade	Coefficient of friction μ (in flow direction)	
		Static	Dynamic
Glass-fiber-reinforced	A115	0.11	0.11
	A130	0.14	0.14
Carbon-fiber-reinforced	A230D-3	0.19	0.12
PTFE modified	A430	0.11	0.11
	A435 FDA	0.16	0.18
Graphite	A625	0.21	0.15

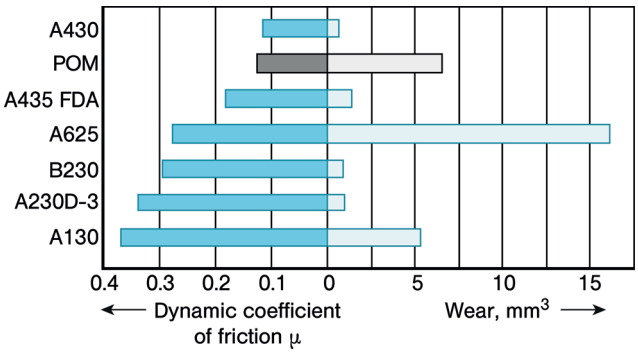


Figure 20. Coefficient of friction μ and wear (average from longitudinal and transverse to flow direction) of several modified LCP grades and standard POM [144]

moving parts in automotive lighting applications where the temperatures actually go up to 200 °C [145].

6.2.2. Thermal Properties

Thermodynamics. LCPs have a significantly lower heat of fusion than semicrystalline thermoplastics. Figure 21 shows the differential scanning calorimetry (DSC) curves for Vectra A130 (LCP GF30) and two other thermoplastics.

The curve for the LCP resembles more that of an amorphous thermoplastic (→ Plastics, Properties and Testing). This is attributed to the liquid crystalline structure of LCPs. In LCPs, the transition from the solid to the melt phase is associated with only a minor order change because the melt maintains the high orientation of the solid. There is nearly no entropy increase when melting an LCP.

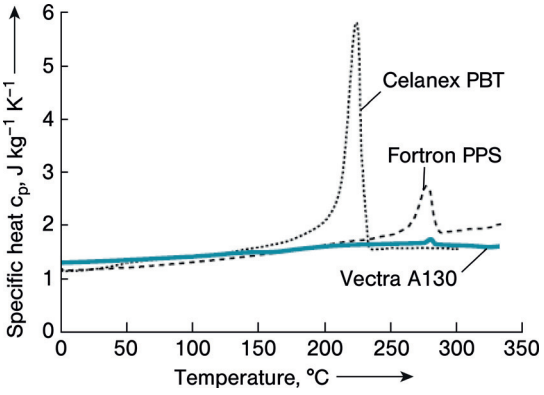


Figure 21. DSC curves of Vectra A130 (LCP GF30), poly (butylene terephthalate) (PBT), and poly(phenylene sulfide) (PPS) [144]

Because of the high order of the melt state and its ability to solidify with minimal change in structure, the transition energy during melting or freezing of LCPs is one to two orders of magnitude lower than that of semicrystalline thermoplastics (Fig. 22) [144, 145].

Dynamic Mechanical Analysis (DMA). Because LCPs are anisotropic, both the orientation of the test specimen and the direction of the mechanical stress have a significant influence on the test results. Dynamic mechanical analysis (DMA) of two or more LCP grades can be used to compare their retention of stiffness at increasing temperatures (Fig. 23). The higher the stiffness at any temperature, the more creep-resistant the LCP will be at this temperature [144].

Table 16 gives the temperatures at which the moduli G′ fall to 50% of the ambient-temperature moduli for various commercial LCP grades.

In general, the higher the temperature $T_{1/2G'}$, the more creep-resistant the grade will be at elevated temperatures. For example, Vectra A130 ($T_{1/2G'}$ = 88 °C) is more creep-resistant than Vectra A625 ($T_{1/2G'}$ = 83 °C) in the temperature range 23–90 °C. Likewise, Vectra E130i ($_{T1/2G'}$ = 119 °C) is more creep-resistant than Vectra A130 ($T_{1/2G'}$ = 88 °C) in the temperature range 80–120 °C [144].

Similarly, peaks in the damping factor curve indicate transitions and temperature ranges where the polymer will be more energy-dissipating. Typically, LCPs have two damping peaks, one at the α-transition temperature (T_g) and the other at the lower α-transition temperature. The damping-peak temperatures are listed in Table 16. Glass transitions usually occur in

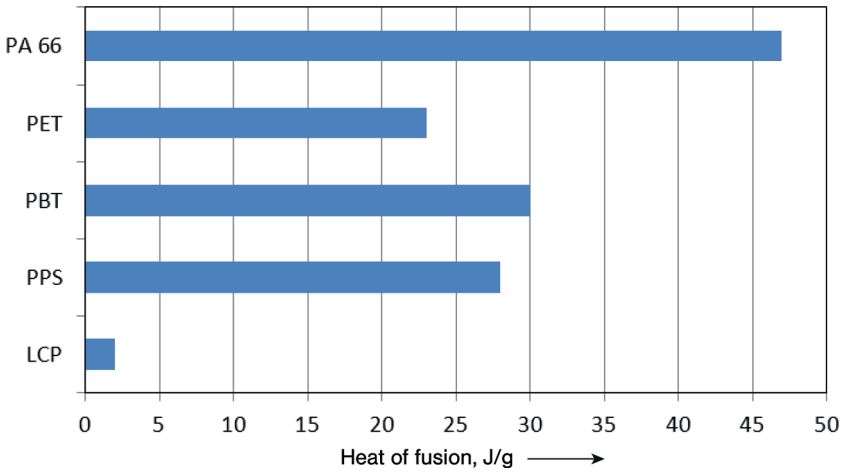


Figure 22. Heat of fusion of an LCP and other engineering thermoplastics [144]

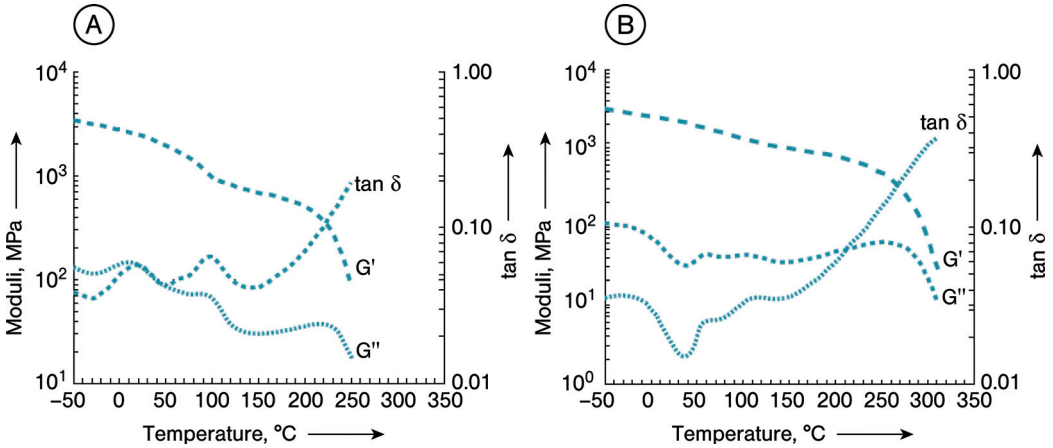


Figure 23. Dynamic mechanical analysis of two LCP grades [144]
G' = shear storage modulus; G'' = shear loss modulus; tanδ = damping factor
A) Vectra A130 (GF30, T_m = 280 °C); B) Vectra E130i (GF30, T_m = 335 °C)

Table 16. DMA data of various commercial Vectra LCP grades [144]

		α-Transition temperature, T_g, °C	β-Transition temperature, °C	Modulus G' at 23 °C, MPa	Half-modulus temperature, $T_{1/2G'}$, °C
A130	30% GF	97	18	2400	88
A230D-3	30% CF	103	21	3200	95
A625	25% graphite	98	22	3000	83
E130i	30% GF	113	59	2300	119
E471i	35% GF/Min	115	57	2500	119
E540i	40% Min	117	61	3200	113
S135	35% GF	128	35	2400	121
S471	45% GF/Min	131	39	3600	119

the 120–155 °C range while the low-temperature secondary loss peaks are at 10–80 °C. In general, a damping-peak temperature just above the ambient temperature makes the LCPs a good sound absorber. When struck, they do not "ring", but they "clunk" or sound "dead" [144].

Coefficient of Linear Thermal Expansion. The coefficient of linear thermal expansion of LCPs is very low compared to that of other thermoplastics. While the coefficient of linear thermal expansion depends on the nature of resin, it is also strongly influenced by the nature and amount of fillers. Most commercial LCPs have coefficients of linear thermal expansion in flow direction of about 10^{-6} K^{-1}. This meets the values of glass, steel, ceramic, or glass fiber/epoxy substrates. The coefficient of linear thermal expansion is up to ten times higher perpendicular to the flow [128, 144].

The low coefficients of linear thermal expansion result in a high dimensional stability. In combination with the high thermal stability (decomposition temperatures >370 °C), this makes LCP suitable, for example, for all common soldering technologies, including vapor-phase (wave) and IR (reflow/SMD/through-hole) soldering [128, 144] (→ Soldering and Brazing).

6.2.3. Behavior on Exposure to Flame

Most LCPs are inherently flame-resistant and self-extinguishing. On exposure to very high flame temperatures, the fully aromatic LCPs form a carbon char layer, which retards the development of flammable gases. Some LCPs have a self-ignition temperature of >540 °C [144, 146].

6.2.4. Electrical Properties

Without any conductive additive, LCPs are, like most thermoplastics, electrical insulators. Surface resistivity typically exceeds 10^{13} Ω m. Volume resistivity is typically in the range of 10^{14} Ω.

Conductive LCPs are usually modified with carbon fibers or conductive carbon black. This modification results in conductive properties comparable to those of other conductive-modified thermoplastics. Surface resistivity can drop down to 10^{0} Ω m, volume resistivity can be reduced down to 10^{1} Ω [144].

6.2.5. Rheological Properties

Solid LCPs have a nematic liquid crystal structure. The melt viscosity decreases continually with increasing deformation (shear) rate. At the shear rates that normally occur during injection molding, the melt viscosity of Vectra is lower than that of conventional filled or reinforced semicrystalline thermoplastics (Fig. 24).

From a technical point of view, it is important that this drop in melt viscosity with increasing shear rates is both continuous and reversible, i.e., not caused by degradation of the polymer backbone. The nonlinear behavior that some semicrystalline polymers show is either caused by nonlinear (or turbulent) flow effects within the measurement or by polymer degradation. The latter can be proved by retesting at lower shear rates.

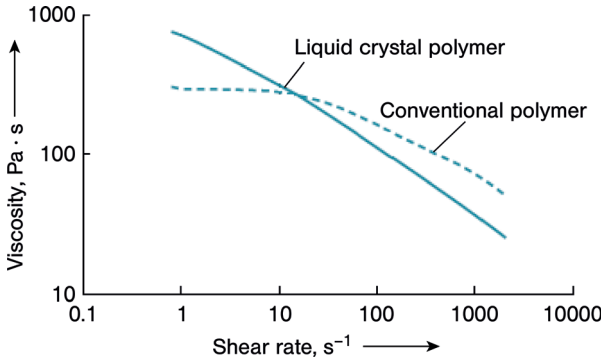


Figure 24. Comparison of the melt viscosity of LCPs and conventional semicrystalline polymers [144]

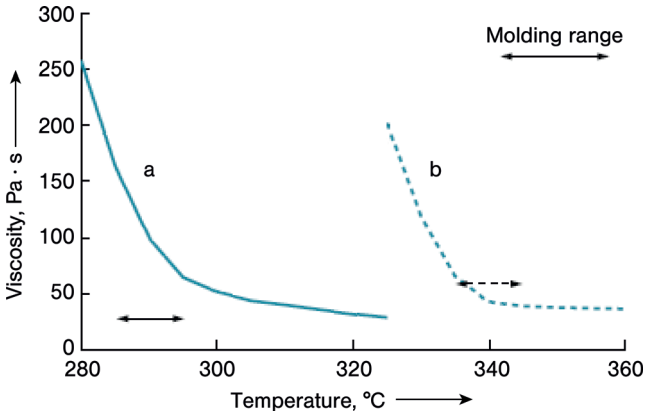


Figure 25. The melt viscosity of two Vectra grades in relation to the temperature [144]
a) A130 (LCP GF30, T_m = 280 °C); b) E130i (LCP GF30, T_m = 335 °C)

This rheological behavior allows LCPs to be processed to thin-walled parts (>0.2 mm wall thickness) or to complicated part structures with high flow lengths. In contrast to other thermoplastics, the flow length can be increased by increasing the shear rate, either by higher injection speeds or (which is unusual for other polymers) by reducing the injection gate diameter [128, 144].

Above the melt-transition temperature (which is in fact the transition temperature from the nematic to the isotropic state), the melt temperature has only a minor influence on the melt viscosity (Fig. 25).

This means that filling problems are rather to be solved by adjusting tools or the injection speed and pressure, and not the temperature.

6.3. Chemical Properties

6.3.1. Chemical Resistance

LCP show a very good resistance to chemicals, particularly to organic solvents (even at high temperatures). Their resistance to concentrated mineral acids and bases (both inorganic and organic) at elevated temperature is reduced. In general, caustic components in the presence of moisture or alcohols are problematic; acids become more critical with increasing acidic and oxidation strength.

The resistance of LCPs to methanol and methanol-containing solvents or fuels depends on the temperature and time of contact. In permanent contact with methanol-containing liquids the temperature is limited to max. 70 °C [144].

Two degradation mechanisms are involved. First, LCPs, similar to any polyester, are generally sensitive to hydrolysis, especially alcoholysis and aminolysis. This sensitivity depends on the reactivity and the size of the groups. In general, primary alcohols are more critical for LCPs than secondary alcohols, while tertiary alcohols are usually uncritical, which might be due to steric effects [127, 147]. Alcoholysis is catalyzed mainly by caustic components. In the case of amines, which are often present in solvents or fuels, primary amines are more critical than secondary amines. Tertiary amines and hindered amine light stabilizers (HALS) are not critical for LCPs.

The other degradation mechanism is oxidation of either the aromatic sections of the backbone (mainly leading to discoloration) or the ester bond.

Discoloration and degradation can also be caused by the presence of iron ions.

6.3.2. Hydrolysis Resistance

LCPs show a higher resistance to hydrolysis than other polyesters. Figure 26 shows the results of immersion tests in hot water.

However, prolonged exposure at high temperatures leads to gradual hydrolytic degradation. Similarly to other polyesters, LCPs have an increased degradation rate in the presence of caustic components and at increasing temperatures.

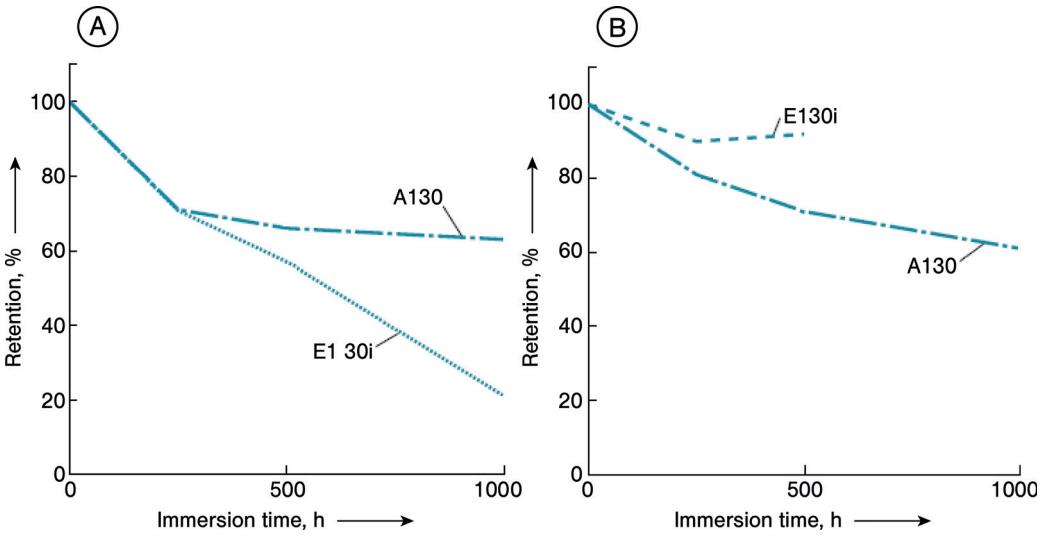


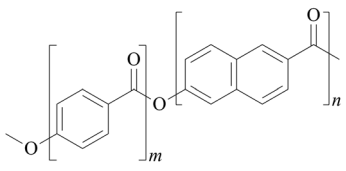
Figure 26. Hydrolysis resistance of Vectra A130 (LCP GF30) and E130i (LCP GF30) tested by immersion in hot water (120 °C, 2 bar) [144]
A) Tensile strength retention; B) Tensile modulus retention

6.4. Production

In general, the fully aromatic LCPs consist of (co) polyesters or polyesteramide copolymers and all common mechanisms for the polymerization of polyesters can be applied to produce LCPs (→ Polyesters, Section 3.2). Technically, all manufacturers use the polycondensation reaction of mesogens with suitable functionalities.

Aromatic hydroxycarboxylic acids are suitable mesogens, but aromatic diols (e.g., hydroquinone) combined with aromatic diacids (e.g., 4,4′-dihydroxydiphenyl (4,4′-biphenol) and terephthalic acid) or combination of hydroxycarboxylic acids with diols and diacids are also possible.

Besides the nonthermoplastic poly(*p*-hydroxybenzoic acid), another simple structure is the copolymer of *p*-hydroxybenzoic acid (HBA) and hydroxynaphthoic acid (HNA), Vectra A950:



In this material, the mesogen HBA builds a rigid, stiff polymer chain. HNA is employed to the backbone as a chain-disrupting comonomer. The addition of a "crankshaft" into the polymer chain reduces the melting point and allows melt processing steps.

A huge number of comonomers for controlling the thermal and mechanical properties of LCPs are available. Most commercial LCPs are based on a selection of HBA, HNA, isophthalic acid (IA), terephthalic acid (TA), hydroquinone (HQ), bisphenol (BP) and naphthoic diacid (NDA). Patents give a broad overview on the comonomers used [135, 137–140].

Three different methods are employed for the polycondensation on a commercial scale.

1. Bulk polymerization in the melt
2. Bulk polymerization in the solid state
3. Suspension polymerization in nonaqueous media

All three methods share a common reaction scheme comprising three steps. The first step involves a complete esterification of the hydroxy groups followed by the formation of a low-molecular-mass prepolymer. In the last step, the molecular mass of the polymer is increased by continuing the polymerization under vacuum.

The polymerization reaction is usually catalyzed by, e.g., sodium alkoxides, titanium

alkoxides, lithium hydroxide, or *p*-toluenesulfonic acid, but also shows good results without a catalyst [148].

In the first step, all hydroxy functions are transferred into acetates with the help of acetic acid anhydride (Fig. 27). This step is required both to reduce the thermodynamic barrier of the polycondensation reaction (reduction of the activation energy) and to achieve milder process conditions because of the lower melting points of the corresponding acetates [127, 147].

For esterification, an excess of 5–20 mol% of acetic anhydride is usually added [149]. Acetylization is performed under reflux at ca. 150 °C for 2–4 h. Then, the mixture is quickly heated up to 240 °C and then heated to 300 °C at a slower rate. The mixture is kept for several hours at this temperature, while the acetic acid and excess acetic anhydride are removed by destillation. This process produces low-molecular-mass polymers [150, 151].

In the suspension polymerization process, an inert solvent remains in the reaction mixture and the polymer will precipitate from the suspension as a powdered material [148].

In the melt polymerization process, the temperatur is increased further above the melting point of the resulting polymer, up to more than 370 °C. The polycondensation then continues in the melt state; the degree of polymerization can be measured by the amount of acetic acid

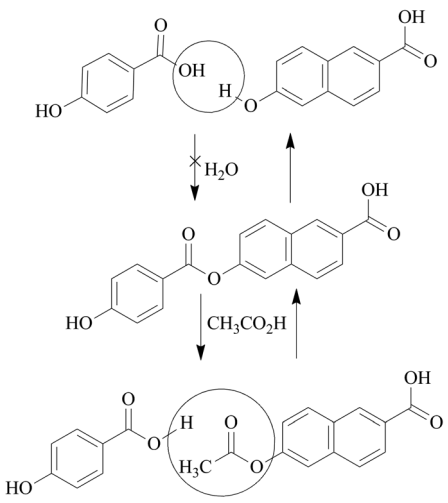


Figure 27. Esterification step in the synthesis of LCP [135]

formed and the viscosity of the melt. At the end of the reaction, the product is driven off the reactor and granuled for further use [151].

In the solid-state polymerization method, the product is driven off the reactor at a lower degree of polymerization and chopped to pellets. This allows a faster and more effective exhaustion of the reactor [151].

Both the powdery products of the suspension polymerization and the prepolymer of the bulk polymerization methods need a post-polymerization step to yield high-molecular-mass polymers. Therefore, the powder or pellets are heated under vacuum to a temperature just below the melting point. Again, acetic acid is formed and removed by vacuum. While the higher surface area of the powder allows shorter reaction times in the post-polymerization step, the occurrence of powder-clotting during solidification is more likely in this process [135].

6.5. Uses

LCPs are obtained in a variety of forms, from sinterable high-temperature compounds to injection-moldable compounds. LCPs can be welded, though the lines created by welding are a weak point in the resulting product.

For the thermoset poly-(*p*-hydroxybenzoic acid) polymers, the fabrication is accomplished by metallurgical techniques which are not normally used for polymers, for example, compression sintering at 420 °C and ca. 70 MPa [134].

Thermoplastic LCPs are usually processed by injection molding or extrusion techniques. The flowability and mechanical stability of the thermoplastic LPCs at thin wall dimensions, combined with soldering resistance and good electrical properties, offers a broad use in the electric and electronics market. Many applications as connectors and microconnectors (e.g., in play consoles, computer and laptops, mobile phones, television, and automotive), switches, and electronic components with small wall thicknesses are reported. But also the automotive market and the application in lightings (e.g., sensors, actuators, lamp sockets, LED sockets, heat shielding in automotive application) offer a broad use [145, 152–154].

Additional properties, e.g., no embrittlement at low temperatures, are relevant for automotive,

aerospace, sporting goods (e.g., rovings and sails). Furthermore, the excellent heat resistance which is interesting for applications in, e.g., protection clothes, bakeware (heat resistance combined with a low surface energy gives non-staining and nonsticking surfaces) offers huge opportunities besides the electric and electronics market [145, 155].

6.6. Trade Names (Examples)

Ekonol (Saint Gobain)
Laxtar (Lati)
Selcion (Samsung)
Siveras (Toray)
Sumikasuper (Sumitomo)
Vectra LCP (Ticona, Polyplastics)
Xydar (Solvay)
Zenite (Ticona)

6.7. Economic Aspects

The ratio for the sales price for nylons to the sales price for the high-temperature LPCs varies from 1:5 to 1:30. However, the mechanical performance of LPCs in combination with their flow performance and the ability to be processed into finest structures allows a miniaturization of parts, which is one of the drivers for the use of LCPs in electronic applications such as cell-phone components. This miniaturization means a significant saving in the consumption of polymers for the production of parts.

Another economic aspect is the high tolerance of most LCP to the use of regrind in injection-molding processes. Typically, amounts up to 50% of regrind can be tolerated in molding processes without a significant drop of material performance [156].

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Reinforced Plastics

ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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1. Introduction, Classification

Reinforced plastics, also called polymer composites, are now an important class of engineering materials. They are distinguished by attractive mechanical properties and corrosion resistance, unique flexibility in design capabilities, and ease of fabrication. The word "composite" means "consisting of two or more distinct parts." Polymer composites consist of one or more discontinuous phases embedded in a continuous-phase polymer matrix.

The discontinuous phase is usually harder and stronger than the continuous phase, and is called the reinforcement. The matrix can be classified as thermoplastic (capable of being separately hardened and softened by increases and decreases, respectively, in temperature) or thermoset (changing into a substantially infusible and insoluble material when cured by the application of heat, or through chemical means).

The properties of composites are strongly influenced by the properties of their constituents and the distribution and interactions among them. The constituents usually interact in a synergistic way, providing properties that are not accounted for by a simple volume-fraction sum of the components. Along with the volume fraction and the distribution of discrete units in the discontinuous phase, the interfacial area plays an important role in determining the extent of interaction between the reinforcement and the matrix and — in this way — the final properties of the composite. The fabrication technology of composites, as well as some of their physical properties, is dominated by the chemistry and rheology of the matrix resin and by the type and physical form of the reinforcement.

The use of reinforcing agents makes it possible for any thermoset – or thermoplastic – matrix property to be improved or changed to meet varying requirements. Most polymer

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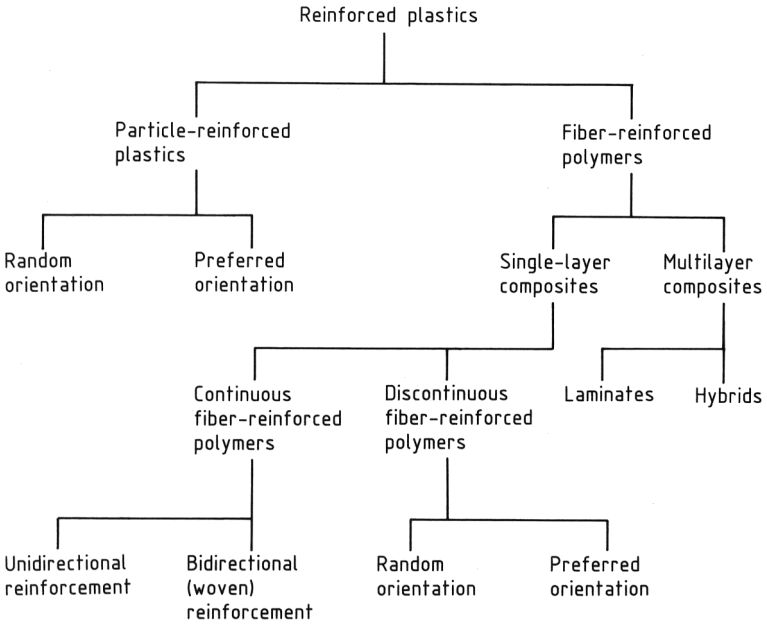


Figure 1. Classification of polymer composites [9]
The single-layer composites include materials composed of identical layers having the same orientation.

composites developed thus far have been fabricated to improve mechanical properties such as strength, stiffness, or toughness. The strengthening efficiency of the discontinuous phase plays the most important role in these products, and the strengthening mechanism depends strongly on the geometry of the reinforcements. Therefore, polymer composites can be classified according to reinforcement geometry [9]. The three major classes of polymer composites are fibrous, laminar, and particulate. The commonly accepted classification scheme for polymer composites is presented in Figure 1.

1.1. Fiber-Reinforced Polymers

Fibrous composites consist of reinforcing fibers embedded in a matrix. All fibers are characterized by a high aspect (length-to-diameter) ratio. This results in a high surface – volume ratio, permitting good anchorage of fibers within a matrix. Fiber reinforcement can be either continuous or discontinuous. Fibers are generally much stronger and stiffer than the surrounding polymer matrix, but they are small in diameter, and bend easily when pushed axially. Although such composites may have outstanding tensile strength, support is essential to prevent individual fibers from bending and buckling. Thus, the principal purpose of the matrix is to function not as a load-bearing constituent but essentially to bind the fibers together and protect them. Fiber-strengthening efficiency is highest when the direction of loading corresponds to the orientation of the fibers. In the transverse direction, properties of the matrix and the quality of the fiber – matrix interface predominate. The combination of matrix and fibrous elements results in a composite structure that may assume different structural forms depending on the forming and processing methods used.

Because the fibers are oriented in a particular direction, material properties may vary with direction. Such a material is referred to as "anisotropic." Many types of anisotropic materials exist, with special designations such as orthotropic, transversely isotropic, and cubic. The fundamental building block for fiber-reinforced plastics is an element with a unidirectional (UD) but transversely random array of fibers embedded in a surrounding matrix, as illustrated in Figure 2. Thus, a unidirectional composite is transversely isotropic (axes O_T and O_P can be selected arbitrarily). In the $O_L - O_T$ plane, however, the properties of a UD lamina

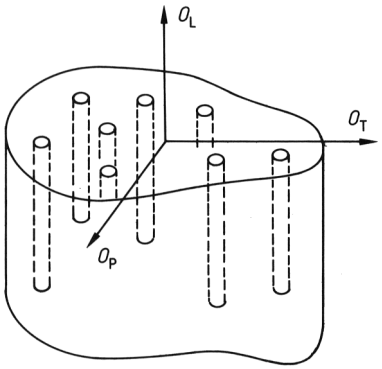


Figure 2. Basic element of fiber-reinforced plastics; coordinate system
O_L = longitudinal; O_T = transverse; O_P = perpendicular

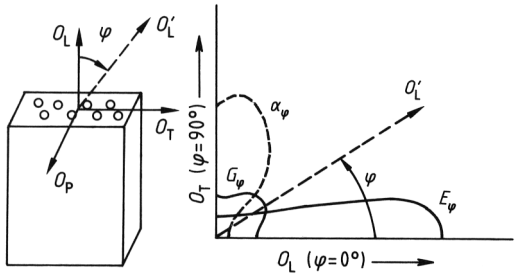


Figure 3. The directional nature of UD lamina properties (E, G, α — Young's modulus, shear modulus, and coefficient of thermal expansion)

are strongly dependent on direction (Fig. 3). The longitudinal properties of UD composites are controlled by the fiber, whereas transverse properties are matrix-dominated. The transverse properties are unsatisfactory in most engineering applications, a problem which is overcome by bonding together two or more laminae to act as an integral structural element displaying the desired properties in all directions. Combining layers with different properties or different orientations gives the designer the ability to tailor a laminate (provide the optimal configuration) for a particular set of loading conditions. However, in applications where the stress may not be predictable, or where stresses are likely to be approximately equal in all directions, the composites themselves must have approximately equal strength in all directions.

An effective way of producing such an isotropic composite material is to use randomly oriented short fibers as reinforcement. Molding compounds consisting of short fibers are usually capable of producing isotropic composites. In short-fiber composites, the so called fiber-end effect plays an important role, and composite properties become a function of fiber length. Loads are not applied directly to the fibers in a composite, but are transferred instead by the matrix to the fiber surface through nonuniform shear stress acting along the fiber – matrix interface (Fig. 4). The tensile stress in the fiber reaches a maximum at the fiber midpoint. The *critical length* of a fiber can be defined as the minimum length at which the ultimate strength of that fiber is reached. Interfacial strength is influenced strongly by the effectiveness of bonding between the fiber and the matrix via coupling agents. The higher the interfacial strength, the shorter is the length that will ensure full exploitation of the fiber's strength.

In the case of short-fiber injection-molded composites, some fibers will have aspect ratios lower than the critical value. These fibers cannot contribute effectively to overall composite strength. Compounding and molding cause fibers to undergo attrition, resulting in a broad distribution in length and a significant fraction of fibers falling below the critical length. In long-fiber injection-molded composites, the mean fiber length is typically 10 times as great as in short-fiber composites. Thus, a higher proportion of the fibers remains effective in load-bearing

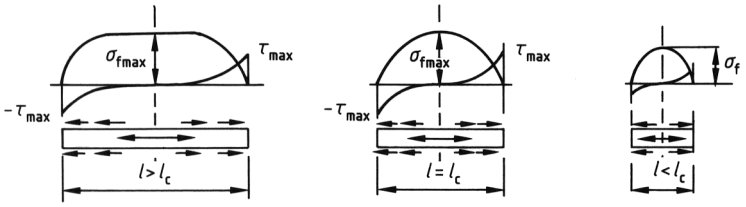


Figure 4. Distribution of tensile stress σ and shear stress τ in short fibers aligned with the load (l = length, l_c = critical fiber length)

situations, and the composites themselves are stronger than their short-fiber counterparts. Figure 4 shows that a small region adjoining the fiber end is subject to less than the maximum fiber stress. This in turn affects the elastic modulus. When the fiber length is much greater than the critical length, composite behavior approaches that of a continous-fiber-reinforced polymer. The tensile strength of a composite is more strongly dependent on interfacial bond strength than is its tensile modulus. This is evident in particulate fillers, where the aspect ratio approaches 1. Here the addition of filler contributes to an increase in modulus but generally to a decrease in the strength of the composite.

In general, the incorporation of reinforcing fibers into a polymeric matrix increases short-term stiffness and strength, increases creep resistance and fatigue endurance, and reduces the influence of temperature on all of these properties. Thermal expansion can be reduced as a way of improving dimensional stability.

Impact strength, which is related to the toughness of a material, is reduced in some polymer composites, a circumstance that can be influenced by several factors. The loading of fibers may transform the failure mode from ductile to brittle, which can in turn lower impact strength. However, this reduction can be counteracted, at least to some extent, if interfacial adhesion between the polymer matrix and the reinforcement permits the absorption of impact energy through debonding. Nevertheless, in systems where matrix-governed ductile failure occurs, increased interfacial adhesion generally improves impact strength.

1.2. Particulate Polymer Composites

By definition, a particle is nonfibrous; it generally lacks a long dimension, and is not effective in improving fracture resistance when added to a polymer matrix (with the exception of rubberlike particles in brittle polymer matrices, which contribute to an improvement in fracture resistance by promoting and then arresting crazing). Despite this definition, polymers containing very short fibers are generally classified as particulate composites. The introduction of hard particles into a polymer matrix leads to a reduction in strength due to stress concentration in the adjacent matrix material.

The two basic reasons for adding particulate filler or reinforcement to a polymer are (1) to fill the system (i.e., replace some of the more expensive polymer with less expensive filler) and (2) to modify properties of the matrix material (e.g., thermal or electrical conductivity), improve processibility, reduce friction or shrinkage, improve performance at elevated temperature, increase wear or abrasion resistance, improve fire retardancy, provide color, and improve appearance.

Platelet-shaped particles, such as flakes, can also serve as reinforcing agents. They offer two-dimensional geometry and, when placed parallel to each other, can be packed more closely than fibers or spherical particles. However, such possibilities have not been fully exploited due to fabrication difficulties. In terms of reinforcement, the longer the particles, the better is the reinforcement. Most particle-filled polymers are manufactured by injection molding, however, so a balance must be struck in terms of a particle length that gives both optimum properties and good processibility. If relatively long fiberlike particles are used as filling, their distribution and orientation may change within the molding. The flow of fiber-filled plastics into a mold during injection molding is a very complex process, and ensuring flow-induced orientation in the optimum direction is difficult. On the other hand, sometimes the challenge is to minimize undesirable effects of anisotropy (e.g., warping and postmolding shrinkage), which may be accentuated by the flow-orientation of fibers. In these cases particulate fillers may be preferable to fibers.

1.3. Laminar Polymer Composites

Laminar composites consist of at least two different layers (laminae) bonded together into one composite piece. Such layers may differ in material, form, or orientation. Combinations of matrix, fibrous mat, aligned fibers, cloth, paper, and other materials can be laminated together in either continuous or discontinuous processing.

Because of the nearly unlimited variety of possible combinations of layers, material forms, and orientations, generalization regarding laminar design is difficult. This great variety offers the designer considerable freedom in both

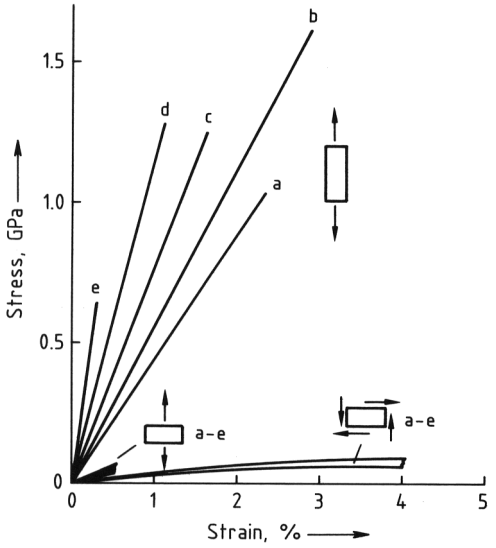


Figure 5. Stress – strain relationships for UD composites under loading in different directions
Matrix = epoxy resin; fiber volume fraction = 0.6
Fiber reinforcement: a) E-glass; b) R-glass; c) Aramid; d) HS graphite; e) UHM graphite

laminate composition and product form. The unique properties obtained with layered construction encourage the designer to develop composite materials that meet new and innovative design parameters.

The principal design criterion is appropriate fiber orientation within each layer. Polymeric composite structures that incorporate continuously oriented fibers laid in plies can be radically anisotropic in nature. Strength, stiffness, and coefficients of thermal or moisture expansion can all vary more then tenfold in different directions (cf. Fig. 5). Whereas the in-plane strength of such materials may be comparable to the strength of metals, for example, strength in the through-thickness direction can be lower than that of pure matrix. Differing properties of the different layers (e.g., thermal expansion, stiffness) may lead to considerable residual stress when a polymer matrix is cured at elevated temperature. Interlaminar stresses induced through external loading may also be significant, and can cause distortion when the layer-stacking sequence is not symmetric and situated symmetrically to the midplane (Fig. 6).

The theory of laminates has been elaborated [9–17], and many computer programs are now available to help determine the optimal

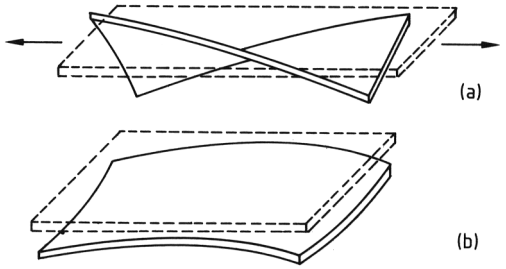


Figure 6. Distortion of an unsymmetrical laminate due to (a) load and (b) temperature change

configuration of a laminate under specific conditions; [e.g., LAMINATE (Engineering Software, Dallas, Texas), COMPCAL and CYCLAN (American Society for Composites, Dayton, Ohio), MIC-MAC (Think Composites, Dayton, Ohio), and CADFIBER (IKV, Aachen, Germany)]. In addition to these general programs, many special software packages are being developed for special tasks (e.g., computation of fatigue and crack propagation).

2. Reinforced Plastic Components

2.1. Reinforcing Fibers

As a rule, fibers used for reinforcement purposes are rather fine, ranging from 2 to 20 μm in diameter. The main exception is boron fiber, available in diameters up to 200 μm. Fibers are typically stronger and stiffer than a corresponding bulk material. Fiber strength generally decreases with increasing diameter and length

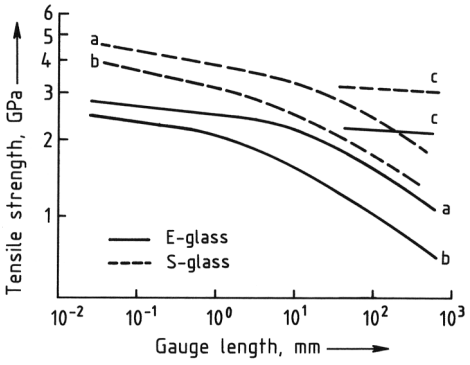


Figure 7. Dependence of fiber strength on gage length
a) Mean filament strength; b) Strength of fiber roving; c) Strength of fiber roving saturated with polyester resin

(Fig. 7). A high fiber aspect ratio permits an effective transfer of load to the fibers via the matrix, which makes such fibers an excellent reinforcing agent.

The major categories of synthetic reinforcing fibers are glass, graphite (carbon), boron, organic, metallic, and ceramic. Natural fibers (asbestos, jute, and sisal), formerly used for economic reasons, have now been generally supplanted by synthetics (in the case of asbestos, because of adverse health effects).

Synthetic fibers are usually prepared in continuous processes and then converted into a form suitable for their intended composite application. The major finished forms are continuous roving, woven roving, fiber mat, chopped strand, and yarn for textile applications.

The form of reinforcement varies with the fabrication process. Three categories can be distinguished: In the first, fibers are placed directly on the component being manufactured. Examples are the filament winding (Section 3.3) and spray-up contact (Section 3.2) molding processes. The second group includes those processes in which a sheet, web, or preform of fibers is prepared and placed in position on a mold where it comes in contact with a resin (e. g., resin-transfer molding, Section 3.11). The third category consists of processes involving the preparation of a compound of fiber and plastic that can flow during molding. Sheet molding compounds (Section 3.6), bulk molding compounds (Section 3.8), and short-fiber-reinforced thermosets and thermoplastics are typical examples within this category.

2.1.1. Glass Fibers (→ Composite Materials; → Fibers, 12. Glass Fibers)

Glass fibers constitute the most widely used form of synthetic composite reinforcement. Chemically, glass is an amorphous material consisting essentially of a silica network. Other chemical components are added to decrease its viscosity to levels suitable for melting and fiber formation. Both the physical and the chemical properties of the resultant glass are altered to varying degrees by the type and amount of modifiers.

The four main glass compositions used to create continuous fibers for reinforcement are high-alkali glass (A-glass), low-alkali or electrical-grade glass (E-glass), chemically resistant glass (ECR-glass), and high-strength glass (S-glass). Properties of glass fibers are listed in Table 1.

Table 1. Properties of glass fibers

Property	A-glass	ECR-glass	E-glass	S-glass
Density, kg/m^3	2500	2490	2540	2480
Tensile strength, GPa	3.0	3.0	3.5	4.6
Elasticity modulus, GPa		69	72	85
Coefficient of thermal expansion, 10^{-6} K^{-1}	8.6	7.2	5.0	5.6
Tensile elongation, %		2.5	2.4	2.9

Glass fibers are supplied in several basic forms, including rovings, chopped strands, mats, yarns, woven fabrics, woven rovings, nonwoven fabrics, tapes, and other special configurations.

The principal advantages of glass fibers are low cost and high strength. The disadvantages are a low modulus, poor abrasion resistance, and poor adhesion to the polymer matrix. Fiber *sizing* (containing a coupling agent) is used to improve fiber – matrix adhesion; its basic function is to form a chemical link between the glass surface and the matrix. Typically, a coupling agent consists of a silane that is adsorbed onto the glass and is capable of reactions with functional groups in the resin (→ Fibers, 11. Inorganic Fibers, Survey, Section 1.5.3.). The precise mechanism of action is not known, but silane sizing performs a useful role in glass-reinforced systems involving unsaturated polyester, epoxy, vinyl ester, or thermoplastic matrices.

Glass fibers generally have good chemical resistance, are noncombustible, and do not absorb water. Substantial reduction of thermal dilatation can be achieved by the addition of glass fibers because their thermal expansion coefficient is an order of magnitude lower than that of most plastics. The useful temperature range is quite large: glass does not soften significantly until a temperature > 400 °C is reached. Glass fibers are isotropic.

2.1.2. Graphite (Carbon) Fibers (→ Composite Materials, Section 4.1.1.; → Fibers, 15. Carbon Fibers)

Graphite and carbon fibers are generally prepared by the thermal decomposition of three fibrous organic precursors: polyacrylonitrile (PAN), rayon (cellulose), or pitch. They are available in tows containing typically 2000 – 10 000

Table 2. Properties of graphite (C) and aramid fibers

Property	C, high strength	C, high modulus	C, ultrahigh modulus	Aramid
Density, kg/m^3	1800	1900	2000	1440
Tensile strength, GPa	2.5	1.8	1.0 – 1.3	2.3
Young's modulus, GPa				
Longitudinal E_L	230	390	520 – 620	124
Transverse E_T	14	8	6	5
Shear, G_{LT}	10	8	7	2.6
Poisson ratio [1]				
Longitudinal ν_{LT}	0.25	0.2	0.2	0.35
Transverse ν_{TT}	0.35	0.3	0.25	0.35
Coefficient of thermal expansion, $10^{-6}\,K^{-1}$				
Longitudinal	– 1.0	– 1.2	– 1.5	– 4.0
Transverse	10	12	15	52
Elongation, %	0.9	0.3	0.2	1.6

untwisted individual filaments. Fiber cross sections may be circular, dog bone, or irregular, with a diameter of ca. 6 – 10 μm. The primary advantages of graphite over glass fibers are higher modulus, improved creep-rupture resistance, better fatigue endurance, and lower density. However, they are also characterized by a lower limit of elongation, which results in a relatively low fracture energy. Therefore, impact resistance for graphite-fiber composites is lower than for glass-fiber composites. The high strength and stiffness of graphite fibers result from a high degree of structural orientation. They are strongly anisotropic, with transverse tensile and shear moduli generally an order of magnitude lower than the corresponding axial modulus. Graphite fibers have a negative thermal expansion coefficient in the axial direction, which permits the construction of a multi-ply laminate with zero in-plane expansion. This is achieved, however, at the expense of large deformations in thickness.

Graphite fibers are usually subjected to a surface treatment which results in an increase in hydroxyl and amine groups on the fiber surface, thereby improving the adhesion between fiber and matrix and the laminate shear performance. To improve handling, a light sizing is often applied, consisting of a resin that is compatible with the designated matrix. Graphite fibers are available in various forms: continuous, chopped, woven fabric, or mat. Hybrid fabrics (made of a combination of graphite and glass or aramid fibers) are also available. The graphite fibers applicable as reinforcement are offered in high-strength, high-modulus, and ultrahigh-modulus forms. Representative properties are listed in Table 2. Other grades with intermediate properties have also been produced, and production processes continue to be improved.

2.1.3. Aramid Fibers (→ Composite Materials; → High-Performance Fibers)

Aramid (aromatic polyamide) fibers have been used in advanced composites since the early 1970s. The most widely known are Kevlar fibers. Among commercially available aramid fibers, the two types of interest for reinforcing plastics are high-modulus (Kevlar 49) and, to a lesser extent, low-modulus (Kevlar 29) materials.

Aramid fibers have stiffness and strength characteristics intermediate between glass and graphite. Their bonding to polymeric matrices is rather poor. Plasma amination of the fiber surface seems to be the most promising method for improving this property. In addition to high tensile strength, aramid fibers offer excellent toughness, outstanding heat resistance, fairly good chemical resistance, exceptional wear resistance, good frictional properties at elevated temperature, excellent tensile – tensile fatigue resistance, and a negative axial coefficient of thermal expansion.

Aramid fibers are strongly anisotropic (Table 2). Like graphite, their transverse tensile and shear moduli are about an order of magnitude lower than the axial tensile modulus. The fibers are also weak in compression, a result of their fibril microstructure, leading to use predominantly in tension-loaded construction

elements. Their very low density makes them ideal for applications requiring critical weight saving, such as components for aircraft, space vehicles, missiles, and sporting goods. However, an elevated water-absorption capacity results in low values for dielectric properties. Aramid fibers are available in a variety of forms, such as continuous-filament yarns, rovings, woven fabrics, discontinuous staple, and pulp.

2.1.4. Other Continuous Fibers

Almost any organic fiber can be incorporated into a composite. For years, natural fibers such as cotton, jute, hemp, and silk have been studied as reinforcements. They are inferior to synthetics in tensile strength and modulus, but exhibit significantly higher elongation, which results in better composite damage tolerance. Low cost makes natural fibers attractive for applications with low load requirements (e.g., housing construction). A major problem, however, is their susceptibility to fungal and insect attack and to degradation by moisture.

From the category of synthetic fibers, cellulosics, polyamides, polyvinyls, polyacrylonitrile, polyethylene, and polyesters have found application in the preparation of composites because of their favorable contribution to impact strength, electrical properties, and chemical resistance.

2.1.5. Other Discontinuous Fibers

Some fibers, such as single-crystal whiskers and alumina and silicon carbide fibers (→ Composite Materials, Section 4.1.3.) lack a corresponding continuous form. They offer very high stiffness and strength, but their full potential for composites has not been realized for two reasons: (1) their original length approaches the critical length, and this low aspect ratio is further reduced during compounding and molding; (2) controlling their alignment in the product is extremely difficult.

2.2. Fillers

Fillers are used to alter certain properties of composites — including price, because they are generally much less expensive than the polymer they replace. Many fillers are available, and in a variety of shapes: fibrous, plate-like, spherical, and irregular. Because of their low aspect ratio, fillers do not improve the tensile strength of a plastic; in fact, strength is usually decreased, especially at higher filler content.

With the addition of most fillers, such as calcium carbonate, kaolin, glass (milled glass fibers, hollow and solid glass spheres, glass flakes), mica, talc, silica, wollastonite, and aluminum oxide, the composite modulus increases, cure shrinkage and thermal expansion decrease, and the heat generated during cure is reduced. Aluminum oxide trihydrate and antimony oxide act both as fillers and as fire retardants; mica and silica improve chemical resistance.

Electrically conductive fillers, such as metallic powders and carbon particles (carbon fibers, carbon black), are used to reduce the accumulation of static charge. Carbon black is used to improve the UV-radiation resistance of polyolefins. Some fillers, such as carbon black, chalk, and titanium dioxide, act as pigments. Addition of extremely fine silica particles affects the thixotrophy of liquid resins. Magnetic properties can be obtained by incorporating such magnetic mineral fillers as barium sulfate.

2.3. Polymeric Matrices (→ Composite Materials, Section 4.2.)

Certain physical and chemical properties of the matrix are particularly significant with respect to the properties of a composite. The main advantages conferred by polymer matrices are low cost, easy processibility, good corrosion resistance, good dielectric properties, and low density. Low strength, low stiffness, and (usually) low service temperatures, on the other hand, limit their applications. The primary functions of a matrix are to bind the reinforcing elements together, distribute the loading among them, and protect the reinforcing system; this in turn presupposes good adhesion between matrix and reinforcement. Stress-transfer capability is generally higher in thermosets than thermoplastics. However, thermosets are more difficult to process, and they require longer molding cycles. They are also high molar mass materials, and therefore inherently relatively brittle. Their creep resistance, particularly at elevated

temperature, is generally higher than that of thermoplastic matrices.

Traditionally, thermoplastics were reinforced primarily with discontinuous fibers, but high-temperature resins such as polyether ketone, polysulfone, and polyimide have made thermoplastics competitive with thermosets in the area of high-performance continuous-fiber composites as well.

The most important matrices generally are alkyds, allyl esters, epoxies, furans, melamines, phenolics, polybutadienes, polyesters, polyimides, polyurethanes, silicones, ureas, and vinyl esters. The most widely used, however, are polyesters, epoxies, and vinyl esters. For thermosets, the dominant resins are unsaturated polyesters, followed by acrylic resins, phenolic resins, epoxies, vinyl esters, and unsaturated polyester – urethane hybrids. The complete list of applicable thermoplastic matrices is more extensive, however, and includes acrylonitrile – butadiene – styrenes, acetals, acrylics, fluoropolymers, polyamides, polyamide – imide, polyarylsulfone, polycarbonates, thermoplastic polyesters, polyetherether ketone, polyethersulfones, polyethylenes, polyimides, poly(phenylene sulfides), polypropylenes, polystyrenes, polysulfones, poly(vinyl chloride), and styrene – acrylonitriles.

3. Fabrication of Polymer Composites (→ Composite Materials, Chap. 5.; → Plastics, Processing, 2. Processing of Thermosets)

A typical feature of thermoset composites is that material formation and product fabrication occur simultaneously during final molding (e. g., hand lay-up, spray-up, vacuum-bag molding). In some cases, especially with thermoplastic matrix composites, compounding occurs first, and the shape is formed or molded in a second stage. However, in all cases, final composite properties are influenced significantly by processing conditions. Fabrication processes for thermosetting matrices can be classified broadly as wet forming processes and processes involving premixes or prepregs. The wet processes include hand lay-up, filament winding, pultrusion, bag molding, reinforced reaction injection molding (RRIM), and resin transfer molding (RTM). In processes using premixes, compounding is performed separately to yield bulk molding compounds (BMC), sheet molding compounds (SMC), and prepregs. The use of premixes facilitates automation.

Conventional molding and thermoforming methods, (e.g., injection molding, press molding, stamping) are used when processing thermoplastic matrix composites. However, the addition of fibers or filler particles to thermoplastics significantly alters their rheological properties and thermal conductivity, which can greatly affect molding conditions [2].

3.1. Hand Lay-up Technique

Hand lay-up is an open-mold process based on stacking the plies of reinforcing material in a special orientation and sequence, saturating them with resin, and brushing or rolling them to compact the material and remove entrapped air (Fig. 8). The hand lay-up techniqe is the simplest, most commonly used method for the manufacture of both small and large reinforced products. Typical applications include boats, radomes, pools, and tanks. This process is commonly employed with room-temperature-cure polyester resin and glass reinforcement, but it can also be used with vinyl ester and suitable epoxy systems as well as with carbon or aramid fiber reinforcement. The reinforcement is usually in the form of chopped strand mat or woven roving. A gel coat, formed from a thixotropic

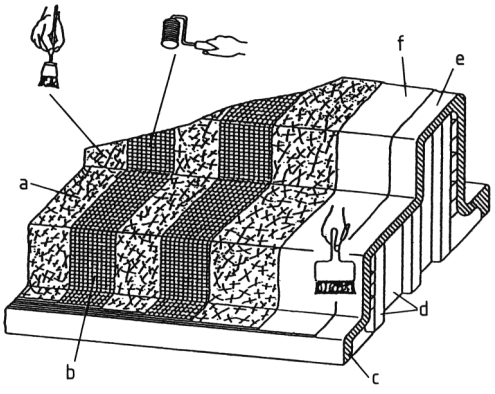


Figure 8. Basic cold-cure contact molding process
a) Strand mat; b) Fabric; c) Mold; d) Mold stiffeners; e) Mold release agent; f) Fine surfacing tissue

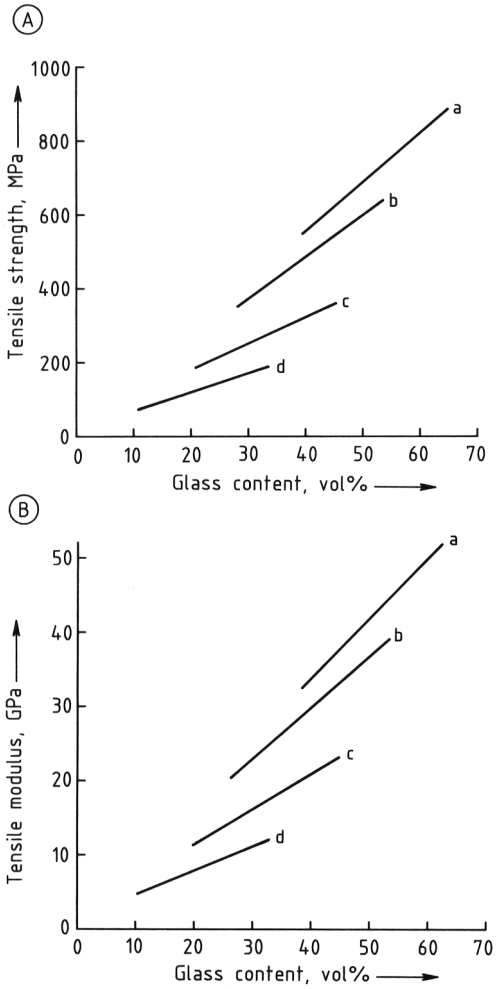


Figure 9. A) Tensile strength and B) stiffness of various glass – polyester laminates as a function of fiber content a) UD laminate; b) UD fabric; c) Balanced fabric; d) Chopped strand mat

pigmented resin, is widely used to produce a high surface finish.

Performance may be altered greatly by varying the resin-to-reinforcement ratio, the type of resin, the form and direction of reinforcement, and the additive content (Fig. 9).

3.2. Spray-up

Spray-up is a partially automated form of hand lay-up. A spray nozzle is used to propel chopped fiber and liquid resin against the mold surface until the desired thickness is reached (Fig. 10).

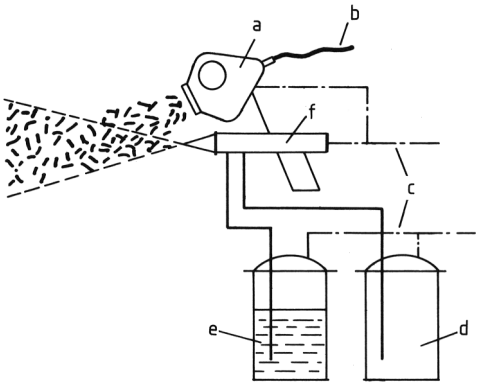


Figure 10. Schematic representation of spray-up process a) Chopper; b) Fiber strand; c) Pressurized air; d) Resin and accelerator; e) Resin and catalyst; f) Spray nozzle

As in hand lay-up, the quality of the product depends heavily on the skill of the operator, but labor and raw material costs are lower than in hand lay-up operations. Spray-up operations can be automated, and are more practical for fabricating large parts (e.g., boat hulls) or creating protective surface coating.

3.3. Filament Winding

Filament winding is an automated process in which continuous filament (or tape) passes through a resin bath and is then wound on a mandrel. The winding angle and placement of the reinforcement are controlled through specially designed machines in which filament feed is synchronized with mandrel rotation. The device has the capacity to vary the winding angle, filament tension, or resin content in each layer of reinforcement. The winding angle may vary from longitudinal through helical to circumferential or "hoop" (Fig. 11), which permits the design and fabrication of structural parts with a high degree of precision and very

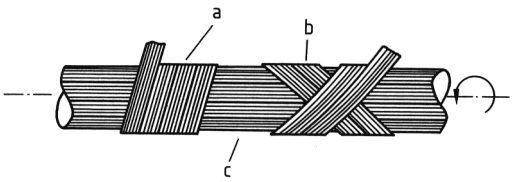


Figure 11. Alternative filament winding patterns a) Circumferential or hoop; b) Helical; c) Axial

high strength. The two basic techniques for filament winding are

1. Wet winding, in which the reinforcement and matrix resin are applied during the winding stage
2. Dry winding, which uses preimpregnated reinforcement

Resin content in the laminate can be controlled more accurately with prepregs.

Reinforcements are available in a number of forms: rovings, fabrics, tapes, mats, foils. Computer-aided design (CAD) methods are widely used to establish optimal laminate composition and fabrication conditions. Filament-wound applications include components subject to very high loads, such as pressure vessels, rocket engine cases, radomes, storage tanks, pipes, helicopter blades, and other aerospace parts.

3.4. Pultrusion

Pultrusion is a continuous processing method for obtaining composites with a constant cross section. The process consists of pulling continuous reinforcement (usually in the form of a roving or mat) through a resin bath (with removal of superfluous) into a shaping die, where the resin is subsequently cured (Fig. 12). A number of profiles, such as rods, tubes, and various structural shapes, with very high longitudinal strength and stiffness, can be produced via appropriate dies. The process is suitable for thermosetting resins (polyester, epoxy).

3.5. Bag Molding

In this process, a sheetlike reinforcement is laid up in a mold, into which the resin is introduced by spreading or coating. A flexible bag or diaphragm is used to apply pressure uniformly over one surface of the laminate. The general process can be subdivided into three basic molding methods: pressure bag, vacuum bag, and autoclave, the last of which is represented schematically in Figure 13. Heat may be applied in the form of steam in the autoclave itself or through the rigid mold. Large parts can be prepared with high-quality surface finishes. Mats, fabrics, preimpregnated forms of reinforcement, and honeycomb materials are used, and excellent adhesion to composite or sandwich core surfaces can be achieved. These features make bag molding attractive in the aerospace and high-technology areas.

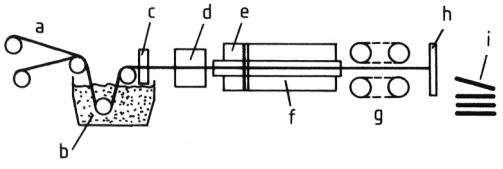


Figure 12. Schematic of the pultrusion process
a) Let-off; b) Impregnation bath; c) Resin control; d) Preformer die; e) Cold die section; f) Heated die section; g) Puller; h) Cut off; i) Product

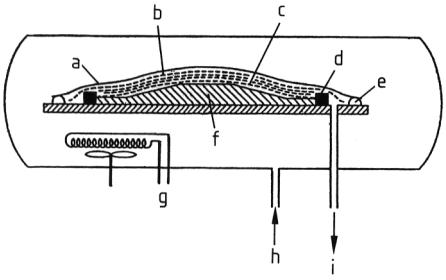


Figure 13. Schematic of an autoclave molding device
a) Bag; b) Bleeder pack; c) Prepreg pack; d) Flexible dam; e) Seal; f) Mold; g) Heater; h) Pressure; i) Vacuum

3.6. Sheet Molding Compounds (SMC)

Sheet molding compounds are produced as continuous flat sheets of ready-to-mold composite material containing fibers, usually together with mineral filler, dispersed in a thermosetting resin. Chopped E-glass fibers 20 – 60 mm long are most often used as reinforcement, although carbon or aramid fibers are also applicable, either separately or as a hybrid. Both short (discontinuous) and continuous fibers are used in SMC. Short fibers, randomly oriented in the plane of the sheet, are common in applications requiring isotropic material properties. The resin is in an uncured but highly viscous state, achieved by addition of a thickener (MgO). Curing of the resin takes place during the compression-molding operation. With the application of heat and pressure, SMC first flows into and fills the mold cavity, and then cures into a

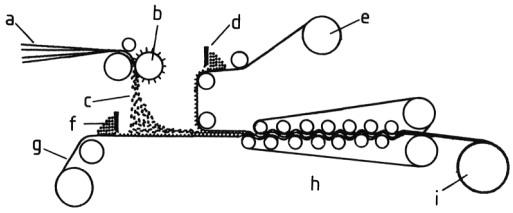


Figure 14. Processing equipment for sheet molding compounds
a) Continuous-strand roving; b) Chopper; c) Chopped roving; d) Doctor blade; e) Carrier film; f) Resin–filler paste; g) Plastic carrier film; h) Compaction section; i) Take-up roll

solid. Volume change on cure can be controlled by the addition of various shrinkage compensators, permitting high dimensional stability to be achieved. A schematic of an SMC device is presented in Figure 14.

Several types of SMC are distinguished as a function of the form of reinforcement (Fig. 15):

SMC-R	randomly oriented fibers
SMC-O	oriented SMC
SMC-CR	combination of continuous, parallel, and random fiber orientation
XMC	criss- crossed continuous fibers in a sheet
HMC	SMC with a high fiber content (no filler)

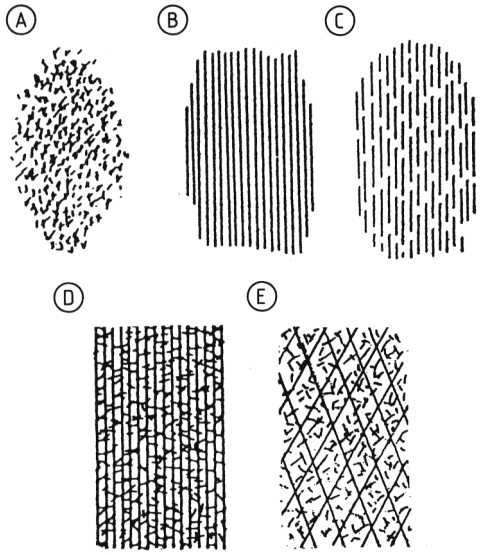


Figure 15. Fiber reinforcement structures of various sheet molding compounds
A) SMC-R; B) SMC-C (HMC); C) SMC-O; D) SMC-CR; E) XMC

A numeral at the end of the letter designation indicates the fiber content in weight percent. For example, SMC-C (HMC) 20 R 15 contains 20 wt % of continuous parallel and 15 wt % of randomly oriented fibers.

The performance of SMC composites depends primarily on a combined effect of the amount and length of the reinforcement as well as the orientation of the reinforcement in the finished part. Many properties can be influenced favorably by the addition of fillers or other additives. SMC composites can be used to produce structural parts with complex shapes in relatively short molding times. For this reason SMC composites have found broad application in mass production, especially in the transportation industry and appliance manufacture (e.g., washing machines, refrigerators, furniture, computer housings).

3.7. Thick Molding Compounds (TMC)

Thick molding compounds differ from sheet molding compounds only in thickness. This may range up to 50 mm with TMC, whereas a thickness of 3 – 6 mm is achieved with conventional SMC. Greater thickness allows chopped fibers to assume a three-dimensional random arrangement. For this reason, strength and stiffness are both lower with TMC than with SMC.

3.8. Bulk (or Dough) Molding Compounds (BMC, DMC)

BMC is prepared by mixing chopped strands with a filled polyester resin paste. For reinforcement, BMC usually contains glass fibers, with lengths ranging from 3 to 12 mm, but cellulose, cotton, and other fibrous materials can also be used. Bulk molding compounds are manufactured by compression molding at 130 – 160 °C, depending on the resin formulation. Temperature control is extremely important in the molding process to reduce internal stresses and ensure reproducible physical properties of the product. Major markets for BMC are the transportation and appliance industries. The products are quickly molded, light, and strong, and may possess complex shapes.

3.9. Prepregs

Prepregs are materials that have been impregnated with partially cured polymer matrix. The matrix differs from that in SMC by the absence of fillers, thickening agents, and pigments. Most prepregs are based on epoxy resins. Reinforcements include glass, carbon, and aramid fibers in the form of roving, woven fabric, or mat. Continuous unidirectional fiber sheets give high-performance multilayer composites, used in high-load-bearing construction parts in the aviation and automobile industries. Prepregs are molded by hand lay-up, bag molding, or autoclave molding.

3.10. Reinforced Reaction Injection Molding (RRIM)

By reaction injection molding (RIM), two chemically reactive liquid streams are injected into a mold where polymerization and formation of the part occur. When short fibers or fillers are added, the process is referred to as reinforced reaction injection molding (RRIM). The fibers and particles must be sufficiently small to fit through the mixing head orifice (< 2 mm). Since viscosities of the essentially monomeric materials used in the RRIM process are low, the injection mixture flows into the mold under relatively low pressure and at low temperature, resulting in savings in energy and equipment.

Polyurethane-based polymers have been widely molded by RRIM. Various mineral fillers (e.g., milled glass fibers, glass fibers, glass flakes and beads, mica, wollastonite, and kaolin) are used to improve the modulus and reduce thermal expansion.

3.11. Resin Transfer Molding (RTM)

In this approach a dry reinforcement material is placed in a mold cavity before the mold is closed and resin is injected. Resin flows through the reinforcement preform, expels air in the cavity, and impregnates the reinforcement. After curing, the molded part is removed and the resin reaction may be allowed to continue to completion through postcuring. RTM resins are low-viscosity polyester epoxy and vinyl ester resins. A broad variety of reinforcements is used, such as continuous strand, cloth, woven roving, long fiber, and chopped fiber mat made of glass, aramid, or carbon.

Resin transfer molding has the potential to become an efficient, low-cost manufacturing process for the fabrication of large, integrated, high-performance products.

4. Physical and Chemical Properties

The properties of a resin – matrix composite depend on many factors, among them the properties of the constituents. The form of the reinforcement (particulate, chopped fibers, woven, etc.); its volume fraction; fiber length, distribution, and orientation; interfacial bond strength; and void content all play important roles. Many of these factors depend strongly on the nature of the fabrication process. The constituents of a composite can be combined in various ways. Therefore, determining the properties of all possible combinations is a practical impossibility. Analytical methods have been developed to permit derivation of a set of predicted properties based on the properties of the composite constituents [9–16].

The fundamental building element upon which fiber-reinforced plastics theory is based is a unidirectionally reinforced layer. Many applications involve components in the form of thin plates or shells [17]. For such structures the components are commonly assumed to be in a state of plane stress; that is, through-thickness deformations and stresses are neglected. As a result, material characteristics in the plane of the structure become of primary interest. In such a case, four elastic constants and two thermal expansion coefficients are necessary to describe the elastic behavior of the UD layer. Like stiffness, strength is a directionally dependent parameter in composites. The strength properties of UD composites are governed by complex internal failure modes and cannot be described in a way similar to that used for elastic characteristics. Although no universally accepted law currently exists for the prediction of composite failure under arbitrary loading conditions, a number of basic strength properties do allow the structural efficiencies of composites to be evaluated. For typical fiber composites, these properties are listed in Table 3. One of the most important factors affecting composite properties

Table 3. Representative mechanical properties of several UD composites (fiber fraction 60 vol %)

Property	E-glass – polyester	E-glass – epoxy	C-HM – epoxy	C-HS – epoxy	Aramid – epoxy
Density, kg/m^3	2000	2000	1650	1600	1400
Young's modulus, GPa					
Longitudinal E_L	43	44	180	140	76
Transverse E_T	12	14	6	8.5	5
Shear G_{LT}	5	6	4	4.5	2.5
Poisson ratio ν_{LT}	0.31	0.30	0.27	0.30	0.36
Tensile strength, MPa					
Longitudinal	800	1000	800	1400	1400
Transverse	25	40	47	50	28
Compression strength, MPa					
Longitudinal	400	450	630	1000	300
Transverse	120	150	190	200	140
Shear strength, MPa					
In-plane	45	80	46	63	60
Interlaminar	40	70	46	70	50
Thermal expansion, 10^{-6} K^{-1}					
Longitudinal	7	7	− 0.7	− 0.3	− 2.7
Transverse	28	26	28	28	54

is the amount of reinforcing agent present (see Fig. 9). Here the important parameter is percentage by volume, not by weight. Therefore, volume fractions of components must be used to compare composites of different composition.

As can be seen from Table 3, maximum strength and stiffness are reached in the fiber direction. To provide improved transverse properties, composites are commonly arranged in laminates such that individual layers have different orientations. In this way, the transverse properties of the laminate are enhanced at the expense of some of the potential inherent in a UD layer. An isotropic arangement of reinforcement therefore leads to much lower strength and stiffness values (Figs. 9 and 16). Composites reinforced with discontinuous fibers, such as bulk molding compounds, generally have nonuniform properties because local fiber content and orientation are difficult to control. As a result, material properties vary from point to point throughout the material, which contributes to great variation in measured characteristics, especially strength. Relatively high scatter with respect to properties is a typical feature of composites. For generalized comparisons of material weight-savings potential, the strength – density ratio is an adequate guide when loading is uniaxial. This comparison is very favorable for advanced composites (Fig. 16 C). Although reinforcing fibers and fillers are elastic over a wide temperature range, the behavior of a polymer matrix is strongly temperature- and time-dependent. Such behavior can be observed in polymer – matrix composites as well, especially for matrix-governed properties [9], [16–19].

The polymer matrix also plays a dominant role in the chemical resistance of composites. One of the most important tasks of a matrix is to bind the reinforcing elements and protect them against hostile environments. To prevent fiber corrosion, the fiber volume-fraction must be kept low so that absorption and subsequent diffusion of the corrosive medium are minimized. This can be accomplished by protecting the load-carrying layer with a corrosion barrier consisting of thin, resin-rich veil liners. Chemical corrosion of composites can be prevented by careful choice of resin, reinforcement, and additives [20], [21], with the behavior of the resin being most important.

Of the two categories of polymers used as matrices — thermoplastics and thermosets — thermoplastics show excellent resistance to most acids, bases, and solvents. Among thermoset-based composites, polyester-based resins are generally resistant to acids and solvents, whereas epoxies are more appropriate when resistance to bases is necessary. Special resin systems, such as furans, are also available for specific chemical exposures. Phenolics and epoxies provide superior resistance to various forms of radiation [22].

Good resistance of components to environmental effects can be sustained by good manufacturing practice, appropriate material

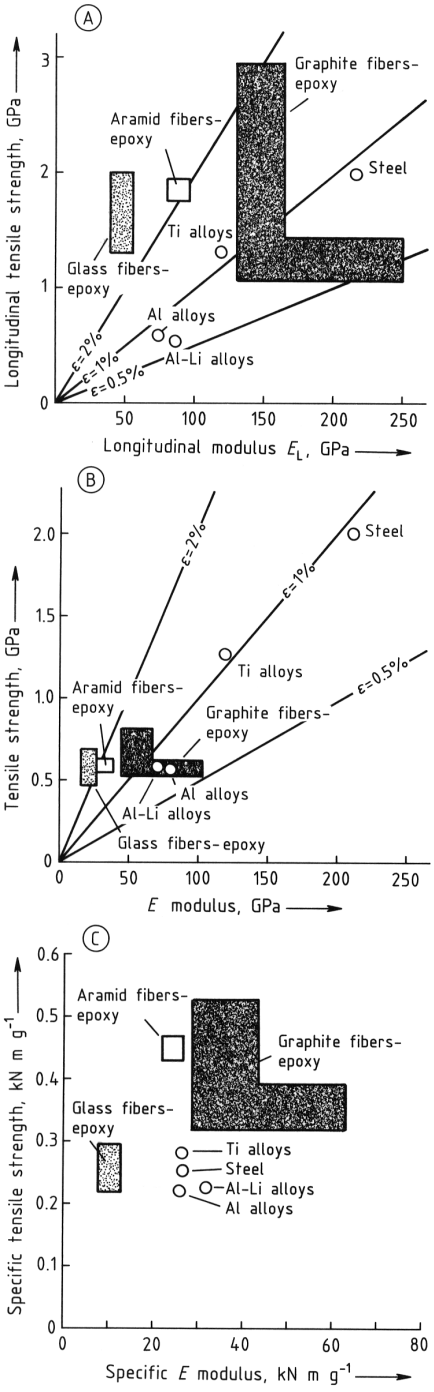


Figure 16. Comparison of strength and stiffness properties of advanced composites with those of high-strength metallic materials

A) UD properties; B, C) Properties of plane-isotropic reinforced composites

ϵ = typical limit elongation

handling, and the application of consistent control standards. Prolonged storage of resins and fibers, or their exposure to high temperature, UV light, or moisture, may result in degradation and subsequent loss of corrosion resistance [23]. In addition to the effects of temperature, time, and environmental exposure, mechanical loading or fatigue also contributes to the acceleration of corrosion. Stress corrosion can be controlled by a reduction of stress levels, choice of the appropriate laminate structure, and the use of resins with high ultimate elongation [21].

Extensive literature on corrosion and environmental resistance is available from resin and fiber manufacturers, research laboratories, and several government agencies. Corrosion data banks are being developed by the manufacturers and users of composites.

5. Quality Specifications

Quality specification is accomplished by tests to determine the suitability of materials, processes, and designs for the intended applications.

The broad range of applications for reinforced plastics and their diverse properties have necessitated the development of a large number of specialized tests for evaluating mechanical, optical, thermal, electrical, physical, chemical, and durability characteristics. Standard test methods and necessary equipment are described in various sources [24], [25], and new testing procedures are constantly being developed [26]. Details about individual methods can be obtained from the literature [27–29]. Specific material features that must be considered when testing polymer composites include:

1. Composition of the constituents. Determination of the fractions of individual components is of prime importance.
2. Anisotropy of properties. The direction of a test (e.g., load application or heat conductivity) should be specified and recorded with the test results.
3. Inhomogeneous structure of the material. With laminates the stacking sequence of layers may play an important role under certain test conditions (e.g., bending, static as well as dynamic fatigue, environmental resistance).

4. Rheological behavior as a function of time. Loading rate and duration, frequency, and loading history must be specified carefully.
5. Relatively great variation in data. A sufficient number of samples must be examined to ensure reasonably reliable test results for the material under evaluation. Statistical analysis of the test data is necessary.
6. Influence of the fabrication process on product properties. Specimens must be prepared and tested under conditions identical to those specified for the product in question.

Tests may be destructive or nondestructive, depending on whether a sample is destroyed or degraded during the test. Nondestructive methods (e.g., ultrasonics, X-ray inspection, acoustic emission, microwave techniques) are becoming increasingly important in ensuring the integrity, reliability, and safety of composite structures [30].

6. Economic Aspects

Based on modern trends in materials technology, the reinforced plastics industry should continue to enjoy rapid growth. The trend can be seen in total shipments of reinforced plastics to the United States, which reached 1.21×10^9 t in 1988 compared to 0.91×10^9 t in 1978, for a mean annual growth rate of nearly 12 %. A similar development can be observed in Europe, where the mean annual growth rate in the 1980s was 9 %. Worldwide growth of composites during 1985 – 1988 averaged 5.5 %, and all predictions for 1990 – 1995 anticipate a growth of ca. 1.5 – 2 times the rate of growth of gross domestic product. Exceptional growth is expected [31] for reinforced plastics with the following characteristics: high performance, high performance – cost ratio, high flame resistance and low smoke index, good adhesion, and corrosion resistance.

Among composites generally, thermosets still dominate thermoplastics as matrix materials. Nevertheless, although thermosets accounted for about 75 % of the demand in the 1980s, this decreased to 70 % in 1990, and the growth in demand for thermoplastics over the first five years of the 1990 s is expected to be double that of composites in general [32].

More than 80 % of the reinforced thermoplastics market belongs to injection-molded resin matrices of nylon, thermoplastic polyesters, olefins, styrene, and polycarbonate. High-performance reinforced thermoplastics in the fastest growing material sector include polyimide, polyetherketone, polybenzimidazole, and polyarylene sulfone. This sector is expected to grow > 10 % annually [33].

The potential exists for significant further advances in composites, in contrast to the relatively minor improvements possible in such wrought sheet-type metals as steel or aluminum. Past and present performance, as well as current areas of research and development, have laid the groundwork for future growth of the composites industry. Effective exploitation of new opportunities is the key to potential large-scale market penetration and consequent profitability for reinforced plastics.

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Specialty Plastics

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1. Introduction

In this article, "specialty plastics" are defined as those plastics which do not fit into other keywords, either because they are prepared from unusual monomers or because they possess unique structures and/or properties. However, the term "specialty plastics" is in general often used as a synonym for "high-performance plastics", which are a special class of engineering plastics (technical plastics, technoplastics; see → Plastics, General Survey). Engineering plastics provide the engineer with a combination of useful properties, whereas highperformance plastics often exhibit only one outstanding property albeit one which surpasses the corresponding property of engineering plastics, e.g., a high continuous service temperature.

"Specialty plastics" are also not necessarily identical with either "functional plastics" or "functional polymers." Functional plastics are those plastics which are useful for one application only; examples are ethylene–vinyl alcohol copolymers with high contents of vinyl alcohol units, which are exclusively used as gas and aroma barriers in the packaging industry. The term "functional polymer" or "functionalized polymer", on the other hand, refers to polymers with functional chemical groups, i.e., specific chemical reactivities.

The polyphenylenes and poly(*p*-xylylenes) described in this article are typical functional plastics since they are used for only one purpose: coatings. The group of polymers known as ionomers, on the other hand, comprises functional plastics, engineering plastics, elastomers, and thermoplastic elastomers.

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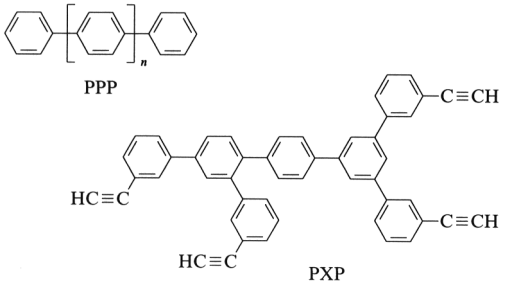
2. Polyphenylenes

2.1. Chemical Structure

Polyphenylenes are oligomeric to polymeric compounds composed of phenylene units and related units such as naphthalene or anthracene; these units are connected to each other via *ortho*, *meta*, and/or *para* links. Their molecular architecture thus ranges from linear to highly branched compounds; they may or may not become cross-linked on further processing. Polyphenylenes are also known as polyphenyls, oligophenyls, oligophenylenes, or polybenzenes [1–7].

Polyphenylenes exhibit two remarkable properties. As compounds of low hydrogen content and free of readily activated chemical bonds, they show good thermal, oxidative, and hydrolytical stability. As aromatic compounds, they have the potential of becoming electrically conducting materials. Commercial developments are thus along two lines: polyphenylenes are either prepared as thermosetting resins with high service temperatures or as base materials for electrically conducting polymers.

The two classes of polyphenylenes differ in their chemical structures. Polyphenylenes for conductors are linear polymers with phenylene units interconnected in 1,4-position (PPP [*25190-62-9*]), whereas polyphenylenes for thermosets are highly branched oligomers [*9033-83-4*], often with reactive end groups such as acetylene (schematically shown as PXP). This section is exclusively concerned with the latter type of polymers; poly(1,4-phenylenes) are discussed in → Polymers, Electrically Conducting, Section 5.5.



PPP PXP

2.2. Polybenzenes

Melting temperatures of simple poly(1,4-phenylenes) increase strongly from biphenyl H $(C_6H_4)_2H$ (70 °C) to hepta(1,4-phenylene) H $(p\text{-}C_6H_4)_7H$ (ca. 540 °C). Poly(1,4-phenylenes) were thus expected to be very temperature stable compounds. All classic stepwise syntheses of such polyphenylenes are, however, too expensive for the industrial manufacture of plastics but may be utilized for electrically conducting polymers [1], [2], [6], [7].

The first industrial branched polyphenylenes were prepared by oxidative cationic polymerization of benzene with stoichiometric amounts of aluminum trichloride/copper dichloride, iron trichloride, molybdenum pentachloride, etc. [3–5], [8–10]. The arylation reaction proceeds via radical cations [7], [11]. The polymers still contain 1 – 4 % chlorine, < 5 % oxygen, 0.1 – 0.2 % copper, and 0.3 – 0.6 % aluminum after purification [5].

The resulting brown to black masses have densities of ca. 1.25 g/cm^3, tensile strengths of 65 MPa, Young's moduli of 160 MPa, elongations at break of 10 %, and linear expansion coefficients of ca. 3×10^{-5} K^{-1}. They melt above 530 °C and decompose above 700 °C. Their melt viscosities are so high that they cannot be processed by injection molding or similar fabrication techniques. The polymers can, however, be molded at high pressure; the moldings can then be machined. Such materials are produced as Eimac 221 by Eitel–McCollough, United States.

2.3. Polymers from Higher Aromatic Hydrocarbons

The oxidative cationic polymerization of terphenyl isomers, with or without addition of other compounds such as biphenyl, reduces the probability of cross-linking reactions as compared to benzene. The resulting branched prepolymers are soluble; their solutions in chloroform or chlorobenzene are used as impregnating varnish for laminates. Filled prepolymers can be processed in the melt. The prepolymers are cross-linked to give insoluble and unmeltable polymers by the addition of catalysts such as *p*-toluenesulfonic acid, sulfuryl chloride, or boron trifluoride etherate. These techniques are mainly being developed by Hughes Aircraft Co.

2.4. Acetylene Group Containing Polymers

Other types of branched polyphenylenes are the so-called H-resins of Hercules [12–15]. These prepolymers are obtained by cyclotrimerization of *p*-diethynylbenzene (DEB) in aromatic solvents [16] or by copolycyclotrimerization of DEB with phenylacetylene [17]; catalysts are $AlR_3/TiCl_4$, $NiCl_2/P(C_6H_5)_3/NaBH_4$, or $CoBr_2/(C_6H_5O)_3P$.

The prepolymers (B-stage resins) are oligophenylenes with the schematic structure PXP (see Section 2.1). For B-stage resins from the polymerization of DEB by $TiCl_4/(C_2H_5)_2AlCl$ at 86 % monomer conversion, a number-average molar mass of 2300 g/mol and a mass-average molar mass of 8060 g/mol were found. Higher DEB conversions resulted in gelation.

These polymers contain acetylene end groups that form cross-links under the action of titanium(IV) chloride/diethylaluminum chloride, nickel(I) acetyl acetonate, and similar catalysts. The chemical structure of these cross-links is unknown; they are probably not benzene rings.

B-Stage H-resins dissolve in aromatic hydrocarbons, chlorinated hydrocarbons, ketones, and cyclic ethers. They are insoluble in water, aliphatic hydrocarbons, and aliphatic alcohols. The resins can be processed with simultaneous cross-linking by molding, injection molding, extrusion, and powder coating; different grades are provided for these purposes. Molding cycles are 2 – 5 min at 160 – 170 °C [13]. Molding stability starts at 160 °C but improved mechanical stabilities and better solvent resistance require post-curing at 230 – 300 °C.

The cured resins are hard, nonporous materials which are resistant to hot solvents, acids, bases, brine, superheated steam, and salt melts. They become brittle in molten alkali metals. Continuous service temperatures are 200 – 300 °C in air and ca. 400 °C in an oxygen-free atmosphere; the limiting oxygen index is 55 %. Slow carbonization starts at ca. 500 °C.

Molded parts show flexural moduli of several gigapascal and high flexural strengths (Table 1). These properties can be enhanced by fillers such as talc, silica, or asbestos. They are often preserved over a wide temperature range.

Table 1. Properties of cured H-resins

Physical property	Temperature, °C	Property value after filling with		
		none	50 wt % talcum	50 wt % silica
Flexural modulus, GPa	23	4.8	9.7	11.4
	250		6.3	5.9
	300	3.5		
	350		6.8	4.6
Flexural strength, MPa	23	<69	<69	<83
	250		<62	62
	350	<55	<55	46
Barco hardness	23	85		
Taber abrasion (17) (1000 g load)	23	0.0015		
Volume resistivity, Ω cm	23	10^{17}		
Dissipation factor (60 Hz)	23	0.002		
	100	0.0009		

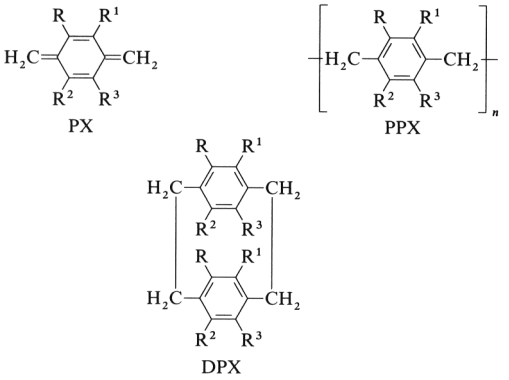
Unmodified H-resins exhibit low elongation and low adhesion to polar substrates. The adhesion of H-resins to metal surfaces can be improved by the use of polymer blends and polymeric fillers such as epoxy resins, phenolic resins, polysulfones, and polyimides.

H-Resins serve as corrosion-resistant coatings, for example, for pipes and processing equipment for hot sour petroleum or gas wells, pump linings, high-temperature sodium and lithium batteries, and high-temperature processing equipment. They are also used as nonflammable coatings for electric and electronic components and as self-lubricating coatings for metals.

3. Poly(*p*-Xylylenes)

3.1. Introduction

Poly(*p*-xylylenes), PPX, are polymers of the unstable *p*-xylylenes (*p*-quinodimethanes) PX; they are produced industrially from the dimeric *p*-xylylenes DPX:



The syntheses, structures, and properties of PPX are described in [18–25]. Although PPXs with many different substituents R, R^1, R^2, and R^3 have been prepared in the laboratory (see the list in [23]), only three of them are industrially important. These polymers are based on DPX as monomer and have no (N) or one chlorine (C) substituent, or are disubstituted (D) with chlorine:

PPX-N ($R = R^1 = R^2 = R^3 = H$) [*25722-33-2*]

PPX-C ($R = R^2 = R^3 = H$; $R^1 = Cl$) [*9052-19-1*]

PPX-D ($R = R^3 = H$; $R^1 = R^2 = Cl$) [*52261-45-7*]

The systematic names are:

PPX-N	poly(1,4-phenylene-1,2-ethanediyl)
PPX-C	poly[(chloro-1,4-phenylene)-1,2-ethanediyl]
PPX-D	poly[(dichloro-1,4-phenylene)-1,2-ethanediyl]

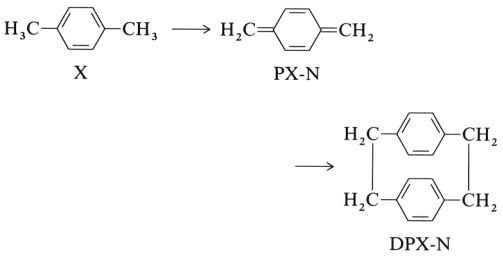
The designations monochloro and dichloro PPX for technical products are misleading since these polymers do not have one or two chlorine substituents on each ring. Monochloro and dichloro rather refer to the average number of chlorine ligands per ring, i.e., there is a distribution of chlorine substituents amongst the rings; each ring in PPX-C or PPX-D may bear between 0 and 4 chlorine substituents.

Poly(*p*-xylylenes) from the Gorham process (see below) are known as parylenes. Coatings produced by this process are correspondingly named parylene N, parylene C, and parylene D. The sole producer of dimeric *p*-xylylenes DPX-N, DPX-C, and DPX-D is Union Carbide, which also custom-coats parts with PPX-N, PPX-C, and PPX-D.

3.2. Synthesis

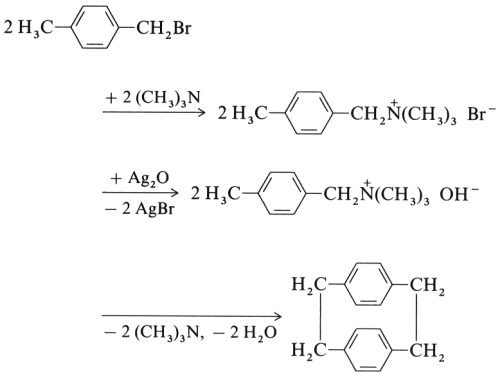
3.2.1. Monomer Synthesis

Two synthetic routes have been used commercially for the synthesis of dimeric *p*-xylylenes DPX, also known as [2.2]-paracyclophanes: direct pyrolysis and Hofmann elimination. In direct pyrolysis, *p*-xylene X is pyrolyzed at ca. 950 °C in the presence of steam. The pyrolysis dehydrogenates *p*-xylene X to *p*-xylylene PX-N which is converted into di-*p*-xylylene DPX-N on quenching with liquid xylene at ca. 20 °C:



A major byproduct is the polymer PPX-N. Its simultaneous formation can be minimized by using an excess of liquid xylene (Ruggli–Ziegler dilution principle), controlled rates, etc. The polymeric byproduct has no commercial value since it can be neither processed nor recycled.

The Hofmann elimination proceeds under far milder conditions and does not need special equipment, unlike the direct pyrolysis. α-Bromo-*p*-xylene is first quaternized and the resulting product converted into the quaternary ammonium hydroxide; amine elimination then leads to DPX-N:

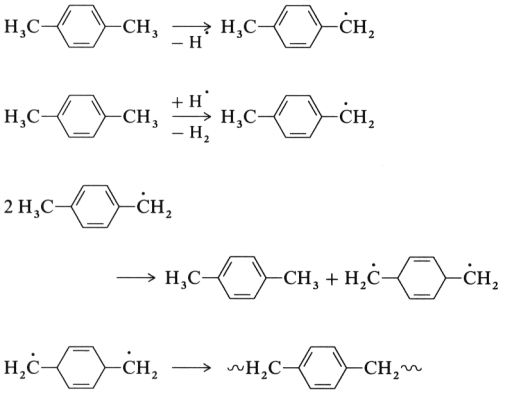


The yields of DPX-N vary between 17 and 50 %, depending on the reaction conditions (e.g., use of polymerization inhibitors).

Chlorine-containing dimeric *p*-xylylenes are produced industrially by chlorination of DPX-N using standard procedures for aromatic ring chlorinations. Chlorination gives mixtures of unreacted DPX-N with various chlorinated compounds (from mono to tetra substitution per ring) and their isomers.

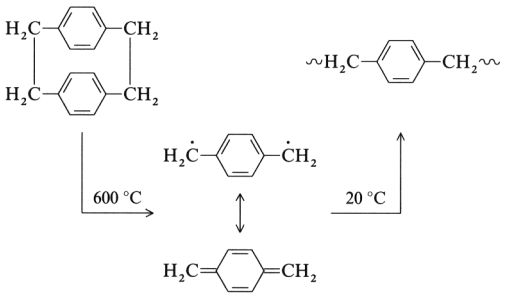
3.2.2. Polymerization

Poly(*p*-xylylenes) can be synthesized by the Szwarc or the Gorham process. In the Szwarc process [26–28], *p*-xylene vapor is passed rapidly (residence time < 1 s) in vacuum (< 100 Pa) through quartz tubes heated to 800 – 1150 °C. The pyrolysis gases are subsequently quenched to temperatures below 25 °C. The mechanism was assumed [26–28] and later confirmed [29–32] to consist of the formation of monoradicals (either spontaneously or by radical transfer), followed by disproportionation to give *p*-xylylene, and finally polycombination of the diradicals to give poly(*p*-xylylene):



The diradical and not the *p*-xylylene is the intermediate species since the former is stable in the gas phase between 120 °C and 200 °C and in liquid phases (such as quenched hexane solutions) at low temperatures (half-life 21 h at −78 °C). The resulting poly(*p*-xylylene) is slightly cross-linked; it always contains 10 – 25 wt % of low molar mass impurities. Furthermore, since the yield never exceeds 25 %, the process was technically and economically useless.

The Gorham process, on the other hand, leads to colorless, linear (uncross-linked) polymers that are free of low molar mass compounds [34], [34]. The process uses di-*p*-xylylene DPX as monomer and proceeds in three stages: (1) DPX is vaporized at ca. 200 °C and 133 Pa, (2) on heating to 680 °C at ca. 67 Pa, DPX dissociates quantitatively [21] to *p*-xylene which, after cooling to 25 °C and 13 Pa, (3) polymerizes to poly(*p*-xylylene) PPX on the surfaces of parts in a deposition chamber at <−70 °C:



p-Xylylene PX can be represented by quinoid (diamagnetic) or benzoid (paramagnetic) structures. The vapor of PX is diamagnetic [24].

The polymerization is thus probably started by paramagnetic diradical structures; such species may be the dimeric diradical from a one-sided ring-opening of DPX-N, the benzoid structure of PX, or the dimeric diradical from the coupling of two *p*-xylylene molecules. The polymerization seems to be propagated by addition of the diamagnetic quinoid structures to the growing macrodiradicals and not (or only slightly) by the polyrecombination of macrodiradicals. The polymerization proceeds as living polymerization with radical concentrations of $(5 - 10) \times 10^{-4}$ mol of free radicals per mole of xylene units of the final polymers.

Polymer yields are 100 % at −50 °C and drop rapidly at temperatures above ca. 0 °C (Fig. 1). Molar masses are almost independent of polymerization temperature in the range −50 °C to +50 °C [35].

The Gorham process can be applied to substituted [2.2]-paracyclophanes, provided the threshold condensation temperatures for the condensation on surfaces are not exceeded. These threshold temperatures are 30 °C for poly(*p*-xylylene), 60 °C for poly(2-methyl-*p*-xylylene), 90 °C for poly(2-chloro-*p*-xylylene),

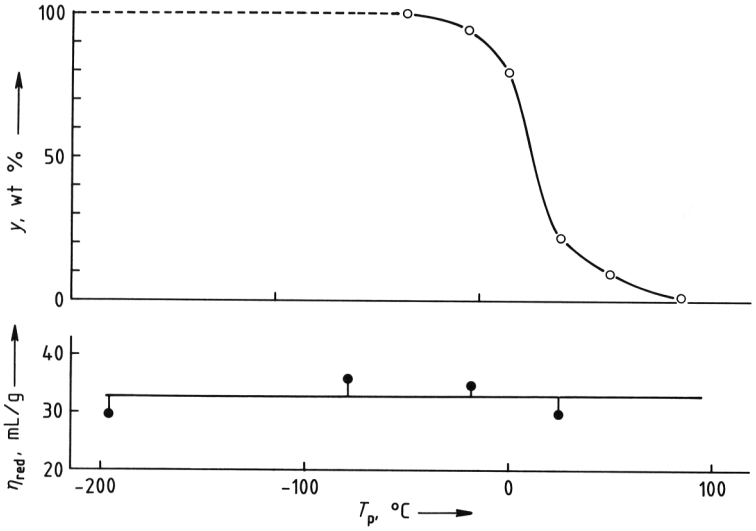


Figure 1. Dependence of polymer yield γ and reduced viscosity η_{red} (1×10^{-3} g/mL polymer in α-chloronaphthalene at 238 °C) of poly(*p*-xylylenes) on the polymerization temperature T_p (data from [35])

and 130 °C for poly(2,5-dichloro-*p*-xylylene) [34]. The physical meaning (other than the phenomenological) of the threshold temperature is unclear since the most obvious interpretation as thermodynamic ceiling temperatures is made difficult by reports of very high estimated thermodynamic ceiling temperatures of more than 200 °C for a gas pressure of 0.08 torr (11 Pa) [35] and calculated ceiling temperatures of 1149 °C (gas) and 3035 °C (liquid) for PX [25]. However, such calculations suffer from the absence of knowledge about the true nature of the polymerization: true equilibria between all species (monomers, monomeric diradicals, macrodiradicals), equilibria between monomers and macrodiradicals only, or even kinetically-controlled reactions.

Poly(*p*-xylylenes) can also be obtained by other methods [25], [36], [37], none of which seem to be used industrially since the monomers are too expensive and/or the polymers are obtained in low yield, with low molar masses, or with many low molar mass impurities.

3.3. Structure

Chemical Structure. Poly(*p*-xylylenes) from the Gorham process are linear polymers, whereas those from the Szwarc process are slightly cross-linked. The number-average molar mass, as calculated from the free-electron concentration of living PPX-N polymers [33], is ca. 200 000 – 400 000 g/mol. Osmometry of soluble fractions in chloroform gave 24 000 g/mol [24].

The commercial chlorinated monomers DPX-C and DPX-D are complex mixtures with 0 – 8 chlorine groups per molecule and 0 – 4 chlorine substituents per ring. On pyrolysis and subsequent vapor deposition polymerization, DPX-C with an average of one chlorine substituent per ring thus gives mainly base units $-CH_2-(p-C_6H_3Cl)-CH_2-$ besides considerable amounts of base units $-CH_2-(p-C_6H_4)-CH_2-$ and $-CH_2-(p-C_6H_2Cl_2)-CH_2-$. Chlorinated units may be arranged head-to-head, head-to-tail, and tail-to-tail so that the resulting constitutional copolymers also show regio-isomerism.

Physical Structure. PPX-N has two crystal modifications [38], [39]. The monoclinic α-modification is formed between −17 °C and +30 °C, while the triclinic β-modification exists below −78 °C and above 220 – 260 °C. The unit cell of the α-modification consists of two monomer units. The phenylene units are parallel to each other; the angle between the plane of the benzene rings and the methylene chain is 90°. The $\alpha \rightarrow \beta$ transition at 220 °C is accompanied by a marked increase in brittleness. At 270 °C, a reversible smectic transition is observed.

Vapor deposition polymerization is carried out below the melting and near the glass temperatures of the polymers (see Table 2); any crystallization must thus occur simultaneously with the polymerization on surfaces. At polymerization temperatures between 0 °C and 60 °C, the α-modification is formed, whereas mixtures of α and β are found for polymerization temperatures above 80 °C.

The degree of crystallinity of parylene N has been reported to be 57 % [25]. The density of amorphous PPX-N, as calculated from the experimental density of 1.11 g/cm^3 and the theoretical density of the α-modification of 1.185 g/cm^3 (from the unit cell), is thus 1.070 g/cm^3.

Table 2. Properties of poly(*p*-xylylenes) [25], [34], [40], [41]

Property	Property values of		
	PPX-N	PPX-C	PPX-D
Density at 23 °C, g/cm^3	1.11	1.29	1.42
Refractive index n_D^{23}	1.661	1.639	1.669
Water uptake (24 h, 23 °C), %	0.01	0.06	< 0.1
Melting temperature, °C	420	290	380
Glass temperature, °C	13		
Continuous service temperature (air), °C	100	130	
Continuous service temperature (inert), °C	220		220
Linear expansion coefficient (25 °C), K^{-1}	6.9×10^{-5}	3.5×10^{-5}	
Specific heat capacity (25 °C), J g^{-1} K^{-1}	1.3	1.0	
Thermal conductivity (25 °C), kW m^{-1}K^{-1}	12	8.2	
Flexural modulus (23 °C), MPa	2450	2800	2800
Modulus of elasticity, MPa			
at 23 °C	2400	3200	2800
at 200 °C	170	170	170
Tensile strength (23 °C), MPa	45	70	75
Yield strength (23 °C), MPa	42	55	60
Elongation at break (23 °C), %	< 30	200	< 10
Rockwell hardness R (23 °C)	85	80	
Relative permittivity (23 °C)			
60 Hz	2.65	3.15	2.84
1 kHz	2.65	3.10	2.82
1 MHz	2.65	2.95	2.80
Dissipation factor (23 °C)			
60 Hz	0.0002	0.020	0.004
1 kHz	0.0002	0.019	0.003
1 MHz	0.0006	0.013	0.002
Surface resistivity, Ω (23 °C)			
50 % RH	1×10^{13}	1×10^{14}	5×10^{16}
90 % RH	9×10^{11}	7×10^{11}	
Volume resistivity (50 % RH, 23 °C), Ω cm	1.4×10^{17}	8.8×10^{16}	2×10^{16}
Dielectric strength at 23 °C, kV/mm	260 – 280	145 – 220	200 – 215
Permeability (at 25 °C) 10^{14} P, cm^{2}s^{-1} Pa^{-1}			
N_2	0.35	0.020	0.20
O_2	1.76	0.32	1.44
Cl_2	3.32	0.016	0.025
CO_2	9.64	0.35	0.58
He	18.8	7.4	
H_2	24	5.0	
H_2S	35.7	0.58	0.065
SO_2	85.1	0.49	0.21
H_2O	428	150	

3.4. Manufacture

Parylenes are exclusively prepared and applied by vapor deposition polymerization of DPXs on surfaces (Gorham process). Total production is estimated to be several tonnes per year.

Film formation by vapor deposition polymerization differs from other coating techniques in that the coating is formed from the gaseous phase rather than from a liquid one (no surface tension effects on wetting) and that the film grows from the substrate upwards and not downwards as in drying films. The films are self-adherent; coupling agents are usually not necessary.

The technique produces pinhole-free coatings of uniform thickness even on complex, three-dimensional substrates with hidden areas. Films have thicknesses between 0.050 and 100 μm. They are flexible even at low temperatures and possess good dimensional stability.

These features, together with good electrical and mechanical properties and low gas and water vapor permeability, make parylenes especially suitable for surface coating of electrical and electronic components such as printed and integrated circuits, capacitors, transistors, and miniature electrical components. Parylenes are also applied for particle encapsulations, thin membranes, lubricants, and long-term implantation devices.

3.5. Properties

Properties of poly(*p*-xylylenes) are listed in Table 2.

Solubility. Poly(*p*-xylylenes) from the Gorham process are sparingly soluble. PPX-N dissolves to 1.5 % and PPX-C to 10 % in methylene chloride at 25 °C [25]. The solubility of

PPX-N in xylene is ca. 10 % at 140 °C. PPX-N and PPX-D can be dissolved in chlorinated biphenyls or in benzyl benzoate at temperatures above 200 °C, and PPX-C in 1-chloronaphthalene at 150 °C [33]. Cooling the solutions to below 150 – 200 °C leads to gel-like precipitation of the polymer. Repeated dissolution and precipitation cause degradation.

Aromatic and halogenated aromatic compounds swell parylenes at room temperature, but stress corrosion has not been observed. Parylenes are resistant to concentrated sulfuric acid and 5N nitric acid.

Thermal Properties. Melting temperatures of symmetrically substituted poly(*p*-xylylenes) PPX-N and PPX-D are higher than those of unsymmetrically substituted PPX-C. The glass temperature of PPX-N is fairly low (T_g = 13 °C) [25], and lower than the earlier reported 80 °C [21]. Similar low glass temperatures can be expected for PPX-C and PPX-D; earlier reported glass temperatures of 80 – 110 °C are definitely too high since no sudden upswing of relative permittivity (dielectric constant) $_r$ due to the onset of segmental motions is observed in the temperature interval 20 – 190 °C, only a continuous increase of $_r$ from 3.0 to 4.7.

Since the glass temperature is lower than ambient temperature, structural changes occur upon aging and/or annealing of parylenes; freshly deposited polymers have other properties than old ones.

The stability of parylenes is determined by the dibenzyl groups, which are easily oxidized and thermally cleaved. The continuous service temperature of PPX-N is thus only 100 °C in air and 220 °C under an inert atmosphere (see Table 2).

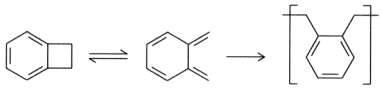
Mechanical Properties. Parylenes have tensile strengths and elastic moduli (Table 2) similar to those of other engineering plastics. The unusually high elongation at break of PPX-C refers to freshly deposited films; such films have high dimensional stability if subjected to high relative humidities. Films remain tough and flexible down to −165 °C. Since further crystallization takes place on annealing, density, hardness, and abrasion resistance also increase.

Permeability. Gas permeabilities (O_2, N_2) of parylenes are similar to those of poly(ethylene terephthalate), and water vapor permeabilities compare favorably with those of high-density polyethylene. PPX-C and PPX-D have also low permeability for SO_2 and H_2S.

Electrical Properties. Parylenes from the Gorham process have low relative permittivity (dielectric constant) and dielectric loss (dissipation factor) due to their chemical structures (only carbon and hydrogen, no hydrophilicity, no dipoles) and the absence of low molar mass impurities and catalyst residues. Dielectric strengths are high compared to other polymers, which is in part due to the thinness of the test films (0.025 mm) since dielectric strengths decrease with increasing thickness and dielectric strengths of other polymers are usually measured at thicknesses of 3.18 mm.

4. Polybenzocyclobutenes

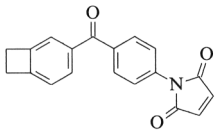
Polybenzocyclobutenes are polymers and copolymers of various benzocyclobutenes [42–46]. On heating, the parent compound, benzocyclobutene (BCB), is converted to the unstable *o*-quinodimethane, OQDM (*o*-xylylene, OX), which polymerizes thermally to polybenzocyclobutene (PBCB):



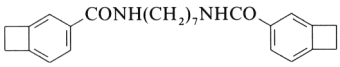
BCB [*694-87-1*] OQDM, OX PBCB (**1**) [*51774-83-5*]

The intermediate is not a biradical but has an *o*-quinone structure (ground-state singlet) according to theoretical calculations. This intermediate is the true monomer; the polymer can thus also be called a poly(*o*-quinodimethane) or a poly(*o*-xylylene).

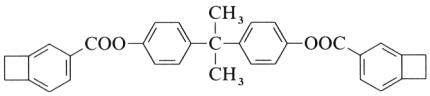
Syntheses of benzocyclobutene derivatives start with either benzocyclobutene or 3-bromobenzocyclobutene. Monobenzocyclobutenes (functionality 2) such as **2** lead to linear polymers, and bis(benzocyclobutenes) (functionality 4) such as to cross-linked polymers:



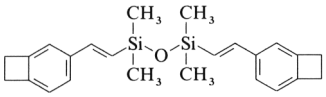
2
Monomer: [*112903-01-2*]; Polymer: [*112903-02-3*]



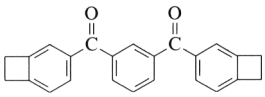
3
Monomer: [*99716-25-3*]; Polymer: [*99716-26-4*]



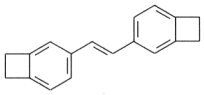
4
Monomer: [*99716-21-9*]; Polymer: [*99716-22-0*]



5
Monomer: [*117732-87-3*]; Polymer: [*124221-30-3*]



6
Monomer: [*137662-13-6*]; Polymer: [*137662-14-7*]



7
Monomer: [*67237-37-0*];

The polymerization proceeds without formation of volatile products. It does not require catalysts or initiators and it is first order in benzocyclobutene groups. The polymerization temperature of BCB is 200 – 250 °C; it is lower for substituted benzocyclobutenes , regardless of whether the groups are electron donating or electron withdrawing.

The polymerization mechanism of the bis-benzocyclobutene monomers is not known with certainty: intermolecular reactions **1** may either lead to random cross-linking or to ladder-type structures.

All polymers of have high thermal stability. The good mechanical properties (Table 3) are retained at temperatures up to 200 – 250 °C.

5. Ionomers and Related Polymers

5.1. Overview

5.1.1. Introduction

Terms such as ion-containing polymer, ionic polymer, ionomer, polyelectrolyte, etc., are commonly used in polymer literature. None of these terms are defined by international standardization bodies and their meaning often differs from similar ones in other branches of science.

The term "ion-containing polymer" in its literal sense does not specify whether ions are part of the polymer molecules or whether they are extraneous to the polymer molecules, for example, catalyst residues or other impurities. In the polymer literature, the term "ion-containing polymer" is used as a shorthand notation for

Table 3. Physical properties of polymers from a benzocyclobutene 2 and various bisbenzocyclobutenes 3 – 7

Property	Property values of polymer					
	2	3	4	5	6	7
Young's modulus (25 °C), MPa		2500	2660			
Shear modulus (25 °C), MPa		940	1000			
Flexural modulus (25 °C), MPa	3550 *			3310	4250	5150
Flexural strength (25 °C), MPa	200				152	
Elongation at break (25 °C), %	6				4.1	
Glass temperature, °C	310	> 270	> 270	> 350	310	> 350
Expansion coefficient ($\times 10^5$), K^{-1}		4.1	8		3.5	
Water absorption (48 h, 100 °C), %		1.4	0.9	0.25		0.87
Relative permittivity (1 MHz)				2.57		2.7
Dissipation factor (1 MHz)				0.0008		0.0004

* 30 °C

"ion-containing polymer molecules"; i.e., it refers exclusively to ionic structures attached to polymer molecules.

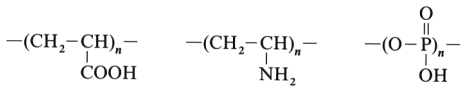
Polymer molecules with ionic structures are often called ionic polymers. They are usually subdivided into two groups [47]: water-soluble and water-insoluble. Water solubility is commonly shown by polymer molecules with high contents of ionic groups; these polymers are called polyelectrolytes (Section 5.1.2). Polyelectrolytes may, for example, contain basic groups such as $-NH_2$ or acidic groups such as $-COOH$.

The terminology is less clear for water-insoluble polymers with small contents of ionic groups. If these groups are acid groups such as $-COOH$ or $-SO_3H$, the polymers are termed acidic but never ionic. The term "ionic" is reserved here for polymers with small proportions of salt groups such as $-COONH_4$, $-COONa$, or $(-SO_3)_2Zn$. The designation of these polymers as "ionic polymers" is furthermore not meant to imply that the ionic structures are indeed present as ions, i.e., with charge separation (Section 5.1.3).

The incorporation of small amounts of acidic and/or ionic groups into apolar backbone chains causes these groups to associate ("aggregate") in the solid state. The resulting intermolecular physical cross-links lead to higher moduli and strengths. The cross-links dissociate at higher temperatures and the polymers can then be processed conventionally.

5.1.2. Polyelectrolytes

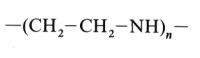
The ionic groups of polyelectrolytes may be in side chains as in **8** and **9** or in backbones as in :



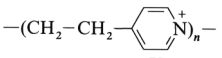
8

9

10



11



12

Polyelectrolytes may be polyacids such as poly(acrylic acid) **8** and poly(phosphoric acid) **10**, or polybases such as poly(vinyl amine) **9** and poly(ethylene imine) **11**. In water and other highly polar solvents, they dissociate into polyions and oppositely charged counterions. Upon dissociation, polyacids lose protons and become polyanions (e.g., $\sim[CH_2-CH(COO^-)]_n\sim$). The salts of these polyanions are thus called polysalts (e.g., $\sim[CH_2-CH(COO^-Na^+)]_n\sim$). Polybases can quaternize by adding protons, methyl groups, etc., and become polycations; the quaternization may be in the substituent as in **9** or in the main chain as in **11**. Polymers which only exist as polycations but not as polybases are called ionenes, an example of which is **12**, the polymer of 4-vinylpyridine by polymerization via the 1,6-positions.

Polyacids, polybases, polyanions, and polycations contain many acidic, basic, anionic, and cationic groups per molecule. They are to be distinguished from macroacids, macrobases, macroanions, and macrocations, which have only one such group (as in, e.g., living anionic polymerizations with monofunctional initiators), and from macrodiacids, etc., with two such functional groups, etc.

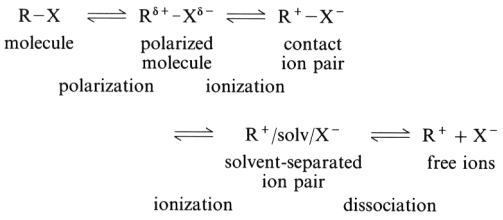
Polyampholytes are polymers whose chains carry both acidic and basic (or anionic and cationic) groups; an example is the copolymer of acrylic acid $CH_2=CHCOOH$ and acrylamide $CH_2=CHCONH_2$. Complexes of polyacids and polybases are called polyelectrolyte complexes or symplexes; they may or may not be water soluble, depending on their chemical structure (see also [47]).

5.1.3. States of Ions

In science "ion" denotes an electrically charged atom or molecule (cation or anion) which shows ionic conductivity as a free entity (in solution or as gas) or in its assemblies (in crystals or melts). Each ion possesses an oppositely charged counterion due to the principle of electroneutrality; the electric charges are separated. In polymer science, "ion-containing" does not necessarily refer to charge-separated entities, especially not in the solid state; it is merely necessary that these entities may be able to generate ions under favorable (polar) conditions.

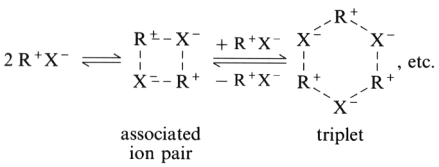
Under less polar conditions, ions can form ion pairs consisting of oppositely charged ions

bound together by Coulomb interactions but not by covalent bonds. In contact ion pairs, these ions are in direct contact. In the presence of polar solvents, the ions may be also more loosely held together in solvent-separated ion pairs; such ion pairs may share one solvent molecule or two or more.



Triple ions arising from Coulombic interactions such as ~~$COO^-/M^{2+}/^-OOC$~~ from two carboxylate groups ~~COO^-~~ and a metal ion M^{2+} are especially stable ionic structures since the sum of the repulsion between two anions and the attraction between the cation and two anions results in a negative potential energy [48]. The same reasoning applies to higher ion aggregates; such structures are responsible for the stability of ion crystals such as NaCl. Triple ions are sometimes called triplets although the latter term should refer exclusively to multiplets of ion pairs.

Ion pairs can associate to form tightly aggregated ion multiplets consisting of associated ion pairs (2 ion pairs), triplets (3 ion pairs), etc.:



The maximum number of ion pairs in such multiplets should be six to eight if the multiplets are spherical. Ion multiplets do not contain polymer chain segments; sizes of spherical multiplets cannot exceed ca. 0.6 nm because of geometrical constraints on the multiplet structures by the chain segments to which the multiplets are attached. Because of their small size, they are not separate phases in solid polymers; they thus directly affect matrix properties such as segment mobilities. No size restriction is imposed on nonspherical geometries.

Multiplets may aggregate into ion clusters [49] which contain significant amounts of polymer segments in addition to the ionic structures [51], [51] (for a review of these and other theories, see [52]). The domains of these clusters are thus considerably larger than those of multiplets; their size is limited to 2 – 10 nm by the elastic forces generated by the backbone chains. These clusters approach the size of true phases. Clusters thus do not markedly affect matrix properties except that they may behave as cross-links with reinforcing action.

Free ions and solvent-separated ion pairs conduct electricity, but contact ion pairs, contact multiplets, and ion clusters do not. Most ion-containing polymers are electrical insulators in the solid state; since obviously no ions are present, they really should not be called ion-containing polymers.

5.2. Acidic Copolymers

5.2.1. Introduction

Acidic copolymers are defined as copolymers of a parent monomer (or several thereof) and a small amount of an acidic comonomer. The polymers may be thermoplastic or elastomeric, depending on the glass transition temperature of the parent monomer segments.

The first acidic elastomers were copolymers of butadiene with small amounts of various unsaturated acids, patented by I. G. Farbenindustrie in 1930 [53]. In 1950, B. F. Goodrich started to introduce a series of acidic elastomers from butadiene, acrylonitrile, and small amounts of acrylic acid [54], [55]; the trade name Hycar now refers to polymers of different compositions and grades with many different CAS numbers. These and other acidic elastomers are also known as carboxylated elastomers or carboxylated rubbers; they are produced by many companies [56].

Hycar rubbers can be neutralized with zinc oxide or zinc salts; these neutralized acidic polymers were the first elastomeric ionomers. However, the ionomeric structures served only as reinforcing entities since the rubbers were still conventionally vulcanized to covalently cross-linked elastomers.

Neutralization of suitable acidic copolymers without chemical cross-linking leads to

thermoplastic elastomers. The first thermoplastic elastomers were the cured Hypalon polymers of Du Pont. Hypalons are based on sulfochlorination of polyethylenes [57] and are available in many grades. The curing of these polymers by metal compounds leads to ionomers which behave as thermoplastic elastomers.

In the mid-1960s Du Pont began production of the first thermoplastic acidic copolymers from ethylene (E) with small amounts of methacrylic acid (MAA). These copolymers were not commercially available but were converted in-house to ionomers (Section 5.3.6).

Thermoplastic acidic EAA copolymers of ethylene (E) and up to 15 wt% acrylic acid (AA) were first commercially manufactured in various grades by Dow Chemical and Union Carbide (Section 5.2.3). They were followed by Du Pont's E-MAA copolymers with up to 15 mol % MAA (Nucrel).

Du Pont also manufactures a 1 : 1 copolymer of ethylene and methyl acrylate with small amounts of (meth) acrylic acid (Vamac) (Section 5.2.4).

5.2.2. Structure and Properties

Acidic copolymers can be amorphous or partially crystalline, depending on the crystallizability of the segments of the parent monomer units. The crystalline domains are composed of lamellae formed by folded chains of parent segments and do not contain acidic units, the latter being confined to the amorphous regions where they may be present as dimers. Associated acidic units do not form separate phases. Acidic copolymers are thus one-phase materials if amorphous, and two-phase polymers if crystalline.

Properties of such polymers depend on intramolecular and intermolecular interactions between their segments and groups. COOH groups in polyethylene segments tend to associate; the associated groups act as cross-links. At low COOH content, this association can hardly take place since the COOH groups are not free but bound to polyethylene; the geometrical constraints imposed upon the groups reduce the probability of association. Since the crystallinity of the polymer is not markedly affected, Young's moduli of ethylene–methacrylic acid copolymers remain constant up to 4 – 5 mol % of methacrylic acid groups. At higher COOH group concentrations, intermolecular association is increasingly possible. Intermolecularly associated groups act as cross-links and the moduli and yield strengths increase sharply (Fig. 2).

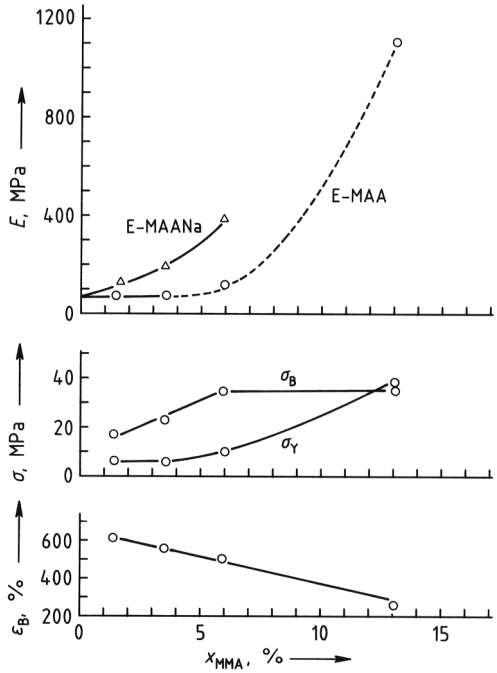


Figure 2. Tensile modulus E, yield strength σ_Y, tensile fracture strength σ_B, and elongation at break $_B$ of ethylene – methacrylic acid copolymers (○) and their sodium salts (▲) (100 % neutralization) as function of the mole fraction x_{MAA} of methacrylic acid units (experimental data from [58])

Polyethylene yields easily and exhibits stress-softening. The increasing association of COOH groups impedes the flow of segments, and the elongation at breaks decreases. Tensile fracture strengths of ethylene–methacrylic acid copolymers increase with increasing COOH content, eventually becoming independent of the proportion of COOH groups.

5.2.3. Thermoplastic Acidic Copolymers

Syntheses. EAA copolymers of ethylene (E) and up to 15 wt % acrylic acid (AA) are produced by Dow Chemical and Union Carbide in various grades. Du Pont manufactures an EMAA copolymer of ethylene and <15 mol % methacrylic acid MAA (Nucrel [59]) and an 1: 1 EMA copolymer of ethylene and

Table 4. Industrial copolymers of ethylene and (meth)-acrylic acid

Parent monomers	Comonomers	Trade name	Manufacturer
Ethylene	acrylic acid	EAA 469	Dow Chemical
Ethylene	acrylic acid		Union Carbide
Ethylene	methacrylic acid	Nucrel	Du Pont
Ethylene + methyl acrylate	(meth)acrylic acid	Vamac	Du Pont

methyl acrylate (MA) with small amounts of (meth)acrylic acid (Table 4).

None of the industrial polymerization processes have been disclosed. They are most likely high-pressure free-radical polymerizations. Since the Q, e values of ethylene ($Q_E = 0.015$; $e_E = -0.200$) and methacrylic acid ($Q_{MAA} = 2.34$; $e_{MAA} = 0.65$) are unfavorable for random arrangements of comonomeric units, copolymerizations are probably limited to ca. 10 % conversion in order to prevent the formation of long blocks of methacrylic acid units. Calculation of copolymerization parameters r from $r_i + (Q_i/Q_j)\exp[-e_i(e_i - e_i)]$ $r_i = (Q_i/Q_j)\exp[-e_i(e_i - e_i)]$ gives $r_{MAA} = 2.07$ and $r_E = 0.234$ and thus number-average sequence lengths $N_{MAA} = 1 + r_{MAA}([MAA]/[E])$ of methacrylic acid units of only $N_{MAA} \approx 1.23$ if the monomer ratio is $[MAA]/[E] = 90/10$. Q,e values of acrylic acid or copolymerization parameters of the ethylene–acrylic acid system have not been published but they should be similarly unfavorable.

Structure and Properties. High-pressure radical polymerization of ethylene leads to polyethylenes with a few short and long branches. The more or less random distribution of fairly bulky acid or salt units along the chains reduces the chain lengths of crystallizable segments of such polyethylenes. Melting temperatures thus decrease with increasing size of the substituents, e.g., for ethylene polymers with ca. 3 mol % comonomer units from 115 °C (LDPE with no comonomer units) to 104 °C (ethylene–acrylic acid), 95 °C (ethylene–sodium acrylate), and 90 °C (ethylene–methyl acrylate). Since the physical cross-linking caused by such comonomer units shortens the segments between cross-links, glass transition temperatures increase from −80 °C (LDPE) to −35 °C (ethylene–methyl acrylate), 0 °C (ethylene–acrylic acid), and 50 – 60 °C (ethylene–sodium acrylate).

The density of EAA copolymers increases linearily with the content of acryl acid units AA, reaching 0.95 g/cm^3 at 15 wt % AA units. Tensile yield strengths first decrease with increasing AA content, pass through a minimum at 12 – 15 wt % AA units, and increase again. The fracture strength exhibits a maximum at approximately the same AA content. Elongations at break are ca. 600 %.

Ethylene–acid copolymers show outstanding toughness since incorporated acrylic acid units reduce the formation of spherulites by polyethylene segments and simultaneously promote intermolecular association. Toughness is maintained at low temperatures; the brittleness temperature is ca. −70 °C for polymers with ca. 3 – 9 wt % acid units.

Ethylene acid copolymers show excellent adhesion to metals, glass, and paper due to the polar COOH groups and the low melt viscosities of the polymers. They also adhere well to polyethylene because of their polyethylene segments. Adhesion to other plastics can be improved by oxidation of EAA and EMAA surfaces.

Processing. EAA and EMAA can be processed similarly to LDPE. Since the acid groups are somewhat corrosive to metals, corrosion-resistant metals or nickel or chromium plating are recommended for processing equipment.

Certain ethylene acid copolymer grades can be dispersed in hot aqueous ammonia solutions to give dispersions stable at room temperature. They lose ammonia upon drying and form surface coatings with the same properties as copolymers processed otherwise.

Applications. Present applications comprise inner laminate layers on aluminum foil for pouches (towelettes, condiments) and tubes (toothpaste), cable sheathing, pipe coatings, and laminates on metals and glass fiber for automotive and building applications, and on polyurethane foams for carpet underlay.

FDA regulations for direct food contact with ethylene acid copolymers exist for EAA resins containing up to 10 % acrylic acid units and EMMA resins with up to 20 % methacrylic acid units.

Prices of resins are between those of low-density polyethylenes and Surlyn A ionomers.

5.2.4. Elastomeric Acidic Copolymers

Since 1976, Du Pont has offered Vamac, a copolymer with ethylene units $-CH_2-CH_2-$ and methyl acrylate units $-CH_2-CH(COOCH_3)-$ in the molar ratio 1: 1 and a small amount of undisclosed cure site units $-R(COOH)-$. The polymer is probably synthesized by free-radical emulsion polymerization. Two carbon-black-filled masterbatches (e.g., type B-124 with 24 parts SRF carbon black and auxiliaries per 100 parts polymer) and two neutral masterbatches (e.g., type N-123 with 23 parts siliceous earth per 100 parts polymer) are available [60].

All Vamac grades can be vulcanized by diamines or hexamethylene diaminocarbamate, and N-123 also by free radicals. Vulcanized Vamacs are EE–EH elastomers according to ASTM D-2000 and SAE J-200 classifications, i.e., elastomers with continuous service temperatures up to 175 °C (E) and swelling between 20 % (H) and 80 % (E) after 70 h in ASTM oil no. 3. Vamac is resistant to hot oils, hydrocarbons, glycols, and engine cooling fluids but not to brake fluids. Its weatherability is excellent.

The heat distortion of Vamac is surpassed only by the more expensive fluoroelastomers and silicones; however, Vamac has better mechanical properties. After 30 min vulcanization at 177 °C, the rebound elasticity of B-124 is 35 %, the tensile strength 14 MPa, the ultimate elongation 440 %, and the 100 % modulus 2.9 MPa. After 7 d at 177 °C, the modulus increases to 5.3 MPa and the tensile strength to 16.5 MPa, whereas the elongation decreases to 240 %, all probably due to an after-vulcanization.

Vamac is used for tubes and seals and as a damping material. It can replace sulfochlorinated polyethylene in cables and electrical systems since it burns with little smoke of low toxicity.

5.3. Ionomers

5.3.1. Introduction

The name ionomer was originally introduced by Du Pont for (partial) salts of copolymers of olefins with small amounts of carboxyl group containing monomers, such as ethylene–methacrylic acid copolymers [61]. The term ionomer is now used as a generic term for thermoplastic and elastomeric hydrocarbon polymers with small amounts of partially or completely neutralized pendant acid groups which show typical ionomer properties (Table 5). Total acidic group contents (free or neutralized) are usually under ca. 10 mol %. The syntheses, structures, properties, and applications of ionomers have been described in many books [62–64], reviews [50], [65–71], handbook articles [72–74], and symposia [75–77].

The acidic monomer units of such copolymers may be directly introduced by copolymerization as in ethylene/acrylic acid copolymers, or subsequently by chemical transformation of a primary copolymer as in the sulfonation of copolymers of ethylene, propylene, and a nonconjugated diene (Table 5). In ionomers, acidic monomer units are furthermore partially or completely converted into their salts. Polymer literature restricts the term "ionic" to these salts: polymer molecules with salt groups such as $-COONa$ or $-COONH_4$ are called ionic, whereas those with groups such as

Table 5. Industrial ionomers

Parent monomeric unit	Ionomeric unit	Ions	Trade name	Manufacturer
Thermoplastics				
Ethylene	methacrylic acid	Zn, Na	Surlyn A	Du Pont
Tetrafluoroethylene	perfluoro vinyl ether A *		Nafion	Du Pont
Tetrafluoroethylene	perfluoro vinyl ether B *		Flemion	Asahi Glass
Styrene	styrene *p*-sulfonic acid			Exxon
Elastomers and thermoplastic elastomers				
Ethylene	post-sulfochlorination		Hypalon	Du Pont
Ethylene + propylene+ nonconjugated diene	post-sulfonation		Thionic	Uniroyal
Butadiene + acrylonitrile	acrylic acid	Zn	Hycar	Goodrich

* Perfluoro vinyl ether: $CF_2=CF[O(CF_2CF(CF_3)O)_mR]$with R = $(CF_2)_2SO_3Na$ (A) orR = $(CF_2)_nCOONa$ (B).

$-COOH$ or $-SO_3H$ are not considered ionic but are sometimes referred to as acidic copolymers. Ionic and acidic copolymers with small proportions of ionic and/or acidic groups are always insoluble in water.

At present, only three thermoplastic ionomers (Surlyn A, Nafion, Flemion), two thermoplastic elastomers (Hypalon, Thionic), and many carboxylated rubbers (Hycar and others) are manufactured. Many other ionomers have been reported in the literature, e.g., carboxylic, phosphonic, sulfonic, and thioglycolic salts of polypentenamers [78], carboxylated and sulfonated polystyrenes [79], [80], and telechelic poly(isobutylene sulfonate) ionomers [81].

5.3.2. Structure

The first thermoplastic ionomers were copolymers of ethylene and methacrylic acids, partially neutralized with zinc or sodium compounds [82]. These Surlyn A polymers of Du Pont have much better clarity and tensile properties than comparable polyethylenes, which stimulated much research.

The enhanced properties of Surlyn A polymers were first thought to be due to decreased crystallinity and the presence of cross-linking triple ions of one bivalent metal cation (Zn^{2+}) and two carboxyl anions. It was subsequently shown that crystallinities are not markedly lower than those of the parent polymers, and that the good transparency was due to the absence of spherulites. These property changes also occur with monovalent metal cations (such as Na^+) so that other ionic cross-links must be present; these were later found to be ion multiplets and ion clusters.

Ionomers may be amorphous or partially crystalline, depending on the crystallizability of the segments of the parent monomer units. Amorphous ionomers are two-phase polymers. The continuous phase of these ionomers is amorphous and composed of parent segments with interdispersed ion pairs and ion multiplets. The discontinuous phase of amorphous ionomers consists of ion clusters of ion pairs and ion multiplets with interdispersed polymer segments. Crystallizable ionic copolymers possess crystalline regions as a third phase in addition to the amorphous phase and the ion clusters [49] (Fig. 3).

Crystalline domains do not contain acidic or ionic units; the segments in these domains are chain-folded. Acidic units are confined to amorphous regions, whereas ionic units are either in

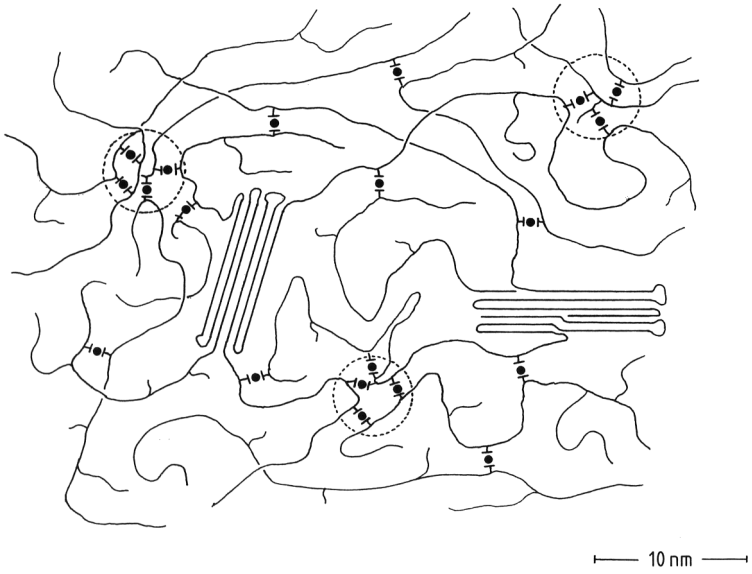


Figure 3. Schematic representation of the structure of crystallizable ionomers with crystalline (lamellar) domains, amorphous regions with ion triplets (and multiplets), and ion clusters with interdispersed chain segments (e.g., zinc-neutralized low-density ethylene – methacrylic acid copolymers)

amorphous regions or in ion clusters. The amorphous regions contain polymer segments with acidic or ionic units, acidic units as dimers, and ionic units as ion pairs and/or ion multiplets in a single phase. Ion clusters are separate phases that contain ion multiplets and polymer segments. The exact structure, size, and size distribution of amorphous and crystalline phases, ion clusters, ion multiplets, ion pairs, and associations of acidic groups are not known.

5.3.3. Properties

Ionic Group Content. Ionomers behave either as physically cross-linked thermoplastics or as thermoplastic elastomers, depending on the segment mobility of the parent monomer units. In amorphous polymers, the mobility is determined by the glass transition temperature, and in crystalline polymers also by the melting temperature, both relative to the service temperatures. Melting temperatures of crystalline polymers are mainly affected by the segments of the parent units and only secondarily by acidic or ionic units, which merely reduce the segment lengths of crystallizable units.

However, the glass transition temperatures T_G reflect the structure and mobility of noncrystalline phases, i.e., amorphous phases and ion clusters. Ionomers thus show two glass transition temperatures [61].

Ion pairs and ion multiplets act as cross-linking agents in amorphous phases. The higher the concentration of these physical cross-links, the shorter are the segments between cross-links. Cooperative movements of the units in segments are affected if the segment lengths are shorter than $N_c = 30 - 50$ chain atoms. At $N_c < 30 - 50$, glass transition temperatures of amorphous phases increase linearily with the concentration of ionic units (Fig. 4).

Glass transition temperatures of ion clusters are strongly influenced by ion pair and multiplet formation. Ions of an ion pair can only move away from each other above T_G; the required work W_{el} must be proportional to kT_G. This work is given by the electrostatic interaction F_{el} and the internuclear distance a. Because $W_{el} \sim kT_G \sim \int F_{el} da$, one obtains $TG \sim q_{cat}q_{an}/a$, where $q$cat and q_{an} are the cation and anion charges. The anion charge is constant in ionomers and thus $TG \sim q_{cat}/a \sim q/a$ [83]. In

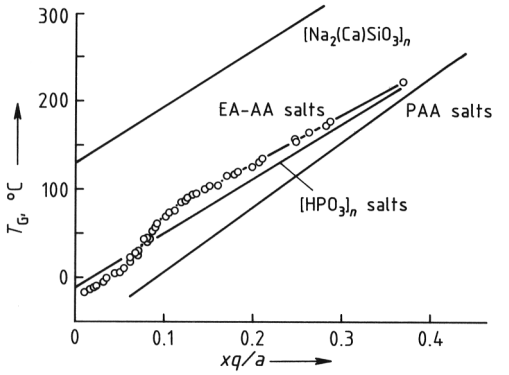


Figure 4. Glass transition temperature T_G as function of the linear charge density xq/a where x is the "metal carboxylate content" (probably in mol % of ionic units), q the cation charge (in "units of electron charges"), and a the distance between centers of charge (probably in 0.1 nm) [85]
○ = T_G of ion clusters of ethyl acrylate – acrylic acid copolymers EA – AA with Li, Na, K, Cs, Ca, and Ba [84]
— = T_G of amorphous domains of $[Na_2(Ca)SiO_3]_n$ glasses, salts of $[HPO_3]_n$, and salts of poly(acrylic acid) PAA

copolymers, only a fraction x of the monomeric units are ionic; the glass transition temperature of ionomers must be therefore proportional xq/a [84] (Fig. 4). The glass transition temperatures of ionic clusters usually show a sigmoidal dependence on either xq/a or x.

Effect of Neutralization. Elastic moduli of ethylene–methacrylic acid polymers with COONa groups are higher than those of the same polymers with COOH groups (Fig. 2). Increasing neutralization of COOH groups thus leads to an increase of moduli up to degrees of neutralization of $f_N \approx 30$ mol % (Fig. 5); moduli become constant at higher degrees of neutralization, which indicates that no new cross-linking sites are formed beyond this concentration.

The situation is quite different for partially neutralized copolymers of ethylene and acrylic acid. Tensile moduli first increase with higher degrees of neutralization f_N, but do not become constant as in ethylene/methacrylic acid copolymers; instead they decrease if $f_N > 0.3$ (Fig. 6). Fracture strengths σ_B increase monotonically with higher degrees of neutralization; they do not become constant. The variation of modulus and fracture strength with degree of neutralization seems to be independent of the type of monovalent cation, whereas the elongation at break depends on the ion type, especially at high

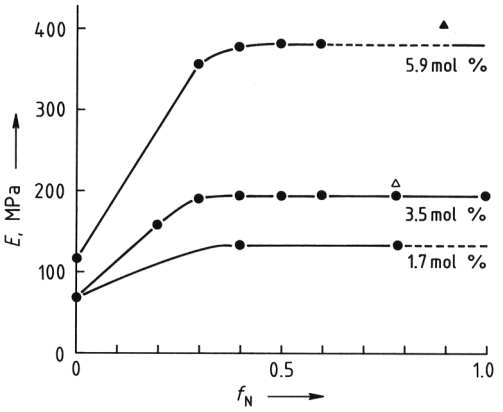


Figure 5. Young's modulus E of ethylene/methacrylic acid copolymers with 1.7, 3.5, and 5.9 mol % methacrylic acid units as function of the degree of neutralization fN of COOH groups by NaOH (●), $Sr(OH)_2$ (▲), or $Cu(OH)_2$ (△) Reproduced with permission from [58].

degrees of neutralization. These effects are probably due to differences in the structure and/or concentration of ion clusters; experimental data are not available.

Ionic domains are present in neutralized ethylene–methacrylic acid copolymers at temperatures up to 300 °C, far above the crystallite melting temperature, according to small-angle X-ray and neutron-scattering experiments. The number of ionic domains increases with the degree of neutralization f_N. Since they represent physical cross-linking sites, they are responsible for an increase of melt viscosity with increasing

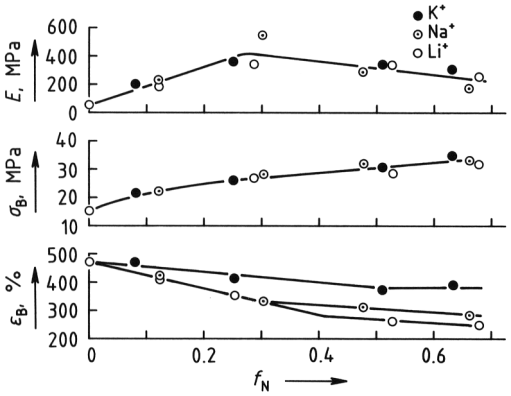


Figure 6. Variation of tensile modulus E, fracture strength σ_B, and elongation at break $_B$ with degree of neutralization f_N of ethylene – acrylic acid copolymers (experimental data from [85])

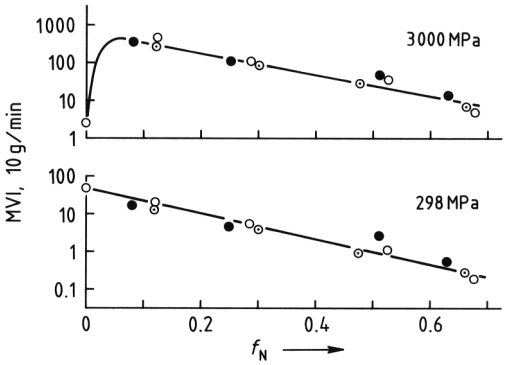


Figure 7. Effect of the degree of neutralization by Li^+ (○), Na^+ (⊙), and K^+ (●) on the melt volume index MVI (at 298 and 3000 MPa) (melt flow index) of copolymers of ethylene with 15 wt % acrylic acid (experimental data from [85])

neutralization, i.e., a decrease in melt volume index (melt flow index) MVI (Fig. 7). The size of these ionic domains is not affected by the type of monovalent ion nor by the applied pressure as the similar slopes of the functions log MVI = f (f_N) show.

Influence of Counterion Type. The association of salt groups depends on the coordination number of the counterions and not on its valency. Monovalent ions such as Li^+, Na^+, and K^+ and bivalent ions such as Mg^{2+}, Ca^{2+}, and Zn^{2+} cause multiplet and cluster formation (Fig. 3). The effects are however quantitatively different: at 25 °C and the same elongations at break, bivalent ions lead to higher tensile fracture strengths than monovalent ions

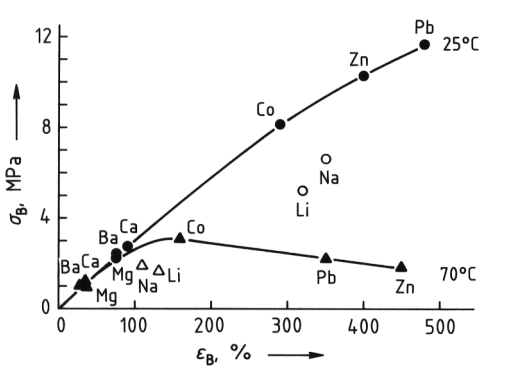


Figure 8. Tensile fracture strength σ_B as a function of elongation at break $_B$ of salts of sulfonated EPDM polymers (32 milli-equivalents of sulfone groups per 100 g polymer) at 25 °C (●, ○) and 70 °C (△, ▲) (experimental data from [86]) ●, △ = Bivalent metals; ○, ▲ = Monovalent metals

(Fig. 8). At this temperature, higher strengths are accompanied by higher elongations for the two series of bivalent and monovalent metal cations. In each series, these properties increase with increasing atomic number of the metal.

At the higher test temperature of 70 °C, ionomers with bivalent metals of group 2 of the periodic table (Mg, Ca, Ba) still follow the $\sigma_B = f(_B)$ relationship for 25 °C but the members of higher groups (Co, Zn, Pb) now not only lead to much lower fracture strengths but to a decrease in strength with increasing elongation at break (Fig. 8). These changes indicate that the structures of physical cross-linking sites formed by metals with higher group numbers change at higher temperatures.

5.3.4. Ethylene–Methacrylic Acid Ionomers

Many thermoplastic ionomers have been reported in the literature but only three have been commercialized: Surlyn A (Du Pont) for films, coatings, and molded articles, and two perfluorinated ionomers for membranes (Nafion from Du Pont, Flemion from Asahi Glass).

Synthesis. Surlyn A (Du Pont) is a copolymer of ethylene with ca. 10 wt % methacrylic acid; 50 % of the COOH groups are present as the sodium salt [*25608-26-8*] or zinc salt [*28516-43-0*]. CAS registers these copolymers as "2-propanoic acid, 2-methyl-, polymers," i.e., as polymers of methacrylic acid, although methacrylic acid is clearly the minority component.

The commercial synthesis of Surlyn A polymers has not been disclosed. Most likely, it is a high-pressure free-radical copolymerization of ethylene and methacrylic acid. The acid groups are then partially neutralized by rolling the polymers with metal acetates, alkoxides, carbonates, or hydroxides with release of acetic acid, alcohols, carbon dioxide, or water, respectively.

Commercial products contain either sodium or zinc. Polymers with ammonium derivatives or lithium can also be processed but these polymers are not commercial. Magnesium- and barium-containing polymers possess such high viscosities that they can no longer be processed.

Structure. Surlyn A polymers have a multiphase structure consisting of crystalline regions with chain-folded polyethylene segments, amorphous regions containing ion multiplets, and ion clusters with interdispersed polyethylene segments.

The introduction of acid/salt groups into polyethylene chains prevents the formation of spherulites but does not markedly change the crystallinity. Surlyn A polymers therefore have good optical clarity (haze < 2 %), especially the low-crystallinity grades. Transparency increases with increasing degree of neutralization; it becomes constant at neutralizations >ca. 30 – 50 %.

Surlyn A polymers have chemical structures similar to those of alkali metal salts of long-chain fatty acids. Since the latter are nucleating agents, similar behavior can be expected from Surlyn A polymers. Upon annealing, the crystallinity of these polymers does indeed increase. Spherulites form at temperatures above ca. 90 °C, leading to haziness.

Properties. Some properties of Surlyn A resins are listed in Table 6. Crystalline regions and ion clusters all act as physical cross-linking sites for the rubbery, ion-multiplet-reinforced amorphous domains; Surlyn A polymers thus have the characteristics of high-impact multiphase polymers. Tensile strengths are higher than those of comparable polyethylenes and increase with the proportion of acid units and the degree of neutralization (Fig. 9). Stiffness and hardness are similar to those of LDPE. The various grades retain impact strengths up to their brittleness temperatures, which are between −100 and −130 °C. The continuous service temperatures of ca. 70 °C are fairly low. The elongation at

Table 6. Properties of Surlyn A Resins

Property	Na Resin	Zn Resin
Density, g/cm^3	0.94	0.94
Melting temperature, °C	94	95
Heat deflection temperature (455 kPa), °C	40	41
Thermal expansion coefficient, K^{-1}	14 × 10–5	16 × 10–5
Melt flow index, g/10 min	1.3	5.5
Flexural modulus, MPa	220	130
Tensile strength at yield, MPa	12.4	8.3
Tensile strength at break, MPa	29	21.4
Elongation at break, %	450	500
Tensile impact strength, kJ/m^2	1160	925
Notched impact strength, J/m	610	no break
Hardness (Shore D)	60	54

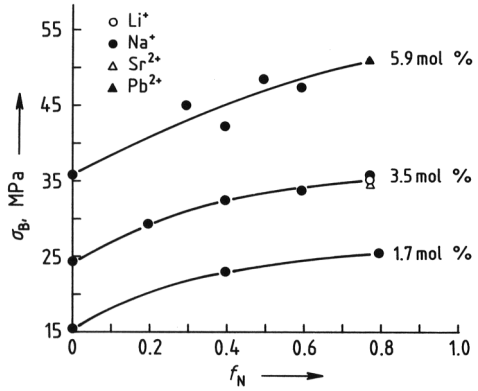


Figure 9. Tensile fracture strength σ_B of copolymers of ethylene with various mole fractions x_{MAA} of methacrylic acid as function of the degree f_N of neutralization
Reproduced with permission from [58].

break is ca. 350 %, and the abrasion resistance is excellent.

The physical cross-linking of chains by ion clusters causes high melt viscosities (low melt volume indices) which are much higher than those of comparable polyethylenes. Melt strengths are high. The cross-linking also reduces the creep under constant load.

At room temperature, Surlyn A ionomers are insoluble in all common organic solvents. They dissolve at temperatures above ca. 70 °C in 60/40 vol/vol mixtures of toluene/isobutanol, toluene/methyl isobutyl ketone, or tetrachloroethylene/butanol, or in a 70/20/10 mixture of decahydronaphthalene/diethylene glycol dimethyl ether/dimethyl sulfoxide. The polymers have good resistance to stress corrosion, except by certain combinations of detergents and alcohols. The permeability for oils and fats is low, while water vapor permeabilities correspond to those of low-density polyethylene. The polymers are readily degraded by light; UV absorbers extend outdoor service lives to ca. 2 years. Surlyn A polymers burn slowly when in contact with flames.

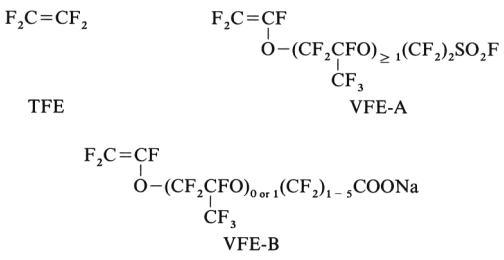
Carboxyl groups provide Surlyn A polymers with good adhesion to metals, glass, and paper; the adhesive properties depend on the carboxyl group content. Adhesion on impact is good, as e. g., required by the painted surfaces of molded golf balls.

Applications. The combination of good impact strength, high melt viscosity, high melt strength, good transparency, and relatively low continuous service temperatures is ideal for the manufacture of extremely thin packaging films. Such films have high tear strengths and are especially well suited for the packaging of sharp objects. Co-extruded ionomer–LDPE films are used for sterilizable packaging of foods and pharmaceuticals. Coatings of zinc-containing Surlyn A grades make glass bottles splinter-resistant. The combination of toughness and good abrasion resistance recommends the polymers for shoe soles and heels. Other applications are sheathing of electric cables and wires, automotive parts, and floor mats. Molded articles can be directly painted.

Closed-cell Surlyn A foams with densities of 50 – 700 kg/m^3 can be produced by extrusion or injection molding. Applications include carpet backings, ski boots, hockey sticks, helmets, and tennis court foundations.

5.3.5. Fluorinated Ionomers

Precursors of fluorinated ionomers are manufactured by free-radical copolymerization of tetrafluoroethylene (TFE) with perfluorovinylethers (FVE)



in molar ratios of 5 – 10 mol TFE per mole PVE [88], [88]. VFE-A is synthesized by reaction of hexafluoropropylene oxide (from the oxidation of TFE) with the sultone from the addition of sulfur trioxide to tetrafluoroethylene. Copolymers of TFE and VFE-A are known as XR Resins (Du Pont) whereas copolymers of TFE and VFE-B are called Flemion (Asahi Glass).

XR Resins can be melted and fabricated into membranes and tubes by conventional processing methods for thermoplastics. The $-SO_3F$ end groups are then saponified by hot caustic soda to give $-SO_3Na$ end groups, which in turn are

converted into sulfonic acid groups with, for instance, nitric acid.

Du Pont manufactures articles with free sulfonic acid groups as films, tubes, or laminates under the trade name Nafion. Similar carboxylated fluoro ionomers are produced by Asahi Glass under the trade name Flemion. These polymers are permselective [89]: they allow the passage of cations but not of anions and are therefore used as membranes for electrochemical processes, e.g., for the production of sodium hypochlorite. The exchange capacity of such resins is ca. 0.85 mmol/g, the fracture strength of resins with ca. 25 % water content ca. 21 MPa, and the elongation at break ca. 150 %. The strength can be increased by reinforcement with fabrics made from polytetrafluoroethylene fibers [90].

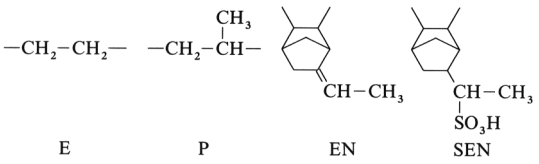
5.3.6. Sulfochlorinated Polyethylene

Simultaneous chlorination by Cl_2 and sulfonation by SO_2 of polyethylenes in homogeneous solution under the action of free-radical initiators or light leads to polymers with $-CH_2-$, $-CHCl-$, and $-CHSO_2Cl-$ groups in the approximate ratio 100 : 30 : 1. The polyethylene segments of these polymers are too short to crystallize, and the polymers thus behave as elastomers because of the low glass transition temperature (actual data unknown). Du Pont manufactures chlorosulfonated polyethylenes (CSM) in various grades (different CAS numbers) under the name Hypalon. Apart from a handbook article [91], little has been published about CSM polymers.

CSM polymers can be cured by way of the SO_2Cl groups [92]. The white polymers need no reinforcing fillers and can be used for many colored products. The presence of polar Cl and SO_2Cl groups provides the elastomers with excellent resistance to oil and ozone compared to standard synthetic rubbers. The maximum service temperature is ca. 120 °C.

5.3.7. Sulfonated EPDM Polymers

Synthesis and Structure. EPDM polymers are produced by Ziegler–Natta copolymerization of ethylene (E), propylene (P), and a small amount of a nonconjugated diene, preferably 5-ethylidene-2-norbornene (EN). The amorphous, rubbery polymers contain the monomeric units E, P and EN; the latter can be sulfonated by $H_2SO_4/(CH_3CO)_2O$ to sulfo units SEN [73]:



Sulfo-EPDMs can be neutralized with metal alkoxides or other bases, either in solution with subsequent precipitation of the neutralized polymer or by reactive milling of the polymer in an extruder. These thermoplastic elastomers were developed by Exxon and are now being commercialized by Uniroyal under the trade name Thionic.

Properties. Mechanical properties of sulfo-EPDM ionomers depend strongly on the type and concentration of cations (Fig. 8). Tensile strengths of these ionic polymers are typically much more enhanced over those of the acidic base polymers as compared to other ionomers.

The strong associations caused by ion clusters decrease with increasing temperature (Fig. 8). Even then the melt viscosity is very high at the usual processing temperatures. The Mg, Ca, Co, Li, Ba, and Na ionomers of Figure 8 typically have apparent melt viscosities between 55×10^4 Pa · s (Mg) and 51×10^4 Pa · s (Na) at 200 °C and a shear rate of 0.88 s^{-1}; for unknown reasons, melt viscosities of Pb and Zn ionomers are much lower (33×10^4 and 12×10^4 Pa · s, respectively [86]. Lead and zinc ionomers also exhibit melt fracture at higher shear rates (88 and 147 s^{-1}) than the other ionomers (< 0.88 s^{-1}).

The high melt viscosities can be lowered by ionic-domain "plasticizers" such as zinc stearate [86]. Such additives interact preferentially with the ionic clusters, lessen the bonding in the cluster region and thus decrease the melt viscosity. Despite its designation as local or specific "plastification", the phenomenon is not a plastification in the scientific meaning of the word since glass transition temperatures are not affected. "Plasticized" zinc and lead sulfo-

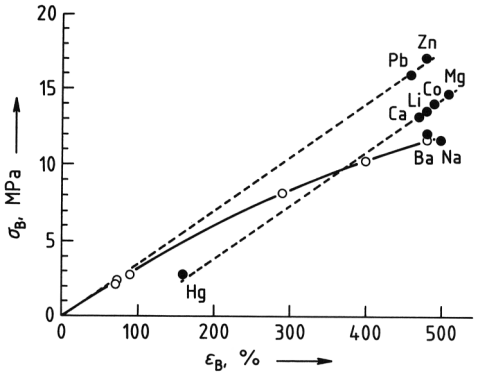


Figure 10. Tensile fracture strength σ_B as function of elongation at break $_B$ of sulfonated EPDM ionomers before (•—•, bivalent ions only) and after (▷ – – – ▷) plasticization with zinc stearate (experimental data from [86])

EPDMs show also higher fracture strengths than the corresponding unplasticized ionomers (Fig. 10). The phenomenon seems to be due to a reduction of the strength of the cross-linking ion clusters upon shearing the melt

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Thermoplastic Elastomers

ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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1. Thermoplastic Polyolefin Elastomers

1.1. Introduction and Definition

The significant growth of thermoplastic elastomers in the marketplace since the 1970s can be attributed to the family of thermoplastic polyolefin elastomers because of the wide range of products available, their favorable price–performance relationship, and their acceptance by the automotive industry. Historically, Uniroyal Chemical Company was the first company in 1972 to introduce a thermoplastic polyolefin elastomer to the market.

In 1971, W. K. FISHER [1, 2] filed patent applications on thermoplastic elastomer (TPE) blends based on rubbers that are copolymers of monolefinic monomers—such as ethylene–propene copolymer (EPM) or ethylene–propene–diene terpolymer (EPDM)—with crystalline polyolefin resin, e.g., polypropylene (PP). FISHER employed partial vulcanization of the rubber component to maintain the thermoplastic processibility of the blend by limiting the amount of peroxide. Cross-linking was performed while mixing under dynamic shear, a process known as dynamic vulcanization. However, the dynamic vulcanization process and the first EPM–PP blend were discovered independently by GESSLER et al. [3] (Exxon) and HOLZER et al. [4] (Hercules) in 1958 and 1961, respectively. Two types of thermoplastic rubber (TPR) were produced. One type consisted of simple blends of EPDM and PP; the other contained *partially vulcanized rubber* in the blend. In 1972–1976, most major EPDM producers commercialized products based on simple blends. In general, the TPR products were elastomeric according to DIN 7724 and ISO 1382–1982 definitions, yet these products were not seriously considered for true rubber replacement applications.

Significant improvement in the properties of these blends was achieved in 1975 by CORAN et al. [5] by *fully vulcanizing the rubber phase* under dynamic shear without affecting the thermoplasticity of the blend. This discovery was advanced by ABDOU-SABET et al. [6] in 1977 by the use of phenolic curatives to achieve further improvement in rubber-like properties and processing characteristics.

Therefore, the field of thermoplastic elastomers based on polyolefin rubber–plastic blends grew along two distinctly different product lines or classes: one class consists of a simple blend of α-olefin rubber in a crystalline polyolefin resin and classically meets the definition of thermoplastic polyolefin (TPO). In the production of the other class, the rubber component in the TPO is subjected to dynamic vulcanization to generate a TPE with true rubber-like properties. This class is called thermoplastic vulcanizates (TPVs) or dynamically vulcanized alloys (DVAs).

These two classes of materials share a common basic composition. The plastic phase is a semicrystalline polyolefin such as isotactic and syndiotactic polypropylene, propene copolymer, high-density polyethylene, low-density polyethylene, linear low-density polyethylene, ethylene–vinyl acetate copolymer, ethylene–methacrylate copolymer, or ethylene–ethyl acrylate copolymer. The rubber phase may consist of EPM, EPDM, isobutene–isoprene copolymer (butyl rubber), halobutyl rubber, isobutene–*p*-methylstyrene copolymers, halogenated isobutene–*p*-methylstyrene copolymers, natural rubber, styrene–butadiene copolymers, nitrile–butadiene copolymers, styrene–isoprene–styrene block copolymers and their hydrogenated version, etc. (The component polymers are described elsewhere in this encyclopedia).

1.2. Thermoplastic Polyolefin Blends

Thermoplastic polyolefin compositions based on the blends of a polyolefin rubber and a semicrystalline polyolefin have increased

dramatically in popularity in recent years. The first thermoplastic polyolefins blends commonly referred to as TPOs were *mechanical blends* of polyolefin polymers. The most common types of TPO are composed of polypropylene and ethylene–propene rubber (EPR). In principle, there is a wide variety of starting materials, an almost unlimited number of formulations for this type of TPOs in major part custom-tailored to meet the varied requirements of the most demanding low temperature high impact applications.

In addition to these mechanical blends, advances in Ziegler–Natta catalysis and reactor design have allowed the preparation of such blends in the polymerization reactor from ethylene and propene monomers. These are commonly called *reactor thermoplastic polyolefins* (RTPO). The amount of EPR content in RTPO can be varied from less than 15 wt%, which is most common, to around 70 wt%. Commercial demand for TPO and RTPO has been particularly strong in the automobile bumper application, especially in Europe and Japan. Such dominance has overshadowed the opportunities for TPO in other market sectors. Advanced compounding technology is being used to generate TPO compounds specific to the application; such technology can also be applied to RTPO.

Mechanically prepared blends are produced by using either batch or continuous mixing techniques. The most common batch mixers are internal intensive mixers, such as the Banbury. Continuous mixing techniques can be performed in either single- or twin-screw extruders. Mixing procedures can be extremely varied because of the wide range of TPO recipes in use, as well as the mechanical characteristics of individual process lines.

Reactor thermoplastic polyolefins are the newest variety of TPO. The amount of rubber (generally EPR) that may be included in a reactor-generated TPO is strongly dependent on the catalyst and process used. The development of a new generation of Ziegler–Natta catalysts (4th generation) with long-lived activity and the capacity of providing PP particles with very high porosity permit the polymerization of a high-rubber component (up to 70 wt%, soft component) inside a shell or skin of crystalline PP. This has been accomplished by the *Cataloy process* [7], which is based on a three-stage reactor. The first stage consists of a tubular loop reactor that produces semicrystalline polypropylene. In the second and third reactors, ethylene and other olefinic monomers are introduced, and ethylene copolymerizes with propene to form the ethylene–propene copolymer rubber inside the semicrystalline homopolymer PP produced in the first reactor; this minimizes reactor fouling. The formation of a continually growing polymer skin and porous particle provides a reaction bed within which the copolymer is produced. This advanced technology in Ziegler–Natta catalysis has been referred to as *Reactor Granules Technology* [8] because the growing polymer particle itself has become the polymerization reactor.

1.2.1. Morphology

Thermoplastic polyolefins possess primarily a two-phase morphology. At least one phase—the thermoplastic component of the blend—is continuous. The second, or rubber, phase can be either co-continuous or dispersed, depending on the composition of the blend. The mixing conditions, surface energy, viscosity, and molecular masses of the two polymers determine at what polymer ratio the two phases are co-continuous [9, 10], since at extreme concentrations (i.e., a 10 : 90 or 90 : 10 ratio) the minor component is expected to be the dispersed phase.

Onogi and coworkers [11, 12] reported phase inversion in the blends of crystalline polypropylene with EPR or EPDM elastomers when the polypropylene content reaches 50 to 60%.

Lohse [13] describes the morphology of the simple blend as unstable because the polymers are not miscible, especially at a 50 : 50 polymer ratio. The rubber phase, particularly when present as the dispersed phase, tends to agglomerate or coalesce. Such phase growth is undesirable and would lead to changes in properties and performance as a function of mixing and processing. To stabilize against phase growth, additives or *compatibilizers* are usually added. The

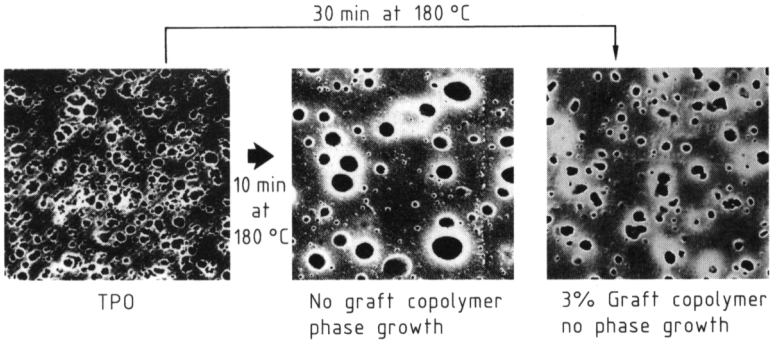


Figure 1. Morphology of EPDM–PP thermoplastic polyolefins containing 0 and 3 mol% compatibilizer

preferred compatibilizer is a graft or block copolymer of isotactic PP and EPR. One approach has been described in [14]. The compatibilizer is generated from EPDM containing vinylnorbornene as the diene; the pendant double bond is then used to graft to the PP. The addition of 3% of a compatibilizer to the blend improves adhesion between the phases and leads to finer dispersion of the phases. This is demonstrated by the smaller size of the rubber phase and the considerably decreased phase growth (Fig. 1).

1.2.2. Elastomer Component, Soft Domain

Either ethylene–propene or ethylene–propene–diene rubber is suitable for these blends. The double bonds in the EPDM are not used as chemically active sites for curing. However, they provide considerably wider choices in raw material selection and undoubtedly affect the green strength properties of the elastomer by changing the number of branch points in the rubber molecule. The diene most commonly used in the EPDM is ethylidene norbornene (ENB), but 1-4 hexadiene (1,4 HD), dicyclopentadiene (DCPD), or vinylnorbornene (VNB) may be used.

EPR rubbers contain 45–85 mol% ethylene, 55–15 mol% propene, and 0–10 mol% diene. EPDM with an ethylene content > 75 mol% exhibits crystallinity that can be examined by differential scanning calorimetry or ^{13}C NMR by measuring the ethylene sequence index [15]. The net effect of ethylene crystallinity is that it greatly strengthens the rubber and, consequently, the blend.

1.2.3. Plastic Component, Hard Domain

In most commercial TPO, the hard domain is isotactic polypropylene homopolymer or a copolymer (random or block) with a small amount of ethylene as comonomer for random PP and until 25 mol% ethylene for block copolymer PP. These resins are semicrystalline. The homopolymer has an *mp* of 155–165 °C, while the random copolymer has an *mp* of 140–155 °C. Ethylene decreases the rigidity of the polymer and improves the low-temperature properties at a sacrifice of the upper performance temperature.

1.2.4. Compounds, Trade Names

The two main components of a TPO blend are ethylene–propene rubber and polypropylene. Additional materials, such as other elastomers, processing oils, antioxidants, reinforcing and nonreinforcing fillers, colorants, and other additives to enhance the adhesion or the paintability of the product, are often used. Typical TPO compounds and their properties are listed in Table 1, and the suppliers and trade names of such materials are listed in Table 2.

Automotive and electrical applications are the major markets for TPO. Automotive constitutes by far the largest market because of the excellent weatherability and low cost of TPOs. Some examples are bumper covers, interior trim, fender extensions, etc.

TPOs have good electrical properties in combination with good ozone resistance, which makes these materials a good choice for low voltage wire and cable applications where hot

Table 1. Typical TPO compositions and properties

Components, properties	TPO type		
	1	2	3
EPDM, parts by weight	20	57	85
PP, parts by weight	80	43	15
$CaCO_3$, parts by weight	60	8	8
Irganox 1010, parts by weight	0.2	0.2	0.2
Tinuvin 327, parts by weight		0.15	0.15
N-110 black, parts by weight	3.0		
Calcium stearate, parts by weight	0.10		0.10
Process oil, parts by weight		7.0	64.00
T.S.,* MPa	16.55	13.50	5.50
U.E.,** %	200	740	750
Flexural modulus B, MPa	1240	415	
Shore hardness	62 D	54 D	65 A
Gardner impact (at −29 °C), J	20	36+	

* T.S. = Tensile strength.
** U.E. = Ultimate elongation.

tension set at 200 °C is not a requirement. Such applications can be found in automotive booster cable, flexible cord, and welding cable insulation.

Table 2. Suppliers of TPO

Trade Name	Producer	Location
Vistaflex	AES	Europe
Dexflex, Sequel, Depro, Ontex, Fortilene	Solvay	North America, Europe
Hifax, Adflex	Basell	North America, Europe
Flexathene	Equistar	North America
Kelburon	DSM	Europe
Keltan TP	DSM	Europe
Polytrope	A. Schulman	North America
Telcar	Teknor Apex	North America
Tefabloc	Cousin Tessier	Europe
Multiflex	Multibase	Europe
Vestolen EM	Pawtucket, RI, United States	North America
Vestoprene	Chem. Werke Hüls	Europe
Exxtral	ExxonMobil	North America
Plastomer	Yukong	Asia
Garaflex O	Alpha Gary	North America
Dong II	Deayoung	Asia
Zeonex, Zeonor TPO	Zeon	Asia
Silac	Lucent	North America
WPP TPO	Washington Penn	North America
Vyflex	Lavergne	North America
Novalast	Nova Polymers Inc.	North America
Elastamax	PolyOne	North America
Salflex	ABC Group	North America
J-Prene	J-Von	North America
Tamfer	Mitsui	Asia
Thermoran	Mitsubishi/JSR	Asia
P.E.R.	Tokoyama Soda	Asia

1.2.5. Processing

TPOs can be processed on most common thermoplastic equipment. Products can be formed by injection molding, extrusion, vacuum forming, injection blow molding, extrusion blow molding and so on. The versatility of the compounding TPO products permits designing of compounds to fit the available process and equipment.

1.3. Thermoplastic Vulcanizates

Thermoplastic vulcanizates made via a dynamic vulcanization (TPV) are rubbery engineered polymer blends with fabrication characteristics of a conventional thermoplastic and perform the properties of a conventional thermoset rubber.

TPVs offer a variety of practical advantages over conventional thermoset rubbers. These advantages are:

1. Little or no compounding or blending. Most TPVs are fully formulated and ready for use.
2. Simpler processing with fewer steps. TPVs have the processing simplicity of thermoplastic.
3. Shorter fabrication cycle time and consequently higher productivity for fabrication parts.
4. Recycling of scrap material (regrind). After each step, the scrap from thermoset rubber should be discarded while with TPVs all the eventual scrap is reground and used as virgin material.
5. Lower energy consumption
6. Better quality control and closer tolerances on finished articles
7. In most cases a density lower than a comparable thermoset rubber.

1.3.1. Dynamic Vulcanization

Dynamic vulcanization was discovered by GESSLER et al. [3]. In an attempt to improve the impact properties of PP they partially vulcanized halobutyl rubber in a polypropylene matrix under continuous mixing. Dynamic curing generates the same necessary cross-links or three-dimensional polymer structures as static curing.

In dynamic curing, however, these structures are generated in small rubber particles dispersed in the uncross-linked thermoplastic polymer matrix as a microgel. The formation of such dispersed-phase morphology depends on establishing a high degree of cure (CORAN et al. [5]). The rubber phase is fully vulcanized in a plastic matrix (thermoplastic vulcanizate). The rubber particles are in the order of 1–2 μm in size. Fully curing the rubber phase has led to significant improvement in the material properties including

1. Higher ultimate tensile strength
2. Lower tension and compression set
3. Better property retention at elevated temperature
4. Greater resistance to attack and swelling by fluids
5. Greater flexural fatigue resistance
6. More consistent processibility

Partially cross-linked blends give modest improvement [1, 2].

The effect of the size of the rubber particles and the degree of cure on material properties can be seen in Figures 2 and 3. By proper choice of the curatives, S. ABDOU-SABET et al. [6] demonstrated that rubber-like properties can be improved beyond those achieved by CORAN. Improvements in compression set, oil resistance, and the processing characteristics of the material were achieved by applying phenolic curatives (e.g., dimethyloloctylphenol). These improvements are beyond those expected from the state of cure. They probably are due to in situ formation of a graft copolymer between EPDM and PP that optimizes the interfacial adhesion between the rubber particle and the polypropylene matrix, thus allowing for better elastomeric properties. The graft copolymer could have been generated through the functionalization of PP with dimethyloloctylphenol, which then reacts with EPDM [16].

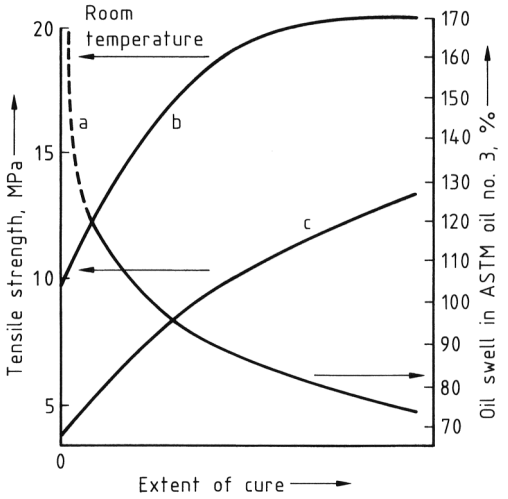


Figure 3. Effect of the degree of cure on mechanical properties
a) Percentage of swell in ASTM oil no. 3; b) Tensile strength at 100 °C; c) Tensile strength at room temperature

More importantly, significant improvement in processing was achieved over that obtained with the sulfur cure, as shown in Table 3. The use of dimethyloloctylphenol as curative allowed the generation of very soft TPV (as soft as 35 Shore A, with compression set approaching that of a thermoset rubber) while maintaining excellent thermoplastic processing. The poor processing characteristics of sulfur-cured TPV are due to phase growth of the dispersed rubber particles. The polysulfidic bonds generated during vulcanization undergo sulfur exchange reactions leading to significant coalescing of the rubber particles.

Other vulcanization systems are used to cure the rubber phase of TPV. Peroxide with an adequate coagent is the most common curing system after phenolic curatives. The role of

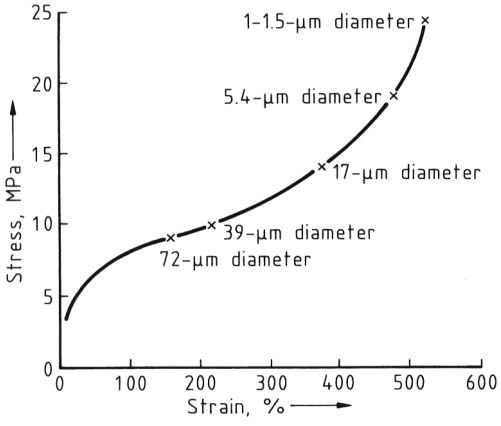


Figure 2. Effect of particle size on stress–strain relationship

Table 3. Effect of cross-linking agent on properties of EPDM rubber–PP TPV

Property	Cross-linking agent			
	None	Sulfur	Dimethylolalkylphenol	Peroxide
Hardness Shore D	36	43	44	39
T.S.,[a] MPa	4.96	24.3	25.6	15.9
M_{100},[b] MPa	4.83	8.00	9.72	8.07
U.E.,[c] %	190	530	350	450
ASTM oil no. 3 swell, %	disintegrated	194	109	225
Comp. set,[d] % (22 h at 100 °C)	91	43	24	32
Processing characteristics[e]	+	−	+++	+

[a]T.S. = tensile strength.
[b]M_{100} = modulus at 100% elongation.
[c]U.E. = ultimate elongation.
[d]Comp. set = compression set.
[e]+ = good; − = poor; +++ = excellent.

coagent is to enhance the cross-linking efficiency for the rubber phase. Apart from cross-linking efficiency, the use of a coagent can also affect the molecular structure of the cross-links. The most common type of coagents are polyfunctional organic molecules.

Another effective vulcanization system reported in several patents [17, 18] uses a hydrosilylation agent with platinum-containing catalysts. This cross-linking system works with rubber containing diene groups, preferably with sterically unhindered carbon−carbon double bonds.

A new cross-linking system to make TPV based on hydrolyzable organosilane-grafted rubber molecules is reported in [19–21]. The organosilane function is hydrolyzed during the dynamic mixing of rubber with the thermoplastic phase (PP) followed by condensation reaction with help of an organotin derivative catalyst such as dibutyltin dilaurate.

1.3.2. Production and Morphology

Melt mixing of the two polymers prior to dynamic vulcanization is the first requirement for a good TPV. The phase morphology of the uncross-linked blend will be influenced by the same variables discussed for TPO. S. Abdou-Sabet et al. [10] demonstrated for an 80 : 20 EPDM–PP blend that PP is the dispersed phase in an EPDM matrix. During dynamic vulcanization of such a blend, EPDM and PP have to undergo a phase inversion to maintain the thermoplasticity of the blend. In the initial stages of dynamic curing, two co-continuous phases are generated, and as the degree of cross-linking increases during mixing, the continuous rubber phase becomes increasingly elongated and then breaks up into polymer droplets. As these droplets form, PP becomes the continuous phase. This can be seen in the SEM electron micrograph (Fig. 4), in which the EPDM phase appears white and the PP phase is black. Photograph 4 B shows that both phases are co-continuous. Figure 5 shows a TEM electron micrograph of a very soft TPV where EPDM phase appears in black and PP in white color.

Reactor TPO can also be used as a raw material to make a TPV [22]. Reactor TPO, however, is not yet commercially produced with a diene function or other functionality in the rubber molecules. Therefore, cross-linking of the rubber phase can be performed only with peroxide. Peroxide curing is carried out while the necessary precautions are taken to protect polypropylene from chain scission and unzipping by the peroxy radical. Protection can be achieved via the incorporation of compounds in the blend that preferentially undergo reaction with the peroxides without affecting PP [23]. Such compounds include polyisobutylene, polybutadiene (PB), and polybutene. Even then, achieving full cure is quite difficult, and only partial curing of the rubber phase is usually accomplished.

To achieve the best improvement in properties of TPV, certain conditions must be satisfied:

1. The higher the crystallinity of the plastic component, the better are the mechanical and elastomeric properties

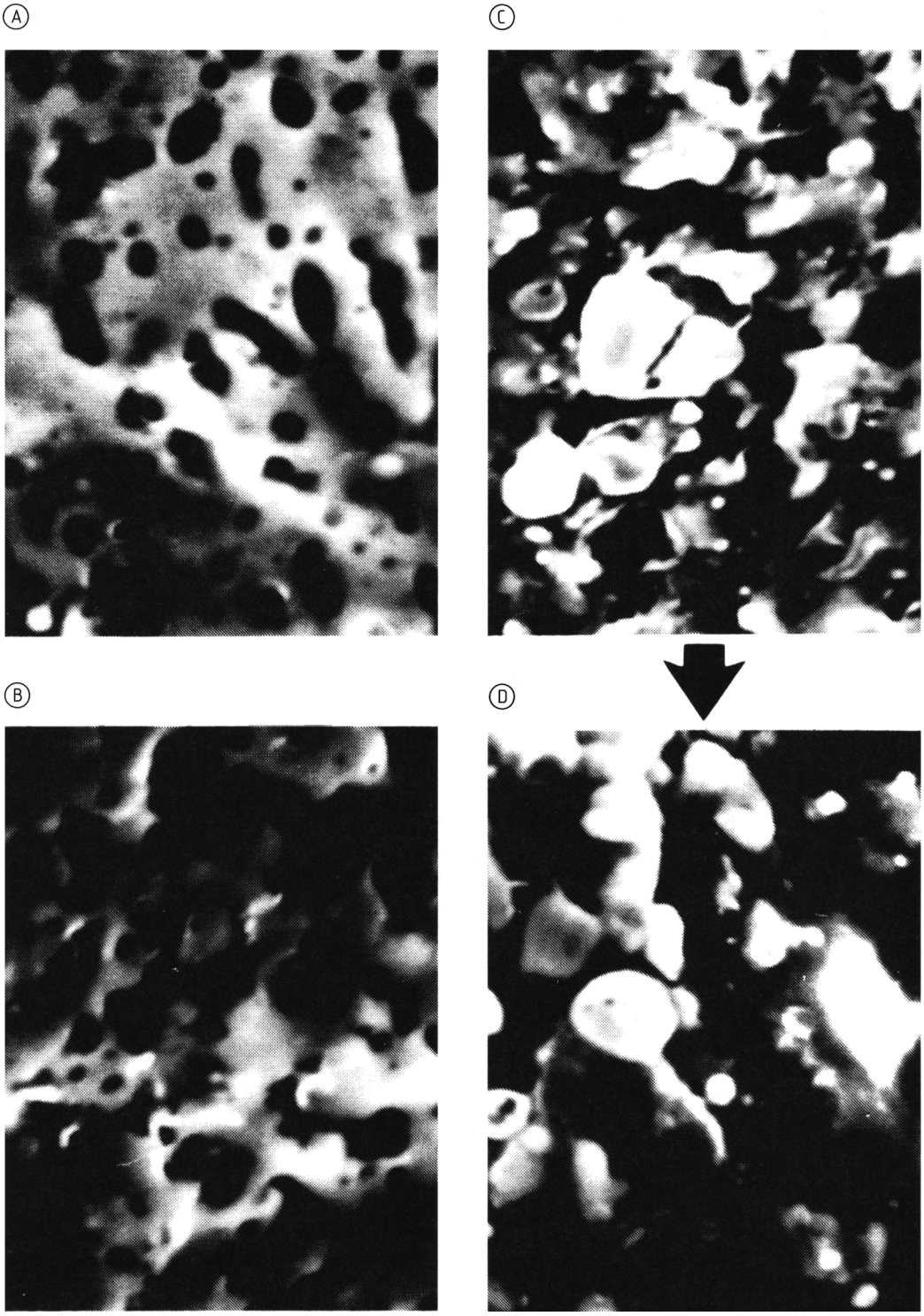


Figure 4. SEM-Electron micrograph of an 80 : 20 EPDM–PP thermoplastic vulcanizate
A) Unvulcanized blend; B) Partially vulcanized; C) Fully vulcanized; D) Fully vulcanized and diluted to 20 : 80 EPDM–PP

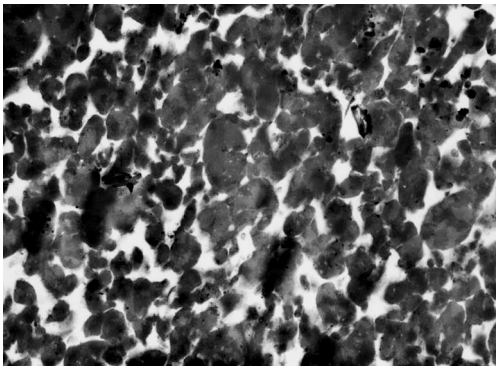


Figure 5. TEM-Electron micrograph of a very soft TPV based on EPDM/PP

2. The smaller the difference in critical surface tension between the rubber and the plastic, the smaller is the size of the dispersed rubber phase
3. The lower the entanglement spacing of the rubber chain, the better are the properties of TPV

1.3.3. Types

Theoretically it should be possible to make a large number of different classes of TPV by combination of at least one type of rubber with one type of thermoplastic. But practically, there is a limitation in the number of commercial TPV families due to limited number of compatible rubber–thermoplastic pairs. Obviously by use of adequate compatibilizing agent between a given rubber and a given thermoplastic, it is possible to expand the number of TPV families.

The discussion in this section is limited to those containing at least one polyolefin polymer.

EP/EPDM rubber–polypropylene based TPVs are the most common types of TPV [24]. The EP/EPDM–PP pair is the mostly used rubber (except for tire application) and thermoplastic material due to the excellent rubbery properties, heat and weathering resistance of EP/EPDM rubber and the excellent versatility, chemical resistance and inertness, and mechanical properties of PP. A broad range of vulcanization systems can be used as mentioned earlier to cross-link EPDM while only peroxide system can be used as cross-linking agent for EP rubber.

Natural rubber (NR)–polyolefin based TPVs [25] have been thoroughly investigated in an attempt to develop commercial products that take advantage of the attributes of natural rubber. Most of the research work was focused on *polypropylene-based material*. These NR–PP TPV thermoplastic natural rubbers (TPNRs) exhibited significant disadvantages compared to their EPDM counterparts and were not acceptable. Drawbacks stemmed from the poor thermal stability and the generation of excessive odor from the natural rubber component on processing at higher temperature. Again, partially cross-linked products exhibited co-continuous morphology, while those cross-linked to 95% or higher of the natural rubber phase showed dispersed-phase morphology. Properties of this type of TPV are listed in Table 4.

Natural rubber–polyethylene-based compositions [26] have also been studied extensively. These TPVs should possess good low-temperature flexibility and elastic recovery for low-temperature applications.

Butyl rubber–polypropylene based TPVs are another family of TPVs where a butyl or halobutyl rubber is used as elastomer component. In 1988, R. C. Puydak et al. [27] introduced *butyl rubber-based TPV* for applications requiring impermeability to oxygen and water vapor transmission. Such products are useful in sports bladders and blood vial stoppers.

Polymers with significantly different critical surface tension [28] can still be mixed together with the help of a compatibilizer to improve wetting characteristics or interfacial adhesion [29] between the two phases, thus allowing for the generation of preferred morphology prior to dynamic vulcanization. The application of compatibilization technology allowed the mixing of polar rubbers (e.g., *nitrile rubber* [30, 31] and *acrylate rubber* [32]) with polypropylene, followed by dynamic vulcanization to improve the properties as much as possible. Figure 6 illustrates the effect of the compatibilizer (maleated polypropylene) on polypropylene–ethylene–acrylate rubber TPV.

Table 4. Typical properties of thermoplastic natural rubbers

Property	Rubber type				
	1	2	3	4	5
Shore A hardness	50	60	70	80	90
M_{100},[a] MPa	3.1	4.1	5.3	6.3	8.2
T.S.,[b] MPa	6.5	8.8	11.2	13.2	15.3
U.E. at break,[c] %	285	315	340	370	405
Tear strength, die C (kN/m)	22	31	38	43	51
Tension set, %	9	10	14	18	23
Comp. set,[d] %					
72 h, 23 °C	26	28	31	34	39
24 h, 70 °C	30	35	36	41	55
22 h, 100 °C	38	42	43	47	57
Volume swell after 7 d in					
ASTM oil no. 1, 23 °C	14	9	9	7	
ASTM oil no. 2, 23 °C	19	13	12	9	
ASTM oil no. 3, 23 °C	71	53	47	35	
ASTM oil no. 1, 100 °C	101	80	67	61	
ASTM oil no. 2, 100 °C	151	123	108	82	
ASTM oil no. 3, 100 °C	190	164	139	116	

[a] M_{100} = modulus at 100% elongation.
[b] T.S. = tensile strength.
[c] U.E. = ultimate elongation.
[d] Comp. set = compression set.

Only a small amount of compatibilizers is needed for compatibilization. The function of the compatibilizer is analogous to that of a surfactant that emulsifies and stabilizes a water–oil mixture. Effective compatibilizers are generated by forming a graft or block copolymer; the structures of the blocks must be similar to the phases to be compatibilized. In that case, one block of the copolymer is soluble in the polyolefin resin, while the other is soluble in the polar rubber phase. Graft formation must be controlled to achieve the desired interfacial adhesion while preserving a dispersed phase morphology. Generation of primary chemical bonds between the two phases could lead to an interpenetrating network morphology. Such networks could result in thermoset characteristics and the loss of the thermoplastic processing advantage.

1.3.4. Processing

Thermoplastic vulcanizates or block copolymers that are made of soft and hard blocks are processed or fabricated by the same techniques normally used for rigid plastics. This enables the fabrication of elastomeric articles with improved efficiency and economy over

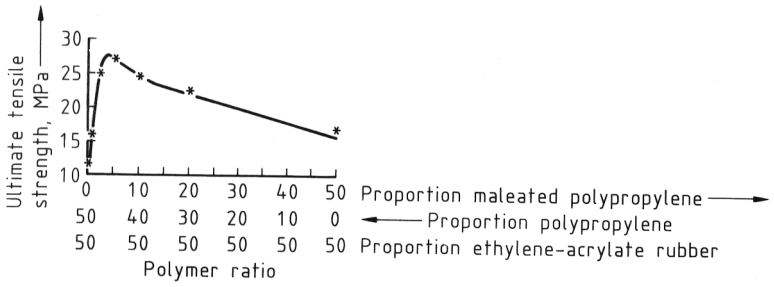


Figure 6. Effect of compatibilizer (maleated polypropylene) on ultimate tensile strength of polypropylene–ethylene–acrylate rubber TPV

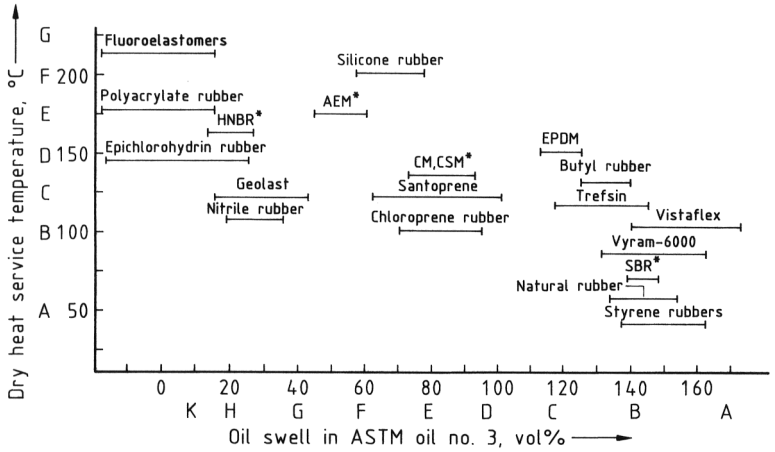


Figure 7. Classification of elastomers according to heat and oil performance
*AEM = ethyl acrylate–ethylene copolymer; CM = chlorinated polyethylene; CSM = chlorosulfonated polyethylene; HNBR = hydrogenated acrylonitrile–butadiene rubber; SBR = styrene–butadiene rubber; Geolast, Santoprene, Trefsin, Vistaflex, and Viram-6000 are registered trade names of commercial TPVs (see Table 5)

those of a conventional thermoset rubber. Scrap from TPV can be recycled readily, whereas thermoset rubber scrap is generally discarded, resulting in a sizeable cost penalty. The thermoplastic nature of TPV enables fabrication by methods unavailable to thermoset rubbers. These include blow molding, thermoforming, and heat welding. Thermoplastic vulcanizates have extremely non-Newtonian flow properties, and their viscosity is highly sensitive to shear [33]. At low shear rates, they flow very poorly; at high shear rates, however, they are quite fluid, enabling rapid injection molding cycles.

1.3.5. Performance and Product Positioning

ASTM D-2000 attempts to classify rubber products according to their performances in dry heat (dry heat service temperature) and ASTM oil no. 3 (see also → Rubber, 3. Synthetic Rubbers, Introduction and Overview). Conventional thermoset rubber occupies certain regions on a performance chart. Such classification is, however, insufficient because other characteristics such as dynamic properties, stress relaxation, barrier properties, UV resistance, adhesion, and colorability, also play an important role in material selection. Nevertheless, according to the ASTM D-2000 classification, EPDM–PP TPVs have performance characteristics superior to chloroprene (Neoprene) rubber. The properties of TPO, however, are considerably less elastomeric, and TPOs occupy a lower-performance category (Fig. 7).

1.3.6. Uses

Since their introduction in 1981, TPVs have found thousands of commercial uses worldwide. Generally speaking, these materials have been used in most rubber applications with the exception of tires. Thermoplastic vulcanizates are employed, e.g., in automotive and construction applications, in foods, hardware, appliances, business machines, mechanical rubber goods, and sporting goods, as well as electrical and medical applications. The uses can vary from the syringe stoppers in medical syringes to the rack-and-pinion boots on the steering mechanism of a front-wheel-drive automobile.

1.3.7. Commercial Products and Trade Names

Advanced Elastomer Systems who commercialized the first TPV (Santoprene) in 1981, is leading the market for this family of products. Global market demand for TPVS is forecast to

Table 5. Suppliers of thermoplastic vulcanizates

Trade name	Supplier	Polymer type	Degree of cure
Santoprene [a]	AES	EPDM–PP	full
Trefsin [b]	AES	butyl-PP	full
Dytron [c]	AES	EPDM–PE	full
Sarlink 3000	DSM	EPDM–PP	partial
Sarlink 2000	DSM	butyl–PP	partial
Hifax-XL	Himont	EPR–PP	partial
Vyram [d] 9000	AES	EPDM–PP	partial
Vyram [d] 6000	AES	natural rubber–PP	full
Milastomer	Mitsui	EPDM–PP	partial
Sumitomo TPE	Sumitomo	EPDM–PP	partial

[a]Santoprene is a registered trademark of Monsanto Company, licensed to Advanced Elastomer Systems, L.P.
[b]Trefsin is a registered trademark of Advanced Elastomer Systems, L.P.
[c]Dytron is a registered trademark of Advanced Elastomer Systems, L.P.
[d]Vyram is a registered trademark of Advanced Elastomer Systems, L.P.

increase 8 to 10% per year. The strong gain anticipated for TPVs results from an intense product development activity led by Advanced Elastomer Systems. Currently, a number of products are on the market (see Table 5). Only fully vulcanized materials achieve the full benefit of dynamic vulcanization.

2. Thermoplastic Polyurethane Elastomers (Polyurethane Rubbers, see → Rubber, 7. Synthesis by Polyaddition, Polycondensation, and Other Mechanisms, Chap. 2; see also → Polyurethanes)

2.1. Introduction

Thermoplastic polyurethanes (TPUs) are a group of elastic materials whose common structural feature is the urethane group −O−CO−NH− arising from the reaction between diisocyanates and long- and short-chain diols. The long-chain polyester or polyether diols form flexible soft segments in the temperature range of use, while the short-chain diols and diisocyanates form rigid or hard segments. Since soft and hard segments are arranged alternately along the molecular chain, TPUs belong to the $[AB]_n$-type block copolymers. Intermolecular interactions between the hard segments lead to the formation of glassy or paracrystalline hard domains, which, as physical cross-linking points, can be reversibly melted during thermoplastic processing. Variation in the ratios of soft and hard segments and monomers permits the production of materials in the modulus range of ca. 5–700 MPa, corresponding to ca. 60 Shore A to 70 Shore D. Because of their very good mechanical properties, especially extraordinary resistance to abrasion, the great choice of monomers available for the production of "tailor-made materials", and efficient thermoplastic processibility, TPUs have found a wide range of applications since their introduction to the market at the beginning of the 1960s. Further information on the production and properties of TPUs can be found in [34–37].

2.2. Raw Materials (→ Isocyanates, Organic; → Polyesters; → Polyoxyalkylenes)

The raw materials used in TPUs are diisocyanates, short-chain diols with molecular masses of 61–ca. 600, and long-chain polyester and polyether diols with average molecular masses between 600 and 4000, so-called polyols.

Diisocyanates. 4,4′-Diisocyanatodiphenylmethane (4,4′-methylenediphenyl diisocyanate, MDI) [101-68-8] is industrially by far the most important diisocyanate. It can be used to produce materials that offer the most favorable compromise between price, thermoplastic processibility, and mechanical properties. Other *aromatic diisocyanates* used are 3,3′-

dimethyl-4,4′-biphenyl diisocyanate (3,3′-tolidene-4,4′-diisocyanate, TODI) [38] and 1,4-phenylene-diisocyanate (PPDI) [104-49-4] [39]. Among the *aliphatic diisocyanates* the following are important: 4,4′-dicyclohexylmethane diisocyanate (H_{12}-MDI) [5124-30-1] (as the isomeric mixture) [40] and 1,6-diisocyanatohexane (hexamethylene diisocyanate, HDI) [822-06-0]. The aliphatic diisocyanates are much less reactive toward alcohols than MDI [41].

Short-Chain Diols. The most important short-chain diol used as a chain extender is 1,4-butanediol. For TPUs with improved dimensional stability at elevated temperature, 1,4-bis(2-hydroxyethoxy)benzene [hydroquinone bis(2-hydroxyethyl) ether] [104-38-1] is also used. The use of diol mixtures (e.g., with ethanediol or 1,6-hexanediol) gives products with a broader processing range [42].

Polyols. *Polyester Polyols.* The most important polyols are polyadipates of short-chain diols with two to ten carbon atoms. Butanediol, hexanediol, ethanediol, and mixtures of these diols are most commonly used. The resistance to hydrolysis of the polyol and TPU increases as the molecular mass of the diol increases. Polycaprolactones and polycarbonate diols with their good to excellent resistance to hydrolysis are also employed. The most widely used products have average molecular masses of 1000–2000. As polycondensation products, polyadipates have a broad molecular mass distribution [43]. They frequently contain unreactive ring esters formed as byproducts. For TPU production the acid number of the ester polyols should be as low as possible, preferably < 1 mg of KOH/g, because carboxyl groups react with isocyanates and impair the resistance to hydrolysis.

Polyether Polyols (→ Poly(propylene oxide) (PPO)raw material for thermoplastic elastomersPolyoxyalkylenes). Poly(tetramethylene oxides) are the most important polyether polyols for the production of TPUs. Poly(propylene oxides) [poly(propylene glycols)] and copolymers with ethylene oxide give products with poorer properties; normally, they are used together with polyester polyols. The molecular mass distribution of the polyether polyols follows the Poisson distribution and is thus considerably narrower than that of the corresponding polyesters. Poly(propylene oxides) have predominantly secondary hydroxyl groups as terminal units and are therefore considerably less reactive than other polyols.

Additives. Internal release agents, such as esters of montanic acid (octacosanoic acid), silicones, or amide waxes in quantities up to 2%, are used as *processing aids*. TPUs based on polyesters can be protected effectively against *hydrolytic degradation* by the addition of carbodiimides [44]. Protection against *microbial degradation,* for example on prolonged contact with soil, is also possible. Sterically hindered phenols and amines are used as *antioxidants,* mainly to protect against discoloration and degradation, particularly in the case of polyether TPUs at the high production and processing temperatures often required. Yellowing because of the effect of light can be slowed considerably through the use of *light stabilizers* such as benzophenones, sterically hindered amines (HALS), or benzotriazoles [45].

Plasticizers are used only to achieve hardness levels below ca. 70 Shore A [46–48]. Short glass fibers are used mainly to *reinforce* TPUs. Many additives, such as colorants, antiblocking agents, antistatic agents, and flame retardants, are supplied as concentrates.

2.3. Production

General. The industrial production of TPUs is carried out virtually exclusively in continuous, solvent-free processes [49]. According to Flory statistics [43] the required high molecular masses are achieved only at high conversions and an essentially stoichiometric ratio of NCO and OH groups. At an NCO : OH ratio < ca. 0.97, products with the required properties are generally not obtained [50]. Too high an excess of NCO can lead to cross-linking through allophanate and biuret formation even after long periods [51]. A prerequisite for maintaining exact stoichiometric ratios is the use of raw materials that are as pure—especially anhydrous—as possible and of exact metering devices. Prepolymer and one-shot processes

can be used to carry out the reaction (→ Polyurethanes, → Polyurethanes, Section 5.4). In the one-shot process, OH- and NCO-functional reactants are mixed with each other in one step. In the prepolymer process, a prepolymer with terminal NCO groups is first formed from a long-chain polyol and diisocyanate. This prepolymer is then mixed with the chain extender. Reactivity differences (e.g., between polyether polyols and butanediol) can be overcome with this process. The process used affects the segment length distribution and thus the morphology of the final product [52, 53].

Belt Process [54]. Liquefied raw materials are mixed continuously in a mixing head and poured onto a continuous belt, which passes through an oven heated to ca. 70–130 °C, where the reaction proceeds further. The congealed product is ground to irregular pellets. It can be melted in extruders, possibly along with additives, and formed into regular pellets. According to a modification of this process [55] the reaction is carried out to a desired degree of conversion, generally > 80%, on the belt, and the congealed mixture is then fed immediately into an extruder where the reaction is continued and the mixture is homogenized. Finally, the polymer is pelletized. In the belt process the temperature and residence times in the heated zone can be adapted to the requirements of the particular product.

Reaction Extruder Process. A twin-screw extruder serves as the reactor [56–59]. The screws are conrotating and can be set to the required shearing ratios by a combination of kneading and transporting parts. Temperature is controlled by using barrel sections that can be heated separately. The reactants and additives can be charged at different locations. In this way, a continuous prepolymer or one-shot process is possible without additional equipment. The bulk temperatures are generally > 200 °C. The product is extruded continuously and pelletized immediately after the head or after passage through a cooling area. As in the belt process, subsequent sieving and drying processes occur. In the reaction extruder process, finished pellets can be obtained from starting materials with the addition of all additives (including glass fiber or other thermoplastics) in one process step [60].

Comparison of Products. Because of different shearing and temperature conditions, the type of process used significantly affects the morphology and thus the processing properties of the products. Starting from identical raw materials more opaque products are formed in the belt process with larger hard segment domains that melt at higher temperature, whereas the reaction extruder process gives more transparent, lower-melting products.

2.4. Properties

Morphology [37, 61, 62]. The physical properties of TPUs are determined by their polyphase structure consisting of soft segments with very low glass transition temperatures, hard segments with high melting ranges, and mixed phases. This structure arises from the incompatibility of the hard and soft segments, which, on cooling from the melt during production and processing, leads to partial or complete separation of the phases that are bonded covalently with each other. The extent of separation and the phase structure are determined mainly by the stoichiometric composition of the polymer; the statistical distribution of the hard and soft segments [52]; the structure of the polyol [63], the diisocyanate and the chain extender, and the thermal history. The latter results from the kinetics of the separation and crystallization processes and from the cleavage and transurethanization during production, processing, and possible tempering of the product [64–67]. In polyethers, phase segregation is more pronounced than in polyesters and increases as the molecular mass of the polyol increases. Many investigations of the structure [65, 68, 69], phase interactions [69–71] and structure–property relationships of TPUs have been carried out, mainly on model substances [72–74]. Macroscopically, the soft segments determine the elastic ductility, the low-temperature properties, and the basic chemical properties, while the hard segments are important for dimensional stability at high temperature and the processing properties.

Table 6. Typical mechanical properties of TPUs with different hardness based on polyester polyols (example Desmopan, Bayer)

Property	Test standard (ISO)	Desmopan			
		385	345	359	372
Density, mg/m^3	1183	1.2	1.21	1.23	1.24
Hardness, Shore A/D	868	86 A	47 D	59 D	73 D
Tensile stress at break, MPa	527-1, -3	52	52	60	70
Elongation at break, %	527-1, -3	550	450	400	330
Tear resistance, kN/m	34-1	70	100	160	220
Flexural modulus, MPa	178		70	180	650
Abrasion loss, mm^3	4649	30	30	35	30
Compression set, %					
70 h/22 °C	815	30	25	30	
24 h/70 °C	815	55	42	60	

Technical Properties. By varying the proportion of the hard segment the modulus of elasticity can be varied over a range of ca. 5–700 MPa without the use of plasticizers or reinforcing agents. Typical contents of the long chain diol range from 30–75 wt%. Products containing no [41] or only very small proportions of soft segments can no longer be regarded as thermoplastic elastomers [75]. Table 6 gives an overview of some properties of different types of products.

Figure 8 shows the dependence of tensile modulus on temperature for adipate-based TPU with different hardness; typical stress-strain diagrams are shown in Figure 9.

High extension with very low residual extension, high tensile and tear strength, high moduli of elasticity at a given Shore hardness, and excellent abrasion resistance are common to all TPUs. Polyester TPUs are superior to polyether products with regard to strength and resistance to oxidation or swelling by oils, fats, and water, while they are inferior with regard to resistance to hydrolysis or microbial attack and impact resistance at low temperature. Hybrid types from polyester and polyether polyols combine the advantages of both types to a certain extent [76, 77].

Unstabilized TPUs based on MDI turn yellow through the action of light, initially without the impairment of mechanical properties. TPUs based on aliphatic diisocyanates do not show this discoloration. The lower temperatures of use are determined by the glass transition temperature of the soft phase (−20 to −60 °C), and the upper ones by the onset of softening of the

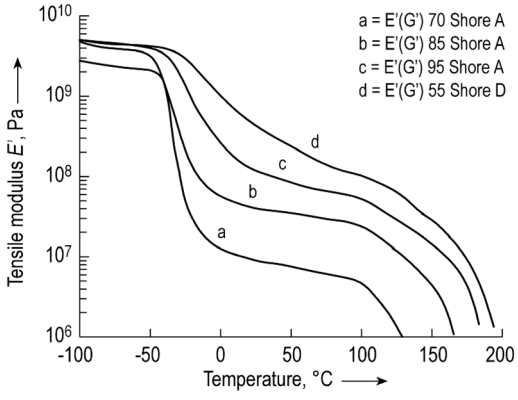


Figure 8. Tensile modulus of elasticity vs. temperature for polyadipate based TPU (example Desmopan, Bayer)

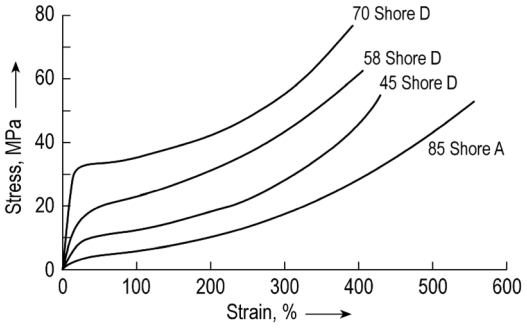


Figure 9. Stress-strain curves of polyadipate-based TPU with different hardness (example Desmopan, Bayer)

hard domains. Depending on the hardness, softening starts at ca. 80–100 °C (see → Polyurethanes). Hard products can be kept at up to ca. 120 °C for short periods. TPUs are soluble in polar, aprotic solvents such as *N,N*-dimethylformamide, methyl ethyl ketone, or *N*-methylpyrrolidone.

2.5. Processing and Use [34, 35, 37, 78, 79]

TPUs can be processed by all methods available for thermoplastics, such as injection molding, extrusion, blow molding, sintering, and calendering, although not all types are suited to every processing method. Melt temperatures range between 180 and 250°C, depending on hardness and other parameters. Typically, the melt viscosity of TPU is strongly temperature-sensitive. Generally only products with hardnesses up to ca. 50 Shore D can be extruded. Generally, extrusion becomes more and more difficult with increasing hardness above ca. 50 Shore D, due to formation of gel particles resulting from crystallization effects or side reactions.

TPUs are used in all those areas where their high strength and excellent resistance to abrasion, oil, and many other solvents are important. The large number of uses includes bases for shoe heels, soles and studs, or sports shoes, screens for the classification of minerals, rollers, tool parts, toothed belts, gaskets, electrical plugs, coupling elements, ear tags for animals, parts for car bodies, instrument panels, bearing shells, ski boots, seals, cable sheathings, tubing of all types, blown films, profiles, coatings, and medical equipment such as tubing and catheters. TPUs are also used for melt spinning of elastic fibers and modification of the impact resistance of polyacetals and as blend components for polycarbonates and acrylonitrile–butadiene–styrene (ABS) polymers [80, 81].

2.6. Economic Aspects

TPUs are produced in Europe, the United States, and Japan by the three large producers BASF, Bayer, and Noveon (quantities of > 20 000 t/a) and a number of medium and small producers (Table 7).

Table 7. Important producers of TPU and trade names

Region	Producer	Trade Name
Europe	Bayer	Desmopan
	Elastogran (BASF)	Elastollan
	Noveon	Estane
	Huntsman	Avalon, Irogran
	COIM	Laripur
	Mercquinsa	Pearlthane
USA	Bayer	Texin, Desmopan
	Noveon	Estane
	Huntsman	Krystalflex
	Dow	Pellethane
	BASF	Elastollan
Asia	Dainichi Seika	Resamine
	Nippon Miractran	Miractran
	DIC Bayer Polymers	Pandex, Desmopan
	BASF	Elastollan
	Hosung	Neothane
	SK Chemicals	Skythane

Almost all producers offer materials of differing hardness based on different polyols within several product ranges. In 2000, the estimated market volume was ca. 150 000 t/a. The regional distribution has a peak in Europe (40%), followed by North America (30%) and Eastern Asia (27%). The chances of growth are estimated to be positive in view of the possibilities for replacing rubber and plasticized thermoplastics by TPUs and the versatility of this class of materials.

2.7. Toxicology and Occupational Health

Since the production process involves polyaddition in a melt, very small quantities of byproducts are formed. Correctly dimensioned and efficiently functioning air extraction allows the permitted workplace concentrations for diisocyanates to be adhered to with certainty by producers and processors. Generally neither aromatic amines nor diisocyanates can be extracted from properly produced TPU articles. If only the allowable raw materials are used, TPUs comply with health authority guidelines for contact with foods (FDA: CFR 175.300, 175.105, 177.1680; European Commission Directive 2002/72/EC). Because of their good compatibility with blood and tissue, some products also fulfill the requirements of the ISO standard 10993/1 [82, 83].

3. Thermoplastic Copolyester Elastomers

3.1. Introduction

Thermoplastic copolyester elastomers are segmented block copolymers, consisting of repeating, high-melting, rigid "hard" blocks and amorphous, flexible "soft" blocks, which have a very low glass transition temperature. These polymers exhibit a remarkable combination of properties as a result of microphase separation of the hard block (in the form of crystalline domains) from the matrix of the amorphous soft blocks. The crystalline domains impart excellent mechanical properties (tensile strength, toughness, resistance to creep, good retention of properties at elevated temperature, etc.) and outstanding chemical resistance to the polymer. Concurrently, the amorphous domains provide exceptional flexibility and fatigue resistance over a broad temperature range. By varying the ratio of hard to soft blocks, products ranging from relatively rigid plastics to very flexible elastomers can be produced.

Copolyester elastomers are typically produced by condensation of an aromatic dicarboxylic acid or ester with a low molecular mass aliphatic diol and a polyalkylene ether glycol (molecular mass generally between 1000 and 4000) [84–86]. Reaction of the aromatic dicarboxylic acid with the diol leads to the crystalline hard segment phase, while the soft segment is the product of the diacid (or diester) and the long-chain glycol. Other combinations are possible, however (see Sections 3.4.2, 3.4.3).

3.2. Raw Materials

Polyester elastomers are produced from aromatic dicarboxylic acids or diesters, polyoxyalkylenes, and an excess of short-chain diols [84]. The most common raw materials follow:

Dicarboxylic Acids. *Terephthalic Acid* [100-21-0]. For production and properties, see → Terephthalic Acid, Dimethyl Terephthalate, and Isophthalic Acid.

2,6-Naphthalenedicarboxylic Acid [1141-38-4]. For production, see → Carboxylic Acids, Aromatic.

Polyoxyalkylenes. *Poly*(*tetramethylene oxide*); *poly*(*propylene glycol*) [25322-69-4]; *poly*-(*ethylene glycol*) [25322-68-3]; for production and properties, see → Polyoxyalkylenes.

Short-Chain Diols. *1,4-Butanediol* [513-85-9]. For production and properties, see → Butanediols, Butenediol, and Butynediol, Section 1.3.

Ethylene glycol [107-21-1]. For production and properties, see → Ethylene Glycol.

3.3. Production

(see also → Polyesters, Section 3.2.1, → Polyesters, Section 3.2.2, → Polyesters, Section 3.2.3, → Polyesters, Section 3.2.4).

Polyester elastomers are manufactured by a *multistage melt polymerization process*. Soluble titanium alkoxides are generally used as catalyst. In the first stage of the process, all reactants are mixed and heated at atmospheric pressure to 190–220 °C to form a low molecular mass prepolymer. In the latter stages the prepolymer is converted to high molecular mass polymer by increasing the temperature to 250–260 °C while lowering the pressure to < 133 Pa to distill off the excess short-chain diol. The degree of polymerization is monitored by the viscosity change of the molten reaction mass by measuring the torque on the reactor agitator. To protect the polyether ester from oxidative degradation during synthesis and in end-use applications, polymerization is usually carried out in the presence of an antioxidant. Hindered phenols such as Irganox 1098 (Ciba–Geigy) and Ethanox 330 (Ethyl Corp) or an aromatic secondary amine [i.e., Naugard 445 (Uniroyal)] are examples of antioxidants that are added during the preparation stage of the prepolymer. At the end of polymerization, the polymer is extruded, quenched, and cut into pellets. Predominantly hydroxyl and carboxylic acid end groups are produced by this process. The acid end groups are formed by the thermal cleavage of polymer chains or by degradation of a butanol end group with simultaneous elimination of tetrahydrofuran.

Both batch and continuous processes produce materials of sufficient viscosity to be fabricated by either extrusion or injection molding. However, a polymer with ultrahigh viscosity is

required for blow molding operations and in extrusion processes where very precise dimensions are required. Generally, the polymer viscosities required for these methods of processing cannot be obtained by a melt condensation process. One technique used to manufacture ultrahigh-viscosity copolyester elastomers is *solid-phase polymerization* [87–90]. In this process the solid polymer is heated to just below its melting point under reduced pressure. This leads to the reaction of acid and hydroxyl end groups or of two hydroxyl end groups with elimination of water or short-chain glycols. They diffuse out of the polymer, and the molecular mass increases. A second method of increasing viscosity is by polymer chain extension in a postcompounding step. In numerous examples [91–93], diisocyanates have been used as chain extenders to increase the viscosity of low and moderate molecular mass polyesters through the reaction of the polyester hydroxyl end group to form a urethane.

Thermoplastic copolyester elastomers are stable for an indefinite period of time. However, they will absorb moisture, reaching equilibrium with existing atmospheric conditions very rapidly. Since the ester group hydrolyzes at processing temperature, these products must be dried thoroughly prior to fabrication. The moisture content should not exceed 0.1 wt% when molding or extruding [94].

3.4. Microstructure and Composition of Segments

3.4.1. Short-Chain Ester Units (Hard Segments)

The hard segment employed in the polyester elastomer strongly influences the load-bearing capabilities and processing characteristics of the polymer. Because of its high melting point, rapid crystallization, and low cost, the predominant hard segment in commercial use is tetramethylene terephthalate (4GT), an ester of 1,4-butanediol (4G) and terephthalic acid (T). Hard segments based on ethylene glycol (2G) and terephthalic acid (2GT) are high melting and yield polymers with excellent physical properties. However, crystallization of this hard segment is very slow, requiring 36 h to completely develop the physical properties of the polymer. This limitation greatly reduces the usefulness of 2GT thermoplastic elastomers in injection molding and extrusion applications [95]. WOLFE [96] has prepared a series of copolyester elastomers with a wide range of short-chain diols and compared their properties (Table 8). The properties of the elastomers resulting from 2G, 3G, (1,3-propanediol), and 4G are very similar except for tensile and tear strength. Hard segments based on diols with five, six, and ten carbon atoms do not form high-melting crystals, and as a result, copolyesters made with these diols generally have inferior properties.

Substituting a cycloaliphatic glycol, 1,4-cyclohexanedimethanol, for 1,4-butanediol produces a high-melting polyether ester elastomer that crystallizes somewhat slower than one containing tetramethylene terephthalate but rapidly enough to be blow- or injection molded. Because of their slower crystallization characteristics, finished parts made of these elastomers are clear [97, 98].

Naphthalenedicarboxylic acid, in place of terephthalic acid, in combination with 1,4-butanediol provides products with improved thermal properties compared to their 4GT counterparts [99]. Some mechanical properties such as tear strength are also improved. A major limitation in using naphthalenedicarboxylic acid in

Table 8. Properties of 50% alkylene terephthalate–PTMO terephthalate copolymer as a function of diol structure [96]

Properties	Diol					
	2G	3G	4G	5G	6G	10G
Melting point, °C	224	198	189	106	122	106
Shore D hardness	46	48	48	32	33	35
Stress at 100% elongation, MPa	11.4	11.7	11.7	4.5	5.2	6.1
Tensile strength, MPa	45.5	22.8	48.4	15.4	13.5	15.5
Elongation, %	675	660	755	880	750	640
Tear strength, kN/m	42	15	48	25	18	7.8

commercial thermoplastic copolyester elastomers, however, is its high price.

3.4.2. Long-Chain Polyether Soft Segments

The long-chain polyether soft segments are formed by reaction of poly(ether glycols) and diacids. The predominant poly(ether glycols) used in commercial thermoplastic copolyester elastomers are poly(tetramethylene oxide) (PTMO) and poly(propylene glycol) end-capped with ethylene oxide (EOPPG). In general, the chemical resistance and certain physical properties of thermoplastic elastomers, such as tear strength, are influenced by the poly(ether glycol) segment. For example, products based on PTMO have much higher tensile and tear strengths and significantly better resistance toward oxidative degradation than polymers made with EOPPG. Melting point, modulus, and hardness are generally independent of the type of polyether employed.

Because of their polarity, polymers made using poly(ethylene glycol) (PEO) show the greatest water swell, yet the least swell in nonpolar oils [100]. These products have high moisture vapor transmission rates.

A comparison of typical properties of thermoplastic polyester elastomers containing soft segments based on PTMO, EOPPG, or PEO is shown in Table 9 [101].

Through a novel set of reactions, polyethers end-capped with amino groups [102] also have been utilized to manufacture copolyester elastomers. These polyoxyalkylenamines are first converted to acid-terminated polyethers by reaction with benzene-1,2,4-tricarboxylic acid, followed by copolymerization with terephthalic acid and a short-chain diol. Since the backbone of the polyoxyalkylenamines is based on ethylene and propylene oxides, the resulting thermoplastic elastomers have properties similar to EOPPG-based products [103].

Table 9. Properties of 57% 4 GT polyether elastomers as functions of polyoxyalkylene structure [101]

Properties	Polyoxyalkylene		
	PTMO	EOPPG	PEO
Nominal molecular mass	1000	1000	1000
Stress at 100% elongation, MPa	13.4	11.7	13.2
Tensile strength, MPa	47.2	27.2	42.6
Elongation, %	660	675	705
Tear strength, kN/m	62	23	31
Volume swell, % [97]			
Water (3 d/24 °C)	0.5	1.0	17.0
ASTM oil no. 3 (7 d/100 °C)	13.0	12.0	4.0

3.4.3. Hydrocarbon Soft Segments

Unsaturated straight-chain aliphatic carboxylic acids can be dimerized to form high molecular mass dicarboxylic acids, generally referred to as dimer acids [104]. When purified, these dibasic hydrocarbons have been used in place of poly (ether glycols) as soft segments in the preparation of thermoplastic copolyester elastomers. HOESCHELE [105] prepared several of these polymers and demonstrated the striking similarities with their polyether counterparts.

One major difference is that products based on dimer acid exhibit poor low-temperature properties because of their high glass transition temperatures. However, due to the hydrocarbon nature of the backbone, these polymers have much better heat aging characteristics and resistance to UV degradation. MCCREADY [106] has noted that the heat aging of thermoplastic polyether esters can be improved by using a mixed soft segment of dimer acid and poly(ether glycol).

3.4.4. Polyester Soft Segments

The use of low molecular mass polyester glycols as soft segments gives thermoplastic copolyester elastomers with improved heat aging characteristics and stability toward UV degradation compared to their polyether counterparts. However, the preparation of these products presents special problems because of the randomization that can occur between the hard and soft ester segments during synthesis. This negatively affects formation of blocks, and the resulting polymers are low melting with poor mechanical properties [107].

One approach to solving this problem is to react preformed hard and soft polyester segments in the presence of a titanate catalyst until the reaction mass becomes clear. At that point the catalyst is deactivated by addition of a phosphorus compound [108]. On further

processing into end use articles, very little ester exchange occurs between the hard and soft blocks, and as a result, parts with good mechanical properties are obtained. Generally, better results are obtained by chemical coupling of the blocks with diisocyanates [109] or acylating agents such as diacylbis(*N*-lactams). A detailed description of diisocyanate coupling between poly(tetramethylene terephthalate) and various aliphatic polyester diols has been published by VAN BERKEL [107]. After deactivating the catalyst used for formation of 4GT, coupling is carried out by using either toluene diisocyanate or methylene diisocyanate. A slight excess of isocyanate is used to obtain optimum mechanical properties. These thermoplastic polyester ester products show improved heat aging and UV resistance, but also have poor hydrolytic stability and stiffen much faster than polyether ester elastomers at low temperature.

3.5. Properties

Physical and Chemical Properties. Polymers prepared by the method described in Section 3.3 have the molecular mass distribution expected from a condensation polymerization. A number-average molecular mass in the range of 20 000–25 000 can be obtained. The two-phase hard–soft segment structure of these segmented polyesters has been demonstrated clearly by differential scanning calorimetry [110]. By varying the ratio of these two segments, thermoplastic polyesters ranging from soft, transparent rubber-like elastomers to semirigid plastics can be prepared. Melting points ranging from 140 to 220 °C have been reported for polymers containing 20–80 wt% 4GT [111]. As expected, the glass transition temperatures of this same series of polymers increase from −70 to 25 °C.

Thermoplastic copolyester elastomers have good to excellent resistance to hydrocarbons. Products containing > 50% 4GT are particularly well-suited for contact with oil, grease, or hydraulic fluids. These polymers offer better resistance to hot hydrocarbons than nitrile rubber.

Resistant to

- Nonpolar fluids
  - Oil
  - Fuels
  - Hydraulic fluids
- Polar fluids at room temperature
  - Glycols
  - High molecular mass alcohols
  - Weak acids and bases

Not resistant to

- Hot glycols
- Hot alcohols
- Strong acids and bases
- Amines

Resistance to polar fluids, including water, acids, bases, amines, and glycols, is a function of both the composition of the polymer and the temperature of use. At > 70 °C, polar fluids attack the polymer.

Mechanical Properties. The predominant hard segment in thermoplastic copolyester elastomers is poly(tetramethylene terephthalate). WOLFE [96] has shown that a hard segment content of 30 to 80 wt% produces a wide range of useful products (Table 10). A complete

Table 10. Properties of tetramethylene terephthalate–PTMO terephthalate copolymer as a function of tetramethylene terephthalate content [96]

Properties	Percentage 4GT				
	30	**40**	**50**	**57.4**	**80**
Melting point, °C	152	172	189	197	212
Shore D hardness	34	44	48	54	70
Stress at 100% elongation, MPa	5.9	8.3	11.7	13.4	24.4
Tensile strength, MPa	24.6	31.0	48.4	46.7	54.5
Elongation, %	900	830	755	660	535
Tear strength, kN/m	13	26	48	63	108

summary of mechanical properties for these elastomers has been published [112].

3.6. Blends

The low melt viscosity and good processing characteristics of thermoplastic elastomers facilitate their use in polymer blends to give products that are otherwise not easily obtainable. In many instances the properties of these blends are an average of the properties of the individual components, for example, the combination of poly (vinyl chloride) (PVC) and a polyester based on 4GT and PTMO [113, 114]. The addition of 10–30% of thermoplastic polyester elastomer provides PVC with improved heat resistance, low-temperature flexibility, and resistance to oils and fuels. Another important advantage is that the polyester elastomer cannot be extracted from the blend, which extends the service life of PVC molded parts.

In other instances, blends offer improved physical properties that are not obtainable by direct synthesis. Blending poly(butylene terephthalate) with a thermoplastic copolyester elastomer containing 58 wt% hard segment provides a polymer with improved low-temperature impact resistance compared to a directly synthesized polymer of identical composition [113]. The improvement in low-temperature properties is said to result from the incompatibility of the components of the resultant blend.

High-melting, crystalline thermoplastic copolyester elastomers can be softened (thus improving their low-temperature properties) by blending with an amorphous or very low melting polyester made from PTMO, 4G, and a diacid [115]. Since the melting point of the resultant blend is similar to that of the unblended crystalline thermoplastic, evidence that the two components of the blend are not miscible is good. Soft thermoplastic copolyester elastomers can also be prepared by blending the polyester with ethylene copolymers. Shih [116] reports blends with EPDM that retain the melting point of the polyester yet exhibit reduced stress–strain properties. In an extension of this work, blends of polyesters have been prepared with ethylene–carboxylic acid copolymers that had been partially neutralized [117]. This novel combination of polymers provides blends with enhanced melt viscosity, which greatly improves the processibility by blow molding and film extrusion of the thermoplastic copolyester elastomers.

Very efficient mixing is required to achieve good dispersion of polyester homopolymers and thermoplastic copolyester elastomers because of their incompatibility [113]. If the materials being blended differ greatly in polarity, homogeneous blends can sometimes not be achieved unless *compatibilizers* are employed. These compatibilizers generally contain reactive functional groups to assist in dispersing the components of the blend. In two separate examples, polycarbonate resins having improved flexibility and impact strength were obtained by blending with copolyester elastomers. To obtain optimum properties, polystyrene grafted with organosiloxanes or styrene–butadiene copolymerized with acrylic acid derivatives has been used to compatibilize the blend components [118, 119].

3.7. Uses

Thermoplastic copolyester elastomers are available in grades ranging from soft, rubber-like to semirigid plastics. This provides customers with products covering a wide spectrum of load-bearing characteristics, flexibility, and low-temperature properties. These materials are simple to process and can be made into high-performance products by a variety of polymer-forming processes, including injection molding, extrusion, blow molding, rotational molding, and melt casting. All thermoplastic copolyester elastomers have sharp, well-defined melting points, crystallize rapidly, and have good melt stability.

Grades having a Shore D hardness of 50–80 have excellent chemical resistance, which makes them suitable replacements for specialty rubber such as nitrile and epichlorohydrin rubbers in hose and tubing applications. They can be extruded into long, continuous lengths with relatively low wall thickness, thereby providing lightweight constructions. Compared to competing flexible polyamide compounds, no plasticizer is required, so the material remains flexible over long periods of

time. Overall, hose construction costs using thermoplastic copolyester elastomers are comparable to those using conventional rubber. This is due to the less expensive plastics processing techniques involved and the fact that thermoplastic copolyester elastomers require no postcuring [112].

The good impact strength and toughness, dimensional stability, and good paintability of thermoplastic copolyester elastomers have been utilized in automotive applications to replace metal in exterior automotive bumpers and front and rear end spoilers. The use of thermoplastic copolyester elastomers is not limited, however, to the exterior of automobiles. Overmolded interior parts such as door handles having good "feel" properties also have been commercialized [120].

In a very demanding application requiring excellent flexural fatigue resistance, thermoplastic polyesters have replaced polychloroprene rubber in constant-velocity joint boot bellows for front-wheel-drive automobiles. In addition to the necessary flexibility, this application also requires a product with good thermal properties, high tear resistance, very good low-temperature properties, and resistance to lubricating greases [121].

Thermoplastic copolyester elastomers containing either EOPPG or PEO soft segments absorb significant quantities of water. Because of this characteristic, thin films produced from these materials have high moisture vapor transmission rates. In addition to their use in laminated films for moisture-proof sports and rain wear [122, 123], these materials have also found application in the medical field [124]. By varying the EOPPG or PEO content, a wide range of moisture vapor transmission rates can be obtained. These products are suitable for medical wound care treatment, transdermal patches, and surgical drapes [124].

3.8. Producers, Trade Names

Thermoplastic copolyester elastomers were originally introduced by DuPont in 1972 under the trade name Hytrel and are manufactured by DuPont in the United States and Luxembourg, and by DuPont–Toray in Japan. Other U.S. producers include General Electric (trade name Lomod), Hoechst–Celanese (trade name Riteflex), and Eastman Chemical Products (trade name Ecdel). Both copolyether esters and copolyester esters are manufactured by DSM in the Netherlands, under the trade name Arnitel, and by Toboyo in Japan, under the trade name Pelprene. Pibiflex is manufactured in Europe by Montedison. More recent manufacturers entering this field include two South Korean producers, Kolon Industries (Kopel) and Cheil Synthetics (Esrel).

4. Thermoplastic Polyamide Elastomers

4.1. Introduction

Polyamides have been highly regarded thermoplastics for more than 50 years because of their high heat deflection temperatures, rigidity, and excellent resistance against solvents and aggressive chemicals. Their low melt viscosity permits easy processing, e.g., in injection molding. These and other positive properties have been transferred successfully to a greater or lesser extent to intrinsically softened polyamide elastomers.

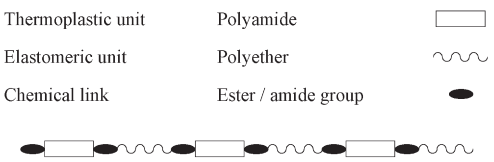
In the early 1980s, Chemische Werke Hüls (today Evonik) and Ato-Chimie (today Arkema) independently developed processes for the synthesis of multiblock copolymers containing sequences of different polyamides and various kinds of polyethers linked by either ester or amide bonds. These polyamide elastomers (PAE, TPE-A or TPA)–more often referred to as Poly Ether Block Amides (PEBA)–behave like thermoplastic elastomers, i.e., they combine elastomeric properties over a wide range of temperature with an easy thermoplastic processibility. Because their properties are closely related to the basic polyamides, PEBA can be assigned to the high-performance class of thermoplastic elastomers.

4.2. Raw Materials

Polyamide elastomers consist formally of difunctional crystallizable oligoamides (hard segments) and difunctional soft segments having a low glass transition temperature. In many

cases, this sequential co-condensation is also a viable preparative procedure. Various embodiments of this "internal plastification" concept have been described such as the use of (co-) polyolefin derivatives [125–131], polysiloxane soft segments [132], polyester soft segments [133, 134] and, in 2002, polycarbonate diols as soft segments [135]. However only polyether derivatives have become technologically significant on a commercial scale so far [136–140].

Polyether diols and diamines undergo condensation with dicarboxylic acid terminated oligoamides to form sequential multiblock copolymers via polyesterification or polyamidation, respectively [139, 140]. The typical structural patterns of these copolymers can be simply visualized as shown below.



Typical PEBA building blocks are polyamides with carboxylic acid terminal groups, e.g., poly(laurolactam) (PA12), and polyethers with hydroxyl terminal groups or polyethers with amino terminal groups, e.g., poly(tetramethylene glycol) (PTMG).

4.2.1. Oligoamide Unit

Oligoamides having carboxylic terminal groups are obtained by reacting a dicarboxylic acid with a lactam, e.g., Lactam 12 (laurolactam) or Lactam 6 (caprolactam), or an aminocarboxylic acid, e.g., Amino 11. In the case where a nylon salt is used, an excess of the dicarboxylic acid is employed [140]. The ratio between monomers and dicarboxylic acid excess controls the number average molar mass, M_n, of the oligoamide, usually around 600 to 4000 g/mol.

4.2.2. Polyether Units

Polyether diols applied in commercial PEBA grades are based on poly(ethylene glycol) (PEG), polypropylene glycol (PPG), and most frequently on poly(tetramethylene glycol) (PTMG or PTMEG), also named polytetrahydrofuran (PTHF) or poly(tetramethylene oxide) (PTMO). Poly(tetramethylene glycol) diols are commercialized worldwide, e.g., by Invista (Terathane) or BASF (PTHF).

Polyether diamines have been commercialized by Huntsman–formerly by Texaco–as Jeffamine D-grades (polypropylene glycol diamine) and as Jeffamine ED-grades (polyethylene glycol diamines), but are now commercialized under the tradename Elastamine R or H depending on the nature of the chain ends. PTMG-based diamines are also available.

4.3. Manufacture of Block Polyetheramides

The most important group of PEBA is derived from polyamide 12. The monomer basis is laurolactam which is converted to polyether block amides (PEBA) usually in a two-step process [136, 140]. The intermediate is an oligoamide dicarboxylic acid, which is then condensed to a PEBA by forming ester or amide links (Fig. 10).

4.3.1. Polyetherester Amides

The first step—ring opening polymerization of laurolactam—requires either acidolytic conditions, i.e., sufficiently high amounts of dicarboxylic acids [141] or the presence of water at high temperatures [142]. It may be advantageous to enhance the miscibility of oligoamide and oligoether by pressurizing the reaction mixture with water vapor [143].

The second polyesterification stage usually requires addition of a catalyst. Recommended classes of catalysts are dialkyltin(IV) compounds [140], phosphoric acid [144], tetraalkyl titanates [144, 145], tetraalkyl zirconates [146], tin(II) salts [147], or antimony oxide [148], the latter also being applied as a mixture with tin and phosphorus compounds [149].

A *single-step batch synthesis* has been described [144], in which both lactam polymerization and polyesterification are performed in the same reactor: Usual polyamidation equipment can be employed, such as stirred autoclaves, provided that sufficient water vapor pressure up to 25 bar (25×10^5 Pa)

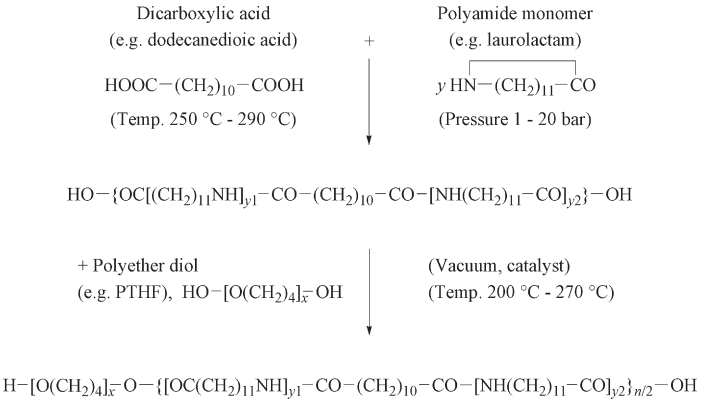


Figure 10. Two step formation of polyetheresteramide type PEBA

for the lactam cleavage can be applied and the reaction vessel can be evacuated for the second stage.

The one-pot synthesis, i.e., charging the reaction vessel with both polyamide forming monomers, including excess dicarboxylic acid and polyether diols or diamines is always the method of choice when polyamide monomers more reactive than laurolactam are used: Drastic reaction conditions necessary for the ring opening of laurolactam—high temperatures over an extended period of time may cause thermal degradation of polyethers—can be avoided in these cases, in particular for caprolactam [150], aminocarboxylic acids [151], nylon salts, or equimolar mixtures of diamines and dicarboxylic acids [152] as polyamide-forming monomers.

A continuous process applying *thin layer evaporation* has been described by Atofina (now Arkema) [153–155], it requires, however, a separate synthesis of oligoamide dicarboxylic acid. This dicarboxylic acid-terminated oligoamide is fed with a stoichiometrically equivalent amount of polyether diol via a static mixer into one or several thin-layer reactors equipped with rotating film-forming wipers. These elements are inclined to promote a reverse flow in the initial phase of the polyesterification, whereas in the final stages they are positioned in a way to promote downstream flow of the higher viscous melt [153]. The published procedure makes use of three sequential thin-layer reactors [153].

4.3.2. Synthesis of Polyetheramides

Condensation of oligoamide dicarboxylic acids with polyetherdiamines can be performed without the necessity of applying vacuum in the final phase of polycondensation [156, 159].

Polyamide elastomers based on this structural pattern have been developed by Ube, Ems (Grilamid ELY), and former Rhône Poulenc (Dynyl) [156, 160]. An additional benefit of the amide link instead of the ester group is the increased hydrolytic stability. The synthesis is usually performed batchwise in pressurized polyamide reactors. Both a single-step process [161] and a two-step process comprising a separate preparation of oligoamide dicarboxylic acids [162] have been described by Ube. Cocondensation of polyetherdiamines with low molar mass aliphatic diamines has also been described [163]. In the Ube synthesis a dimeric fatty acid is preferred both as a nylon chain terminator and as a link between polyetherdiamine segments.

Hybrid elastomers based on polyetheramides terminated with both amino and hydroxyl groups have been described [164, 165]: Reaction with isocyanates converts these polyetheramides into polyurethanes or polyureas, respectively.

Polyetheramides with very high melting points derived from nylon 46 segments have been prepared [166, 167] employing polyethers terminated by two primary amine moieties.

Table 11. Variation of block types and correlations with PEBA properties

Variable	Influenced property
Type of polyamide block:	melting range (upper service temperature)
	water absorption
PA 12, PA 11, PA 6, PA 66, PA 612	chemical stability
	density
PA 11	enhanced elastomeric properties
Length of polyamide block	melting range (upper service temperature)
	crystallinity
	transparency
Type of polyether block:	glass transition temperature (lower service temperature)
	water absorption, water permeability
PTMG (or PTHF), PEG, PPG	electrostatic properties
	chemical and thermal stability
Block composition Polyamide/polyether	rigidity, hardness, flexibility

4.4. Physical and Chemical Properties

4.4.1. Block Variations

The properties of PEBA can be varied and determined by the selection of both hard and soft block types (Table 11). The choice of hard blocks defines the upper service temperature, corresponding with the melting temperature of the base polyamide. Also water absorption, chemical stability, and density are determined by the chosen polyamide. The length of the hard blocks is controlled by the amount of chain-limiting dicarboxylic acid and affects the melting range, the crystallinity, and the transparency of the PEBA.

The choice of the soft segment type determines the glass transition temperature and, hence, the lower service temperature. Using hydrophilic soft segments, such as polyethylene glycol, the moisture absorption and permeability is enhanced and permanent antielectrostatic as well as breathable properties induced. Using polyethers with amino end groups, the resulting polyetheretheramides have higher hydrolytic stability.

Finally, the block composition of polyamide and polyether blocks can be varied in a wide range and the resulting products encompass an outstanding range of rigidity. This is demonstrated in Figure 11 in terms of Shore hardness. PEBA with high polyamide block contents have a Shore hardness D up to 72, i. e., close to polyamides themselves. With lowest polyamide block contents PEBA can be very soft with Shore hardness A down to 60, hence, in the domain of soft rubbers. Such soft grades cannot be achieved using other TPEs.

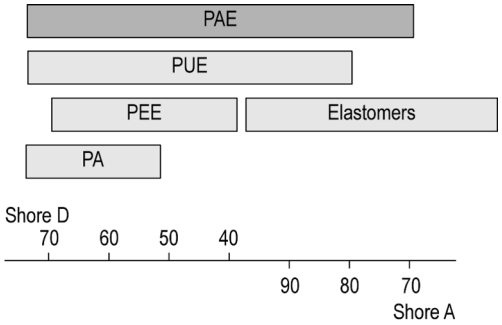


Figure 11. Range of hardness for PEBA
PEBA = Polyamide elastomer; TPU = Polyurethane elastomer; PEE = Polyester elastomer; PA = Polyamide

Figure 12 shows a series of tensile stress-strain curves of PA 12–PEBA with varied PA 12 block content. PEBAs rich in PA 12 exhibit the

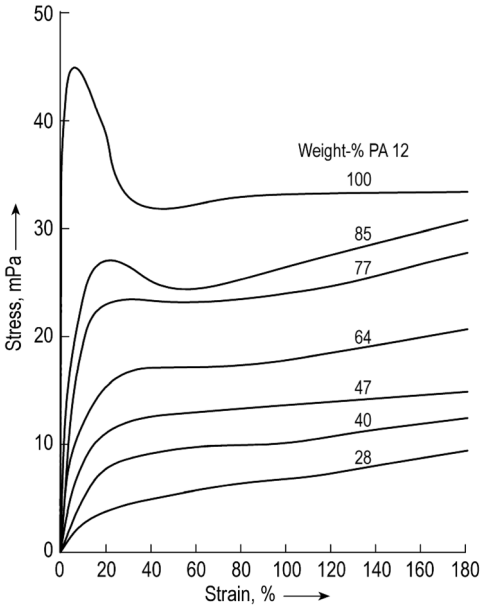


Figure 12. Stress–strain diagrams of PA 12–PEBA from tensile tests according to ISO 527

typical behavior of thermoplastics with yielding. With increasing polyether content there is a transition to more and more elastomeric characteristics. Better elastomeric properties for rigid grades can also be obtained when using PA 11 blocks (PEBAX, R = new range from Arkema) [168]. Indeed, PA 11–PEBA usually crystallizes in two arrangements: a triclinic one as well as an hexagonal one. Since the triclinic phase can change into a pseudo-hexagonal one, under thermal or mechanical stress, PA11–PEBA grades are more elastic, have better impact resistance and even the more rigid grade does not show any yield on their tensile stress-strain curve.

4.4.2. Morphology

The specific mechanical properties of PEBA are strongly determined by the phase morphology of the principally incompatible polyamide and polyether blocks. Four different phases have been identified by thermo-analytical methods and electron microscopy [169–171]. Differential scanning calorimetry revealed two melting signals, the dominant one corresponding with the melting of PA 12 blocks, the other one with a little content of crystallized PTMG blocks (Fig. 13). With decreasing level of PA 12 hard blocks, the melting temperature drops indicating that the size of crystallites is becoming smaller. Amorphous phases have been

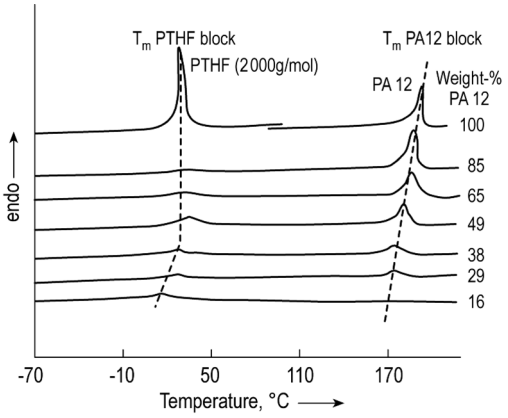


Figure 13. Melting point diagrams (DSC) indicating two crystalline phases in PA 12–PTMG–PEBA (T_m = melting temperature)

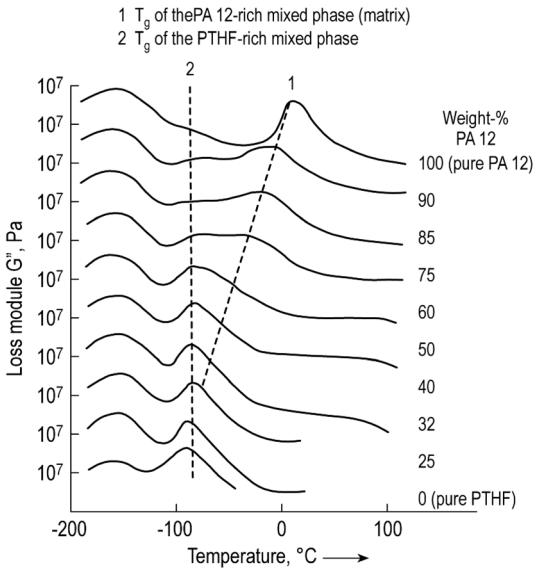


Figure 14. Loss modulus curves from torsional vibration analyses indicating two amorphous mixed phases in PA 12–PTMG–PEBA (T_g = glass transition temperature)

detected by torsional vibration analysis. Figure 14 shows the loss modulus plots of the investigated PA 12–PEBA series. The maximum values of the plots correspond with the glass transition temperatures of amorphous phases. In a range of higher PA 12 block content, glass transition temperatures of two mixed amorphous phases with different block compositions are observed. At higher PTMG block content, the loss modulus plots are dominated by the signal of a PTMG-rich mixed phase.

With the aid of highly sophisticated contrast-enhancing techniques, transmission electron microscopy (TEM) images were obtained, demonstrating the unique morphology in PEBA. Crystallized lamellae of PA 12 blocks form the same spherolitic superstructures as known from polyamides (Fig. 15). These crystalline superstructures form an interpenetrating reinforcing "physical network" for the amorphous mixed phase of PA 12 and PTMG blocks between the lamellae. At lower PA 12 content, only fragments of spherolites or single lamellae can be formed with a weak reinforcing effect on the soft amorphous PTMG-rich mixed phase (Fig. 16). For completeness, it should be mentioned that PTMG-rich PEBA molecules build



Figure 15. Transmission electron micrographs showing spherolitic superstructures of crystallized lamella in PA 12–PTMG–PEBA (PA 12-rich PEBA)

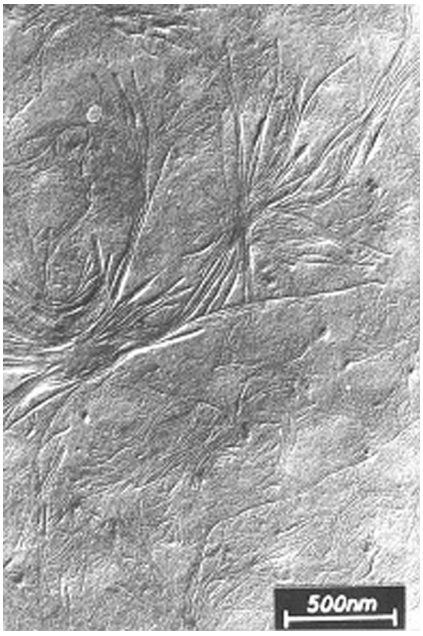


Figure 16. Transmission electron micrographs showing spherolitic superstructures of crystallized lamella in PA 12–PTMG–PEBA (PTMG-rich PEBA)

up a separate disperse phase due to the strong incompatibility between both blocks. This is the second amorphous mixed phase with the low glass transition temperature observed in torsional vibration analysis.

A number of the unique mechanical properties which distinguish PEBA from all other TPE can be deduced from the interpenetrating network of crystallized polyamide blocks. This is valid, for example, for the lower temperature dependence of stiffness and elasticity compared to other TPEs.

4.4.3. Outstanding Properties

The specific advantages of PEBA (mainly PA 12–PTMG, unless otherwise mentioned) compared with other TPE can be summarized as follows:

- Low density: 1.01–1.03 g/cm^3 (TPU, copolyester elastomer: 1.14–1.25 g/cm^3),
- High stability against chemicals and solvents,
- Easy processing, coloring, and overmolding,
- Excellent ability to be decorated by thermodiffusion printing,
- Excellent cold impact strength,
- Wide range of hardness and flexibility,
- High elasticity and resilience,
- Low temperature dependence of mechanical properties,
- Excellent abrasion resistance (only surpassed by TPU),
- Highest service temperatures (especially PEBA with PA 6 blocks).

Some of the outstanding properties of PEBA are listed in Table 12 for a series of commercial products (PEBAX® from ARKEMA) based on PA 12 and PTMG: The density (close to 1 g/cm^3) is up to 20% lower than that of competing TPE. The flexural modulus of PEBA comprises a full decade of magnitude, from about 10 to 500 MPa. The cold impact strength of PEBA is excellent, as demonstrated by Charpy notched impact data at −30 °C in Table 12. Very soft and medium soft PEBA do not break at all, stiffer

Table 12. Major properties of PA 12-PEBA compared with PA 12

Properties	Test-method	Unit	PA 12-PEBA (PEBAX) with Shore D hardness (ISO 868)						
			27	33	42	54	64	69	69
Density at 23 °C	ISO 1183	g/cm^3	1.00	1.00	1.00	1.01	1.01	1.01	1.01
Flexural modulus	ISO 178 −1/−2	MPa	12	21	77	170	285	390	513
Charpy notched impact strength at −30 °C	ISO 179	kJ/mm^2	No Break	No Break	No Break	No Break	20	20	10
Vicat softening temperature Method A/10 N	ISO 306	°C	58	77	131	142	157	164	164

grades with Shore hardness D > 60 and tensile moduli above 250 MPa have still excellent toughness data.

The uptake of water is a crucial property for many PEBA applications. In this regard PEBA based on PA 12 and PTMG blocks do not differ significantly from PA 12 which has the lowest water absorption of all polyamides. With increasing polarity of polyamide and polyether building blocks the water uptake of PEBA increases dramatically (Table 13). This creates a strong influence on the electrical behavior of the PEBA. PEBA with PA12 and PTMG blocks are good insulators, while, e.g., PEBA based on PA 6 and poly(ethylene glycol) blocks are permanent antielectrostatic due to their fast and high moisture uptake from the ambient air. High water uptake of PEBA is not tolerable for applications where dimensional stability of parts is crucial. On the other hand PEBA with higher absorption and permeability of moisture have found applications as, for instance, antistatic modifier and for moisture-breathing film.

4.4.4. Chemical Resistance

Due to their close relationship to polyamides, PEBA exhibit high stability against many chemicals and solvents compared with other TPE. The stability of PEBA against diluted hydrochloric and sulfuric acid as well as bases should be especially noted. Rigid PEBA grades show only low swelling in ASTM oil, even at 100 °C. This is also valid for hydraulic liquids, aliphatic solvents, and alcohols. With softer PEBA grades, the swelling in aromatic solvents and fuels is rather high; however, the mechanical properties are not affected dramatically.

4.4.5. Processing

PEBA can be processed on standard equipment and with processing conditions usual for polyamides. For injection molding of PA 12-PEBA melt temperatures of 190–230 °C are recommended for rigid grades and 170–210 °C for softer grades. Mold temperatures of 20–40 °C are suitable for all grades. Because of the very low melt viscosity and rapid crystallization, short injection cycle times are possible.

At extrusion temperatures of 210–230 °C, thin sheets, hoses, tubes, profiles, plates, and monofilaments can be processed. Other processing techniques applied for PEBA are blow molding, rotational molding, thermoforming, and powder coating.

Table 13. Density and water absorption of various PEBA in comparison

TPE-type	Density	Water absorption (saturated)	
	ISO 1183 g/cm^3	20 °C/65% R.H., wt%	20 °C/24 h water storage, wt%
PA 12-PTMG	1.01–1.03	0.5	1.2
PA 6-PPG	1.10	2.4–2.8	6.1–6.4
PA 6-PEG	1.14	4.5	120
TPU*	1.14–1.25	0.1–5	0.5–15
Copolyester TPE*	1.17–1.25	0.2–0.4	0.6–0.8
Rubber*	>1.20	0.6–0.8	0.1–15

* Strongly varying for different types.

4.5. Uses

Since the polyamide block building monomers are rather expensive because of their multistep synthesis, PEBA are ranking at the high end of the scale of prices of TPE together with TPU and copolyester TPE. As a consequence, they are only used where one or more of their outstanding product and processing properties are required.

Polyamide elastomers are especially acknowledged for the construction of lightweight soles for specialists sport shoes. PEBA are used primarily because of their low density, but also because of their good resilience, cold impact strength, and low temperature dependence of flexibility. The excellent processing and overmolding properties allow high sophisticated sole constructions. This has been applied for designs with sole parts of different stiffness and for decorative effects in overmolding of parts with different colors (Fig. 17). Even PA 12-based composites and PA 12-coated metal sheets have been incorporated in sole constructions. Recently, the combination of overmolding and decorative printing techniques have been applied for new sports shoe soles constructions.

Another main application field for PEBA are winter sports goods such as lightweight ski boots or PEBA films for decorative ski and snowboard surfaces. By means of thermodiffusion printing processes brilliant decorations are applied often on the bottom side of a PEBA film. The colorants penetrate only about a 100 μm into the film of typical 500 μm total thickness. The film itself then acts as a protective layer for the decoration and the print motifs are almost indestructible (Fig. 18).



Figure 17. Sport shoe soles with overmolded PEBA parts and PA 12 composites

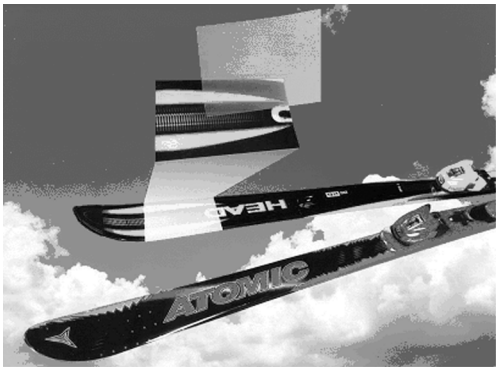


Figure 18. Design of skies with decorative PA12–PEBA films, sublimation printed from the bottom side

Soft PEBA grades, with Shore hardness D below 40, have been used in such applications as straps of watches. Beside flexural properties, the dermatological compatibility, UV stability, and translucence of PEBA is striking. For frames of sunglasses, dermatological compatibility, easy processing, and coating stability of these elastomers is important.

Medical uses are, e.g., catheters, or controlled drug release carriers. Hydrophilic grades are applied for moisture breathable film in surgical drapes and garments.

The excellent processing and demolding properties and the dimensional stability of PEBA make them well suited for manufacturing precise moldings. PEBA gear wheels (Fig. 19), for example, contribute to the noiseless operation of tape recorders or CD players.

For permanent antistatic housings, hydrophobic PEBA can be compounded with special conductive carbon blacks which have still good impact resistance in spite of the necessary high loadings. Hydrophilic PEBA grades can also be used as antistatic additives to reduce the surface resistivity of various thermoplastic resins (PE, PP, ABS, PS, PMMA, PA etc). Applications are permanently antielectrostatic parts, for example, castor wheels (Fig. 20), conveyor belts, rollers, and paint spray hoses, clean room equipment, surface and flooring, containers for flammable or



Figure 19. Precisely molded PEBA wheels for noiseless gears

explosive goods, carried/reel tapes, medical (inhalers, bags).

4.6. Trade Names

PEBA play only a niche role in the TPE market due to their high-end positioning. The main and historical suppliers of PEBA are Evonik AG/Germany (Vestamid E-grades, Shore hardness D 30–70, PA 12 base) and Arkema/France (Pebax, Shore hardness D 25–72, PA 12, PA 11, and PA 6 base, including hydrophilic and transparent grades). Other suppliers are EMS Chemie/Switzerland (Grilamid ELY, Grilon ELX, Shore hardness D 50–63, PA 12 and PA 6 base), Ube/Japan (Ubesta, selected grades), and Sanyo/Japan (Pelestat, hydrophilic grades).



Figure 20. Tough antielectrostatic PEBA parts highly loaded with conductive carbon blacks

5. Styrenic Block Copolymers

5.1. Introduction

Thermoplastic elastomers known as styrenic block copolymers (SBC) have emerged from developments and research in the organometallic-initiated polymerization of diene monomers in hydrocarbon solvents (→ Rubber, 5. Solution Rubbers). Commercial block copolymers are essentially based on styrene, butadiene, and isoprene monomers. The first commercial quantities were produced by Shell in 1964 in its production plant in Torrance, Ca., and marketed under the trade name Kraton [172]. Worldwide capacity for styrenic block copolymers in 1993 was estimated at 500 000 t/a.

Styrenic block copolymers combine rubber performance with thermoplastic processibility on the basis of their specific structure. Anionic polymerization allows the selective polymerization of butadiene or isoprene and styrene in such a way that the resulting polymer is essentially a polybutadiene or polyisoprene molecule tipped at both ends with a polystyrene molecule [173]. Such a structure is commonly identified as ABA, where A represents the plastic and B the elastomer. More specific notations used are SBS or SIS polymers. Styrenic block copolymers with saturated rubber blocks are produced from SIS or SBS precursors by selective hydrogenation. This process converts the polyisoprene into poly(ethylene–propene) and the polybutadiene into poly(ethylene–butene). To provide rubber performance, the volume fraction of plastic (polystyrene) in these structures must be < 50%, and commercial hydrogenated grades usually contain around 30%. Newer variants of the styrene–ethylene/butene–styrene S–E/B–S or styrene–ethylene/propene–styrene S–E/P–S polymers are functionalized with maleic anhydride or other reactive comonomers. Functionalization levels are between 0.2 and 5% and the reactive group is grafted onto the rubber mid block [174].

5.2. Synthesis

The first step in the production of SBCs is activation of purified styrene in a hydrocarbon solvent with butyllithium and subsequent

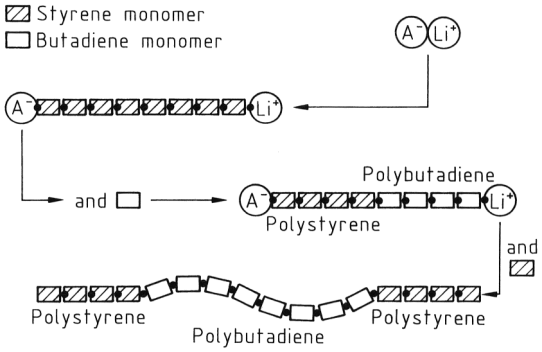


Figure 21. Formation of block copolymers by anionic polymerization (A^- = butyl anion)

anionic polymerization. The molecular mass of the first polystyrene block is determined by the butyllithium : styrene ratio (see Fig. 21). The formed living polymer, PS–Li, is then reacted with purified butadiene to form the second block. When all the diene has been converted, two routes can be followed to complete the formation of SBC:

1. Addition of a coupling agent to produce linear or branched copolymers
2. Addition of a second amount of styrene monomer to form the third block

Technically feasible coupling agents include di-, tri-, tetra-, or multifunctional compounds that allow formation of a multitude of different polymer structures [175].

The procedure for production of the precursor for *saturated block polymers* is the same. To ensure a rubbery mid block after hydrogenation in the S–E/B–S polymer, a modifier is added during polymerization of the polybutadiene mid block to increase its vinyl content (1,2-content) (→ Rubber, 5. Solution Rubbers) to approximately 40% which will ensure optimum elastic properties after hydrogenation. This allows optimization of the ratio of ethylene and butene units in the hydrogenated polymer. After preparation of the precursor, polymer solution is transferred to the hydrogenation section where the double bonds of the polydiene are reacted with hydrogen in the presence of a catalyst.

Functionalized saturated block copolymers are made by extruder grafting of an S–E/B–S or S–E/P–S molecule. The polymer is contacted in an extruder with a peroxide to create free radical sites along the rubber mid block. These react in the extrusion step with a compound containing the functional group and a group able to react with the free radical sites (e.g., maleic anhydride). The process requires careful optimization of the amount of peroxide and reaction conditions to minimize polymer degradation.

The result of the polymerization process is a solution of polymer in hydrocarbon solvent. At this stage, additives such as stabilizers, antioxidants, or plasticizers can be added to the solution which is subsequently converted into solid polymer during finishing. The following systems are used industrially:

Direct Desolventizing. The polymer solution (cement) is introduced directly into a special vacuum extruder; the solvent is evaporated into a recovery system and the extruded polymer melt is face-cut and cooled at the die head of the extruder to form compact transparent pellets.

Coagulation with Steam. Cement is pumped to a vessel where steam is passed into the solution. The resulting coagulate separates from the solvent, and the polymer–water mixture is dried to remove water. The usual form resulting from the coagulation–drying route is referred to as crumb.

5.3. Properties

Thermoplastic rubbers based on styrenic block copolymer can be considered polybutadiene [or polyisoprene, poly(ethylene–butene), or poly (ethylene–propene)] tipped with polystyrene end blocks. Polybutadiene (butadiene rubber, BR) and polystyrene of sufficiently high molecular mass are incompatible, which forms the basis for the performance of these thermoplastic rubbers. At temperatures above the softening point of polystyrene, the SBC molecule is quite mobile and can be melt-processed by, e.g., extrusion or injection molding. On cooling, the PS end blocks separate from the BR mid blocks, and two distinct phases are formed. The separate, discrete phase of the PS domains acts both as a cross-linking material and as a reinforcing filler analogous to the sulfur and carbon black in vulcanized rubber. Figure 22

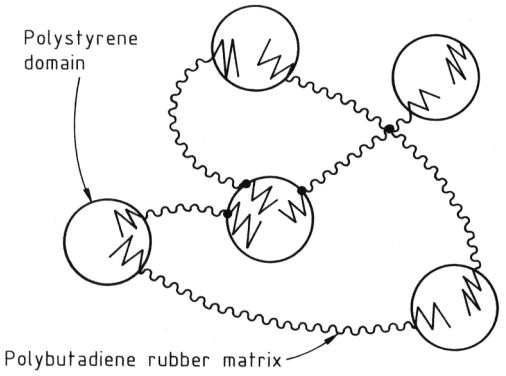


Figure 22. Schematic phase structure of an SBS block copolymer

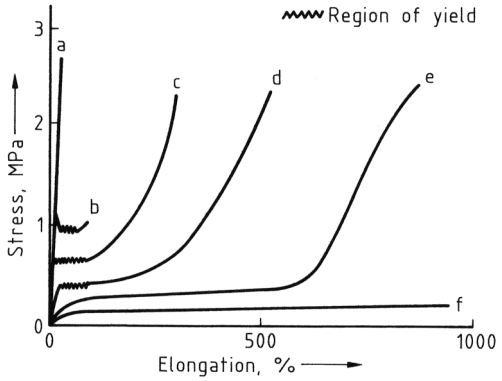


Figure 23. Stress–strain curves for various SBS copolymers
a) 80% styrene; b) 65% styrene; c) 50% styrene; d) 40% styrene; e) 30% styrene; f) 10% styrene

shows an SBC where the PS domains hold together a rubbery BR network. The tensile strength (Table 14) and resilience data (-Table 15) illustrate the truly rubbery behavior of a linear SBS polymer with a polystyrene content of 30%.

The *molecular structure* of an SBC can be varied by changing the proportion of PS in the base polymer. Furthermore the total molecular mass can be varied, but practical limits exist to the processibility in the melt. Figure 23 shows the effect of altering polystyrene content in a series of linear polymers. Polymers can be made that range from very low strength at low (10%) PS content, through rubbery materials of about 30% PS, to those with 80% PS content that behave much like toughened polystyrene. SBC polymers can be linear or branched; branched types are usually higher in molecular mass than linear ones and have a higher melt viscosity at equal strength levels. Furthermore, a minimum molecular mass of the end block exists below which no phase separation occurs, no domain structure forms, and hence unsatisfactory properties are obtained [176]. A comparison of properties of polymers differing in the molecular mass of the PS blocks and in total molecular mass is given in Table 16.

The *processing properties* of SBCs can be derived from their basic chemical structure. The molecular mass of commercially available grades varies from about 75 000 to 400 000. Their behavior in the molten state is similar to that of polyethylene and polystyrene, for example. However, even in the molten state the tendency to form PS domains persists, especially for those types with a saturated rubber mid block. *Melt processing SBCs* at higher shear rates leads to lower apparent viscosity; this effect is relatively independent of temperature (see Fig. 24). Reprocessing of SBCs at < 200 °C has little effect on their properties; saturated

Table 14. Comparison of tensile strengths of BR and SBS

Polymer	Tensile strength, MPa
Unvulcanized BR	0.2–0.5
Vulcanized BR	4.0–5.0
Vulcanized + carbon black reinforced BR	5.0–20.0
Unvulcanized pure SBS	30.0–35.0

Table 15. Resilience (Lüpke-rebound) of different polymers

Polymer	Resilience, %
Unvulcanized SBS	65
Vulcanized BR	65
Unvulcanized SIS	60
Vulcanized NR/IR	60
Vulcanized SBR	50
Vulcanized EPDM	45
Unvulcanized EVA (28% VA)	40

Table 16. Properties of styrenic block copolymer structures with different PS block and total molecular mass

Polymer structure	Molecular mass		Viscosity	Strength
	PS block	Total		
Linear	12 000	80 000	low	high
Branched	12 000	160 000	medium	high
Branched	6000	80 000	very low	low

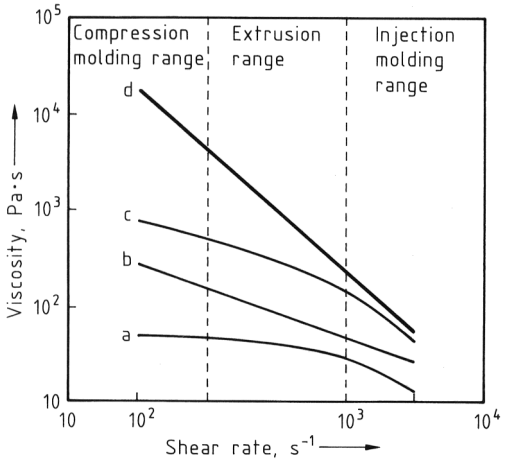


Figure 24. Viscosity–shear rate relationship at 200 °C
a) Clear polystyrene; b) SBS; c) polypropylene melt flow rate (MFR) = 5; d) S–E/B–S

grades can be processed and reprocessed at up to 280 °C.

Solution processing of SBCs is possible, provided that solvents of sufficiently high solubility are used to dissolve the PS end blocks. Solvents with solubility parameters between 8 and 10 are usually employed. Because of the easy solubility of SBCs, adhesive, sealant, and coating systems can be designed that have low viscosity and high solids content. A consequence of their good solubility in organic solvents is that the oil and solvent resistance of parts based on SBC is limited. However, their resistance to dilute aqueous solutions of the most commonly encountered chemicals is generally satisfactory.

The *service performance* of SBCs and the products derived from them is also related to their basic chemical structure. Because of their moderate molecular mass and their physical and reversible cross-linking, they flow under pressure and exhibit creep. Block copolymers with *BR or IR mid blocks* are unsaturated and sensitive to aging. Exposure to elevated temperature can result in polymer degradation with simultaneous decrease in viscosity and tensile strength. With the exception of black compounds, exposure to UV light for any length of time will result in discoloration and surface cracking, which becomes more pronounced on prolonged exposure. These block copolymers are also susceptible to ozone attack, and in shaped products at points with local stresses, microcracks develop on exposure to atmosphere containing ozone. The use of antioxidants, UV stabilizers, and antiozonants reduces these degradation effects to workable limits in end uses.

The *hydrogenated S–E/B–S or S–E/P–S types*, in contrast, have a saturated rubber mid block and are therefore highly resistant to degradation by oxidation, ozone, and UV light. They can be processed over a much wider processing temperature range.

5.4. Uses

Because of their rubbery characteristics (especially at low temperature), high strength, compound ability, and thermoplastic nature, SBCs are used in a variety of applications as highlighted in Figure 25.

On the left-hand side of Figure 25 the list includes outlets that use SBC as an additive or modifier for other materials. The polymers are delivered to the end user who will incorporate them in his existing process. The right-hand column lists applications that utilize a compounded product with performance tailored to the specific end use and plastic conversion technology. A comprehensive review of the applications of thermoplastic rubber is given in [177, 178].

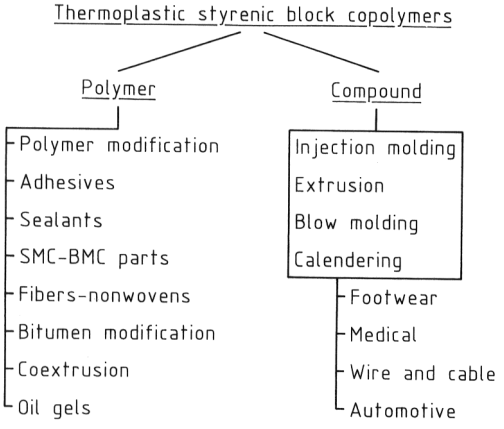


Figure 25. Applications of styrenic block copolymers
SMC = sheet molding compounds; BMC = bulk molding compounds

5.4.1. Adhesives, Sealants, and Coatings

Adhesive properties are determined primarily by the styrenic block copolymer type chosen for a typical application. SBS polymers with high cohesive strength (high polystyrene content) are commonly used in contact adhesives, whereas SIS polymers with low polystyrene content that can be tackified easily are preferred for pressure-sensitive adhesives. For applications in hot melt form, low molecular mass polymers with a high melt flow rate are selected. When high UV resistance is required, hydrogenated block copolymers should be considered as base polymer. Furthermore, adhesive properties are also determined by the nature and the concentration of the various resins and plasticizers used and their degree of compatibility with the respective mid or end block phase of the block copolymer [179].

Table 17. Pressure-sensitive adhesive formulations and properties

Composition, property	Formulation number			
	1	2	3	4
Parts by weight				
SIS polymer *	100	100	100	100
Piccotac 95	90		25	
Escorez 1310		120		90
Hercures C 10	10	50	125	
Wingtack 10				40
Irganox 1010	1			3
ZDBC		3	3	
Properties				
Melt viscosity (175 °C), Pa · s		20		60
Rolling ball tack, cm	2	3	3	1
Probe tack, N	10	>10		10
Loop tack, N/25 mm	25	30	8	27
180° peel adhesion, N/25 mm	17	15	5	16
SAFT, °C	115	100	80	100
T_g (Fox), °C	−20	−19	−33	−29

* Kraton D-1107 from Shell Chemicals.

Pressure-sensitive adhesives are materials that remain permanently tacky and adhere instantaneously to solid surfaces on the application of light pressure. Major applications are tapes and labels. Tapes require high shear strength and holding power, while labels require less shear strength but good convertibility. For general-purpose solvent-based pressure-sensitive adhesives, SIS block copolymers are combined with resins that are compatible with the mid block, such as wood rosins, polyterpenes, or synthetic hydrocarbon resins. A typical composition is shown in Table 17, formulation no. 1. The formulation for an adhesive used for permanent labels is given in Table 17, formulation no. 2. Pressure-sensitive adhesives for peelable labels have a relatively high cohesive strength and a low peel strength (Table 17, no. 3). Labels that are applied under cold conditions must have a low T_g, and formulations usually contain low amounts of high-melting resin but large proportions of plasticizer (Table 17, no. 4).

In outdoor applications where the adhesive must withstand UV light, saturated block copolymers are employed. Pressure-sensitive adhesives with very high temperature resistance can be obtained by UV or electron beam curing (→ Kraton D-1320XRadiation Chemistry). A special polymer developed by Shell for this application is Kraton D-1320X. The shear adhesion failure temperature (SAFT) of a pressure-sensitive adhesive based on this polymer is increased from 80 °C to ca. 140 °C by either UV or electron beam curing [180].

Contact adhesives are applied as liquid onto one or two substrates; after a certain time to allow partial evaporation of the solvent (open time) the coated substrates are pressed together to form a strong bond. SBCs are ideal for these types of adhesives because they offer high cohesive strength without vulcanization and are readily soluble in many solvents. For some applications, the contact adhesive is allowed to dry completely to a tack-free non-blocking adhesive film. Exposure to heat reactivates the adhesive, and a firm bond forms under pressure. Large surfaces are commonly coated by spraying with a uniform adhesive layer (e.g., on flexible foams used in the furniture and automotive industries). Because of their molecular structures, SBC-based adhesives combine high strength with low viscosity and ease of spraying. A variety of melt adhesives are used in the construction of hygienic products such as disposable diapers, sanitary napkins, etc. These adhesives can be applied by spray or slot-die coating techniques. Selection of the styrenic block copolymer depends on the properties required and the application technique used.

Sealants. Styrenic block copolymers with *saturated rubber mid block* are ideally suited as base polymers for both hot-melt and solvent-based sealants that require resistance to long-term degradation and weathering [181, 182].

Coatings. In several applications, SBCs are used to formulate *protective coatings* based on solvent systems, but the trend is toward solvent-free systems, for example, in chemical milling.

5.4.2. Modification of Bitumen

The addition of SBCs to bitumen increases its upper and decreases its lower operating service temperature, which results in substantial performance improvement in applications such as roofing felts, waterproofing membranes, and asphalt pavement. Selective development of SBS polymers has enabled bitumen to maintain its strength and integrity at elevated temperature without flowing and to remain flexible and ductile at temperatures well below the freezing point [183]. Moreover, SBCs greatly enhance the lifetime of bitumen-based products (e.g., roofing felts). This is achieved by development of a three-dimensional network. To optimize the effect of SBS addition, bitumen with the right degree of compatibility must be selected to ensure effective formation of the elastomer network. For roofing felts, SBS addition levels are commonly between 8 and 12%. Blending into the bitumen is carried out at 170–190 °C. For fast dissolution, especially when low-shear paddle mixers are employed, SBS polymer is ground to a powder with particle size of ca. 1000 μm. For most applications, high-shear mixers are used with regular polymer crumb [184, 185].

The use of polymer-modified bitumen for asphalt pavements is growing rapidly and offers large potentials for SBC in the future. The SBS addition levels for road applications are lower than for roofing: typically 3–7%. In addition to improved deformation and flexibility, laboratory data clearly demonstrate that the durability of asphalt roads is increased by addition of SBS polymer [186]. Many test roads have been installed that are being monitored to gain experience and evidence for performance under practical conditions. For documentation of the most important practical experiences so far, see [187–193].

5.4.3. Compounded Products

As mentioned earlier, end use parts that are made via established plastic processing techniques do not employ pure SBC polymers but rather—like traditional vulcanized rubber—compounded and end use-tailored compositions. Depending on their requirements, such compounds have hardnesses in the range from 35 Shore A to as high as 55 Shore D. The actual SBC content can be as low as 15 wt% but is usually between 25 and 40 wt%. SIS block copolymers are rarely used as base polymer for compounds. The main classes of compounding ingredients include the following:

Mineral oil is used as plasticizer to increase flow and reduce cost. Paraffinic or naphthenic oils are used that compatibilize with the rubber mid block. Aromatic oils or polar plasticizers such as dioctyl phthalate (DOP) are avoided because they strongly plasticize the end blocks and reduce strength.

Polystyrenes are important compounding ingredients to increase hardness, strength, and wear resistance, particularly in SBS polymers. Both clear and high-impact polystyrenes are used.

Polyolefins, particularly polypropylene, are important ingredients in S–E/B–S and S–E/P–S block copolymers.

Fillers, mainly cheapeners and nonreinforcing types, are used to decrease cost and increase hardness. They also increase density, which is exploited in formulations for sound-deadening applications.

Additives such as antioxidants, UV stabilizers, and antiozonants, as well as additives that induce special effects, can be used. Examples are pigments, surface-active slip agents, blowing agents, and antistatics.

Compounding is carried out at elevated temperature and at shear conditions that result in a fine, stable dispersion of the various ingredients. Compounding equipment originates from both the rubber industry with two-roll mills, Banbury-type internal mixers, and Farrel continuous mixers, and the plastic processing industry with mainly single- and double-screw compounding extruders. Modern compounding plants are fully instrumented robots in which a twin-screw

conrotating compounder with a length : diameter ratio ($L : D$) up to 42 is the key unit. Screw types with feeding, kneading, homogenization, and venting sections are designed for the specific compounding operation. Ingredients are added either as preblended mixture or via separate weigh feeders and oil injection pumps. The granulating section at the end of the extruder is important because it is responsible for formation of the homogeneous, free-flowing pellets required in subsequent plastics conversion equipment. Depending on line capacity and product characteristics (i.e., soft or hard), die plates with knife cutters, water-ring pelletizers, underwater pelletizers, or a strand die with water cooling bath and rotating knife granulator can be used.

Detailed compositions and selection of base polymers have been published by SBC suppliers in the form of technical bulletins or formulating guides. Compounding know-how and formulations based on SEBS or SEPS polymers is rather specific [194]. Table 18 lists properties of typical SBC-based compounds tailored for selected end uses. The largest volume of SBCs in compounded form is consumed by the footwear industry. Here, SBS-based compounds are established mainly as high-quality soling materials. An important aspect is the multitude of colors that can be combined in shoe design. Compounding aims to optimize the end products with respect to melt flow rate (for ease of processing), high abrasion resistance (for durability), and good resistance to repeated flexing. Hardness for most typical soling materials falls within the Shore A 55 to 75 range.

Table 18. Properties of compounded SBCs

Property	Reference no*, base SBC polymer				
	1 SEBS	2 SBS	3 SEBS	4 SEBS	5 SEBS
MFR (E or G), dg/min	50 G	35 E		3 G	17 G
Density, g/mL	0.91	1.0	1.94	0.91	1.01
Hardness, Shore A/D	45 A	65 A	36 D	60 A	82 A
Tensile strength, MPa	5.0	7.6	4.8	7.5	17.3
Elongation, %	610	650	250	480	670
DIN abrasion, mm^3		180			
Haze, %	7				
UL 62**, Class 34 rating, °C					105
Compression set 22 h at 100 °C, %				42	

* 1 = Transparent medical molding; 2 = soling material; 3 = automotive sound deadening; 4 = high-temperature performance; 5 = electrical wire insulation.

** UL = Underwriters Laboratories code.

Compounds designed for use in medical devices and articles intended for food contact are also important outlets and take advantage of the high purity of polymers made by anionic polymerization. SBS- and SEBS-based compounds which meet the requirements set in the United States by the FDA and in Germany by the BfArM ■correct?■, are used for syringes, tubing, bottle nipples, stoppers, i.v. bag systems, etc. Contact of SBS and SEBS with fatty food is restricted.

Thermoplastic rubber products can be recycled, and scrap, trimmings, and off-specification parts can to a certain extent be reintroduced in the manufacturing stream.

5.4.4. Modification of Plastics

Most plastics are brittle and lack impact resistance, particularly below 0 °C. Rubber is added to achieve

1. Increased impact strength (Izod, Charpy, FWIS, Dart, etc.) especially at low temperature
2. Increased environmental stress corrosion resistance

The addition of a rubber to a thermoplastic also changes properties such as stiffness, tensile strength, yield modulus, surface friction, softening point, clarity, electrical properties, vapor transmission, and gloss.

With many plastics, an impact resistance improving rubber fraction can be incorporated in the polymerization reaction. Examples are propene–ethylene copolymers, high-impact polystyrene (HIPS), and ABS. Nevertheless, styrenic block copolymers are used as melt-blended component in plastics that do not allow reactor modification or to obtain impact performance in excess of that achievable in the reactor. Polystyrenes are often compounded with flame-retarding additives and then require the addition of SBS polymer to compensate for the loss in impact strength due to addition of the flame retardant [195]. Engineering plastics require processing temperatures beyond the operating range of SBS. Here, saturated SEBS and SEPS block polymers are used, especially

as modifiers in polycarbonate (PC) and poly (phenylene ether) (PPE). The more polar engineering plastics such as polyamides and polyesters can be adequately impact modified by SEBS or SEPS functionalized with maleic anhydride [196].

Styrenic block copolymers are also capable of compatibilizing different and dissimilar plastics into useful and workable blends. Addition of SBS or SEBS to a blend of polystyrene and polypropylene or polyethylene, for example, creates a ductile material that can be extruded or molded without the delamination or phase separation encountered in the absence of block polymer addition [197]. Similar results are obtained when SEBS is used in blends with polycarbonate and polypropylene, as well as polyethylene–poly(ethylene terephthalate) (PETP) blends. Functionalized block polymers are good compatibilizers for, e.g., polyamides and polypropylenes. SBCs can also be used in thermoset resin systems, particularly as additives for sheet molding or bulk molding processes with unsaturated polyesters. Moldings modified with specifically developed SBS or SEBS polymers to control shrinkage show high-quality surface appearance [198, 199].

The use of SBCs as compatibilizers for mixed plastic streams is becoming more and more important with respect to waste management and upgrading and compatibilization of used plastics [200].

Abbreviations for polymers and monomers:

2G	ethylene glycol
2GT	dimethylene terephthalate, ethylene terephthalate
3G	1,3-propanediol
4G	1,4-butanediol
4GT	tetramethylene terephthalate, butylene terephthalate
5G	1,5-pentanediol
6G	1,6-hexanediol
10G	1,10-decanediol
ABS	acrylonitrile–butadiene–styrene copolymer
BR	butadiene rubber
DOP	dioctyl phthalate
DVA	dynamically vulcanized alloys
EOPPG	poly(propylene glycol) capped with ethylene oxide
EPDM	ethylene–propene–diene terpolymer
EPM	ethylene–propene copolymer
EPR	ethylene–propene rubber
EVA	ethylene–vinyl acetate copolymer
H_{12}-MDI	4,4′-dicyclohexylmethane diisocyanate
HDI	hexamethylene diisocyanate
HIPS	high-impact polystyrene
IR	isoprene rubber
MDI	4,4′-methylene diphenyl diisocyanate
NDI	1,5-naphthalene diisocyanate
NR	natural rubber
PEBA	thermoplastic polyamide elastomer
PB	polybutadiene
PC	polycarbonate
PEO	poly(ethylene glycol); poly(ethylene oxide)
PETP	poly(ethylene terephthalate)
PP	polypropylene
PPE	poly(phenylene ether)
PS	polystyrene
PTHF	poly(tetrahydrofuran)
PTMG	poly(tetramethylene glycol)
PTMO	poly(tetramethylene oxide)
PVC	poly(vinyl chloride)
RTPO	reactor thermoplastic polyolefins
S–E/B–S, SEBS	styrene–ethylene/butene–styrene copolymer
S–E/P–S, SEPS	styrene–ethylene/propene–styrene copolymer
SBC	styrenic block copolymers

SBS	styrene–butadiene–styrene block copolymer
SIS	styrene–isoprene–styrene block copolymer
T	terephthalic acid
TODI	3,3′-tolidine-4,4′-diisocyanate
TPE	thermoplastic elastomer
TPNR	thermoplastic natural rubber
TPO	thermoplastic polyolefin elastomer
TPR	thermoplastic rubber
TPU	thermoplastic polyurethane elastomer
TPV	thermoplastic vulcanizates
VA	vinyl acetate

Other abbreviations used

BMC	bulk molding compound
MFR	melt flow rate
SAFT	shear adhesion failure temperature
SMC	sheet molding compound
T. S.	tensile strength
U. E.	ultimate elongation
UL	Underwriters Laboratories code

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Part 3

Films, Fibers, Foams

Ullmann's Polymers and Plastics: Products and Processes
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Films

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1. Introduction

The term *film* is applied to thin materials present in a continuous planar form, which are at the same time self-supporting and flexible. A film may consist of one or more layers, usually of differing composition. The term generally encompasses both metallic and polymeric substances, which

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Table 1. Worldwide consumption of some of the most important types of film in 2005*

Material	Consumption, 10^6t
Low-density polyethylene (LDPE)	11.00
Polypropylene, biaxially oriented (BOPP)	3.70
Poly(vinyl chloride) (PVC), rigid and plasticized	0.8
Polyesters	2.20
Cellophane	0.07

* http://www.pardos-marketing.com

may be either homogeneous or made heterogeneous by the presence of incompatible additives or blending components. In this article, a film is assumed to be a polymeric material which can be wound into a roll. Film thicknesses range from 0.5 μm to ca. 1 mm.

The characteristics of a film are determined primarily by the raw materials employed, but they are additionally affected by processing methods, modification, and converting (e.g., stretching, coating and lamination).

Film materials are of considerable economic importance. In 2005, the annual worldwide consumption of film for packaging and technical applications was ca. 50×10^6 t. Figures for the worldwide consumption of the more important film materials are listed in Table 1.

Films are used as flexible packaging materials, as insulation for electrical conductors, as protective layers on sensitive surfaces, and as windable base materials for subsequent application of magnetic coatings, electrically conducting, and light-sensitive layers as well as printing inks. Multitudes of film and sheet types have been developed to meet the increasing demands of these applications. These products provide a broad spectrum of mechanical, optical, and electrical properties, as well as various degrees of permeability and stability to temperature and aggressive media.

Historical Aspects [1]. Polymeric films were first developed at the end of the 19th century, when cellulose nitrate was introduced as a base material for photographic emulsions. Other cellulose-based films followed, the most important of which were derived from cellulose acetate and cellulose hydrate. Cellulose triacetate films quickly replaced the highly flammable cellulose nitrate films in the photographic industry; cellulose hydrate films (cellophanes) became important packaging materials, maintaining their dominance until polyolefin films were introduced in the 1950s. Cellophane coated with cellulose nitrate or poly(vinylidene chloride) also played a key role in this respect due to its low permeability to water vapor and oxygen, coupled with desirable sealing properties.

All cellulose-based films are prepared from polymer solutions, however the subsequent introduction of totally synthetic polymers has led to new film production methods, as well as new types of films with unique properties. These developments have been encouraged by the close working relationship between fiber and film producers, particularly in terms of polymer compositions and processing technology.

Important milestones in the development of films included the introduction of

1. poly(vinyl chloride) films in the late 1930s
2. low-density polyethylene films in the late 1940s
3. biaxially oriented polyester and polypropylene films in the 1950s

Parallel and subsequent to these developments, a series of specialty films has emerged. These films are distinguished either by high mechanical or thermal stability, or by special properties such as impermeability to oxygen, advantageous electrical characteristics, or resistance to chemical attack.

2. Production Technology [2]

Generally speaking, the manufacture of films from both natural and synthetic polymers relies on two basic techniques:

1. solution casting
2. thermoplastic film forming

The method chosen is generally determined by the behavior of the starting materials with respect to solvents and temperature. However, in certain cases the desired product characteristics are decisive.

For *solution casting*, the raw materials must first be dissolved in an appropriate solvent. The solution is then pressed through a slot die either onto a moving belt or into a precipitation bath.

Thermoplastic film forming can be divided into two categories: (1) calendering (film formation in a rolling process) and (2) film formation from a melt (an extrusion process).

2.1. Solution Casting

Solution casting is applicable to soluble polymers that are difficult or impossible to thermoform. It also has advantages in the preparation of films for optical applications. Cellulose acetate, polycarbonate, and polyimide films are prepared in this way.

Solution casting consists of three stages:

1. preparation of the casting solution
2. film formation on a moving surface (drum or endless belt) or in a precipitation bath
3. removal of residual solvent

Figure 1 is a schematic illustration of a belt casting machine that is suitable for the production of cellulose acetate film.

The casting solution is prepared in a large agitator vessel, if possible using a low-boiling solvent. The solution is normally very viscous (ca. 20 Pa · s) and is passed through a filter press equipped with a cotton filter. After the viscosity has been checked, the solution finally enters the casting reservoir. Entrapped air is removed either by evacuation or by heating.

The solution is fed from the reservoir under pressure through the die and is cast onto a rotating drum or a moving metal belt. The die gap is adjusted according to the desired thickness of the film.

The metal belt may be made of copper, nickel, or steel, and its surface finish is of critical importance in determining the characteristics of the resulting film. For optical-grade films, the surface must be polished and filtration must be highly effective. Belt dimensions range from 25 to 55 m in length and 1 to 2 m in width; belt speed varies from 1 to 60 m/min, depending on the desired thickness of the film.

The film is dried on the belt by a countercurrent of warm air and is then removed, further dried, and wound. Typical thicknesses of films prepared in this way are 15 – 250 μm.

In some cases, the polymer solution emerges from a slot die directly into a liquid precipitation bath. The polymer solvent is miscible with the bath fluid, whereas the polymer is insoluble in this fluid. Consequently, the polymer coagulates in the bath to form a gel film with a microporous structure. Thus, this process is frequently employed for the preparation of membranes (→ Membranes and Membrane Separation Processes, 3. Membrane Preparation and Membrane Module Constructions).

Cellulose hydrate (cellophane) films [3] are produced by a modification of this process in which the gel film undergoes a chemical reaction. The casting solution is prepared by reacting cellulose with caustic soda solution and carbon disulfide to form viscose. The resulting xanthate solution is then pressed into a spinning bath containing sulfuric acid, causing decomposition of the xanthate and forming a gel web composed of regenerated cellulose (see also → Cellulose).

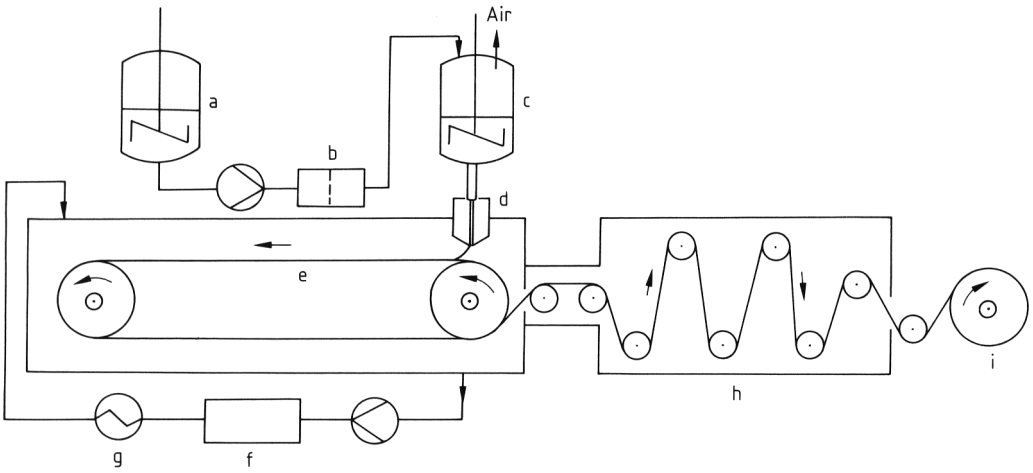


Figure 1. Film production by solution casting on an endless belt
a) Agitator vessel; b) Filter; c) Degasser/casting reservoir; d) Die/caster; e) Metal belt; f) Solvent recovery; g) Air heater; h) Final dryer; i) Winding

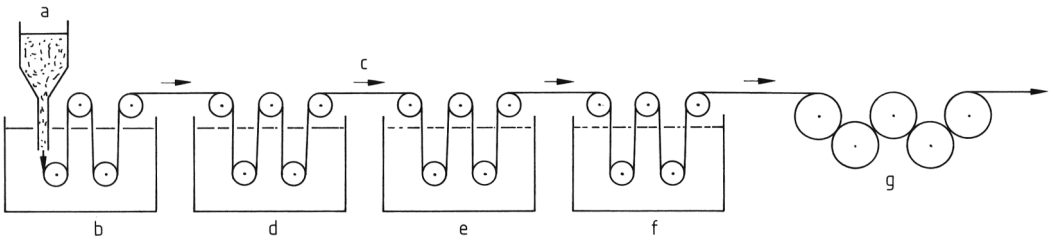


Figure 2. Production of cellulose hydrate film by casting into a precipitation bath
a) Casting solution, slot die; b) Precipitation bath; c) Regenerated film web; d) Regeneration bath; e) Wash and bleaching bath; f) Plasticizer bath; g) Drying rolls

A slot die is immersed in the precipitation bath (see Fig. 2). Shortly after its formation, the gel film possesses sufficient stability to permit its transport over rollers. The film is subsequently washed and bleached, passed through plasticizer baths, dried, and wound.

Film thickness ranges from 12 to 45 μm with a typical width of ca. 2 m. Production rates of 80 m/min are common for films in the mid-thickness range. The normal slot die may be replaced by an annular orifice, in which case the product is a tube of regenerated cellulose [4]. Further processing is as described above for flat cellulose hydrate films.

2.2. Thermoplastic Film Forming

2.2.1. Calendering [5–7]

Only polymers with a broad range of plasticity and high viscosity can be processed by the calendering method; these criteria are met by homo- and copolymers of poly(vinyl chloride) (PVC).

The production of calendered (e.g., PVC) film is shown in Figure 3; three steps are involved:

1. preparation of a blend of the components in a mixer
2. homogenization and plastification
3. film formation in the calender

The powdered mixture is usually converted into a fused mass by continuous compounding in a kneader or planetary-gear extruder using heat, shearing forces, and pressure. The mass is then rolled into a film web, ideally with a four- or five-roll calender, in which the nip rolls are mounted in an "L"-form. These rolls are made of steel or cast iron and they generally have a smooth surface. The nip rolls are heated to 180 – 220 °C, depending on the process and the polymer mixture; heating must be uniform. The calendered web then passes over cooling rolls followed by an edge-trimmer, in some cases a stretching facility, and finally a winding unit. Calendering equipment operates at high

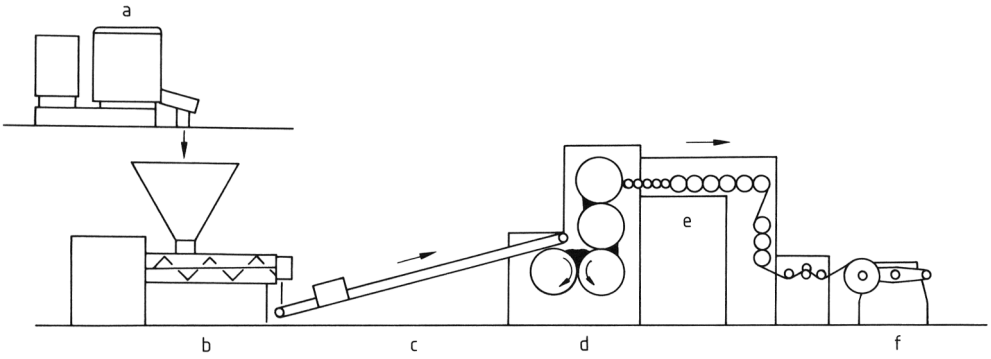


Figure 3. Film production by calendering
a) Mixer; b) Kneader; c) Feed band; d) Calender; e) Cooling and tempering rolls; f) Winder

pressure and must, therefore, be solidly constructed, making it very expensive. The largest production facilities for processing plasticized PVC have nip rolls 85 cm in diameter and are 280 cm wide. Calenders for rigid PVC utilize rolls up to 70 cm in diameter and are 250 cm wide. Production rates of 50 – 100 m/min are achieved depending on the desired film thickness; with stretching, line speeds approach 300 m/min. These figures correspond to an output of 500 – 2000 kg/h.

2.2.2. Extrusion [8]

Advantages of extrusion include a wide range of attainable film thickness, large-scale processing, and the fact that recovery systems for expensive solvents are not needed.

The technique utilizes an extruder to melt the polymer, a die to confer shape to the melt, and a cooling system to solidify it. The process is applicable only to raw materials for which there is a sufficiently large temperature difference between melting and the onset of decomposition (e.g., polyolefins, polyamides, and polyesters).

Chill Roll Extrusion. Figure 4 is a schematic illustration of a chill roll extrusion line. Moisture-containing raw materials (moisture content usually $\ll 1\,\%$) are subjected to continuous or discontinuous drying, preferably utilizing heated air or a vacuum, prior to melting in the extruder.

Various extruder designs can be used including single-screw and twin-screw extruders, the latter with either corotating or contrarotating screws. Extremely high outputs of 4 – 5 t/h can be achieved with two extruders combined in sequence (tandem extruder). Single-screw extruders are the most common. Screw geometry must be adapted to the raw materials being processed and has a major effect on the output and quality of the melt. The largest single-screw extruders currently in use have a screw diameter (D) of 30 cm and a screw length of 30 D.

The melt is filtered in one of several ways depending on the desired purity: wire mesh, sintered metal, and wire–felt disks are all used. The filtered raw materials are forced through a slot die. The required pressure can normally be achieved with the extruder, however in special cases a gear pump is installed before the filter to ensure constant metering of the melt. In coextrusion (see Section 2.4.2), the die combines several different melt streams. The width of the die and the die gap determine the width and thickness of the film, respectively. In large production units, the dies may be as wide as 3.5 m. Adjustment of the die gap permits the film thickness profile to be corrected during production. Initial adjustment and readjustment can be performed either manually or automatically, e.g., by thermal expansion of adjusting screws that are heated as a function of the relative film thickness.

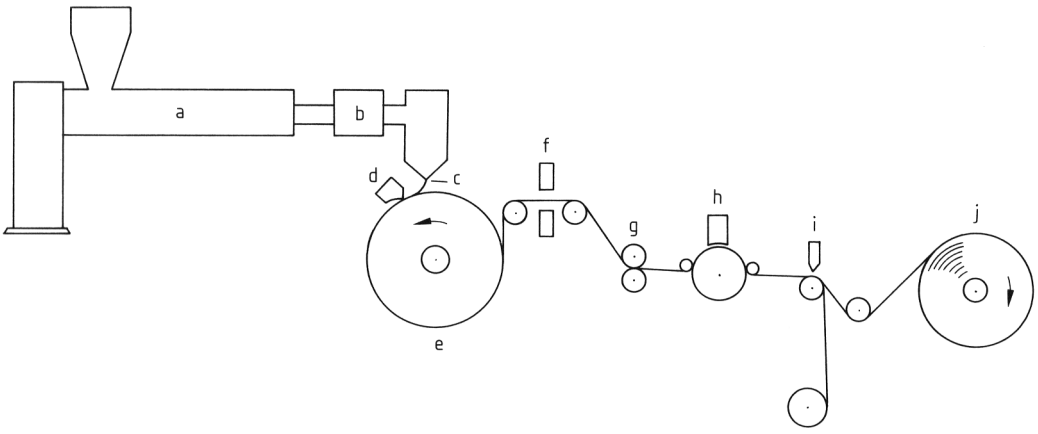


Figure 4. Film production by chill roll extrusion
a) Extruder; b) Filter; c) Slot die; d) Air knife; e) Cooling roll; f) Device for measuring film thickness; g) Tension rolls; h) Corona treatment; i) Edge trimming; j) Winding

When the melt film emerges from the die, it is cast onto a highly polished, chrome-plated chill roll. The takeoff speed depends on both film thickness and output and may be as high as 100 m/min. Entrapment of air between the melt and the roller surface is prevented by using an air jet (air knife), electrostatic "pinning", or a vacuum device.

The thickness of the film is measured with the aid of a traversing radiation source and detector. The film is then edge-trimmed and wound to a roll. If the film is to be printed, corona pretreatment can also be carried out (see Section 2.4.1).

The film is usually cut to the designated width in a separate process—the actual width depending on the application. If monoaxial or biaxial orientation is desired, the film is fed directly into a stretching unit (see Section 2.3) without intermediate winding.

Film Blowing (Blown-Bubble Extrusion). In the film blowing process, the filtered melt is pressed through an annular die instead of a slot die; this results in the production of a tubular film (Fig. 5). The tube (or "bubble") is inflated by means of air blown through the center of the die. The film is thereby expanded at a temperature close to its melting point and is then cooled by an airstream located above the die. A number of techniques are employed for air cooling; the most common involves passing the tube through a cooling ring. Supplementary internal cooling is also usually used if a high throughput is required. If biaxial stretching is to be performed, the melt must be solidified immediately after it emerges from the die (see Section 2.3.2).

The cooled tube is collapsed by transporting it through a convergent collapsing frame and a set of nip rolls. The film can then either be wound directly as a flattened tube or slit open on both sides and directed to two separate winding stations. The largest film blowing systems utilize annular dies with a diameter of 2 m and an output of 1.5 t/h.

The film blowing process is employed mainly for polyolefin and polyamide films. Multilayer films can be produced by coextrusion of tubular films (see Section 2.4.2).

2.3. Stretching [8]

Many films acquire their desired properties only after stretching. Stretching below the softening temperature orients the polymer molecules and crystallites in the direction of stretch, leading to changes in the stress–strain characteristics of the material. Both the modulus of elasticity and the ultimate strength are increased by this process, but elongation at break and dimensional stability with respect to temperature decrease. A number of other characteristics may be altered as well, depending on the type of film involved, e.g. gas permeability, electrical properties, heat sealability, abrasion resistance, coefficient of friction, puncture resistance, density, and optical properties. Stretching can be conducted either solely in the machine (longitudinal) direction (monoaxial stretching) or in both the machine and the transverse directions (biaxial stretching).

Monoaxial stretching (see Section 2.3.1), which is also commonly used in the production of high-strength fibers, produces films of enhanced strength in the direction of manufacture. The resulting films are thus anisotropic.

Biaxial stretching (see Section 2.3.2) can be conducted in one or two steps (simultaneous and sequential stretching, respectively). Sequential stretching may result in either anisotropic or isotropic films depending on the ratio of the final length to the initial length (the draw ratio). Simultaneous stretching tends to produce isotropic films.

The majority of films prepared from orientable polymers are amenable to either sequential or simultaneous biaxial stretching. However, films derived from polymers with a high rate of crystallization during orientation (stress crystallization) [e.g., some polyamides, poly(butylene terephthalate), and ethylene–tetrafluoroethylene copolymer] can only be oriented by simultaneous stretching.

2.3.1. Monoaxial Stretching

Monoaxial stretching is accomplished by subjecting a film to an increasing velocity gradient as it passes through one or more gaps between temperature-controlled rolls. Numerous stretching machines are available; they differ with respect to the number and arrangement of the rolls. Monoaxial stretching is of particular importance in the manufacture of high-strength tape from polyethylene and polypropylene, as well as for the orientation of poly(vinyl

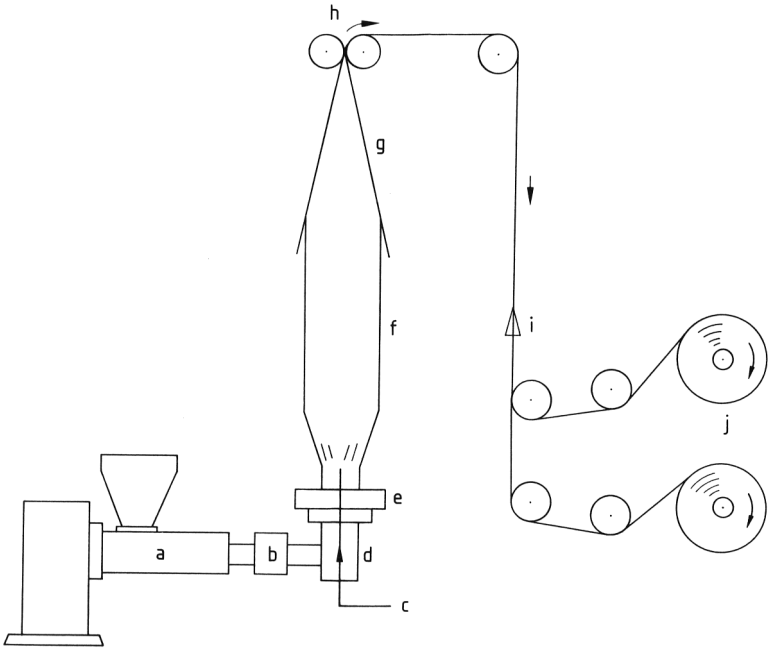


Figure 5. Film production by the blowing method
a) Extruder; b) Filter; c) Blowing air; d) Annular die; e) Air cooling ring; f) Film tube (bubble); g) Flattening; h) Nip rolls; i) Tube separation (slitting); j) Winding

chloride), polycarbonate, and poly(vinylidene fluoride) films. Longitudinal stretching units are also incorporated in film production lines that employ sequential stretching technology for the manufacture of biaxially oriented films (see Section 2.3.2).

2.3.2. Biaxial Stretching

Sequential Stretching. Sequential biaxial stretching is currently the preferred orienting method for example with polyester and polypropylene films. Figure 6 illustrates a production line that uses longitudinal–lateral stretching (the so-called machine direction—transverse direction, MD–TD sequence) for the manufacture of biaxially stretched film. The film line consists essentially of a chill roll facility coupled with forward and transverse stretching units.

The polymer is first dried, melted in an extruder, passed through a slot die, and vitrified on a chill roll. Longitudinal stretching follows using a system of rollers, whereas drawing in the transverse direction occurs in an air-heated oven (stenter) comprising several temperature-controlled zones. When the longitudinally stretched film enters the stenter, it is grasped at both edges by two series of continuously circulating clips which are linked together in a chain. In the zone where the film reaches the stretching temperature, the two series of parallel-running clips are gradually drawn apart and hence stretch the film in the transverse direction (Fig. 6). The film is then heat-set (crystallized), cooled, released from the clips, and wound to a roll. Draw ratios for polyester lie typically between 3 : 1 and 4 : 1 [9, 10].

Facilities for edge-trimming, thickness determination, and, where appropriate, corona treatment (see Section 2.4.1) are located between the stenter and the winding unit. Winding speeds range from 80 to 250 m/min. Film thickness varies from 1 to 350 μm.

Polyester films with a high modulus of elasticity in the machine direction are best prepared by a TD–MD stretching sequence, or in a three-step process with MD–TD–MD stretching.

Simultaneous Stretching. Simultaneous biaxial orientation is most easily achieved by inflation of a tubular film. In the continuous

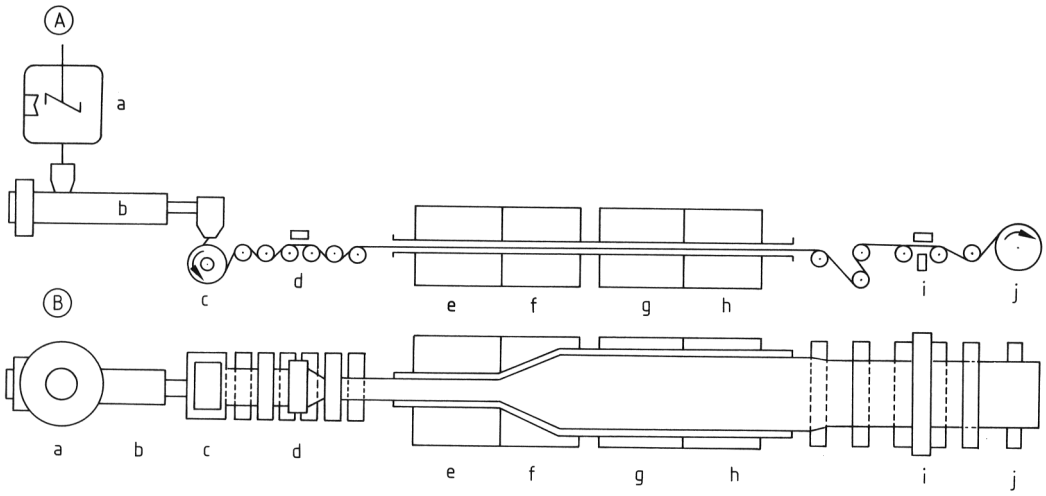


Figure 6. Production of biaxially oriented film by sequential stretching in a machine direction–transverse direction (MD–TD) sequence [production unit viewed from the side (A) and from above (B)]
a) Dryer; b) Extruder; c) Slot die and chill roll; d) Stretching in the machine direction (MD); e) Preheating zone; f) Zone for stretching in the transverse direction (TD); g) Heat-setting (crystallizing) zone; h) Cooling zone; i) Thickness measurement; j) Winding

process, a tube is first created by cooling the melt in a water bath or with a cooling mandrel. This tube is subsequently heated to the stretching temperature with a ring of radiant heaters. It is then inflated, collapsed, and transported as described for blown films (see Section 2.2.2). This technique is widely used for preparing biaxially oriented poly(vinylidene chloride), polyamide, polyester, and especially polypropylene tubular films; all of these films have a high shrinking potential. For this reason, oriented polypropylene tubular films are normally slit, separated, and then heat-set, either with the aid of heated rollers or in a hot-air tunnel.

Simultaneous biaxial stretching of a flat film is technically more complicated than that of tubular materials. Normally, a special stretching (stenter) frame is used in which the clips are not linked in a chain as described for sequential stretching. The clips are individually accelerated as they pass through the transverse-stretching zone by means of a progressive transport system.

2.4. Film Modification and Converting

Films are normally intermediates from which end products are manufactured in subsequent processing steps. The terms *film modification* and *converting* refer to operations such as surface treatment, coating, or lamination, which enhance the value of a film. Commonly encountered end products derived from films include packaging materials (e.g., printed bags and adhesive tapes), capacitors, magnetic tapes, and photographic films.

Untreated films often lack the specific characteristics that are required in the final product, e.g., stability during handling, heat sealability, wettability, adhesion of printing ink or other coatings, and barrier properties. Further processing is then needed to remedy these deficiencies. Sometimes the desired results can be obtained with additives (cf. Chap. 3), which include antistatic agents and lubricants. However, surface treatment or coating is often necessary, and in some cases two or more films must be combined to form a laminate.

2.4.1. Corona Treatment

Corona treatment is the principal method of preparing a film surface for printing or coating. A continuously moving film is exposed to an ionized atmosphere, which is produced by an alternating electrical field [11]. The changes induced in the film surface enhance both its

wettability and adhesion properties. Corona treaters can be integrated into the film production process (see Sections 2.2.2 and 2.3.2) and are widely utilized in the pretreatment of polyolefin films.

2.4.2. Coating

Films may be coated with dissolved, dispersed, emulsified, or molten materials [8, 12]. The techniques employed differ considerably, depending on whether the material is applied as a liquid or as a melt.

Liquid materials are normally coated on one or both sides of a moving film web either by immersion or with the aid of applicator rolls. The coated film is then dried in a heated-air oven or by means of rollers.

Coating is normally performed separately from film production (*off-line coating*), although in some special cases, the two processes can be integrated (*in-line coating*) [13]. In in-line coating (e.g., of polyester films), the coating assemblies are preferentially placed between the MD and TD stretching units.

Coating materials such as nitrocellulose, polyacrylates, and poly(vinylidene chloride) are used to improve heat sealability and gas barrier properties. Adhesion is improved by coating films with polyurethanes, cross-linkable polyacrylate, copolyesters, or epoxides. Other coatings include antistatic or slip agents, scratchresistant and antiadhesive materials.

Films with a different functional coating on each surface possess a combination of properties (e.g., sealing and barrier properties) and can be produced on a large scale.

Molten materials are applied to films with the aid of a die by a process analogous to chill extrusion (see Section 2.2.2). The film itself is supported by a roller. Extrusion coating can be conducted either off- or in-line; the latter approach is employed with biaxially stretched films.

Coextrusion represents a special case of melt coating [14, 15] in which two or more polymer melt streams are combined either in the melt pipes or in a multimanifold die just before the material emerges from the die lips. In the former case, special adapters of varying design ensure that the melt streams do not mix in the die and hence leave the die gap in the form of a multilayer film analogous to that produced by a multimanifold die. This process is also adaptable to annular die systems.

Coextrusion has gained considerable importance. Sealable, biaxially oriented polypropylene film with a triple-layer structure is a particularly important product in the packaging industry. The thickness of the sealable layer is typically 0.5 μm.

Coextruded, double-layer films are commonly employed for magnetic tape and capacitors; they have a smooth side which can be coated, and a rough side, which ensures a low coefficient of friction for adequate processability.

2.4.3. Lamination [8, 12]

Two or more different films can be bonded to form a composite or multilayer film. Their individual properties are thus combined, resulting in a variety of high-quality materials for both the packaging industry and the technical sector. For example, a heat-sealable film may be laminated to a film that acts as a barrier to gases and/or to a high-strength film. The potential number of property combinations is very large.

Laminated composite films are commonly prepared by the *dry lamination process*, in which a dissolved or dispersed adhesive is coated on the surface of the film. After evaporation of the solvent in a dryer, the coated film is bonded to a second film web in a laminating unit consisting of a pair of nip rolls, one made of rubber and the other of steel.

The simplest laminating system is composed of two unwinding stations, an adhesive applicator, a dryer, a laminating unit, and a windup station. However, many different systems are in use, depending on the desired number of laminate layers and the choice of adhesive. In some cases, adhesion can be achieved without using solvents, e.g., by using hot melts, reactive adhesives, or systems that can be hardened by irradiation.

3. Additives

Nearly all films contain additives which perform two main functions: (1) stabilization of the

polymers and (2) improvement of processability and the potential uses of the film [16, 17] (see also → Plastics, Additives, → Plasticizers).

Additives can be introduced when the polymer is being prepared or processed, or during film production. An additive must withstand all stages of processing without any loss of activity. Additives used in films that come into contact with food must also comply with legal health and safety requirements.

Processing Stabilizers. The thermal decomposition of some film raw materials must be suppressed by addition of processing stabilizers so that the melt can be thermoformed. The choice of stabilizer depends on the decomposition mechanism involved. Thus, sterically hindered phenols effectively stabilize polypropylene, while poly(vinyl chloride) responds to treatment with metal salts (in particular organic tin salts) or *N,N′*-diphenylthiourea [102-08-9]. Additive concentrations range from <1 to 3 wt%.

Plasticizers. Plasticizers are particularly useful for adjusting the flexibility of poly(vinyl chloride), cellulose acetate, and cellulose hydrate films. The plasticizer concentration may be as high as 40% (plasticized PVC); typical examples include esters of phthalic and phosphoric acids.

Slip or Antiblocking Agents. Films with smooth surfaces possess a high coefficient of friction and therefore tend to block during winding and other processing operations. To improve the frictional properties of these films, their surface is finely structured by adding small amounts of finely dispersed pigments. The surface of biaxially oriented polyester films can be improved by adding inert inorganic pigments (e.g., calcium carbonate, silicon dioxide, or calcium phosphate) or particles composed of cross-linked polyacrylates. The particles are < 1 μm in diameter, and are used at a concentration of < 0.5 wt%. Lubricants such as fatty amides or polysiloxanes may also be introduced.

Fillers and Dyes. The optical properties of films can be altered by the incorporation of fillers and dyes. A wide range of concentrations is employed. Many fillers are inert inorganic substances, e.g., titanium dioxide, barium sulfate, kaolin, and carbon black. Colored films are normally produced from raw materials that have been dyed in bulk. However, in special cases the films themselves may be dyed either by a diffusion process or by printing the entire surface.

Antistatic Agents. Films are rendered antistatic by mixing the virgin polymer with a substance bearing hydrophilic groups. The additive migrates to the surface layer. Quaternary ammonium compounds, ethyl sulfonates and, especially with polyolefin films, ethoxylated alkyl amines are used as antistatic agents.

Weathering Stabilizers. Most films for outdoor applications are prone to photooxidative degradation and are stabilized by adding UV-absorbing substances. Piperidyl derivatives, for example, are effective stabilizers of polypropylene.

4. Delivery Forms

Commercial quantities of films are available in various thicknesses (ca. 1 – 1000 μm) and are supplied in the form of rolls with cores of a standard diameter (e.g., 6″).

Standardized thicknesses are demanded for many applications. Attempts are being made to establish a standardized system, since this also simplifies production planning and stock control. Films are offered in widths ranging from a few millimeters to several meters. Standard widths have only been established in a few areas of application.

The maximum length of a film depends on the intended application as well as on the film thickness. For example, with poly(ethylene terephthalate) (PET), films with a thickness of 5 μm are supplied in rolls with a typical length of 30 km.

Films that are precut to size are also marketed, although only to a very limited extent.

5. Test Methods [18–24]

Many of the test methods employed for process control in film manufacture have been

standardized. However, the results obtained are not always compatible because the test conditions specified in different standards often vary.

The *chemical composition* of a film is normally apparent from its IR spectrum. Trace elements are determined by atomic absorption spectroscopy, mass spectrometry, or neutron activation analysis. Relative molecular masses can be measured from the viscosity of a film solution. The identity of a film can often be determined more simply with the aid of systematic analytical schemes (e.g., [20], Appendix B).

The *average thickness* of a film is established according to DIN 53 370 or ASTM E 252. No standard method for measuring thickness in both the machine and transverse directions exists as yet. During manufacture, film thickness can be determined by measuring the absorption of either β- or IR radiation or by a dielectric method. The uniformity of the thickness of a film sample can be determined mechanically, electrically, or optically. The accuracy of measurement in all cases is 0.1 μm.

Methods for determining the *mechanical properties* of films are described in ASTM D 882, D 1822, D 1894, D 1922; ISO 1184 (1983). Individual methods are as follows: tear strength, DIN 53 455; elongation at break, DIN 53 457; modulus of elasticity, DIN 53 448; impact strength, DIN 53 374; tear resistance, DIN 53 375; and tear propagation resistance, DIN 40 634 and DIN 53 363.

The *coefficient of friction* is of considerable importance in the converting of films, and conventional methods for its determination are described in DIN 53 375 and ASTM D 1894. Special techniques have been developed for some applications (e.g., for magnetic tapes).

Film density is determined according to ASTM 1505 IC.

The *electrical properties* of films are tested according to VDE 0345/1.65 and 0303/7/1.65; ASTM D 149, D 150, D 229, and D 252; and DIN/sec 15 C. Parameters that are measured include the dielectric strength, dielectric constant, dissipation factor, resistivity, surface resistance, electrolytic corrosion, and glow discharge ignition voltage.

The melting point, glass transition temperature, crystallization and *softening behavior*, and *decomposition temperature* are easily determined by differential thermal analysis. The *long-term thermal stability* of films designed for use as electrical insulators is normally determined according to VDE 0530 or IEC 216; the films can then be classified according to the temperature at which they may be used, i.e., Class T (90 °C), A (105 °C), E (120 °C), B (130 °C), F (155 °C), H (180 °C), and C (> 180 °C).

The coefficient of expansion, dimensional stability, and *thermal conductivity* can be determined by reference to the following standards, which are not, however, exclusively designed for films: DIN 1341, 40 634, 52 328; ASTM D 229, D 1204; VDE 0530/1/1.66.

The following standards apply to the measurement of *optical properties* (transparency, haze, gloss, refractive index, and color): DIN 5033, 53 491; ASTM 1003, D 307, D 1925, D 2457. The measurements are easy to perform, but interpretation of the results can be difficult.

Determination of *permeability* with respect to liquids, vapors, and gases is relatively complicated, but this parameter is especially valuable, since films are widely used as packaging materials. Appropriate procedures are described in DIN 53 122 and 53 386, and ASTM D 1434 and E 96 (E).

Chemical resistance is most easily determined by examining the changes induced in ultimate strength and elongation at break as a result of exposure to the substances concerned. However, the following standards are also applicable: DIN 53 476; ASTM D 543, D 756, D 1435, E 96; ISO/R 175 and R 511.

Water absorption is determined according to DIN 53 472 and ASTM 0570.

The most useful test of *surface structure* is carried out with a profilometer. Since the 1980s this technique has proved itself to be particularly useful for examining film substrates used in the manufacture of magnetic tapes. The best known procedures are those described in DIN 4760 – 4774, the Japanese Industry Standard JIS 0601–70, and ISO/DIS 4267/1. In special circumstances, additional information can be obtained by using microscopy (interference methods and scanning electron microscopy).

The *roll hardness* of film rolls can be evaluated by using the Shore hardness as a criterion (DIN 53 505, ISO 12 868). A better procedure makes use of a falling sphere [24].

The *flammability* of films is evaluated according to DIN 4102, ASTM D 1433, ISO R 1715, and Underwriters Laboratory Standard UL 94 VTM.

Measurement of the *extraction of low molecular mass components* of films with solvents has not been standardized. Most studies are based on special procedures developed by individual manufacturers and end users. Interest centers on films designed for the packaging industry. Information regarding the extractable components of a film often serves as the basic for its legal approval (e.g., FDA approval) [25].

6. Film Products [20, 26, 27]

A remarkable variety of film materials has been developed as a result of several factors: Film manufacturers have a wide choice of potential raw materials and can also use special processing steps such as stretching to modify certain properties of a film during its manufacture. Further variants are made possible by the introduction of additives, by the application of functional coatings, or by lamination of two or more types of film. The following discussion is limited to representative examples from characteristic film groups. Important physical properties of these materials are compiled in Tables 2–5. (The lists of trade names supplied are by no means exhaustive.)

6.1. Cellulose Derivatives

6.1.1. Cellulose Hydrate (→ Cellulose)

Cellophane [9005-81-6] is a trade name applied to films based on cellulose hydrate (regenerated cellulose).

Cellophane is prepared from cellulose via the sodium xanthate derivative in a solution casting process (see Section 2.1) and is available in thicknesses ranging from 12 to 45 μm. Untreated cellophane film is crystal clear, glossy, and highly permeable to water vapor; it is unstable with respect to water, but stable to fats and oils. Cellophane is not heat-sealable, but can be bonded; it is odorless, tasteless, and authorized for use as a food packaging material by the FDA and similar institutions. It possesses desirable mechanical characteristics at the normal water content of 7 – 8 %. Properties are listed in Table 2.

Cellophane is increasingly being replaced by oriented polypropylene films; only a few niche applications are left.

Manufacturers. Wolff Walsrode, Germany; Chemiefaser Lenzing, Austria; British Cellophane, United Kingdom; Flexel, Atlanta, United States; Futamura, Japan.

6.1.2. Cellulose Esters (→ Cellulose Esters)

Films derived from cellulose acetate [9004-35-7] (CA) (2-acetate, 2 1/2-acetate, and 3-acetate), cellulose acetate propionate [9004-39-1] (CAP), and cellulose acetate butyrate [9004-36-8] (CAB) are available; they all contain plasticizers—phthalate esters, aliphatic alcohols, triphenyl phosphate. Solution casting is the usual production method. Methylene chloride [75-09-2] is used as a solvent [9]. The casting solution has a cellulose acetate concentration of 18 – 26 % and a viscosity of 15 – 30 Pa · s.

Cellulose acetate films are the most important of the cellulose ester films. The properties of cellulose acetate vary as a function of the number of acetate groups per cellulose molecule. The properties of cellulose acetate film (2 1/2 acetate) are listed in Table 2. Films with the highest acetate concentration, corresponding to the minimum number of hydroxyl groups, show reduced sensitivity to moisture as well as minimal absorption of water and low water-vapor permeability. These films are crystal clear in their untreated state; they are dimensionally stable at ambient temperature and humidity and possess good electrical properties. Special surface characteristics (e.g., gloss, roughness) can be conferred during manufacture by casting on an appropriate type of metal belt.

Cellulose acetate films are used as supports for photographic coatings, as transparent windows, release films, decorative materials, and as electrical insulators.

Table 2. Properties of selected films[a]

	Cellophane (uncoated)	Cellulose acetate (CA) [b]	Polyethylene (PE)		Poly(4-methyl-1-pentene) (PMP)	Polypropylene (BOPP)
			low-density (LDPE)	high-density (HDPE)		
Mechanical properties						
Thicknesses, μm	12 – 45	12 – 350	25 – 200	50 – 1000	75 – 300	4 – 80
Density, g/cm^3	1.45	1.3	0.92	0.95	0.83	0.91
Ultimate strength						
longitudinal, N/mm^2	100	100	25 [g]	23 [g]	24	140
lateral, N/mm^2	60	100	20 [g]	23 [g]	24	280
Elongation at break						
longitudinal, %	20	30	400 [g]	400	10	140
lateral, %	60	30	700 [g]	400	10	50
Modulus of elasticity						
longitudinal, N/mm^2	5 300	1500	170	900	1100	2 000
lateral, N/mm^2	2 800	1500	170	900	1100	4 000
Electrical properties						
Dielectric strength [c], kV/mm	100	150	200	200	65	340
Dielectric constant at 1 kHz	3.2	4.5	2.3	2.2	2.1	2.2
Dissipation factor	0.015	0.02	0.0002	0.0004	0.003	0.0002
Volume resistivity, Ω cm	10^{11}	10^{14}	10^{17}	10^{17}	10^{16}	5×10^{17}
Thermal properties						
mp, °C			110	130	235	165
Application temperature range [d], °C	− 15 to + 150	− 15 to + 120	− 60 to + 95	− 50 to + 100	−20 to +130	− 20 to + 120
Optical properties n_D^{20}	1.6	1.4 – 1.5	1.50	1.50	1.46	1.50
Dimensional stability						
Coefficient of thermal expansion, K^{-1}	6×10^{-5}	6×10^{-5}				
Shrinkage at 100 °C (30 min)						
longitudinal, %	0.7 – 3.0	0.4	1.0 (80 °C)	0.5	1.6 (160 °C)	3
lateral, %	0.7 – 3.0	0.2	0	0	0	1
Physicochemical properties						
Water absorption in 24 h, wt %	45 – 115	5	< 0.1	< 0.1	< 0.1	< 0.1
Stability toward						
daylight	good	good	limited	limited	poor	limited
organic solvents	moderate	unstable	good	good	good	good
acid	unstable	unstable	good	good	very good	good
alkali	unstable	unstable	good	good	very good	good
salt solutions	unstable	stable	good	good	very good	good
Permeability						
Water vapor, g m^{-2} d^{-1}	very high	350	2.5	1.0	0.6	1.5
Oxygen [e], cm^3 m^{-2} d^{-1} bar^{-1}	10	1 500	4 000	1 600	38 000	600
Carbon dioxide [e], cm^3 m^{-2} d^{-1} bar^{-1}	100	10 000	16 000	7 000	110 000	1 800
Nitrogen [f], cm^3 m^{-2} d^{-1} bar^{-1}	12	300	1 300	400	9 400	140

[a] Standard values determined as described in Chapter 5.
[b] Cellulose acetate film (2 1/2-acetate) containing plasticizer.
[c] At 50 Hz, film thickness = 40 μm, plate/plate.
[d] Temperature range over which no significant loss in strength or stiffness occurs.
[e] Film thickness = 40 μm, 23 °C.
[f] Film thickness = 200 μm.
[g] Film thickness = 50 μm.
[h] Decomposition temperature.
[i] For biaxially stretched (balanced) film.
[j] 20 °C, 0 % relative humidity.
[k] Film thickness = 25 μm.
[l] 40 °C, 90 % relative humidity.
[m] Film thickness = 100 μm.

Table 3. Properties of selected films[a]

	Polystyrene (PS)	Poly(vinyl chloride) (PVC)		Poly(vinylidene chloride) (PVDC)	Polytetrafluoroethylene (PTFE)	Poly(vinyl fluoride) (PVF)
		rigid	plasticized			
Mechanical properties						
Thicknesses, μm	4 – 500	30 – 700	10 – 1 000	25	12 – 1 000	12 – 50
Density, g/cm^3	1.06	1.38	1.24 – 1.3	1.66 – 1.75	2.1 – 2.2	1.38 – 1.57
Ultimate strength						
longitudinal, N/mm^2	60	50	20 – 35	30 – 50	10 – 30	60 – 150
lateral, N/mm^2	60	50	20 – 35	30 – 50	10 – 30	60 – 150
Elongation at break						
longitudinal, %	10	70	250	150 – 250	100 – 350	100 – 200
lateral, %	10	40	250	150 – 250	100 – 350	100 – 200
Modulus of elasticity						
longitudinal, N/mm^2	3 000	2 500	300 – 1 000	230	400	1 400
lateral, N/mm^2	3 000	2 500	300 – 1 000	230	400	1 400
Electrical properties						
Dielectric strength[c], kV/mm	200	60[f]	50 – 100[f]		28[m]	140
Dielectric constant at 1 kHz	2.5	3.5	3.3 – 5.3	4.5 – 6.0	2.0 – 2.1	8.5
Dissipation factor	0.0005	0.02	0.03 – 0.1	0.06 – 0.07	0.0002	1.6
Volume resistivity, Ω cm	10^{16}	10^{15}	10^{11} – 10^{14}	10^{13} – 10^{14}	10^{18}	10^{13}
Thermal properties						
mp, °C	240	160[h]		150	330	200
Application temperature range[d], °C	− 60 to + 100	− 15 to + 75	− 30 to + 50	0 to + 140	− 190 to +250	−70 to +110
Optical properties n_D^{20}	1.59	1.54		1.62		
Dimensional stability						
Shrinkage at 100 °C (30 min)						
longitudinal, %	25	3	0.5	10 – 35		1
lateral, %	25	3	0.5	10 – 35		1
Physicochemical properties						
Water absorption in 24 h, wt %	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.5
Stability toward						
daylight	limited	good	good	limited	very good	very good
organic solvents	limited	good	good	limited	very good	very good
acid	good	good	good	good	very good	very good
alkali	good	good	good	good	very good	very good
salt solutions	good	good	good	good	very good	very good
Permeability						
Water vapor, g m^{-2} d^{-1}	30	7.5	10 – 100	1.5	thickness < 400 μm	32
Oxygen[e], cm^3 m^{-2} d^{-1} bar^{-1}	3 000	80	700 – 1 000	30	contains	30
Carbon dioxide[e], cm^3 m^{-2} d^{-1} bar^{-1}	17 000	160	3 000 – 5 000	200	micropores	110
Nitrogen[f], cm^3 m^{-2} d^{-1} bar^{-1}	500	12	150 – 1 000	5		25

[a] Standard values determined as described in Chapter5.
[b] Cellulose acetate film (2 1/2-acetate) containing plasticizer.
[c] At 50 Hz, film thickness = 40 μm, plate/plate.
[d] Temperature range over which no significant loss in strength or stiffness occurs.
[e] Film thickness = 40 μm, 23 °C.
[f] Film thickness = 200 μm.
[g] Film thickness = 50 μm.
[h] Decomposition temperature.
[i] For biaxially stretched (balanced) film.
[j] 20 °C, 0 % relative humidity.
[k] Film thickness = 25 μm.
[l] 40 °C, 90 % relative humidity.
[m] Film thickness = 100 μm.

Table 4. Properties of selected films[a]

	Poly(ethylene terephthalate) (PET)	Polycarbonate (PC), monoaxially stretched	Nylon 6 (PA), biaxially stretched	Poly(methyl methacrylate) (PMMA)	Ethylene – vinyl alcohol copolymer (EVOH), biaxially stretched
Mechanical properties					
Thicknesses, μm	1.0 – 350	2 – 500	12 – 25	50 – 500	12 – 25
Density, g/cm^3	1.4	1.21	1.16	1.14	1.19
Ultimate strength					
longitudinal, N/mm^2	200[i]	250	260	40	210
lateral, N/mm^2	200[i]	8	260	40	210
Elongation at break					
longitudinal, %	100[i]	30	100 – 120	75	50
lateral, %	100[i]	100	100 – 120	75	50
Modulus of elasticity					
longitudinal, N/mm^2	4 000[i]	2 100	1 400	1 900	3 600
lateral, N/mm^2	4 000[i]	800	1 400	1 900	3 600
Electrical properties					
Dielectric strength[c], kV/mm	320	300	50	90	
Dielectric constant at 1 kHz	3.3	2.8	3. 4 – 3.7	4.4	
Dissipation factor	0.005	0.0012	0. 016	0.046	
Volume resistivity, Ω cm	10^{18}	2×10^{17}	5×10^{17}	10^{16}	
Thermal properties					
mp, °C	260	260	200[h]	160	181
Application temperature range[d], °C	− 269 to +180	−140 to +140	−200 to +180	−20 to +120	
Optical properties n_D^{20}	1.60	1.60			
Dimensional stability					
Coefficient of thermal expansion, K^{-1}	2×10^{-5}	7×10^{-5}			
Shrinkage at 100 °C (30 min)					
longitudinal, %	< 1	< 1	< 1	−11	−4 (140 °C)
lateral, %	< 1	< 1	< 1	0	−0.5
Physicochemical properties					
Water absorption in 24 h, wt %	0.5	0.35	5	0.5	5.9
Stability toward					
daylight	limited	limited	good	very good	
organic solvents	moderate	moderate	good	good (aliph.) poor (arom.)	good
acid	moderate	moderate	poor	very good	
alkali	stable only at low concentration	stable only at low concentration	good	very good	
salt solutions	good	good	good	very good	
Permeability					
Water vapor, g m^{-2} d^{-1}	8	35	100	75	40
Oxygen[e], cm^3 m^{-2} d^{-1} bar^{-1}	50	8 000	26		0.5[j]
Carbon dioxide[e], cm^3 m^{-2} d^{-1} bar^{-1}	250	25 000	100		12
Nitrogen[f], cm^3 m^{-2} d^{-1} bar^{-1}	12	250	9		0.08

[a] Standard values determined as described in Chapter5.
[b] Cellulose acetate film (2 1/2-acetate) containing plasticizer.
[c] At 50 Hz, film thickness = 40 μm, plate/plate.
[d] Temperature range over which no significant loss in strength or stiffness occurs.
[e] Film thickness = 40 μm, 23 °C.
[f] Film thickness = 200 μm.
[g] Film thickness = 50 μm.
[h] Decomposition temperature.
[i] For biaxially stretched (balanced) film.
[j] 20 °C, 0 % relative humidity.
[k] Film thickness = 25 μm.
[l] 40 °C, 90 % relative humidity.
[m] Film thickness = 100 μm.

Table 5. Properties of selected films[a]

	Polysulfone (PSU)	Polyimide (PI)	Polyether-imide (PEI)	Polyether-sulfone (PES)	Polyether-ketone (PEK)	Poly-(phenylene-sulfide) (PPS)
Mechanical properties						
Thicknesses, μm	25 – 1 000	7.5 – 125	75 – 500	25 – 300	75 – 250	2.0 – 125
Density, g/cm^3	1.24	1.42	1.27	1.37	1.24 – 1.30	1.35
Ultimate strength						
longitudinal, N/mm^2	80	180	100	85	120	220
lateral, N/mm^2	80	180	100	85	120	220
Elongation at break						
longitudinal, %	50	70	70	15	200	55
lateral, %	50	70	70	15	200	55
Modulus of elasticity						
longitudinal, N/mm^2	2 500	2 700	3 000	2 400	330	4 000
lateral, N/mm^2	2 500	2 700	3 000	2 400	330	4 000
Electrical properties						
Dielectric strength[c], kV/mm	200	280[k]	145	125	170	240
Dielectric constant at 1 kHz	3.14	3.5	3.56	3.90	3.5	3.0
Dissipation factor	0.001	0.003	0.0013	0.003	0.002	0.0006
Volume resistivity, Ω cm	5×10^{16}	10^{18}	3.4×10^{16}	1.7×10^{16}	10^{17}	10^{17}
Thermal properties						
mp, °C	370	406[h]	216[h]	223[h]	334	285
Application temperature range[d], °C	− 80 to + 170	− 260 to + 400	≤ 170	≤ 180	≤ 240	≤ 180
Optical properties n_D^{20}	1.63	1.78				
Dimensional stability						
Coefficient of thermal expansion, K^{-1}	5.6×10^{-5}	2×10^{-5}	4.5×10^{-5}	4.4×10^{-5}	4×10^{-5}	3×10^{-5}
Shrinkage at 100 °C (30 min)						
longitudinal, %	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
lateral, %	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Physicochemical properties						
Water absorption in 24 h, wt %	0.4	1.3 – 2.9	1.0[l]	1.4[l]	0.4[j]	0.05
Stability toward						
daylight	good	good	good			good
organic solvents	moderate	moderate	satisfactory	satisfactory	very good	very good
acid	good	good	good	good	very good	very good
alkali	good	stable only at low concentration	good	good	very good	very good
salt solutions	good	good	good	good	very good	very good
Permeability						
Water vapor, g m^{-2} d^{-1}	98	84	43.5	100	28.5	5
Oxygen[e], cm^3 m^{-2} d^{-1} bar^{-1}		3.8		200	55	100
Carbon dioxide[e], cm^3 m^{-2} d^{-1} bar^{-1}		6.9				500
Nitrogen[f], cm^3 m^{-2} d^{-1} bar^{-1}		0.9				50

[a] Standard values determined as described in Chapter5.
[b] Cellulose acetate film (2 1/2-acetate) containing plasticizer.
[c] At 50 Hz, film thickness = 40 μm, plate/plate.
[d] Temperature range over which no significant loss in strength or stiffness occurs.
[e] Film thickness = 40 μm, 23 °C.
[f] Film thickness = 200 μm.
[g] Film thickness = 50 μm.
[h] Decomposition temperature.
[i] For biaxially stretched (balanced) film.
[j] 20 °C, 0 % relative humidity.
[k] Film thickness = 25 μm.
[l] 40 °C, 90 % relative humidity.
[m] Film thickness = 100 μm.

6.2. Hydrocarbon Polymers

6.2.1. Low-Density Polyethylene (LDPE) (→ Polyethylene)

Low-density polyethylene [9002-88-4] (LDPE) has a molecular mass of > 50 000 and is prepared by the high-pressure process. It is converted into film mainly by the film blowing process at a melt temperature of 150 – 210 °C. For properties of the film, see Table 2.

Film thickness of LDPE ranges between 25 and 200 μm. The films are transparent to crystal clear, depending on the choice of relative molecular mass and process technology. They are soft, flexible, and resistant to creases and show high tear and tear propagation resistance. Mechanical properties are stable at low temperature and chemical resistance is very high. Films made from LDPE display low permeability to water vapor but high permeability to gases. They are nontoxic and contain neither plasticizers nor odorous materials. Low-density polyethylene films are easily welded and thermoformed. Specific shrinking characteristics can be imparted to the films by stretching at low temperature.

Films made from LDPE are used for packaging and as protective coverings. They are also employed in the production of composite films. Low-density polyethylene has become commercially important. Worldwide annual production is estimated at about 11×10^6 t.

Trade Names. Petrothene (Lyondell Basell, United States); Cryovac L (Cryovac, United States).

Film derived from a copolymer of ethylene with vinyl acetate (EVM film) is used similarly as a packaging material. Its exceptional adhesive properties make it particularly suitable as a cling and stretch-wrap film.

Trade Name. Montothene (American Can, United States).

6.2.2. High-Density Polyethylene (HDPE) (→ Polyethylene)

High-density polyethylene [9002-88-4] (HDPE) prepared by the low-pressure method is also gaining importance as a raw material for films. Films made from HDPE are produced both by chill roll extrusion and by film blowing. Characteristics of the films are given in Table 2.

Films derived from HDPE have a higher chemical resistance than LDPE films and can be employed over a somewhat wider temperature range; HDPE films are used in construction and civil engineering as insulators. High-density polyethylene film can be welded and bonded, and is readily thermoformable.

The market for HDPE films in 2005 was estimated to be 9×10^6 t.

Trade Names. Petrothene (Lyondell Basell United States); Fortiflex (Ineos, United Kingdom).

6.2.3. Linear Low-Density Polyethylene (LLDPE) (→ Polyethylene)

The 1980s witnessed the development of films derived from linear low-density polyethylene (LLDPE), which are produced in the same way as LDPE films. Linear low-density polyethylene films have better mechanical properties (greater strength and higher ultimate strength) than ordinary LDPE films. As a result, LLDPE films have found applications as sacks for transporting heavy materials. Since LLDPE also has a higher melting point (118 °C) than LDPE (110 °C), these sacks can be filled with hot materials (e.g., freshly produced cement). Stretch-wrap packaging represents another expanding market. Like other polyethylene films, LLDPE films can be combined with additional materials to form composite films.

6.2.4. Polypropylene (PP) (→ Polypropylene)

Polypropylene [9003-07-0] (PP) film is available in an unoriented form as well as in both mono- and biaxially oriented versions.

Unstretched PP film is prepared either by chill roll casting or by blowing. Its properties are comparable to those of LDPE film, but with the advantages of greater transparency and a wider application temperature range. Unstretched PP film is used exclusively for packaging purposes. West European consumption in 1986 was 80 000 t.

Monoaxially stretched PP film exhibits increased strength in the direction of orientation and is used for three major applications: (1) cable insulation, (2) tapes and industrial fabrics, and (3) yarns and ropes.

Biaxially oriented polypropylene (*BOPP*) *film* is the most important type of polypropylene film; its properties are listed in Table 2. Worldwide consumption in 2010 is estimated reach 6×10^6 t of which 1×10^6 t be attributed to can China.

Biaxial orientation can be achieved by any of the standard methods (see Section 2.3.2), but sequential stretching is preferred because this method permits a wide range of thicknesses. Most BOPP packaging films are provided with a separate sealing layer, formed either by coextrusion or in an off-line coating process. Coextruded sealing coatings normally consist of polyolefin copolymers, whereas polyacrylate or poly(vinylidene chloride) is used for off-line coating. Poly(vinylidene chloride) has the added advantage that it simultaneously improves the oxygen barrier properties of the film.

Biaxially oriented polypropylene films range in thickness from 4 to 80 μm. They are used industrially in laminates and as release and capacitor films.

Trade Names. Trespaphan (Treophan, Germany); Propafilm (Innovia, United Kingdom); Walothen (Walothen Germany); Bicor (Exxon Mobil, Belgium); Moplefan (Treofan, Germany).

6.2.5. Poly(4-methyl-1-pentene) (PMP) [29] (→ Poly(4-Methyl-1-Pentene))

Poly(4-methyl-1-pentene) [9016-80-2] (PMP) films are produced by extrusion and possess the lowest density of all available films (0.83 g/cm^3). They have a higher softening point (*mp* 240 °C) than PP films (*mp* 165 °C). Film thickness ranges from 50 to 300 μm. For properties, see Table 2.

PMP films have been used only in combination with other materials, mainly with cardboard for the packaging of oven-ready meals.

6.2.6. Ionomers (→ Specialty Plastics)

The term *ionomer* describes a family of polymers incorporating both covalent and ionic bonds. Ionomers [25608-26-8] are based on polyethylene and have carboxyl groups located along their polymer chains. These groups provide ionic cross-links between chains [20]. The corresponding films are prepared by extrusion.

Many of the properties of ionomer films are comparable to those of LDPE films. However, ionomer films are more resistant at room temperature to fats and oils than LDPE films, and they possess exceptionally good sealing properties. They are also extremely tough and are ideally suited for packaging.

Trade Name. Surlyn A (Du Pont, United States).

6.2.7. Polystyrene (PS) (→ Polystyrene and Styrene Copolymers)

Polystyrene [9003-53-6] (PS) films are available in unoriented as well as in mono- and biaxially stretched form. They are produced by chill roll extrusion or by blowing. For properties, see Table 3. For foamed PS films see → Foamed Plastics.

Oriented films are crystal clear with a high gloss but are extremely brittle. Their most important application is for envelope windows. The polymer must be modified with synthetic rubber to increase its strength. However, the resulting increase in impact strength is obtained at the expense of reduced transparency. Film thicknesses are between 4 and 500 μm.

The favorable dielectric characteristics of PS film result in its use in high-voltage capacitors and as an insulator for cables.

Trade Names. Styroflex (Norddeutsche Seekabelwerke, Germany); Trycite (Dow Chemical, United States).

6.3. Halogenated Hydrocarbon Polymers

6.3.1. Poly(Vinyl Chloride) (PVC) [6] [→ Poly(Vinyl Chloride)]

Films formed from poly(vinyl chloride) [9002-86-2] (PVC) may be either rigid or flexible. Rigid films consist solely of PVC; flexible films are produced by addition of plasticizers or by copolymerization with acrylate esters or vinyl acetate. Both rigid and plasticized PVC films are produced by calendering processes, although chill roll casting and film blowing are also possible. Some PVC films are also subjected to stretching.

Rigid and plasticized PVC films are of great economic importance. Worldwide consumption is estimated at 0.8×10^6 t/a.

6.3.1.1. Rigid PVC

Rigid PVC film is available in a wide range of thicknesses (30 – 700 μm); important properties are listed in Table 3. The material varies from crystal clear to transparent and may be colored by the addition of pigments. Rigid PVC is unaffected by water and is virtually impermeable to odors. It possesses outstanding chemical resistance and is also highly flame resistant. The film can be welded, heat-sealed, embossed, thermoformed, stamped, bonded, imprinted, and (under high vacuum) metallized. These remarkable properties combine to produce a broad spectrum of applications for rigid PVC film both in packaging and the industrial sector. Adhesive tapes account for a particularly large share of the market.

6.3.1.2. Plasticized PVC

Plasticized PVC films have an even wider range of applications than rigid PVC because the properties of plasticized PVC can be modified by varying the type and amount of plasticizer added. Plasticized PVC films are available with a thickness of 10 – 1000 μm; for important properties, see Table 3. The material can be strained and shows little tendency to wrinkle; its consistency varies from soft to hard. Plasticized PVC film is resistant to both tear and tear propagation, and it can be embossed, welded, bonded, and stitched. It is resistant to most inorganic and organic chemicals, as well as to water and light. It also shows good aging and weathering properties. Permeability to water vapor and gases is minimal.

Plasticized PVC film is used mainly in packaging and the building industry, as a protective covering, in laminated films, and for the modification of wood surfaces. It is also processed into commercial adhesive tapes.

Trade Names. Genotherm, (Klockker Pentaplast, Germany); Mipolam (Gerflor, Germany).

6.3.2. Poly(Vinylidene Chloride) (PVDC) [27, 30] [→ Poly(Vinylidene Chloride)]

Poly(vinylidene chloride) [9002-85-1] (PVDC) films are made from a vinylidene chloride–vinyl chloride–vinyl acetate copolymer [9003-20-7]. The comonomers render the product sufficiently stable for extrusion. Plasticizers are also added to improve processing properties. The films are manufactured by the tubular drawing process. Since the stability of the melt is low, the film tube must be cooled as it emerges from the die prior to orientation by blowing (see Section 2.3.2). For properties, see Table 3.

Poly(vinylidene chloride) film has been on the market under the trade name Saran since the late 1940s and is still widely used because of its outstanding water vapor and oxygen barrier properties. Its principal application is in the packaging of perishable foodstuffs.

The material is supplied as a shrinkable monofilm or coextruded film; PVDC laminates are also available. Coextruded products are prepared in both tubular and flat form. The PVDC generally is sandwiched between other polymeric layers which impart strength and toughness. Adhesion problems are overcome by simultaneously extruding an adhesive tie layer.

Trade Names. Saran, Saranex (Dow Chemical, United States); Cryovac (Cryovac, United States); Krehalon (Kureha, Japan); Supralon (Supralon, Liechtenstein).

6.3.3. Fluoropolymers [26] (→ Fluoropolymers, Organic)

Incorporation of fluorine into hydrocarbon chains results in polymers that display antiadhesive characteristics, thermal stability, flame resistance, insulating properties, and, most important of all, extreme stability with respect to weathering and aggressive media. As a result of these properties, which depend on the degree of substitution, these films are used mainly under extreme conditions.

From a chemical standpoint, the fluoropolymers used for film production fall into three categories:

1. perfluorinated polymers,
2. partially fluorinated polymers,
3. polymers containing chlorine as well as fluorine

Polytetrafluoroethylene (PTFE) is a perfluorinated polymer that cannot be processed

from a melt by conventional techniques. Polytetrafluoroethylene films are prepared by isostatically sintering the powdered material, followed by "skiving" (paring) of the sintered block. All other fluoropolymers—including copolymers of PTFE with perfluorinated vinyl components—are extrudable and can, therefore, be made into films either by the chill roll process or by film blowing.

The market for fluoropolymer films in the United States is dominated by films made from poly(vinyl fluoride) (PVF), PTFE and polychlorotrifluoroethylene (PCTFE). Extrudable copolymer films made from tetrafluoroethylene–hexafluoropropylene copolymer (FEP), perfluoroalkoxy polymer (PFA), and ethylene–tetrafluoroethylene copolymer (ETFE) have also become somewhat important, or at least have a considerable potential for development. Film made of poly(vinylidene fluoride) (PVDF) is also worth mentioning because of its piezoelectric properties.

6.3.3.1. Poly(Vinyl Fluoride) (PVF)

Poly(vinyl fluoride) [24981-14-4] (PVF) film is commercially available in both transparent and pigmented form in thicknesses of 12 – 50 μm. For properties, see Table 3. Its antiadhesive characteristics, together with its resistance to mechanical, chemical, and weathering effects, make PVF film suitable for use as a protective lamination on both interior and exterior paneling. It also serves as a release film in the pressing of synthetic resin.

Trade Name. Tedlar (Du Pont, United States).

6.3.3.2. Poly(Vinylidene Fluoride) (PVDF) [31]

Poly(vinylidene fluoride) [24937-79-9] (PVDF) films are solvent cast or extruded with a thickness of 50 –500 μm. They possess excellent resistance to weathering and aggressive media.

Poly(vinylidene fluoride) film has an exceptionally high dielectric constant and a relatively high dissipation factor. Because of its piezoelectric properties, the monoaxially stretched film is often employed as a mechanical–electrical transducer in membranes. The consumption of film for piezoelectric applications is small (ca. 1 t); its price is extremely high.

Trade Name. Fluorex (Soliant, United States); Kynar (Arkema, France).

6.3.3.3. Polytetrafluoroethylene (PTFE)

Polytetrafluoroethylene [9002-84-0] (PTFE) films have the highest resistance to aggressive agents of any polymer film and are thermally stable up to 250 °C. Since PTFE films are produced via sintering and skiving, they are somewhat porous; some properties are listed in Table 3. Most of the PTFE film that is produced is used for sealing pipe joints and flanges.

Two related copolymers are extrudable: FEP [25036-53-7], derived from tetrafluoroethylene and hexafluoropropylene, and PFA [2645-79-6], a copolymer of tetrafluoroethylene and a perfluorovinyl ether. Films produced from these materials are not porous, but otherwise display essentially the same characteristics as PTFE itself. The mechanical and optical properties of the extruded films are superior to those of skived PTFE films. Commercial products are available in thicknesses from 12 –1000 μm. Their principal uses are as release films, in the electrical industry, and especially as container linings.

Trade Name. Hostaflon (Dyneon, Germany); Teflon (Du Pont, United States); Fluon (Asahi glass, Japan).

6.3.3.4. Polychlorotrifluoroethylene (PCTFE)

Films made from polychlorotrifluoroethylene [9002-83-9] (PCTFE) are used widely in the packaging of pharmaceuticals and medical supplies; this is because the films possess excellent moisture barrier properties and chemical resistance, coupled with good processability, sterilizability, and UV stability. These films are available in thicknesses ranging from 12 to 250 μm.

Trade Name. Aclar (Honey well, United States).

6.4. Poly(Methyl Methacrylate) (PMMA) [32] (→ Polyacrylates)

Poly(methyl methacrylate) [9011-14-7] (PMMA) films are prepared either by chill roll extrusion or by film blowing; thicknesses range from 50 to 500 μm. They show high resistance to heat and weathering, but their

ultimate strength and elongation at break are relatively low. For properties, see Table 4.

Poly(methyl methacrylate) film is frequently used as a protective layer on metal and plastic, thereby competing with PVF film.

Trade Name. Korad (Polymer Extruded Products, United States); Plexiglas-Folie (Evonik, Germany); Shinkolite Film (Mitsubishi Rayon, Japan).

6.5. Poly(Vinyl Alcohol) (PVA) [33] (→ Polyvinyl Compounds, Others)

Poly(vinyl alcohol) [9002-89-5] (PVA) is produced by hydrolyzing poly(vinyl acetate). Both the fully and partially hydrolyzed polymers are utilized for film manufacture; the fully hydrolyzed polymer is water-soluble.

Poly(vinyl alcohol) film can be prepared by casting an aqueous PVA solution or by extrusion. Prior to extrusion, the poly(vinyl alcohol) is compounded into a paste with water and a plasticizer. Film thicknesses are in the range of 20 – 75 μm.

The characteristic features of PVA film include its high transparency and gloss, toughness, absence of static charge, and, in the absence of moisture, desirable oxygen barrier properties. Water solubility varies, depending on the vinyl acetate content.

Poly(vinyl alcohol) is employed as a monofilm, but can also be coated with PVDC or laminated with polyolefins. Biaxially oriented films can be produced by simultaneous stretching [34].

Poly(vinyl alcohol) films are used as packaging materials for food, textiles, and as release films in the manufacture of synthetic resin products. They are also employed in the manufacture of water-soluble sachets for disposable packaging of hygienic products and as a basis for polarized films.

Trade Names. Vinylon (Kuraray, Japan); Emblar-OV (Unitika, Japan); Bovlon (Nippon Gohsei, Japan).

6.6. Ethylene–Vinyl Alcohol Copolymer (EVOH)

A partially crystalline copolymer of ethylene and vinyl alcohol, EVOH [25067-34-9] is prepared by hydrolysis of an ethylene–vinyl acetate copolymer. This material first appeared on the market in the 1970s [35]; it can be processed into a film by extrusion.

Films derived from EVOH are excellent gas barriers. Biaxial orientation leads to increased strength and further reduction of gas permeability. Since the gas barrier properties of EVOH films are adversely affected by moisture, they are primarily used in the form of laminates or coextrudates. Some properties of oriented EVOH film are listed in Table 4.

The principal application of these materials is in food packaging.

Trade Names. Eval (Kuraray, Japan); Exceed (Okura, Japan).

6.7. Polyamide (PA) [20] (→ Polyamides)

Polyamide (PA) films (thickness 12 – 25 μm) are made mainly from nylon 6 [25038-54-4] and nylon 66 [32131-17-2] by chill roll extrusion or film blowing. The films display high tensile and tear strengths, as well as high resistance to puncture, abrasion, oils, and fats. Nylon films have a low permeability to gases, depending on the atmospheric humidity. Nylon 11 [25035-04-5] and nylon 12 [24937-16-4] are used for films with lower water-vapor permeability.

Orientation improves the properties of nylon films. Biaxially oriented films are produced from nylon 6 by simultaneous stretching. Properties of these films are listed in Table 4.

Polyamide films are used as monofilms but are employed mainly in composite structures produced by lamination, extrusion coating, or coextrusion with sealing or barrier resins. The world consumption of polyamide films is estimated at 320×10^3 t.

Trade Names. Capran (Honey well, United States); Dartek (Du Pont, United States); Bonyl (Kohjin, Japan); Emblem (Unitika, Japan).

6.8. Polyester [10] (→ Polyesters)

The term *polyester film* generally refers to films prepared from poly(ethylene terephthalate) [25038-59-9] (PET). However, other polyesters are also processed into film, e.g., poly(butylene terephthalate) [24968-12-5] (PBT) and poly (ethylene-2,6-naphthalene dicarboxylate)

[24968-11-4] (PEN) (trade name: Q-Film, Teijin/Japan) [36].

Polyester films are manufactured by extrusion; the majority are biaxially oriented and produced in flat form; only a small amount of tubular film is made.

Biaxially oriented PET films are prepared in thicknesses ranging from 1.0 to 350 μm and vary in appearance from clear to transparent, depending on their end use. Pigments can also be added for coloration.

Polyester films have favorable mechanical and electrical properties, are resistant to solvents, and display long-term thermal stability up to 130 °C (VDE 0530). They can be welded and bonded by special techniques. Furthermore, these films can be printed by flexographic, gravure, and screen printing techniques; they are also suitable for high-vacuum metallization without the need for special pretreatment. Some polyester films can be subjected to further deforming subsequent to their manufacture, for example, by thermoforming or thermally induced shrinking. Properties of PET film are listed in Table 4; its permeability to gases and water vapor can be significantly decreased by coating with PVDC.

Polyester films are used for more applications than any other type of film. They are employed as packaging materials, dielectrics, and electrical insulators, as base films for photographic and magnetic coatings, as release films in synthetic resin moldings, and as color and montage film in the graphics industry. These films also serve as a base for flexible printed circuits, as drafting films, and as decorative film. Polyester films have gained considerable importance in the manufacture of videotapes. The demand for polyester film as a base for thermal transfer tapes is also increasing.

Polyester films can be combined with other materials (PE film, paper webs, and aluminum foil) to produce excellent composites.

The economic importance of polyester film is formidable: The total consumption of PET in 2005 was estimated at 2.2×10^6 t because of sustained growth in packaging application.

Trade Names. Hostaphan (Mitsubishi Polyester film, Germany); Mylar (Du Pont, United States); Melinex (Du Pont Tejin films, United States); Lumirror (Toray, Japan); Tetoron (Du Pont Tejin films, Japan); Diafoil (Diafoil, Japan); Terphane (Terphane, United States); Espet (Toyobo, Japan).

6.9. Polycarbonate (PC) [20] (→ Polycarbonates)

Polycarbonate [25037-45-0] (PC) film first appeared on the market in 1957 and is prepared from bisphenol A and phosgene. The principal manufacturers of both polycarbonate and polycarbonate film are General Electric and Bayer.

Polycarbonate films are produced either by extrusion (chill roll) or by solution casting and are available with a thickness of 2 – 500 μm. The thinner grades are subjected to monoaxial stretching. The properties of monoaxially stretched PC film are listed in Table 4.

The special characteristics of these films include their sterilizability, dimensional stability, thermoformability, and long-term thermal stability up to 130 °C (VDE 0530). They are transparent to crystal clear in appearance, and possess good electrical properties. Applications have been found in packaging, the electrical industry, and above all in the field of graphics. Consumption of PC film in the United States is ca. 3000 t/a.

Increased usage is anticipated, partly as a result of new developments in the raw material sector.

Trade Names. Lexan (Sabic Innovative Plastics, United States); Makrofol (Bayer, Material Science Germany); Pokalon (Lofo, Switzerland).

6.10. Polysulfone (PSU) (→ Specialty Plastics)

The first commercially available polysulfone (PSU) was Udel, which was introduced by Union Carbide in 1965 (see also Section 6.12.2). Udel polysulfone [25135-51-7] is produced by reacting bisphenol A and 4,4′-dichlorodiphenyl sulfone. The material is amorphous, with a glass transition temperature of 190 °C, and can be converted into film either by extrusion or by solution casting.

Polysulfone films are available in thicknesses ranging from 25 to 1000 μm. They are highly transparent, possess high heat and dimensional stabilities, and can be thermoformed. Their electrical properties are comparable to those of biaxially oriented polyester films. Polysulfone films are suitable for long-term use at temperatures up to 150 °C, making them superior in this respect to polyester films. Polysulfone films are also stable to alkali, acid, oils, and detergents, although they are attacked by ketones and chlorinated or aromatic hydrocarbons. The properties of Udel PSU film are listed in Table 5.

Principal applications are in packaging, the electrical industry, adhesive tape manufacture, and display technology [37].

Trade Names. Sumilite FS 1200 (Sumitomo Bakelite, Japan).

6.11. Polyimide (PI) (→ Polyimides)

The most important polyimide [25036-53-7] (PI) for film production is derived from pyromellitic acid and 4,4′-diaminodiphenyl ether [38]. Films made from this material do not melt, and they have the highest thermal stability of any synthetic film. They are suitable for long-term applications at temperatures up to 240 °C and short exposure to peak temperatures of up to 400 °C. For properties, see Table 5.

Polyimide films are prepared by dissolving the appropriate monomers in a suitable solvent (e.g., *N,N*-dimethylacetamide), in which they react to form a soluble intermediate (polyamic acid). The film is cast from this solution and is subsequently converted into the insoluble polyimide by intramolecular condensation at 300 °C.

The combination of high thermal stability and flame resistance, along with stability to radiation and favorable electrical properties, makes this film attractive for applications in the aerospace industry (e.g., as an electrical insulator), and the manufacture of electronic components [39]. Commercial grades range in thickness from 7.5 to 125 μm.

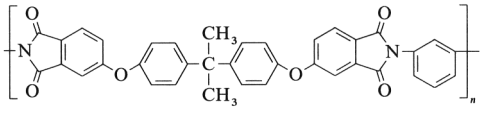
Worldwide capacity in 1986 was 1400 t/a with an expected annual growth rate of 10 %.

Trade Names. Kapton (Du Pont, United States; Toray/Du Pont, Japan); Upilex (Ube Industries, Japan); Novax (Mitsubishi Chemical, Japan).

6.12. Other Films

6.12.1. Polyetherimide (PEI)

The backbone of polyetherimides (PEI) contains both ether and amide linkages. The PEI used for film production was first marketed by General Electric in 1982 under the trade name Ultem and is an amorphous thermoplastic polymer with the structure:



[*61128-24-3*]

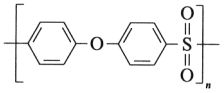
Poly(etherimide) film is prepared by the chill roll process at an extrusion temperature of 350 °C and is available with a thickness of 75–500 μm.

This film is especially suited for electrical applications due to its favorable mechanical and electrical properties. The maximum temperature for long-term use is 170 °C; thus, thermal stability is substantially less than that of conventional polyimides. Nonetheless, stability is adequate for many purposes and significantly higher than that of polyester film [37]. The film is used mainly for electrical insulation. For properties, see Table 5.

Trade Names. Ultem Films (Sabic Innovative films, United States); Sumilite FS-1400 (Sumitomo Bakelite, Japan); Europlex PEI (Evonik, Germany).

6.12.2. Polyethersulfone (PES) (→ Specialty Plastics)

The poly(ethersulfone) (PES) used in film manufacture is an amorphous, thermoplastic material manufactured by ICI under the trade name Victrex. It consists of aromatic rings linked alternately by ether and sulfone groups:



[*25667-42-9*]

Poly(ethersulfone) film is normally manufactured by the chill roll process, although it can

also be cast from solution. Thicknesses vary from 25 to 300 μm. Its range of applications is determined by its electrical and optical properties combined with its thermostability and flame resistant behavior [37, 40, 41].

Poly(ethersulfone) films are used in electrical insulation, interior aircraft fittings, and liquid crystal displays.

Trade Names. Victrex PES-5200 G (Victrex, United Kingdom); Sumilite FS 1300 (Sumitomo Bakelite, Japan); Europlex-Folie (Evonik, Germany).

6.12.3. Poly(ether ketone) (PEK)

Poly(ether ketones) [2738-27-4] can be extruded into either fibers or films in the temperature range 350 –420 °C.

Films made from PEK display high thermal stability (up to 240 °C), solvent and chemical resistance, good dimensional stability, flame resistance, and stability to both radiation and hydrolysis. Properties are listed in Table 5. Since PEK film also possesses favorable electrical properties and is a low-density material, it is used in the aerospace industry.

Both crystalline and amorphous unoriented films are commercially available in thicknesses from 75 to 250 μm [37, 41, 42]. Oriented films are still being developed.

Trade Names. Sumilite FS 1100 (Sumitomo Bakelite, Japan).

6.12.4. Poly(Phenylene Sulfide) (PPS) (→ Specialty Plastics)

Poly(phenylene sulfide) [9016-75-5] (PPS) was marketed as early as 1973 by the Phillips Petroleum Company under the trade name Ryton. However, it was not until 1985 that Phillips, in collaboration with Toray, succeeded in producing the material in film quality.

Poly(phenylene sulfide) is a partially crystalline polymer prepared from sodium sulfide and 1,4-dichlorobenzene. Poly(phenylene sulfide) film is manufactured by extrusion at 300 °C and is similar to PET film in that it can be biaxially oriented and heat-set. Properties of PPS film are given in Table 5. Thicknesses are in the range 2 – 125 μm.

Poly(phenylene sulfide) film combines favorable electrical characteristics with high thermal stability [43]. Thus, it is mainly used in the electrical industry, although it also has potential as a magnetic storage medium.

Trade Names. Torelina (Toray, Japan).

6.13. Composite Films [44]

The most important production methods for composite films are adhesive lamination, extrusion coating (see Section 2.4.3), and, more recently, the simultaneous extrusion (coextrusion) of several raw materials (see Section 2.4.2). The latter approach is unique in that it can produce very thin multilayer films (ca. 12 μm) that still display combined properties.

The incorporation of PET, BOPP, PA, and PVC into composite films permits optimization of ultimate strength, elongation at break, and puncture resistance.

Composite films are especially important as packaging materials, particularly for bulk materials regardless of their state, i.e., gases, liquids, and solids.

Composite films that contain polyethylene can be welded by either heat impulse or thermal sealing methods. Thin polyethylene layers (ca. 30 μm) may suffice for packaging lightweight goods, provided that no need exists for evacuation or a controlled atmosphere. Moderately thick layers (≥ ca. 40 μm) are required for vacuum and inert atmosphere packings. Thicker PE film (≥ ca. 60 μm) is employed if the material to be packaged is a liquid or a paste.

The combination of plastic films with aluminum foil produces semirigid composites with exceptionally low permeability to gases, water vapor, and odors. Special heat-sealable, polyolefin-based layers result in composite films that can be separated by peeling. Composite films incorporating ionomers are especially suitable for packaging oily materials.

7. Summary of Uses [2, 10, 26, 27]

The most important uses of individual films have been described in Chapter 6 and are summarized in Table 6. They can be divided into three main categories: packaging, electrical insulation, and use as bases for other active materials.

Table 6. Uses of films

Application	Film material*																							
	Cellophane	CA	PE	BOPP	PMP	Ionomer	PS	PVC	PVDC	PVF	PTFE	PCTFE	PMMA	PVA	EVOH	PA	PET	PC	PSU	PI	PEI	PES	PEK	PPS
Packaging																								
Food (incl. snack and convenience foods)	x		x	x	x	x		x	x					x	x	x	x	x	x					
Nonfood items	x	x	x	x		x	x	x				x		x		x	x	x					x	
Electrical Insulation																								
Capacitors				x			x										x	x	x					x
Insulation		x		x	x		x				x						x		x	x	x	x	x	x
Printed circuits																	x	x		x	x	x	x	x
Base Film for Functional Coatings																								
Adhesive tapes	x	x		x				x									x		x		x			
Magnetic tapes																	x							
Floppy disks																	x							x
Photographic film		x															x							
Reprography		x															x	x		x				
Decoration	x	x		x				x									x							
Transfer metallization				x													x							
Graphics		x															x	x						
Miscellaneous																								
Office supplies		x	x	x			x	x									x							
Heat mirrors																	x							
Protective lamination			x	x	x			x	x	x	x		x				x				x	x		
Solar collectors																	x			x				
Release film	x	x		x	x					x	x			x			x							
Protective covers			x	x				x																
Display items														x			x		x					

* For explanation of abbreviations, see abbreviations list.

Packaging. Packaging is the most important application of films; virtually every type of film finds some application in the packaging field. Plain and printed films are commonly used in packaging a wide range of foods and nonfood articles. Legal requirements for food packaging are described in [25] (see also → Foods, 4. Food Packaging).

Tubular film prepared either directly by blowing or by the subsequent sealing of flat film is used for the manufacture of a wide variety of bags, sacks, and blister or cushion packs. Thicker films are thermoformed into bottles, containers, cups, trays, and bowls. Shrinkable film is employed in palette packaging. Film is also the basis of skin packings, packing tapes, and even tear-off bands. Decorative iridescent packaging films are available which consist of layers of two or more different polymers with different refractive indices. The iridescent color is produced by light interference [45]. Special characteristics such as impermeability to gases and water vapor can be obtained by applying coatings or using laminated structures.

Electrical Insulation. Films with a high dielectric constant and a low dielectric loss factor are particularly useful in a.c. and d.c. capacitors. Such films may be as thin as 1.0 μm. The films themselves are dielectrics, but they can be converted to electrodes either by vacuum metallizing or by combining them with aluminum foil. Polyester and PI films, either alone or in combination with paper or synthetic nonwoven materials serve as insulating material in electrical equipment. Polymer films are also employed in cable sheathing; thin strips of film are often used as electrical insulation or labels; they also create plasticizer barriers, provide thermal and mechanical insulation, and, in combination with metallic film, confer protection against static charging. Polyester (PET), PC, and PI films are used in the production of flexible printed circuits because of their exceptional dimensional and thermal stability. Film switches represent a new area of application, especially for PET film.

Base Films for Functional Coatings. Polyester film in particular has acquired major significance as a base material for magnetic coatings. Special polyester films combining extra strength with defined surface roughness have been developed for this purpose. Magnetic tapes based on these films are marketed internationally for audio cassette players, video recorders, computers, and other commercial and industrial recording equipment.

Films with a high dimensional stability (e.g. PET) are used as substrates for drafting and photocopying. Films are also used in the printing industry as carriers for transferring color to paper or plastics (stamping foil). Film coated with deformable materials are used as embossing films. Iridescent films and films coated with firmly bonded layers of metal and/or lacquers are frequently used for decorative or display purposes. Films are also the basis for most adhesive tapes. The introduction of a wide range of film-based typewriter ribbons are another application.

Miscellaneous. The furniture industry employs films as veneers for the surface treatment of sheet materials. Thicker films (sheets) are thermoformed into ceiling and wall panels, as well as decorative fixtures and reproductions.

The use of films in heat mirrors and solar collectors (→ Solar Technology) is a more recent development. Heat mirrors employ coated films (mostly PET) that transmit visible light and reflect infrared light. In solar collectors, solar energy is absorbed and passed to a flowing heat-transfer medium (e.g., water). Solar collectors may be constructed from UV-stable film.

Film is frequently used as a protective covering for equipment and materials. Many modern greenhouses are constructed almost entirely from transparent film material. The building industry generally makes frequent use of films on account of their waterproofing properties. Small amounts of films are used for rainwear and clothing.

8. Environmental Aspects

Most of the scrap rolls and waste generated in film production as a result of edge trimming and manufacturing problems is collected and recycled. Special facilities are required for shredding the film and compressing it into granules suitable for reprocessing.

Film constitutes 1 – 2 % of normal household waste. Separate collection and recycling of waste film is in theory possible, but is expensive and requires considerable organization. All films can be regarded as environmentally harmless, provided that they are disposed of properly. Combustion of film waste presents no particular technological problems. Even PVC film can be safely incinerated, although public controversy suggests otherwise; modern combustion facilities are capable of trapping any hydrogen chloride vapor that is formed.

Films can create litter problems; a number of film additives and other chemical modifications have been proposed for accelerating the rate at which films undergo photooxidative decomposition. However, apart from one exception these suggestions have not been implemented, primarily because the required precision in formulation for a given application is difficult to achieve. In addition they conflict with the present ideas of litter prevention. The sole exception is the *mulch film* employed in agriculture for stimulating seed germination and growth; this product is designed to have a lifetime of only one growing season.

Abbreviations used in this article:

BOPP	biaxially oriented polypropylene
CA	cellulose acetate
CAB	cellulose acetate butyrate
CAP	cellulose acetate propionate
ETFE	ethylene–tetrafluoroethylene copolymer
EVM	ethylene–vinyl acetate copolymer
EVOH	ethylene–vinyl alcohol copolymer
FEP	tetrafluoroethylene–hexafluoropropylene copolymer
HDPE	high-density polyethylene
LDPE	low-density polyethylene
LLDPE	linear low-density polyethylene
MD	machine direction
PA	polyamide
PBT	poly(butylene terephthalate)
PC	polycarbonate
PCTFE	polychlorotrifluoroethylene
PEI	polyetherimide
PEK	polyetherketone
PEN	poly(ethylene-2,6-naphthalene dicarboxylate)
PES	polyethersulfone
PET	poly(ethylene terephthalate)
PFA	perfluoroalkoxy copolymer
PI	polyimide
PMMA	poly(methyl methacrylate)
PMP	poly(4-methyl-1-pentene)
PP	polypropylene
PPS	poly(phenylene sulfide)
PS	polystyrene
PSU	polysulfone
PTFE	polytetrafluoroethylene
PVA	poly(vinyl alcohol)
PVC	poly(vinyl chloride)
PVDC	poly(vinylidene chloride)
PVDF	poly(vinylidene fluoride)
PVF	poly(vinyl fluoride)
TD	transverse direction

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Polyamide Fibers

ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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This article deals predominantly with linear polyamide fibers derived from aliphatic monomers, all of the generic class called *nylon*. Linear, aliphatic polyamides are conveniently divided into two groups: those made from aminocarboxylic acids and those made from diamine–dicarboxylic acids. These are characterized by the number of carbon atoms in the monomeric starting material. For example, nylon 11 is the polycondensate of 11-aminoundecanoic acid [$H_2N(CH_2)_{10}COOH$]. Nylon 610 is the polycondensate of 1,6-diaminohexane [$H_2N(CH_2)_6NH_2$] and sebacic acid [$HOOC(CH_2)_8COOH$]. Fibers of aromatic polyamides in which the amide linkages attach directly to two aromatic rings are called aramids, and are covered under → High-Performance Fibers. The history of the beginning and growth of nylon has been reviewed [1].

1. Properties

Nylon fibers are superior to all natural and regenerated fibers with respect to high tenacity and elongation, abrasion resistance, and insensitivity to rotting and moth attack. By heat treatment, fabrics of nylon fiber can be set into stable shapes through formation of additional hydrogen bonds. The highly polar nature of carbonamide groups also results in swelling of nylon fibers in water or in polar solvents, and permits simple dyeing processes with disperse, acid, and metallized dyes. Nylon fibers absorb moisture and swell longitudinally. This limits "outdoor" use because of poor dimensional stability.

Other general properties of nylon are as follows:

- Shrinkage: dependent on conditions; 1–15% when setting in water or hot air
- Abrasion resistance: outstanding; especially suitable for textile floor coverings
- Electrostatic charge: high at low relative humidity; reduced significantly in antistatic fibers (addition of carbon black or polyglycol ether compounds)
- Solubility: at room temperature in concentrated inorganic acids, *m*-cresol, *o*-chlorophenol, and phenol–alcohol mixtures; at the boil in benzyl alcohol and phenylethyl alcohol
- Dyeability: with acid, metal-complex, disperse, and reactive dyes; special types with basic dyes
- Stability:
  - *Light stability:* highly dependent on pigmentation and presence or absence of stabilizers

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Table 1. Physical properties of some Nylon fibers

Property	Nylon 6	Nylon 66	Nylon 11	PACM-12*
mp, °C	214–220	255–260	190	275
ϱ, g/cm^3	1.14	1.14	1.04	1.03
Water absorption,%				
65% R.H., 21 °C	3.5–4.5	3.5–4.5	1.3	1.5–2
Water retention	9–15	9–15	2.9	ca. 3
Tenacity, cN/dtex	3–9	3–9	4–7	2.5–3
Elongation at break,%	80–15	80–15	40–15	30–25
Wet–dry strength,%	80–90	80–90	100	NA**
Loop–straight strength,%	70–90	70–90	NA**	NA**
Elastic modulus, cN/dtex				
Textile fibers	5–30	5–30	45	20–30
Industrial fibers	60–90	60–90	NA**	NA**
Setting temperature, °C	185–195	200–230	NA**	190

* Nylon from bis(4-aminocyclohexyl)methane and dodecanedicarboxylic acid.
** Not applicable.

- *Thermal oxidation:* yellowing and molecular degradation reduced by stabilizers (Cu^+ or antioxidants)
- *Weathering:* relatively poor outdoor life, especially with fine deniers
- *Dilute acid:* adequate resistance
- *Dilute alkali:* good resistance
- *Biological stability:* good to very good resistance against decay-producing bacteria, mold fungi, and moth larvae
- *Shape stability:* good crease resistance with dry materials. On absorbing water, nylon fibers swell in the direction of the fiber axis. The lengthening must be considered in the manufacture of clothing, especially with nylon 6 and nylon 66. With felts for floor coverings, dimensional stability is improved by blending with nonswelling fibers such as polypropylene.

Physical properties of four nylon fibers are given in Table 1.

2. Polyamides for Synthetic Fibers

The high molecular mass, linear polyamides that are useful for synthetic fibers contain mainly methylene groups between the carbonamide groups. They comprise those compositions that can be melted and spun into filaments without decomposing.

The introduction of cyclic segments into an aliphatic polyamide chain generally stiffens the chain and raises the melting point (Table 2). The effect is most pronounced when the ring structure is aromatic and symmetrical, and when the amide group is connected directly to an aromatic ring. Connection of two aromatic rings to the amide group defines the aramid class of polyamides, which usually degrade without melting and cannot be melt-spun. Melt temperature is also strongly affected by ring symmetry, as seen in the 90 °C difference in melting points of the *meta* and *para* isomers of the two xylene diamines.

Introduction of C-alkyl side chains in nylons disrupts molecular order and leads to both a reduction in melt temperature and increased

Table 2. Comparison of melting points for various polyamides

Diamine	Diacid	CAS registry no.*	*mp*, °C
m-Xylylene-α,α'-diamine	adipic	[25805-74-7]	243
1,6-Diaminohexane	adipic	[9011-55-6]	265
p-Xylylene-α,α'-diamine	adipic	[24938-72-5]	333
1,6-Diaminohexane	terephthalic	[24938-03-2]	370
p-Xylylene-α,α'-diamine	terephthalic	[24938-64-5]	> 400

* For the polyamide from the diamine and diacid.

solubility in organic solvents. The influence of *N*-alkyl substituents is even greater, because they eliminate the possibility of hydrogen bonding between polyamide molecules. The polyamide of piperazine and adipic acid, which melts at 185 °C, is of scientific interest because the effect of the missing hydrogen bonds is largely compensated for by chain stiffening through the piperazine radical.

The effect of *C*-methyl and *N*-methyl groups on the melting temperature of nylons made from adipic acid and a diamine is as follows:

$H_2N-(CH_2)_4-NH_2$	251 °C
$H_2N-(CH_2)_2-CH(CH_3)-(CH_2)_3-NH_2$	180 °C
$HN(CH_3)-(CH_2)_6-NH_2$	145 °C
$HN(CH_3)-(CH_2)_6-NH(CH_3)$	−75 °C

Substitution of oxygen or sulfur for a methylene group in aliphatic polyamides also results in a lower melting point. In the low molecular mass region, nylon melt temperatures increase significantly with increasing molecular mass. This effect, however, can be neglected at the high molecular masses necessary for fiber production. The strength of nylon fibers also increases with increased molecular mass, but melt spinning has technological limits because of the difficulty of handling very high melt viscosities.

The melting temperature of nylon decreases with increased ratio of methylene groups to carbonamide groups, and approaches the melting temperature of polyethylene (*mp* 130–150 °C, depending on molecular mass). Thus, nylon 22 melts at 145 °C. However, melting temperatures of the two types of nylon do not decrease uniformly, because nylons in the homologous series with an even number of methylene groups between carbonamide groups melt at higher temperatures than the adjacent nylons with an odd number of methylene groups (Tables 3 and 5). This is because the geometrical symmetry of the even-numbered configuration permits tighter chain packing and better hydrogen bonding. Water absorption and nylon density also decrease with increased number of methylene groups, i.e., as the molecule becomes more alkane-like (Table 3).

2.1. Aminocarboxylic Acid Type Polyamides

Nylons of the aminocarboxylic type can be prepared by the following methods:

1. Polycondensation of ω-aminocarboxylic acids having more than five carbon atoms
2. Hydrolytic polymerization of lactams having more than six ring members
3. Anionic polymerization of lactams with exclusion of water

Tables 1 and 3 list the most important *physical properties* of this type. Fibers are characterized by a high tenacity of 6–7 g/dtex and a break elongation of 20–30%. An exception is nylon 4, with a tenacity of ca. 4 g/dtex.

Nylon 1 [32010-01-8]. Nylon 1 falls into this class by virtue of the linear connection of carbonamide groups; it is a polyamide based on its chemical structure [2]:

$-CO-NH-CO-NH-CO-NH-$.

However, derivatives prepared from monoisocyanates have no polyamide properties.

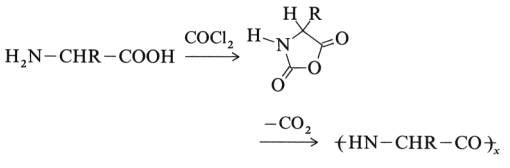
Nylon 2 [25734-27-4]. The polyamide from aminoacetic acid is really the first member of the series defined by the general formula $H[HN-(CH_2)_n-CO]_xOH$ $(n = 1)$. So far,

Table 3. Physical properties of some aminocarboxylic acid type polyamides

Polyamide	*mp*, °C	Water absorption, %		Wet strength as a	ϱ, g/cm^3
		65% R. H.	100% R. H.	% of dry strength	
4	265	9.1	28.0	70–80	
6	223	4.3	9.5	85–90	1.14
7	233	2.8	5.0		1.10
8	200	1.7	4.0	93–97	1.08
9	209	1.5	3.3		1.06
10	188	1.4	3.0		1.04
11	190	1.3	2.8		1.04
12	179	1.3	2.7	100	

preparing nylon 2 with sufficiently high molecular mass for the production of fibers has not been possible. A high order of crystallization would be expected, and spinning would only be possible by a solvent spinning process. Filaments of nylon 2 could resemble natural silk very closely in physical properties.

High molecular mass nylon 2 derivatives alkylated on the α-carbon atom may be also viewed as polypeptides of α-aminocarboxylic acids and can be prepared by ionic polymerization of *N*-carboxylic acid anhydrides:

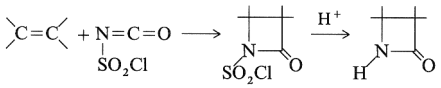


Polymerization can be initiated with a variety of catalysts such as alkali hydroxides and carbonates, phenols, and amines. Spinnable polymers have been obtained only from pure optical isomers, i.e., L- or D-aminocarboxylic acid derivatives. The Japanese have produced semiworks quantities of polypeptide fibers based on L-glutamic ω-ester, which are reported to have unusual properties.

Nylon 3 [25513-34-2]. Nylon 3 would be expected to have good fiber properties, but no economically attractive route to its preparation has been found. It melts at 330 °C and should be spinnable to fibers from superheated aqueous solutions [3].

C-Alkyl derivatives of nylon 3 are of interest for fibers because of new syntheses of corresponding β-lactams [4].

Chlorocyanogen and sulfur trioxide react to form the easily accessible *N*-carbonylsulfamidic acid chloride. Under mild conditions, this reacts with olefins to form the β-lactam-*N*-sulfonyl chloride, which can be converted to the β-lactam through hydrolysis in a weakly acidic medium:



Because both the β-lactams and the corresponding polyamides generally decompose above 250 °C, these nylons are prepared preferably through anionic polymerization in solution, at temperatures of − 15 to 30 °C. For copolymerization, the β-lactams must have reasonably similar polymerization rates. Polymerizations are anhydrous with alkaline catalysts, e. g., alkali lactams or N-alkyl lactams. In contrast to melt-spun polyamides in which molecular masses of 15 000 to 25 000 are adequate for good fiber properties, molecular masses of > 200 000 are required for β-lactams, where fibers are made by solution spinning. Fibers with good textile properties and remarkably good oxidative stability can be prepared from (β,β-dimethyl-β-propriolactam), spun from a ca. 15% solution. Typical solvents are trifluoroethanol, phenol, and dimethyl sulfoxide.

Nylon 4 [24938-56-5]. The polycondensate of 4-aminobutyric acid is prepared by anionic polymerization of γ-butyrolactam in the presence of alkaline catalysts at < 60 °C.

The reaction is carried out in an inert hydrocarbon solvent, and conversion is ca. 80–85%. Precipitated polymer must be washed thoroughly to remove residual monomer, traces of which accelerate decomposition of the polymer at the melting point. Nylon 4 can be melt-spun at 279–280 °C, but residence time in the melt must be short to avoid decomposition or reversion to γ-butyrolactam. Nylon 4 can also be spun from a 45% formic acid solution, but lower tenacity is obtained. Because of its relatively high water absorption (9% at 65% R.H.), nylon 4 can be dyed easily, but it has relatively poor crease resistance. The fibers have not been significant economically, in part because of their poor temperature sensitivity in spinning [5].

Nylon 6 [25038-54-4]. While not ideal for optimum fiber properties, nylon 6 represents about half of the commercial production of nylon fibers and occupies a transitional position in this series. Whereas 4-aminobutyric and 5-aminovaleric acid proceed smoothly to the corresponding lactams on heating above melt temperature, 6-aminocaproic acid forms a temperature-dependent equilibrium condensate. At 250 °C, this consists of ca. 89% linear polyamide, 8.5% caprolactam, and 2.5% larger ring amides. This equilibrium condensate is identical with the equilibrium polymer that

results from hydrolytic polymerization of ϵ-caprolactam.

Problem-free continuous polymerization of caprolactam (→ Caprolactam) can be carried out in perpendicular flow-through tubes, with small additions of water, at 240–270 °C and atmospheric pressure. Batch polymerization in pressure autoclaves can also be carried out, which is a preferred technique for small production units or for polymer with special additives. Anhydrous caprolactam can also be polymerized with alkaline catalysts or cocatalysts, but this "fast polymerization" is not used in the manufacture of fibers. Excess caprolactam and higher ring amides must be removed from the equilibrium mixture before further processing to fibers. The equilibrium melt is extruded, solidified, cut to granules or flake, washed repeatedly with boiling water, and then vacuum dried. This can be done batchwise or continuously. Careful exclusion of oxygen is essential in all processing steps. Nylon 6 can also be polymerized and spun directly by passing the equilibrium polymer through a continuous, thin-film evaporator to remove impurities and then pumping it directly to the spinning machine [5, pp. 121–134].

Because of its relatively low melting point and high water absorption, and the lack of a technically simple way to convert monomer to a continuously spinnable melt, nylon 6 is not the best aminocarboxylic acid type for producing synthetic fibers. The reason for its great importance and large production volume is economic. The high-purity caprolactam required for fiber production is made from favorably priced raw materials (benzene, cyclohexane, or phenol).

Nylon 7 [25035-01-2]. Nylon 7 is generally considered to be the optimum aminocarboxylic acid type polyamide for fibers. In both the condensation of 7-aminoheptanoic acid and the hydrolytic polymerization of enantholactam, yields of linear polymer exceed 99%. This means that nylon 7 can be produced continuously in a technically simple polymerization-spinning process. Textile properties of nylon 7 fibers are superior to those of nylon 6 and, to a degree, those of nylon 66. Of particular interest, compared to nylon 6, are the 10 °C higher melting temperature and reduced water absorption. These two properties lead to important advantages, i.e., a considerably higher wet modulus and improved crease recovery (Table 4).

To date, no economically competitive route for production of the monomer has been reported. Small quantities of nylon 7 are produced in Eastern Europe. For this, 7-aminoheptanoic acid is reportedly prepared by telomerization of carbon tetrachloride and ethylene, via the intermediate 7-chloroheptenoic acid.

Nylon 8 [25035-02-3]. Nylon 8, which melts at 200 °C, is prepared by hydrolytic polymerization of caprolactam. The equilibrium polymerizate contains only traces of ring amide, so that fibers can be produced by using a continuous polymerization-spinning process. Because of the reduced number of carbonamide groups, water absorption is low, which provides relatively good wet strength and wet elasticity. However, raw materials for the synthesis of caprolactam are too expensive for this polymer to be attractive economically.

Table 4. Physical and textile properties of high-strength filaments from nylons 6, 7, and 66 [6]

Property	Nylon 6	Nylon 7	Nylon 66
Tenacity, cN/dtex	8.0–8.5	8.1–8.5	8.2–8.7
Wet strength,% of dry	81	92	85
Elongation at break,%	24	14–16	18
Elastic modulus, cN/dtex*	41	46–49	54
Wet modulus,% of dry**	27	62	31
Boil-off shrinkage,%	12	8–10	10
ϱ, g/cm^3	1.14	1.10	1.14
mp, °C	214–220	225–233	255–260
Water absorption,%			
65% R.H.	4.3	2.8	4–4.5
100% R.H.	9–10	5	9–10

* At 1% elongation.
** In 25 °C water.

Nylon 11 [25035-04-5]. The synthesis of nylon 11 is based on a five-step process from castor oil to 11-aminoundecanoic acid. A 30–40% aqueous dispersion of the acid can be polycondensed in three steps, and the nylon 11 formed can be isolated and melt-spun. Addition of phosphoric or phosphorous acid facilitates spinning by raising the melt viscosity and limiting side-chain growth. As expected from the longer hydrocarbon chain, nylon 11 shows hardly any sensitivity or dimensional change in the presence of moisture. The fibers are too expensive for general use and are restricted to a few special applications in luggage, ropes, transmission belts, and bristles.

Nylon 12 [24937-16-4]. Nylon 12 is prepared by hydrolytic polymerization of lauryl lactam, made by a four-step process from butadiene. The reaction to give polymer is essentially complete, so spun products can be prepared by using a continuous polymerization-spinning process. Because nylon 12 has good thermal stability, polymerization temperatures can be raised to 310–340 °C [7]. Except for a 10 °C lower melting point, fiber properties of nylon 12 closely correspond to those of nylon 11. These fibers are not made in large volume because of cost, and their use is restricted mainly to industrial specialty areas.

2.2. Diamine–Dicarboxylic Acid Type Polyamides

Nylons of this group are prepared for fiber use primarily by thermal polycondensation of equimolar amounts of diamines and dicarboxylic acids or their salts. Monomers that can undergo intramolecular condensation, like glutaric and succinic acids, are not suitable for thermal polycondensation. In commercial practice, aqueous solutions or suspensions of the salt are processed in batchwise or continuous operation. Polycondensation is induced initially by treatment of the concentrated salt under pressure to avoid loss of diamine, and then under vacuum to increase molecular mass to the degree required for fiber production.

This type of nylon can also be prepared from diamines and dicarboxylic acid dichlorides through interfacial polymerization. Some nylons, with melting temperatures in a range suitable for melt spinning, 180–280 °C (Table 5), are obtained by combination of aliphatic diamines and dicarboxylic acids. However, only nylon 66 has any economic significance.

Table 5. Melting temperature of nylons

Diamine	Dicarboxylic acid	Nylon	*mp*, °C
1,4-Diaminobutane	adipic	46	278/295
	pimelic	47	233
	suberic	48	250
	azelaic	49	233
	sebacic	410	239
1,5-Diaminopentane	glutaric	55	198
	adipic	56	223
	pimelic	57	183
	suberic	58	202
	azelaic	59	179
	sebacic	510	185–195
1,6-Diaminohexane	adipic	66	250–265
	pimelic	67	202–228
	suberic	68	220–232
	azelaic	69	185–226
	sebacic	610	209–221
1,7-Diaminoheptane	adipic	76	226–250
	pimelic	77	196–214
	sebacic	710	187–208
1,8-Diaminooctane	adipic	86	235–250
	suberic	88	205–225
	sebacic	810	197–210
1,9-Diaminononane	adipic	96	205
	azelaic	99	165
	sebacic	910	179
1,10-Diaminodecane	adipic	106	230–236
	suberic	108	208–217
	sebacic	1010	194–203

Nylon 46 [24936-71-8]. The fiber from 1,4-diaminobutane and adipic acid is claimed to have better high-temperature properties than nylon 66 [8]. Good strength retention and low shrinkage suggest industrial applications. The advantages of nylon 46 fibers concern the heat capacity, dimensional stability, hydrolytic resistance, processing, fabric softness and dyeability [9]. Further promising end-use opportunities are seen to open up including protective clothing, V-belts, conveyor belts, cord fabrics, and sewing threads.

Nylon 66 [32131-17-2]. Because raw materials are favorably priced for producing both adipic acid (cyclohexane) and 1,6-diaminohexane (acrylonitrile, butadiene, and adipic acid), nylon

66 has outstanding economic importance in the production of synthetic fibers (→ Adipic Acid; → Cyclohexane).

For the production of fiber-grade polymer, a 50–60% aqueous nylon salt solution is heated in a pressure autoclave, with careful exclusion of oxygen. The pressure is released slowly, and the resultant low molecular mass polymer is heated under vacuum in the same vessel to increase molecular mass and melt viscosity to the level required for fiber spinning. Polycondensation can also be carried out continuously [10] and the resultant melt pumped directly to the spinning machine.

Nylon 610 [9008-66-6]. Nylon 610 is prepared under conditions similar to those for nylon 66. Because of low water absorption and high elasticity, nylon 610 is especially suitable for production of bristles. The cost of sebacic acid, produced from castor oil, is fairly high and limits the use of this polymer.

Nylons Containing Aliphatic or Aromatic Rings. There is currently no significant commercial production of linear polyamides containing aliphatic ring structures. Many have been investigated for use in tires for improved flat spotting, for better carpet aesthetics, and for improved wrinkle resistance and tactile aesthetics in nylon apparel fabrics.

One ring-containing nylon fiber, T-472 [26403-85-0], was marketed commercially in the early 1970s by Du Pont. It was based on bis (4-aminocyclohexyl)methane and dodecanoic acid.

The diamine is obtained by catalytic hydrogenation of 4,4′-diaminodiphenylmethane (made from aniline and formaldehyde), resulting in a mixture of *cis* and *trans* isomers. The mixture must be fractionally crystallized to yield the preferred 70% *trans*,*trans* product [11]. This isomeric mixture is polycondensed with dodecanoic acid to yield a melt-spinnable polymer (*mp* 275 °C) and fibers with high tenacity and resilience, and low water sensitivity.

The luxury, silklike fabric made from T-472 fiber was marketed under the registered trade name Qiana. The product was withdrawn from the market in the early 1980s for economic reasons.

Nylons containing aromatic rings are called aramids. Aramids are produced in principle by the polycondensation process [12]. Melt condensation as in the case of the aliphatic polyamides is not possible here because the melting point lies above the decomposition temperature. Aramids can be produced [13] by reaction of diamines with acid dichlorides by means of solution polycondensation, interfacial polycondensation, or emulsion polycondensation. Solution polycondensation has proved successful for the production of aramids. Strong polar organic liquids such as dimethylacetamide, dimethyl sulfoxide, *N*-methylpyrrolidone, etc. are used as solvents. To increase the solubility of the polyamide being produced, lithium chloride, calcium chloride, or other inorganic salts can be added. The reaction is strongly exothermic so the reactive solution has to be cooled and stirred intensively. Reaction times are between 2 and 20 h. After the condensation reaction the byproducts (hydrochloric acid) must be neutralized. This is done, for example, using calcium hydroxide or calcium carbonate. The neutral solution is degassed and as a rule can be used directly in the spinning process.

The base polymers of the aramids which are currently the most important are poly-*m*-phenyleneisophthalamide (MPIA) used to produce the meta-type fibers, poly-*p*-phenylene-terephthalamide (PPTA) used to produce the para-type fibers and poly-*p*-phenylene/3,4-diphenyleneterephthalamide used to produce the copolymer fibers of the para-type [14].

MPIA is produced by polycondensation of *m*-phenylenediamine and the dichloride of isophthalic acid (isophthaloyl dichloride) (Du Pont method). The freshly distilled *m*-phenylenediamine is dissolved in dimethylacetamide (DMAC) and a small quantity of aniline is added as a chain-breaking reagent. After cooling, the solution is placed in a reaction vessel where the polycondensation reaction takes place at a temperature of 70°C. Quicklime is used to neutralize the hydrochloric acid.

PPTA is formed from the components *p*-phenylenediamine and terephthaloyl dichloride (methods used by Du Pont and Akzo/Enka AG). Here too solution polymerization is used with the aid of a mixture of organic solvents such as *N*-methyl pyrrolidone and hexamethyl phosphoramide. For the process to be successful it is important that pure diamine (> 99.5%) and a diacyl chloride (> 92.5%) are used and that the

solvent contains only a small amount of water (< 0.05%). Since the reaction product is a solid, the polymer synthesized must be isolated from the solvent and dried. After that the polymer is dissolved again in concentrated sulfuric acid at a concentration which allows the spinning of liquid crystals as spinning solution [15].

For copolymerization, as in the production of PPTA, terephthalic acid chloride, *p*-phenylenediamine and additionally 3,4-diaminodiphenyl ether (DAPE), which is an aromatic diamine and ether compound, are used. Compared with PPTA this polymer is soluble in organic solvents. Polymerization and spinning are linked directly together and no separation of the polymer is necessary [15]. Because of the low concentration of the spinning solution, hot drawing is necessary here to obtain good fiber properties.

2.3. Copolyamides

Nylon copolymers are formed easily by polycondensation of monomer mixtures. Compared to the corresponding pure polyamides, they have lower melt temperatures and higher solubilities. In the case of copolyamides of 6-aminocaproic acid and 1,5-hexanediammonium adipate, the melt temperature minimum is ca. 160 °C at 60 wt% of the amino acid. The melting temperature of the copolyamides can be reduced still further through ternary monomer mixtures. Low-melting copolyamides are suitable, for example, for thermal bonding of needle felts and nonwoven fabrics. Copolyamides of ϵ-caprolactam and 11-aminoundecanoic acid are especially suitable for fishing lines because of good flexibility and increased transparency.

New low-emission copolyamides were developed for the automotive industry [16].

3. Special Requirements for Polyamides

The *purity* of all nylon starting materials is especially important because reactive impurities result in uncontrolled chain growth and can reduce the quality of the spun product, e.g., by increased yellowing tendency. Mechanical impurities must be removed carefully by filtration before polymerization. The polymer melt is also filtered to remove mechanical impurities and pigment agglomerates, by passing it through a bed of sand or powdered metal and fine screens, just before it is extruded in filament form. This is especially important in the production of fine-denier filaments in which coarse impurities can reduce quality and yield through filament breaks.

Because nylons are particularly sensitive to oxidation at elevated temperature, *oxygen* must be scrupulously excluded in both the polymerization and the spinning steps. The oxygen content of the inert gases used, primarily carbon dioxide and nitrogen, should be maintained below 0.001%. In both the hydrolytic polymerization of lactams and the polycondensation of aminocarboxylic acids, an equilibrium exists whose position is influenced substantially by the water content of the polyamide melt:

$$\mathrm{H[HN{-}(CH_2)_n{-}CO]_aOH + H[HN{-}(CH_2)_n{-}CO]_bOH \rightleftarrows}$$

$$\mathrm{H[HN{-}(CH_2)_n{-}CO]_{a+b}OH + H_2O}$$

Water removal leads to an increase in average molecular mass; water addition reduces average molecular mass. The same is true for nylons of the diamine–dicarboxylic acid type. *Viscosity stabilizers* are added to the monomeric starting materials to control the degree of polymerization and prevent an undue increase in viscosity in remelt. Both monofunctional and bifunctional compounds are used to limit chain growth. Especially suitable for this purpose are primary and secondary aliphatic amines or diamines, aliphatic and aromatic carboxylic acids, and dicarboxylic acids. Examples are cyclohexylamine, 1,6-diaminohexane, acetic acid, benzoic acid, and adipic acid. Trifunctional compounds are undesirable because they lead to molecular branching.

Good *analytical control* of polymer quality is essential to good spinning continuity and high fiber quality for all synthetic polymers. A narrow molecular mass distribution is desirable. Broad distributions can result from improper design or improper operation of a continuous polymerizer for nylon, and this frequently leads to inferior fiber properties.

Molecular mass distribution can be determined by using the ultracentrifuge [17], by

turbidity titration, by fractional precipitation or partition between two liquids, or by chromatography. From the molecular mass distribution, molecular mass can be calculated as the number average (M_n) or the mass average (M_m). The ratio M_m/M_n is always greater than 1 and is a numerical measure of molecular nonuniformity. The absolute value of M_n can be determined cryoscopically, osmotically, or through end-group analysis; M_m can be determined by light scattering [18] or by the hypsometric distribution of macromolecules in ultracentrifugal sedimentation.

The simplest and most commonly used method for obtaining relative values of mass-average molecular mass (M_m) is measurement of solution viscosity [17, pp. 49–67] in a capillary viscometer at constant temperature, where

$$\eta_{relative} = \text{flow time of the solution divided by flow time of the solvent} \quad (1)$$

and

$$\eta_{specific} = 1/\eta_{relative} \quad (2)$$

Suitable solvents are concentrated sulfuric acid, formic acid, and phenol. The specific solution viscosity, $\eta_{specfic}/c$, referred to the polyamide concentration in grams per 100 mL, is concentration dependent. Plotting viscosity as a function of decreasing concentration and extrapolating to zero yield the intrinsic viscosity, which is directly proportional to M_m. In the production of nylon fibers, sufficient control of the process can be achieved by routinely measuring and controlling the viscosity of a standard solution, e.g., 1 g/100 mL. The melt viscosity, of practical importance for melt spinning, can be determined in rotary, torsional viscometers and capillary viscometers, or by using the falling ball method. In measuring melt viscosity, oxygen and moisture must be rigorously excluded and temperature held constant. On melting, polyamides can change by amide ring formation, molecular mass increase, and degradation, so melt viscosity is likely to vary according to method and measuring conditions. In general, the melt viscosity of polyamides for melt spinning is ca. 50–500 Pa · s.

The *free amino and carboxyl end groups* of polyamides are determined by potentiometric or conductometric titration with dilute perchloric acid and alkali hydroxide solution, respectively. A solvent mixture of phenol, ethanol, and water is suitable for amino-group titration. A supersaturated polyamide solution, in benzyl alcohol or α-phenylethyl alcohol, is used for carboxyl end-group determination. This analytical procedure cannot be used for all polyamides.

Water analysis is carried out by heating the flake or fiber, and released water vapor is carried with dry nitrogen into Karl Fischer reagent. In this method, both the physically bound water and that formed by chemical reaction are determined.

Extractable materials in nylon 6, caprolactam, and higher ring amides can be determined by extracting the finely divided polymer for several hours in water or lower alcohols. However, in this relatively simple method, the high ring amides are not extracted completely. For quantitative determination and separation of ring amides, the polymer is dissolved in formic acid and the linear polyamide molecules are then precipitated by addition of methanol. Ring amides can be determined quantitatively in a methanol solution by using gel chromatography.

4. Modifying Additions

Dyeing of nylons that absorb water and swell, such as nylons 6 and 66, can be accomplished relatively easily with disperse, acid, or metallized dyes. The dye molecules migrate readily into the fiber structure. The dyeing of nylon fibers with acid dyes results from reaction with the amino end groups. The number of such reactive sites is influenced by M_n but can be modified by additives such as viscosity stabilizers. For example, carboxylic stabilizers will block amino groups and reduce affinity for acid dyes. The use of primary aliphatic amines or diamines provides additional basic sites and increases acid dyeability. Introduction of tertiary amine groups into the chain strongly increases absorption of acid dyes.

Nylons can be modified to accept basic dyes by introduction of strong acidic groups such as sulfonic acids, e.g., 5-sulfoisophthalic acid, in equimolar mixture with 1,6-diaminohexane [19]. Polycolor effects (graduated color depth,

variable color and shades) can be achieved by dyeing fabrics of mixed nylon fibers with different dyeabilities in a single dye bath containing acid, basic, and disperse dyes.

Delustering is the practice of altering the optical properties of a fiber, usually by incorporation of a white pigment. This is most often done for textile uses. The most common delusterant is titanium dioxide [13463-67-7], added in amounts of 0.03–2%, depending on the effect desired. Of the two forms of titanium dioxide available, the anatase variety is preferred for continuous-filament yarns because the harder rutile modification causes excessive abrasion and wear on guide surfaces and machine parts over which the yarn runs. The rutile form can be used with staple fibers in which guide wear potential is not so serious. Other pigments, such as clay, can also be used. Delustering can also be accomplished by surface roughening or by introducing voids into the filament.

Size distribution [20] of titanium dioxide pigments and pigment aggregates is generally 0.1–1.0 μm, with a frequency maximum in the region of optimum turbidity at 0.2–0.4 μm. However, commercial pigments also contain larger agglomerates, which must be broken down through wet grinding or separated from the aqueous dispersion by fractional sedimentation. Pigment agglomeration must be avoided in pigment addition to the monomer or to the polymer melt, because the particles result in filter plugging as well as weak sections in the filament. For continuous production of nylon flake or fiber, adding a pigment–polymer concentrate of 20–40% titanium dioxide to the melt just before spinning is advantageous. This permits quick conversion to different degrees of delustering, but also imposes strict requirements on control and mixing.

The magnitude of pigment addition can be checked by ash determination or photometric titanium analysis. The uniformity of pigment distribution, as well as the number and size distribution of pigment agglomerates, can be analyzed by microscopic examination of thin fiber cross sections.

Aging and light protection must be provided for some nylons by addition of special additives [21]. Manganese(II) compounds, in amounts as low as 5×10^{-4}%, are especially effective for nylons 6 and 66. Titanium dioxide pigments, especially of the anatase type, reduce light resistance, and one variety of anatase TiO_2 is coated with manganese to offset this effect. Many manganese compounds, such as the acetate, sulfate, phosphate, polyphosphate, and glycerophosphate salts have been proposed. In selecting the type and amount of additive, undesirable side effects, such as yellowing of the filaments and extraction of the manganese (II) during dyeing or wet finishing, must be considered in addition to the light-protective ability desired. Use of a manganese salt with a reducing anion, such as manganese(II) hypophosphite, improves the whiteness of fibers. Addition of sodium phenylphosphinate, in combination with manganese(II) hypophosphite, substantially improves both whiteness and quality [22].

The *heat-aging resistance* of nylons must be improved for uses such as tire cord. The thermooxidative degradation of nylon can be reduced considerably by adding antioxidants (0.1–1.0%), such as substituted aromatic diamines, and their action can be increased by combining them with trialkyl phenyl phosphites. Textile nylon, for which yellowing cannot be tolerated, requires special phenolic antioxidants substituted with alkyl radicals in the positions *ortho* to the — OH group. Examples are the amine salts of 3,5-dialkyl-4-hydroxyphenylcarboxylic acids. Copper(I) salts, in amounts as low as 5×10^{-4}% copper, are also effective. Many synergistically acting stabilizer mixtures are described in the literature, e.g., complex compounds of copper(I) iodide and hydrocarbon phosphines or phosphites are said to be especially effective.

Inorganic and organic pigments for *spin dyeing* of nylons must be stable under melt processing conditions and must give high colorfastness [23]. Pigment particle size should be less than 1–2 μm to avoid impairment of fiber strength, and agglomerates must be carefully milled or separated by sedimentation. Colored pigments are generally added to the starting monomer as aqueous dispersions. They may, however, be added to the melt as pigment–polymer concentrates [24]. This technique is desirable for short commercial runs but requires precise metering and good mixing.

Suitable additives for spun-dyed nylon are the yellow to red cadmium pigments, anhydrous

iron oxide pigments, ultramarine, copper phthalocyanine, perylene, and quinacridone pigments. Because nylon melts generally have a strong reducing action, perylene pigments can be reduced on the surface with a significant change in color. However, reoxidation often occurs in air shortly after extrusion of the filament. Some azo and anthraquinone dyes are also soluble in nylon melts and are sufficiently stable for spin dyeing.

Dyeing of nylon flake in aqueous baths, before spinning, is an economical way to produce a large range of colors from one flake type. However, the resulting colors do not have the outstanding fastness of pigment-spun fibers.

Black nylon fibers are obtained by using carbon black pigments with an average particle size of 10–30 μm. Carbon black pigment in too high a concentration can block carboxyl groups, reduce the degree of polymerization, and impair flow behavior of the melt.

Optical brighteners are frequently used to improve aesthetics of textile fibers, especially to hide the effects of soiling. The more stable brighteners are added to the monomeric starting material, the less stable ones, such as the coumarin type, are injected into the melt.

5. Technology of Melt Spinning

5.1. Melt Spinning of Nylon

All commercially significant nylons are melt-spun at temperatures up to ca. 300 °C [25]. Processes may be continuous from monomer to spun fiber, or they can be staged. When a variety of small-volume products is required, producing nylon flake and remelting it for the spinning process are economically advantageous. This is especially true for nylon 6, which must be washed to extract polycondensation byproducts.

In modern plants, flake is usually stored in large hoppers and then transported pneumatically or in smaller hoppers to the spinning area. Prior to spinning, the flake must be conditioned to proper moisture content because this can have a strong effect on melt viscosity. Great care is taken to store and transport flake with exclusion of moisture. Also, before being delivered to the melt unit, fines and excessively large cuts, as well as contaminating metal particles, are removed.

Nylon flake is commonly melted by using screw extruders or, in the older process, heated grids or grates. In either case, oxygen must be rigorously excluded. Spinning temperature depends mainly on the thermal stability and melt viscosity of the nylon. With nylon 6 and nylon 66, temperatures are usually kept at 280–290 °C. After leaving the melt unit, polymer is delivered to a metering pump and then to a spin pack. The pack contains filter media, passages for distributing polymer within the pack, and a spinneret. The filter section serves to remove mechanical impurities and to provide high shear for the melt. In a typical filter section, the molten polymer passes through layers of either powdered metal or fine sand, then through layers of very fine mesh screen, and finally through a photoetched plate before reaching the spinneret.

The spinneret is a metal plate, usually 6–10 mm thick, filled with holes, each hole forming one filament. Filaments from round spinneret holes have circular cross sections. The cross section can be altered to almost any desired filament shape to achieve unusual luster effects, as well as altered physical and tactile properties. Because the surface tension of the melt leads to a rounded filament, melt temperature, melt viscosity, and cooling rate must all be adjusted to achieve the desired filament cross section.

Spinneret holes of 200–400 μm can be used to produce nylon filament and staple yarns. The molten polymer extruded from the hole is pulled away by downstream rolls, reducing the diameter 5- to 50-fold. The diameter, or the mass per unit length, of the spun filament is determined by the rate at which polymer is metered through the spinneret hole and the rate at which it is pulled away. Small particles that pass through the filter leave weak spots in the filament, which may break in subsequent processing.

Nylons up to ca. 30 dtex/filament can be spun into air, but higher diameters require spinning into water or other liquids. Except for a few specialty uses, such large diameter filaments are generally made for nontextile applications. Turbid monofilaments are usually obtained when spinning into water, because of crystallization and surface corrosion. Clear filaments can be prepared by spinning nylon melts into cooled organic liquids such as carbon tetrachloride.

Unusual and useful filament structures can be prepared with specially constructed spinnerets [25]. Two melts are fed simultaneously to a spinneret hole, which results in a bicomponent filament that crimps spontaneously after drawing and finishing. Suitable melt pairs for this are nylon 66 and a 66–copolyamide [27] or a copolyamide 612 [28]. Spinnerets with two concentric holes yield sheath-core filaments from two melts. Injection of an inert gas into the center hole causes a void to develop and results in a hollow filament cross section.

Grid spinning was the original process for melt spinning of nylon. Flake is gravity-fed from an overhead hopper and melted on a spiral coil or grid heated with diphenyl. An atmosphere of superheated steam is generally provided to control melt equilibration. In starting up a grid-spinning head, melted polymer dropping from the melting grid collects in a conical sump, flows into a pressure pump, and is fed to a metering pump where it is metered through the filter pack and spinneret. Because pump demand must always be smaller than the maximum melt capacity, the sump fills until the melt grid is immersed in the melt, thus automatically regulating melting via the free-grid surface. When the process is interrupted, the grid heat must be shut off, otherwise molten polymer will rise into the cooler zone and solidify to form a bridge that blocks the flake feed. The melting capacity of a grid-spinning unit with a grid diameter of 160–200 mm is ca. 30–60 g/min. Higher capacity can be achieved with larger grids. One melting grid can feed four or more spinnerets.

Extrusion Spinning. More modern spinning equipment uses melt extruders instead of grid units.

Extruders provide a shorter dwell time in the melt, better mixing, and better viscosity control. Their main advantage, however, is the large melt capacity, up to ca. 1500 kg/d for a 150 mm-diameter screw.

Screws with length/diameter ratios of 20–30 are preferred to assure a more uniform melt temperature through the longer compression zone. An additional mixing zone connected to the compression zone improves homogeneity of the melt and permits increased throughput [29].

The melt is fed at constant pressure from the extruder through a jacket-heated transfer line to the spinning machine. One melt extruder can supply 30–40 individual spinning positions, each of which might spin eight or more individual thread lines. Use of a central filter for the melt, located between the extruder and the spinning block, is considered advantageous for some processes. This type of filtration is practical for nylon 6 but not as effective for nylon 66 because of the tendency of the latter to degrade and form gels in, and after, the filter.

Melted polymer must be fed to the individual spinnerets with the same average dwell time. Distribution piping is designed in cascade form to provide the same melt travel distance to each spinneret. In addition, dwell time differences arising from parabolic velocity distribution of melt inside the pipe must be balanced with static mixers ahead of each branch. Local or chronological nonuniformity of the melt can usually be detected first as dyeing differences in filament yarns.

Direct Spinning. Economic and quality advantages result by feeding continuously polymerized melt directly to the spinning machine. This is most easily accomplished with nylon 66, which produces only small amounts of low molecular mass cyclic amides. Direct spinning becomes most attractive when a few products can be made in high volume and such products can be made with little change in overall throughput. Large transitional changes are to be avoided. In such systems, introducing additives into the melt downstream of the polymerization unit is also desirable. This requires additional expenditures for the preparation of melt concentrates, as well as for the melting, metering, and homogenization equipment required for injection.

As noted earlier, nylon 6 fibers can also be made by direct spinning, but the equilibrium mixture, containing substantial amounts of caprolactam and higher cyclic amides, must be dealt with. This is accomplished through *thin-film evacuation*. The melt, prepared continuously in a polymerization tube, is passed to an evacuating assembly at 270 °C [30]. It is distributed through an annular slit onto a cylindrical wall, as a coherent film of melt. As the melt flows down the wall, volatile components

(caprolactam and water) evolve at a pressure of ca. 10 Pa. At the bottom of the assembly, the evacuated nylon 6 melt is homogenized through a mixing stirrer and conveyed by a compression screw through the discharge and to the spinning machine.

5.2. Special Techniques and Products

Fine-Denier Nylon Filament Yarns. Most fine-denier filament yarns are used in wearing apparel and household upholstery. Products are in the region of 10–400 dtex total, with filament counts from 1 to > 100. Single filaments run from 1.5 to ca. 6 dtex (9–36 μm).

Spinnerets for fine-denier textile filaments are usually made of stainless steel, 40–70 mm in diameter and 10–15 mm thick. Because of the high viscosity of the melt, the spinneret hole initially has a large diameter (2–3 mm), called the counterbore, which tapers in a conical section to a smaller exit hole (200–400 μm) from which the melt is extruded.

With a windup speed of 600–1200 m/min, solidification in the quench (cooling) chimney is completed within ca. 50 cm of the spinneret. Cool air is blown at right angles across the filament path, and careful attention must be given to avoiding pulsation or turbulence in air flow.

Filaments leaving the quench chimney are moistened with a spinning finish (oils emulsified in water) to provide static protection and lubrication for further processing. Many filaments are combined after finish application to form the final, multifilament bundle. If the yarn is to be drawn in a separate step, it is normally passed through a steam tube to promote development of the proper crystalline structure. For coupled spinning and drawing, yarn can be forwarded from the feed roll, which pulls the filaments away from the spinneret, directly to a set of faster moving draw rolls and then to a package-winding unit. Textile yarns are commonly drawn three to four times the original spun length to develop the required tensile–elongation properties. Depending on the process and the end-use, packages of ca. 1–20 kg are produced.

Economics of the spinning operation have been improved over the years by winding multiple packages on one winding unit, by winding larger packages for each thread line, and by operating the entire process at higher speed. Filament yarns are now prepared at spinning speeds of 5000 m/min, and useful fiber properties are now achieved in some cases without a separate drawing step [31]. Spinning, drawing, and texturing may also be combined in one continuous operation.

Coarse-Denier Nylon Filament Yarns. Coarse nylon yarns range from 400 to > 35 000 dtex total and from 6 to ca. 20 dtex per filament. Rectangular spinnerets are commonly used, spinning several hundred holes per spinneret. In the production of high-strength nylon yarns (e.g., tire cord), draw ratios of 5–6 are used and drawing is commonly done in two stages, with heating, to develop maximum tenacity and low elongation. Tenacities of 8.0 cN/dtex and 15–17% elongation are common for nylon 66 tire yarns. Package weights of 40 kg are common, and ends from several hundreds of these packages are combined and wound on a larger spool (beam) for shipment to the customer.

Nylon filament yarns for carpets and other floor coverings are usually sold in the range of 1000–3000 dtex total and 15 dtex per filament. Nylon for netting and ropes reach 35 000 dtex total, with 20 dtex per filament. These yarns are drawn four to six times their original length with heat assists and are deposited in rope form in a can. Some of these are then stretched further in a hot water bath to develop maximum tenacity.

Nylon Wires and Bristles Coarser nylon filaments (0.05–5 mm) are generally made with a higher degree of polymerization. Copolyamides are often more suitable for fishing lines.

Several processing steps are frequently coupled in one continuous operation. Flake is melted in a single-screw extruder, and the melt is extruded through spinneret holes (1–10 mm in diameter). The coarse filaments are solidified in a water bath and drawn between rollers in air or hot water at a speed of 200–400 m/min. Thicker wires may be drawn through dies to set the draw point and round the cross section. To improve dimensional stability and stiffness, coarse filaments for bristles are heat-set in boiling water, either continuously or on reels or bobbins.

6. Uses

Nylon fibers are used in a wealth of final products in appropriate make-up form [33]. They are used in applications that need high heat capacitance, high strength, and resilience [34]. Fine count nylon filament yarns with a total count up to approximately 200 dtex are processed largely into stockings, tights, ladies underwear and corset fabrics. Important products from textured nylon yarns are swimwear and sportwear, women's dresses, blouses, shirtings, elastic outerwear, jacket and overcoat fabrics, umbrella, décor and upholstery cover fabrics. In the technical sector, woven fabrics for airbags [32] and parachutes are produced from fine, high-tenacity nylon filament yarns. Coarse count nylon filament yarns are used mainly in carpets and other floor coverings. Other end-uses are high-tenacity tire cord, nets, fishing equipment, as reinforced fibers in driving belts and conveyor belts and also surgical sewing threads, luggage and footwear (so-called Oxford yarns) belts of all types (e.g., car seat belts), tapes and ropes. Nylon staple fiber yarns are processed particularly in blends with cotton, wool and other man-made fibers. By blending with nylon, the strength and wearing properties of a fabric are improved without changing the general character. Typical products are men's socks, warp knitted fabrics, clothing fabrics and also industrial clothing and children's wear, lining fabrics and knitting yarns. Nylon staple fibers are used in carpets and other floor coverings, as an admixture for needle felts, particularly in the running layer, for producing nonwovens and as cut fibers for electrostatic flocking. Nylon staple fiber yarns are processed into technical woven fabrics, filter fabrics, cord belts and inlay fabrics for the rubber industry. Nylon monofils and bristles are used in numerous application fields, such as tennis racket strings, fishing nets, fishing lines, abseiling ropes, safety lines, jump fabrics, screen cloths and other technical fabrics, bristles, tooth brushes (frequently of nylon 610) and paint brushes.

7. Economic Aspects

In recent years, nylon filament yarn and staple has lost share in the global fibers market. Although in 1980 nylon accounted for more than 10% of global fiber production, by 2000 the figure had fallen to 7.4% with a further decline to 5.1% by 2009. In 2020, Tecnon OrbiChem forecasts that the share will have dropped below 4%. Although share has declined, production has been increasing, from around 3×10^6 t in 1980 to almost 3.7×10^6 t in 2009. By 2020, total worldwide production of nylon filament yarns and staple fibers is forecast to reach more than 4.4×10^6 t [35].

Filament yarn is used in a wide range of applications including carpets and industrial end-uses such as high-performance tires and airbags where demand is strengthening. Unlike staple, filament yarn production is more of a global business, with manufacturers in all regions of the world.

In North America, production of nylon filament yarn has fallen by an average of 5.2% per annum since ca. 2005; but the rate is expected to ease to around 3.5% per annum during the forecast period. The change reflects the fact that more than 80% of nylon filament consumption in the USA is in carpets, a product that is less susceptible to substitution by imports because of the highly capital intensive nature of the manufacturing process and the considerable transport costs associated with the bulky product.

Production of nylon filament yarn in Western Europe has been declining more slowly than in North America, falling by an average 2.5% per annum since ca. 2005.

Although now the largest producer of PA filament yarn in the world, China is also the number one importer, accounting for 24% of the world total in 2008, although volumes are in decline as domestic production increases. With nylon 6 being the dominant polymer produced in Asia, the majority of growth in global nylon production this decade has been in fiber produced using this technology. Production of nylon 6 fiber is expected to grow by around 8% per annum during the forecast period with output of nylon 66 in the region remaining stable. As far as exports are concerned, Taiwan continues to be the major exporting nation, accounting for around 20% of the global total, of which more than 80% goes to China. Italy, and Germany also export significant quantities — each accounting for around 10% of the global

Table 6. Trade names and producers of nylon fibers [36]

Trade name	Nylon	Manufacturer
Acelan	6	Tae Kwang Industrial Co./Korea
Aliaf	6	Sherkat Sahami Aliaf/Iran
Alto	6	Aquafil SpA/Italy
Amilan	66/66	Toray Industries Inc./Japan Toray-Monofilament Co./Japan
Amni	66	Rhodia Poliamida/Brazil
Anso	6	Shaw Industries/USA
Antron	66	Invista Canada Inc./Canada Invista Deutschland GmbH/Germany Invista Inc./USA Invista (Australia) Pty/Australia
Aqualon	6	Aquafil SpA/Italy
Arafelle	66	Nilit Ltd./Israel
Asahikasei Nylon	66	Asahi Chemical Industry Co./Japan
Asota	6	Asota GmbH/Austria
Perlon-Draht	6	Perlon-Monofil GmbH/Germany
Borgolon	6	Borgolon SpA/Italy
Bri-Nylon	66	SANS Fibres (Pty.) Ltd/South Africa
Carbyl	6	Inquitex SA/Spain
Chainlon	6	Chain Yarn Co./Taiwan
Coolan	6	Hualon Corp./Taiwan
Cordura	66	Nilit Germany GmbH/Germany
Danamid	6	Zoltek Magyar Viscosa RT/Hungary
Dilon	6	Dilon Ltd./Pakistan
Dimlon	6	Tekstiplik Sanayii A.S./Turkey
Dorix	6	Reinhold GmbH/Germany
Enka NylonEnka Nylon	666	Polyamide High Performance GmbH/Germany Polyamide High Performance, Inc./USA
Enkalon	6	Polyamide High Performance, Inc./USA Enka de Colombia SA/Colombia Polyamide High Performance GmbH/Germany Century Enka Ltd./Italy
Fabelon	6/66	Domo Fibers NV/Belgium
Garware	6	Garware Nylons Ltd./India
Grilon Grilon	6, 12, 6.106	Ems-Chemie AG/Switzerland Nicieza y Taverna SA/Argentina
Islon	6	Insa AS/Turkey
Jayanka	6	J.K. Synthetics Ltd./India
Jacord	6	J.K. Synthetics Ltd./India
Jaykalon	6	J.K. Synthetics Ltd./India
Jinfan	6	Guandong Xinhui Meida Nylon/China
Krasil	6	Dilon Ltd./Pakistan
Kugafil	6	Fugafil - saran GmbH/Germany
Laufaron	6	Laufaron GmbH/Germany
Leona	66	Asahi Chemical Industry Co./Japan
Lilion	6/666	Nylstar SpA/ItalySNIACE S.A./Spain
Long Life	6	Manufacturas del Sur SA/Peru
Meryl	666/666/6666	Nylstar SA /France Nylstar Inc./USA Nylstar SpA/Italy Nylstar SA/Spain
Misrnylon	6	Misr Rayonne Co./Egypt
Mistilon	6	Manufacturas del Sur SA/Peru
Modipon	6	Modipon Ltd./India
Nakron	6	Thai Toray Synthetics Co./Thailand
Nexilon	6/66	Nexis Fibers GmbH/Germany
Nicord	6	Nirlon Ltd./India
Nirlon	6	Nirlon Ltd./India
Noval	666	La Fibra Srl/Italy Sarl Lamato/France
Nurel	6	Nurel SA/Spain
Nylhair	6	Inquitex SA/Spain
Nylpak	6	Bengal Fibre Industries/Pakistan
N.R.C.	6	National Rayon Corp./India
Palmylon	6	Kohap Chemtec Corp./Korea
Pao	6	Jang Dah Nylon Corp./Taiwan
Passorea	66	Rhodia Performance Fibres /France
Perlon	6	Perlon-Monofil GmbH/Germany
Prakarn	6	Asia Fiber Ltd./Thailand
Promilan	66	Toray Industries, Inc./Japan
Pylon	6	Pylon Industries Ltd./Bangladesh

Queen	6	Cheng Chi Fibre Co./Taiwan
Radilon	6/66	RadiciFibres SpA/Italy
Reilon	6	Reinhold GmbH/Germany
Sakorn	6	Hantex Corp./Thailand
Schwarzafil	6	TFG Thüringer Filamente GmbH/Germany
Schwarzalon	6	TFG Thüringer Filamente GmbH/Germany
Sensil	66	Nilit Ltd./Israel
Settestelle	6	Golden Lady SpA/Italy
Shreelon	6	Shree Synthetics Ltd/India
Sifas	6	SIFAS AS/Turkey
Snialon	6	Baroda Rayon Corp./India
Sniater	6	Baroda Rayon Corp./India
Stanyl	4.6	DSM High Performance Fibers BV/Netherlands
Stanylenka	4.6	Polyamide High Performance GmbH/Germany
Sunylon	6	Formosa Chemicals & Fibre Corp./Taiwan
Supplex	66	Invista Brasil/Brazil
	6.66	Invista Srl/Argentina
Sylkharesse	66	Sarl Lamato/France
Tactel	66	Nilit Ltd./Israel, Nilit Germany GmbH/Germany Invista Brasil/Brazil Du Pont (UK) Ltd./UK
Tactel	6, 66	Invista Srl, Argentina
Taftilon	6, 66	INSA AS/Turkey
Tasinlon	6	Chung Shing Textile Co./Taiwan
Taslon	6	Acelon Chemicals & Fiber Corp./Taiwan
Texfiber	6	Hilon Corp./Philippines
Three Gun	6	Chang Shing Textile Co./Taiwan
Timbrelle	66	TWD GmbH/Germany
TNT	6	Toray Nylon Thai Co./Thailand
Toplon	6, 66	Hyosung Corp./Korea
Toray Nylon	6	Toray-Monofilament Co./Japan
Toyobo Nylon	6	Toyobo Co./Japan
Tufcord	6	SRF Ltd./India
Tynex	6, 12	DuPont Filaments/USA
Ultralon	6	Aquafil SpA/Italy
Ultron	66	Solutia Inc./USA
Unitika Nylon	6	Unitika Ltd./Japan
Vanylon	6	Vanylon SA/Colombia
Wellon	6, 66	Wellman International Ltd./Ireland Wellman, Inc./USA
Wellstrand	6, 66	Wellman, Inc./USA
Yuan Pao	6	Jang Dah Nylon Industrial Co./Taiwan

total — though volumes from another former major player, Canada, are in decline.

Trade names and producers of nylon fibers are listed in Table 6. World production of synthetic nylon fibers (yarn and staple) are listed in Table 7.

Table 7. World production of synthetic nylon fibers (yarn and stable)

Year	Production, t
1980	3 185 000
1990	3 776 000
1995	3 911 000
2000	4 118 000
2005	3 924 000
2009	3 467 000

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Polyester Fibers

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ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

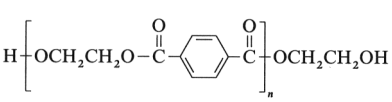
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History. The first spinnable high molecular mass polyesters were prepared by W. H. Carothers and co-workers in the laboratories of E. I. du Pont de Nemours & Co. around 1930 [1]. Dicarboxylic acids in use then were sebacic acid, hexadecanedicarboxylic acid, and others; some diols used were ethylene glycol and propylene glycol. The discovery that hardened spun strands could be drawn to several times their original length and, thereby strengthened, was made with these polyesters [2]. However, their melting points were ca. 75 °C, too low for practical application. For this reason, Carothers turned his attention to the more promising polyamides [3].

In the late 1930s, investigations showed that terephthalic acid and other aromatic acids could yield useful polyamides. Therefore, polyesters containing terephthalic acid as the dicarboxylic acid were studied at several locations [4]. Poly (ethylene terephthalate) was discovered in the laboratories of Calico Printers Association. Beginning in 1940, Whinfield and Dickson devoted themselves mainly to poly(ethylene terephthalate) [5, 6], while Schlack was working on poly(tetramethylene terephthalate) [7].

In 1947, ICI and Du Pont acquired patent rights for Great Britain and the United States, respectively, and initiated the commercial development of polyester fibers [4]. In the early 1960s, ICI licensed its technology worldwide to some large fiber producers whose own developments led to today's mass production. Thus, poly(ethylene terephthalate) has gradually become the most important fiber polymer [8].

According to DIN definition 60 001, fibers are designated polyester if the polymer chain contains at least 85 % of an ester of a diol and terephthalic acid. Poly(ethylene terephthalate) [25038-59-9] (PET), poly(oxy-1,2-ethanediyloxycarbonyl-1,4-phenylene-carbonyl), is a polyester with terephthalic acid [100-21-0] as the dicarboxylic acid and ethylene glycol as the diol ($n = 80 - 150$):



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For a detailed description of the chemistry, raw materials, production, and analysis of polyesters, see → Polyesters. The following discussion contains information pertinent to an understanding of the production and properties of these fibers. Section 2.1 covers aspects of production common to all types of PET fibers; specific information can be found under the individual fibers (Chap. 4).

1. Production

1.1. Starting Materials and Polymer

Ethylene Glycol [107-21-1]. Ethylene glycol is produced commercially by the reaction of ethylene oxide with water, which in turn is obtained by the oxidation of ethylene (→ Ethylene Glycol; → Ethylene). Prerequisites for smooth polycondensation to poly(ethylene terephthalate) and for the desired polymer properties are extreme purity of ethylene glycol and other raw materials and the absence of water.

Dimethyl Terephthalate [120-61-6] (DMT). Until the end of the 1960s, economical production of terephthalic acid in the purity required for fibers was difficult. For that reason, the more easily available dimethyl ester of terephthalic acid was generally chosen as the starting component for PET (→ Terephthalic Acid, Dimethyl Terephthalate, and Isophthalic Acid).

This material is produced commercially primarily by the *Witten process* (identical to the Imhausen or Katzschmann process [9]). *p*-Xylene [106-42-3] is subjected to a two-step, liquid-phase oxidation in air. The *p*-toluic acid thus produced is esterified with methanol to the methyl ester of *p*-toluic acid, which is then esterified with methanol to DMT.

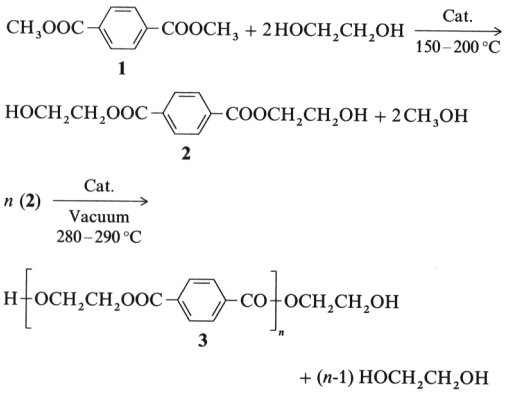
Terephthalic Acid [100-21-0] (TPA) (→ Terephthalic Acid, Dimethyl Terephthalate, and Isophthalic Acid).

Since the early 1970s, extra pure terephthalic acid of fiber quality has been produced commercially primarily by the *Amoco process* [10].

Inhibition of the oxidation of the second methyl group of *p*-xylene is suppressed with the aid of added bromine-containing promoters as cocatalysts. As with DMT, the oxidation takes place in air and produces raw terephthalic acid, which is dissolved at high temperature under pressure in water, hydrated, and thus purified.

Polymer. The polymer is prepared in two steps:

1. Transesterification of dimethyl terephthalate (**1**) with ethylene glycol to bis-glycol terephthalate (**2**) (continuous or batchwise) or direct esterification of terephthalic acid.
2. Polycondensation (continuous or batchwise) to give poly(ethylene terephthalate) (**3**).



The batch process is preferred for special polymer types, particularly for small amounts of polymer. The continuous process is used for standard polymer types in large volume, especially if spinning immediately follows polycondensation.

Poly(Ethylene Terephthalate) from Dimethyl Terephthalate. Commercial transesterification of dimethyl terephthalate with subsequent polycondensation was initially carried out batchwise.

Batchwise Process. First, DMT is esterified as quantitatively as possible with an excess of ethylene glycol (molar ratio range of DMT to ethylene glycol 1:2.5 to 1:4.5) between 150 and 180 °C. Catalysts are primarily zinc, calcium, and manganese acetates. Bis-glycol terephthalate, as well as higher homologues, are formed. Excess glycol is distilled at temperatures up to 250 °C.

Polycondensation is carried out at higher temperatures, up to ca. 285 °C, under vacuum.

In this step, the catalysts are primarily antimony trioxide or oxides of similar amphoteric metals. Phosphorus compounds are added as stabilizers to inactivate the transesterification catalyst.

Other additives, e.g., titanium dioxide for delustering or carbon black for black coloration, can be added to the melt prior to polycondensation. Once polycondensation is complete, the condensate is forced out of the vessel with nitrogen and quenched in water. The melt, which is thus solidified largely in the amorphous state, can then be formed into chips.

Continuous Process. Continuous transesterification and polycondensation occur in several, mostly horizontal, reactors in a manner similar to the batchwise process. As the polyester melt is formed during condensation, care is taken to keep its layer thickness small and its surface correspondingly large. This is necessary because diffusion of excess glycol determines the rate of polycondensation. Discharge from the last reactor occurs by means of an extruder or a pump. The polyester melt is then either passed to the spinning units and spun immediately or chilled in water and cut into chips. Continuous processing units are generally quite large, with throughputs of up to 100 t/d and average holdup times of the material in the unit of 5 – 10 h.

Poly(Ethylene Terephthalate) from Terephthalic Acid. Since highly purified, fiber-grade terephthalic acid has become available at low cost, it is increasingly being esterified directly with ethylene glycol (molar ratio of terephthalic acid to ethylene glycol 1:1.1 to 1:1.5). The reaction occurs at about 260 °C under pressure and generally requires no catalyst. Lower linear oligomers are formed. After the glycol has been distilled, polycondensation follows. Its course is similar to that with DMT as the starting product. A polycondensation catalyst is also required. The economic advantages of this route are that circulation of methanol is eliminated, substantially less excess glycol is necessary, and above all, the amount (in grams) of starting material required is less by ca. 14 % because of the lower molecular mass of TPA vs. DMT. However, direct esterification results in somewhat more diethylene glycol byproduct. This process is used in continuously operating modern plants.

Poly(Ethylene Terephthalate) with Very High Molecular Mass. Industrial end uses require very high molecular masses (corresponding to very high average lengths of molecules) to attain the necessary tenacity and modulus. Because removal of excess glycol in polycondensation is rate-determining, reducing the thickness of the melt layer as the reaction progresses would be appropriate. However, due to the melt viscosity increase during polycondensation, this becomes more and more difficult. Holdup time at high melt temperature is thus increased, which produces thermal degradation in parallel with polymerization. Polymer whiteness thus deteriorates, and COOH end groups are formed in undesirable concentrations in addition to the OH end groups. To get around these problems, PET of very high molecular mass is now generally produced by *postcondensation in the solid phase* (solid condensation).

Granulate PET, produced by melt condensation, is dried and exposed to heat either batchwise in vacuum or continuously under an anhydrous gaseous protective blanket free of oxygen (generally nitrogen) at temperatures up to ca. 250 °C (i.e., somewhat below the melting point). A lamellar structure with noncrystalline regions and voids forms. Polycondensation occurs in parallel with recrystallization and additional crystallization. The glycol – water mixture produced diffuses through the noncrystalline regions and mainly through the interlamellar voids that are being formed. The result, in addition to acceptable polymer color, is primarily the desired low concentration of COOH end groups. Once the desired average molecular mass has been attained, the granulate is chilled and packaged. Alternatively, it can be melted directly with the exclusion of water and sent to the spinning units.

1.2. Spinning

The melting point of poly(ethylene terephthalate) (265 °C) is clearly below the decomposition temperature of the melt; therefore, PET can be melt-spun. During melt spinning, a molecular orientation is created in the filaments by the drawdown tension; this orientation is frozen during cooling. Here, PET exhibits a special characteristic which distinguishes it from other commercial melt-spinnable polymers: because

of its relatively high glass transition temperature (70 °C), the spun material solidifies completely in the spinning shaft to form a stable, supercooled melt with molecular orientation more or less in the yarn direction [4]. This orientation, measured by birefringence, is proportional to the tensile stress along the path of the yarn at the time and place of solidification, [11, 12].

As filaments solidify, they also attain their final speed (winding speed) and thus their final linear density (as-spun fineness). Where the solidification point lies along the path of the as-spun yarn depends on spinning conditions; distances between 20 and 150 cm from the spinneret have been reported [12].

Because of the relatively low tendency of PET to crystallize at room temperature, the as-spun yarn is amorphous as long as drawdown tensions are not too great. Stress-induced crystallization occurs only at higher tensile stress as a result of spinning speeds above ca. 3000 – 4000 m/min or of very intense air quench; this crystallinity also is frozen into the yarn. Under these processing conditions, the as-spun yarn is partially crystalline [13, 14].

At very high spinning speeds (at about 8000 m/min), the crystallinity of the as-spun yarn can be as high as 50 % [15, 16], and the distribution of directions of the crystallites becomes even more narrow. At the same time, the layered structure of crystalline order, which resembles that of PET spun slowly and then drawn, is slowly transformed into a more fibrillar structure of larger ordered regions. Despite the high orientation of the crystalline fractions, the total orientation again decreases somewhat; therefore, orientation of the amorphous material between the fibrils is assumed to decrease [17].

At spinning speeds > 4000 m/min, an additional sheath-core orientation occurs in the filaments [15]. This effect can cause the orientation in the sheath, measured by birefringence, to be almost twice as great as in the filament core [18, 19]. Correspondingly, the sheath of the filaments is also more highly crystalline. These differences remain during further processing of the as-spun yarn and can lead to nonuniformities in dyeing if they are not controlled in the process [20].

As mentioned, the orientation and even the crystallinity of filaments depend on spinning conditions and increase with increasing spinning speed, stronger air quench, and higher molecular mass. Both characteristics decrease with increasing spinning temperature, with higher mass transport, and thus with greater as-spun linear density. If the spinning speed is increased and the fineness is held constant by a proportional increase in mass transport, the effect of spinning speed predominates. The orientation and even the crystallinity increase [12–14]. The diameter of the spinneret holes, hence the spin-to-draw ratio, has relatively little effect on the final spin orientation and crystallinity except when spinning speeds are ≥5000 m/min [17].

Orientation and crystallinity of the filaments are characteristics of the as-spun yarn that must be considered in further processing because of their effect on the properties of the end product. Both factors are held as constant as possible with respect to time and between the spinning units.

As described in Section 1.1, PET is produced either continuously or batchwise. In the continuous process, the spinning and polymerization units can be connected. Thus, freshly condensed melt flows directly to the spinning units. Because the economic advantages of direct spinning are obvious, its use for high-volume end products, e.g., for staple fibers and standard filament yarns, which are always made by the same process, is increasing constantly [21].

The PET granulate that is delivered to a spinning plant is first stored in silos. The granulate must be dried immediately before melting because even the smallest amount of water in the polymer causes hydrolytic degradation of the melt. Residual water content < 0.01 % is desirable. Drying is carried out mostly in continuous shaft dryers. The granulate moves slowly downward, while a hot, often predried, countercurrent air stream blows over it. Since amorphous PET granulate tends to become sticky during heating, a crystallizer in which the chips are slightly crystallized, at least on the surface, often precedes the dryer [22]. Many dryer designs are known, with throughputs amounting to several tons per hour. For some products, drying the PET granulate in a vacuum is better, for example, in batches in large tumble dryers.

From the dryer, the granulate reaches the melt extruder, which transports the melt to one or more spinning machines. Because of thermal degradation of the melt, maintaining equal holdup times in the hot lines between

the extruder and the attached spinning units is important; the temperature of these lines must also be the same. Only then can the uniformity of the as-spun yarn and the end products be assured.

Spinning units differ considerably in construction and processing data, depending on the end product. The same is true for the method of cooling, finishing, drawing down, and collecting the as-spun yarn [4]. Common operational winding speed ranges from ca. 500 m/min for industrial yarns to 6500 m/min for filament yarns spun at the highest speed. Thick filaments, e.g., monofilaments, are spun at a much lower speed. Common to all is the spinning temperature, which is 270 – 310 °C.

1.3. Drawing

The glass transition temperature of PET is ca. 70 °C, which is somewhat above room temperature. Therefore, when PET yarn spun at relatively low speed is elongated slowly, cold drawing occurs with a draw point [23]. From the linear densities on both sides of the draw point or from the length of the plateau of the stress – strain diagram (see Section 2.2), a "natural draw ratio" can be specified. This ratio depends on the orientation of the as-spun yarn, which already represents a part of the total orientation [24]. The product of the orienting spin-to-draw and the natural draw ratio is constant to a first approximation and is equal to ca. 6 – 7 [25].

In commercial practice, as-spun PET yarn is always drawn at a temperature ≥ 80 °C. Because of the added work of drawing, the real yarn temperature in the draw zone is frequently higher than the external temperature, depending on the drawing arrangement.

During drawing [11], the molecular network of the as-spun yarn is oriented further. The increasing parallelism of the molecular chains initiates PET crystallization. With further drawing, the crystalline regions and the amorphous areas between them become more and more oriented [26]. Orientation, crystallinity, and strength of the drawn yarn increase with increasing draw ratio, whereas break elongation decreases [30]. This is illustrated by the stress – strain diagrams of yarns drawn differently (Fig. 1).

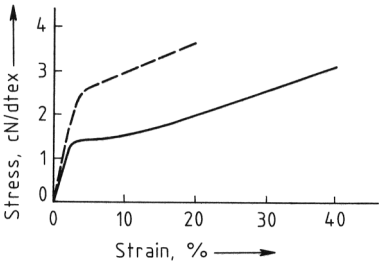


Figure 1. Stress – strain curves of two drawn PET yarns
——— Draw ratio 1 : 1.52; – – – – Draw ratio 1 : 1.83

In addition, the product of orienting spin-to-draw and draw ratio is approximately constant for the maximum possible draw ratio and for drawing to a given break elongation [25]. Thus, PET yarn spun at higher speeds needs to be drawn less to attain a given break elongation. However, this affects the structure of the drawn material [22, 25, 28]. Because less energy is added during drawing, the crystallinity is somewhat lower, and both the total orientation, as measured by birefringence, and the tenacity of the yarn are reduced [29]. These relations begin to change at spinning speeds of ca. 5000 m/min. Then the as-spun yarn is so highly crystalline that the ordered regions are no longer loosened during drawing but orient themselves as far as possible as a whole along the fiber axis. The crystallinity again increases [15].

The more the drawing temperature exceeds the glass transition temperature the more easily can PET be drawn [11]. Drawing tension drops if drawing temperature is increased and also if the glass transition temperature is decreased, either by water absorption by the as-spun yarn [4] or by modifications of the polymer. However, drawing temperature must not be set too high, for then the purely plastic and non-orienting elongation becomes too large a percentage of the total draw.

The draw ratio would have to be set very high to achieve high strength. The yarn in the draw zone would then no longer be able to absorb stresses and would break. As with other polymers, two-stage drawing is necessary; the predrawn yarn enters a second draw zone where it is then capable of withstanding the drawing tension.

In industrial practice, PET as-spun yarn is almost always drawn continuously between two

godets or sets of rolls, whose speeds determine the draw ratio [23]. In so doing, the required draw temperature is imparted to the yarn by heaters or heated rolls [4]. Keeping the draw point stationary is important; otherwise the drawn product will contain differentially drawn areas, which produce defects, particularly nonuniform dye uptake. Details of each drawing arrangement are dictated by the product to be drawn (see also → Fibers, 3. General Production Technology, Section 2.2).

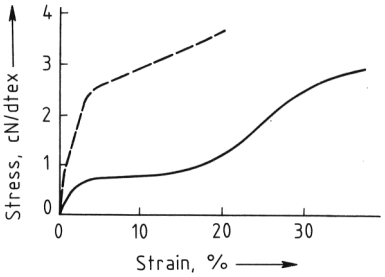


Figure 2. Stress – strain curves of drawn PET yarn, subsequently allowed to shrink freely

1.4. Aftertreatment

Thermal Aftertreatment. At room temperature, oriented and noncrystallized segments of the PET molecular chains in a drawn threadlike structure are frozen and immobile; the entire structure is not in equilibrium. When the yarn is heated beyond the glass transition temperature, the amorphous chain segments begin to move so as to achieve an entropically more favorable, less oriented position, to the extent permitted by their restraints in the crystalline regions. These regions also lose orientation and, as an overall result, the yarn shrinks. The extent of shrinkage depends on the orientation and crystallinity of the drawn structure; it increases with increasing temperature and, initially, also with the duration of heat treatment [11, 27, 31]. Any plasticizers, e.g., water, that have diffused into the structure favor shrinkage.

The thermal instability of drawn PET yarn structures would be quite troublesome during further processing and in textile end products. Therefore, it is often reduced during fiber and yarn manufacture by a thermal aftertreatment called *heat-setting* [4, 32].

Structures that are allowed to shrink without restraint between 110 and 180 °C are thermally stable below the setting temperature. In this process, orientation decreases markedly, which manifests itself on the stress – strain curve as a saddle with a yield stress of ca. 1 cN/dtex (Fig. 2). If the product, which has been heat-set without restraint, is loaded to this yield stress saddle, it is permanently deformed. In general, normal textile applications rarely reach this amount of loading.

During unrestrained heat-setting, crystallinity increases considerably, primarily favoring the ordered regions already present. Degrees of crystallinity up to 50 % have been reported. The amorphous fraction is correspondingly reduced, but the chain segments are disoriented in response to shrinkage. With increasing crystallinity, maximum dye uptake (i.e., the saturation concentration) decreases but dye diffusion becomes much easier as the amorphous chain segments disorient. In this way, dyeability reaches a minimum at heat-setting temperatures of 150 – 180 °C [27, 31, 33].

If heat-setting takes place at constant length without any shrinkage, the effects are intensified with temperature and duration of heat-setting. Crystallinity also increases but less so than during unrestrained heat-setting. The PET products are not completely stable thermally but will retain some residual shrinkage [27, 32]. Therefore, the temperature at which this type of heat-setting is carried out is frequently very high, e. g., 220 °C. Cooling the material under tension after it leaves the heat-setting zone is important to prevent any shrinkage. Heat-setting at constant length decreases extensibility and increases strength.

Hot postdrawing of a previously drawn yarn represents heat-setting with negative shrinkage. Crystallinity and orientation increase markedly, and the initial slope of the stress – strain curve of the yarn and the tenacity increase. The extent of changes in shrinkability depends on processing conditions.

In practice, a middle course is often adopted, i.e., heat-setting while constant shrinkage is allowed [32]. This increases crystallinity and somewhat reduces orientation. The increase in extensibility of the material approximately corresponds to the shrinkage permitted; at the same time, a slight saddle is formed on the stress –

strain curve. The residual shrinkage of material heat-set in this way is smaller by about the amount of shrinkage permitted during setting. The many processing parameters, such as draw ratio, heat-setting temperature, and shrinkage allowed during setting, permit matching the properties of the PET product quite closely to the requirements of each end use.

Heat-setting does more than prevent thermal instability. The structural rearrangements it induces make prior changes in shape impressed on the yarn permanent [4]. This feature is used widely in producing and processing fiber products, e.g., in ironing or pleating when creases are to be set hot. However, in producing the fibrous structure and in further heat-setting, care must be taken to chose conditions which will assure that any subsequent heat-setting will still be effective. "Deadening" a fiber (or a textile structure formed from it), so that it can no longer be heat-set, should not be done.

During setting, primarily the orientation of the amorphous parts changes; however, growing crystalline regions also disorient if any shrinkage has been permitted. This leads to a corresponding change in the superstructure of the PET fiber. In general, the layered structure becomes more pronounced. The orientation angle of the crystalline layers with respect to the fiber axis increases [27].

Structural rearrangements during heat-setting and the resultant changes in textile properties depend in a complicated way on the structure and prior history of the PET yarn and on the conditions of the heat-setting process. Therefore, formulating general, quantitative relationships is impossible. These depend on the given heat-setting process, which differs from product to product. All setting processes are included in the manufacturing process immediately after drawing or deformation.

Deformation. Melt-spun fibers including PET are generally flat and, in this condition, unsuitable for many applications [4]. Hence, all staple fibers and tows must be matched to natural fibers by *crimping*. PET filament yarns for apparel are *textured* → Fibers, 3. General Production Technology, Section 3.3 on a large scale. The processes and installations used in both cases are quite similar for all man-made fibers. The deformations produced are frequently heat-set, either without tension (staple fibers heat-set without restraint) or with tension (texturing), depending on the product.

1.5. Dyeing of Poly(Ethylene Terephthalate) Fiber Products

Dyeing of textiles and dyeing technology in general are discussed under → Textile Dyeing.

As a result of polycondensation and subsequent degradation, PET contains OH and COOH end groups. Neither is suitable for bonding ionic dyes. Therefore, PET is dyed with disperse dyes unless it has been modified to contain ionic end groups (→ Disperse Dyes). These dyes are available in powder or liquid form. They are only slightly soluble in water and are therefore used as aqueous dispersions in the dye bath or even as foam. Dye preparations necessarily contain dispersants.

Migration of dyes into the fiber is controlled by the laws of diffusion [34]. The parameter determining the rate of migration is thus the diffusion constant D, which depends on the size and structure of the dye molecule. The saturation concentration c_∞, reached at very long dyeing times, is the second parameter required to describe the kinetics of dyeing.

Investigations have shown that D is affected substantially by the orientation of the molecular segments in the noncrystalline region of the fiber. With increasing orientation, molecular mobility decreases, and the glass transition temperature T_g, a measure of mobility, increases. Beginning at ca. 68 °C in an isotropic, amorphous PET, T_g can reach 100 °C in a highly oriented, partially crystalline fiber [35, 36].

The diffusion constant is also affected by the ordering of the molecules, though to a much lesser degree. This becomes evident if the temperature of heat treatment prior to dyeing exceeds 180 °C. Above this temperature, the noncrystalline regions (layers between crystalline layers) are loosened, which restores the mobility of the molecular segments in these regions; parts of molecules that up to then had been extended can coil up or even refold, which leads to a growth in crystalline regions transverse to the molecular axis and to an "emptying" of the noncrystalline regions. Material that has been spun at high speed and then

drawn behaves similarly [20]. However, such ordered states in the noncrystalline regions of the fiber are first of all keys to controlling the saturation concentration c_∞.

The fiber can take up dye to any significant degree only at temperatures above T_g. At these temperatures, the polymer is present as a highly viscous liquid in which the mobility of molecular segments in the noncrystalline regions is restricted. The saturation concentration evidently depends on the accessible free volume in the noncrystalline regions and in voids. It is also certainly affected by the structure of the interfaces of these volumes. A quantitative description is not yet possible.

Thus, with reference to fiber structure, the diffusion constant D is the most important orientation-dependent kinetic parameter of dye migration through the "liquid" polymer regions. The saturation concentration is determined by the states of order of the supercrystalline structure (small-angle X-ray structure). However, practical dyeing behavior is essentially determined by the diffusion constant.

Poly(ethylene terephthalate) fibers can be dyed to deep shades without using auxiliary chemicals only at temperatures ca. 50 °C above the glass transition temperature. Such dyeing is carried out in aqueous media under pressure in a closed vessel and is called high-temperature (HT) dyeing. High-temperature dyeing of textiles made of 100 % PET or blends of PET with cotton or other cellulosic fibers presents no problems. Any wool in the blend, however, is damaged.

Carriers are used for open dyeing in boiling water, especially of blends of PET and wool. These chemicals are swelling agents, i.e., poor solvents, for the polyester fiber. They temporarily loosen intermolecular bonds in the fiber and thus increase the mobility of molecular segments. In other words, they lower the glass transition temperature. The problems connected with cleanup of wastewater are a disadvantage.

Therefore, PET fibers have been developed that can be dyed to deep shades in boiling water without carrier (see Section 2.1) [37]. These fibers contain block comonomers, generally polyglycols, and meet all requirements of the apparel and home furnishings trades. However, minor losses in light- and washfastness of the dyeings compared to unmodified PET are unavoidable.

Ionic dyeing for differential dyeing requires appropriate ionic end groups in the molecule. Sodium salts of 5-sulfoisophthalic acid dimethyl ester [138-25-0] and 5-sulfoisophthalic acid [22326-31-4] have been used; they can be added during transesterification of DMT or during direct esterification of TPA [38]. Fibers can be dyed with cationic dyes without difficulty, but the dyeings are much less lightfast.

Dyeing with acid dyes requires basic end groups. Thus far, building such end groups into PET, e.g., via amines, has not been possible without yellowing or high aminolytic degradation, resulting from the high polycondensation and spinning temperatures.

The most important *dyeing processes* are the exhaust process and the continuous process; aftertreatment of PET dyeings is very important for the quality of the dyeing.

The dyeing process most widely used with PET fiber products is the *exhaust process.* Depending on the situation in each dye plant (wastewater) and the chemical composition of the dyed goods (presence of wool), dyeing can be carried out under pressure at HT conditions (60 – 90 min at 125 – 140 °C), or it may be carried out open or under low pressure, respectively, with carrier (60 – 90 min at 95 – 110 °C). Combining both processes is rare and used only if highly oriented PET products are to be dyed to deep shades.

Continuous processes are also used. With the aid of saturated steam, superheated steam (pad steam process, 2 – 8 min holdup time at 160 – 180 °C), or hot air (pad thermosol process, 15 – 90 s holdup time at 180 – 220 °C), high throughputs, which improve the economics of dyeing, can be achieved. Blends of PET with cotton and other cellulosic fibers are preferably dyed by these processes.

Aftertreatment of dyed goods is essential for the quality of the dyeing. This is especially true with regard to their fastness, but also holds for other properties of dyed goods (fibers, yarns, and textile fabrics) such as processibility, appearance, hand, and mechanical properties. In deep dyeing, particularly, residual dye remains on the fiber surface after drying and heat-setting with deleterious effects, particularly on fastness. A reducing, alkaline, postdyeing,

cleaning treatment removes these dyes, as well as any oligomers that are diffused from the interior to the surface of the fibers. Temperature and pH of the postcleaning bath must be carefully controlled because of the danger of hydrolytic degradation.

2. Structure and Properties

2.1. Polymer

Chemical Structure. *Homopolymer.* In addition to the OH end groups of the macromolecules, PET fibers contain 10 – 40 milliequivalents of carboxyl (COOH) end groups per kilogram of fiber. These are produced in the melt at elevated temperature (especially beginning at 280 °C) by breaking of the ester bonds. Because COOH end groups catalyze hydrolytic degradation of the polyester, they are occasionally protected (e.g., with epoxide compounds or carbodiimides), especially in products destined for industrial use [39].

Diethylene glycol, which is present in the PET chain in concentrations up to ca. 1 mol %, affects softening behavior of the polyester, dyeability of the fibers, and to a certain extent, lightfastness. For this reason, diglycol formation is suppressed as much as possible by adjusting the conditions of the reaction.

In addition to macromolecules, the polymer contains ca. 2 % oligomers, primarily cyclic trimers, but also linear oligomers. The former can adversely affect washing and dyeing.

Additional impurities in the polyester are acetaldehyde and degradation products. At higher thermal loading of the melt during further processing, these can lead to formation of gel particles and discoloration.

In the solid state, PET absorbs ca. 0.4 % of water from the atmosphere at 20 °C and 65 % relative humidity. Because even minute amounts of water can cause, or at least substantially favor, hydrolytic degradation, the polyester must be carefully dried to a moisture content below 0.01 % prior to spinning.

Copolymer. The principle of copolymerization of PET with suitable monomers is used to improve certain fiber properties.

The relatively high glass transition temperature of the fibers limits dyeability in boiling water to light and medium shades. Deep shades can be obtained by using higher dyeing temperature (HT dyeing at ca. 135 °C under pressure) or carriers. When these procedures are impractical, e.g., because of the presence of wool or the contamination of wastewater, fibers of block copolymers (PET with polyglycols) can be used [37, 38]. By loosening the noncrystalline regions, the glass transition temperature of these fibers is lowered far enough to attain both the required diffusion and the desired saturation concentration of disperse dyes in the fiber.

In differential dyeing (single bath dyeing of textile fabrics to various shades), fibers are needed that can be dyed with both cationic and disperse dyes. The sodium salt of 5-sulfoisophthalic acid [51876-65-4] is almost exclusively built into the PET molecule for this purpose [38].

The low pilling property of textile fabrics, necessary for practical use, requires low-pilling PET staple fibers. Low molecular mass PET is used for these fibers. In addition, cross-links sensitive to hydrolysis are also built into the polyester with the aid of, for example, organosilicon compounds [40].

A particular requirement for home furnishings is low flammability. For years PET fibers have been used in which flame retardants in the form of suitable phosphorus compounds are cocondensed with PET (→ Flame Retardants) [41, 42]. In this way, flame protection becomes permanent; it cannot be lost in washing or dry cleaning.

Additives. In many cases, the polymer includes additives intended to change the normally transparent and brilliant white appearance of fiber products. The most frequently used additive is titanium dioxide [13463-67-7], mostly anatase but occasionally the harder rutile, which serve to dull the fiber. Particles with average grain sizes between 0.3 and 0.4 μm are added to the transesterification product in concentrations of 0.1 – 3 %.

Dyed fiber products are made by adding soluble dyes or pigments, if extreme lightfastness of dyed goods is required, to the melt. To produce black fibers, carbon black is usually added.

Many attempts have been made to achieve permanently antistatic polyester fibers by

admixture of suitable compounds. Surface resistances of 10^{10} Ω have been attained [43]. However, not much practical use has as yet been made of these possibilities. In general, the desired electrical surface conductivity is obtained by finishes applied to the fiber.

Physical - Chemical Structure. The most important structural variable of fiber-forming polymers is the *average molecular mass*. This describes the mass of the average macromolecule and is the product of the molecular mass of the monomer and the average degree of polymerization. A measure of the molecular mass and hence the length of molecules is the specific viscosity, η_{spec}, measured in dilute solution:

$$\eta_{spec} = (\eta - \eta_0)/\eta_0$$

where η is the viscosity of the solution and η_0 the viscosity of solvent. For poly(ethylene terephthalate), η^c_{spe} is between 0.5 and 1.5, depending on the application of the fiber products.

Generally, molecular mass is described by the intrinsic viscosity [η], often designated as *IV*

$$[\eta] = lim_{c \to 0} \eta_{spec}/c$$

where c is the concentration of polymer in the solution being measured. Again, depending on the area of application, [η] for PET ranges from 0.45 dL/g for low-pilling fibers to 1.05 dL/g for tire cord, which corresponds to a span of 50 to over 200 for the average degree of polymerization.

The *distribution of molecular mass* corresponds to that given by FLORY for condensation polymers [44]. Changes in this distribution function by degradation can be reversed by melting. The distribution function of molecular mass is rarely measured and is not used for product testing.

Melt viscosity is measured with capillary or rotary viscometers. In polymers intended for standard fibers, it is ca. 250 Pa·s at 285 °C. Melt viscosity increases rapidly with increasing [η] and decreasing temperature. It is one of the basic variables of spinnability. The orientation of the macromolecules during filament formation, is particularly dependent on melt viscosity.

The *transition temperatures,* generally measured by differential thermal analysis, are the final determinants of the orientation, crystallization, and melting behavior of PET. The glass transition temperature is measured as ca. 68 °C on the isotropic and amorphous polymer. It depends on the orientation and crystallinity of the polymer and thus can be as high as 100 °C in highly oriented, semicrystalline, industrial, continuous-filament yarns. In the isotropic and amorphous polymer, the crystallization temperature is ca. 100 °C; the maximum rate of crystallization is observed between 140 and 180 °C. The melting point of PET, which depends on crystallinity and crystal size, lies between 255 and 265 °C.

Physical Structure. Poly(ethylene terephthalate) quenched from the melt is isotropic and almost amorphous. The density of amorphous PET is 1.335 g/cm^3. The polymer can be crystallized primarily by the action of heat but also by the presence of agents such as dichloromethane or dioxane. The crystal structure is triclinic; the density of the crystalline regions is 1.515 g/cm^3 [45].

The configuration and conformation of monomeric terephthalic acid and ethylene glycol in the macromolecule are also known. Infrared spectroscopy shows that the terephthalic acid component is present in the trans configuration in the crystalline part, but in the *cis* configuration in the noncrystalline part. The IR method shows that the glycol component exists in the trans conformation in the undisturbed crystalline region and in both the gauche and the trans conformation in the noncrystalline region. The mass ratio of the glycol components in the gauche and trans conformations changes not only during crystallization but also during orientation and disorientation. This ratio correlates to the mechanical properties of shaped PET articles [46].

When PET granulate is melted and the melt is forced through spinneret holes, as-spun filaments are formed. The orientation of the macromolecules in these filaments, characterized by the birefringence Δn of the filaments, depends to a large extent on windup speed. Thus, Δn at a windup speed of 1500 m/min is only ca. 0.010, but at 3500 m/min it is as much as 0.055. Density, too, is subject to this dependence. At 1500 m/min it is ca. 1.34 g/cm^3, and at 3500 m/min it is 1.35 g/cm^3. The degrees of crystallinity behave similarly [47].

During drawing of as-spun filaments, the macromolecules are oriented further, and the birefringence of filament yarns for industrial uses increases to ca. 0.240. The ability of PET to crystallize is exploited in many ways during drawing and also in subsequent aftertreatment. Thus, the fiber density ranges from 1.36 g/cm^3 for drawn high-shrinkage staple fibers up to 1.41 g/cm^3 for highly drawn low-shrinkage filament yarns.

2.2. As-Spun Yarns

Nonuniformities of as-spun yarn along a filament or filament bundle, but also from filament to filament, from bundle to bundle, or even from plant to plant, are reflected in the structure of the final product. There, they appear as differences in textile properties, primarily in dye uptake. For this reason, yarn is carefully monitored during spinning. The glass transition temperature of PET (70 °C) causes the as-spun yarn to be quite stable at room temperature and makes measurement of orientation and even of crystallinity relatively easy. Intervening in the manufacturing process in case of deviation is then possible.

Many physical measurement techniques are available to investigate the structure of PET as-spun yarn. The total orientation of a filament is measured by *optical birefringence.* Except for highly crystalline as-spun yarn, the birefringence is proportional to the orientation factor [11]. If suitably measured, it provides indications of any possible sheath – core structure. Another measure of orientation is the velocity of sound and with it the *sonic modulus* [48, 49]. They change little at lower orientation and increase noticeably only at spinning speeds $\geq$ 2500 m/min [14].

The degree of crystallinity of as-spun yarn can be calculated easily from its *density*; care is required, however, because the densities of completely amorphous and completely crystalline PET, required in these calculations, are not entirely independent of orientation [47]. In addition, true separation of the amorphous and crystalline phases is presumed, which is sometimes questionable.

Much information can be gained from *X-ray* investigations. Wide-angle patterns or goniometry provide data on the size, quantity, and orientation of the crystallites, and the approximate degree of crystallization. With their aid, total orientation can be divided into orientation of the amorphous and of the crystalline fractions of the filament. Small angle X-ray scattering permits conclusions to be drawn concerning the superstructure, i.e., the mutual arrangement of crystalline and amorphous regions and also the state of order of the latter.

Thermal Measurements. If as-spun yarn or tow is heated at constant length beyond the softening point to ca. 100 °C, a *shrinkage stress* that corresponds to the orienting stress during spinning is created [25]. This stress is therefore a measure of orientation and is largely proportional to the optical birefringence. These two quantities diverge only at high spinning speeds.

If as-spun yarn is heated without restraint, it shrinks, sometimes very much. In so doing, the orienting elongation D, frozen in during spinning, is recovered; hence, D can be calculated from the *spun yarn shrinkage* [50]. As expected from theory, the quantity $D^2 - 1/D$ is approximately proportional to birefringence and shrinkage stress at constant length, which are measures of orientation [50, 51]. However, this is true only for spinning speeds up to 1500 m/min with normal quench. Beyond that, shrinkage is impeded by crystalline regions developed in the sample during spinning or by the regions created during measurement. Thus, spun yarn shrinkage goes through a maximum of 60 – 70 % at spinning speeds between 2000 and 4000 m/min and then drops rapidly with increasing speed [13, 20, 25]. In this spinning range, spun yarn shrinkage is again recommended as a measure of crystallinity, even of dyeability of the final product [20, 29].

Differential Thermal Measurements (DTA). The glass transition temperature, the temperature of the maximum rate of crystallization, the melting point of crystallites, and the final melting point can all be determined from DTA curves [14].

Mechanical Tests. If a PET as-spun yarn is elongated at room temperature and its tensile stress is measured at the same time, the stress – strain curves shown in Figure 3 are obtained. For as-spun yarn of lower orientation, a saddle appears after the initial rise in stress, while a draw point crawls along the clamped yarn [23].

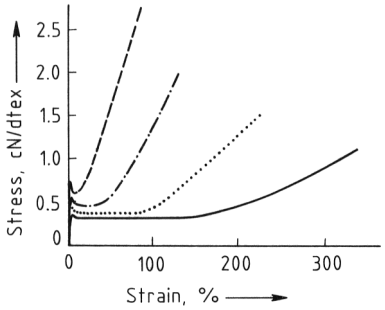


Figure 3. Stress – strain curves of PET as-spun yarns spun at four spinning speeds
Spinning speeds:
———— 1200 m/min
· · · · · · 2000 m/min
—·—·3000 m/min
– – – – 4000 m/min

The percentage of elongation reached at the end of this saddle is called the natural draw ratio R_n of the as-spun yarn. With increasing spinning orientation, shown in the figure by higher spinning speeds, R_n decreases; this is because a greater amount of extensibility has been anticipated during spinning [25]. If spinning orientation becomes too large, R_n can no longer be specified [20, 28]. Then either the elongation of the as-spun yarn at a given load or the force necessary to produce a given elongation is used [25]. In practice, determining the operational draw ratio that imparts a definite property, such as break elongation or dye uptake to the final product might be useful. This, however, assumes that no changes occur in further processing.

To monitor the spinning process and possibly pinpoint defects in commercial practice, tests should be limited to those that can be most readily and accurately carried out and that provide averages over a sufficient quantity of as-spun yarn. Each kind of test, taken separately, is useful only for monitoring, not for control. If a test quantity exceeds the tolerance range, use of another kind of test is recommended to readjust the process conditions.

2.3. Drawn Materials

During drawing, PET crystallizes in the triclinic configuration mentioned in Section 2.1. The supermolecular structure is assumed to consist of somewhat parallel layers, inclined to the fiber axis. With increasing draw, the distance between the layers, measured in a direction normal to the layer surface, decreases, and the layers rotate more in the direction of the fiber axis [27, 52].

In practice, material that has been drawn but not processed further is almost never available as an intermediate product. A posttreatment almost always follows immediately, as described in Section 1.4.

2.4. Dyed Poly(Ethylene Terephthalate) Material

Fastness Properties. The lightfastness of dyed textiles for apparel and home furnishings is important in preserving their coloration. A lightfastness rating of 6 can be achieved readily in articles of unmodified PET fibers with most commercially available disperse dyes. The lightfastness of PET fibers, modified to be dyeable to deep shades at the boil without carrier, may be half a rating lower. Dyeings of PET fibers, modified to be cationic-dyeable, generally do not rate higher than 4 – 5 in lightfastness.

Heat-setting fastness, rubbing fastness, and washfastness of dyeings of PET fibers meet all practical requirements. The only exception is the slightly lower washfastness of modified PET fiber, dyeable without carrier. A wash temperature of 40 °C should not be exceeded.

Degradation and Mechanical Properties. In discussing alkaline postdyeing cleaning treatment, the danger of hydrolytic damage to PET fibers is mentioned. This damage consists of molecular degradation, which can extend to different degrees from the fiber skin to the core. The consequence, in general, is a reduction in tensile strength and breaking elongation of the fibers caused by the embrittlement connected with degradation. At the same time, the hand of the textile fabric can occasionally be changed. However, sometimes such changes of the hand are desired (e.g., by alkalization).

Another change in the properties of PET fibers or textiles is sometimes produced by shrinkage during dyeing, which may be accompanied by crystallization processes. Carefully

controlling the dimensions of, and stresses in, textile fabrics as well as the drying and setting temperatures is required.

3. Poly(Ethylene Terephthalate) Fibers

3.1. Staple Fibers

Special Features of the Manufacturing Process. In the manufacture of PET staple fibers, polymers with intrinsic viscosities [η] of 0.65 – 0.75 are generally used; for special types, polymers of much lower viscosity with [η] ca. 0.5 are occasionally used. The equipment on which PET staple fibers are produced is usually large, with daily production up to 50 t and more. Therefore, feeding the spinning units directly from a condensation unit makes economic sense [53].

A spinning unit for PET staple fibers consists of 8 – 32 spinning positions including their accompanying spinning shafts, aligned side by side. Each position is supplied with melt, either simultaneously or in groups, by an extruder or directly from a condensation unit [4].

Depending on the type of air quench, spinnerets may be circular with uniformly arranged spinneret holes, they may be plates in which the holes are arranged rectangularly, and finally they may be circular with an annular arrangement of holes [53]. The number of holes is based on the as-spun fineness and the feed of the spinning position. The spinneret hole shape is not always round. For profiled fibers with nonround cross sections, such as triangles, five-pointed stars, or even hollow fibers, the holes must have profiles that exaggerate those of the final product because the profile impressed by the hole tends to blur somewhat during spinning.

The output of a spinning position has been increased from 500 g/min to 1500 g/min and more by increasing the number of spinneret holes, by forceful quenching, and by increasing the spinning speed.

For example, a filament bundle with a linear density of 8 dtex per filament is spun from an 1125-hole spinneret at a speed of 1500 m/min. The output per spinning position is 1350 g/min. A 16-position spinning machine then provides about 31 t/d of as-spun yarn in the form of a tow with total length of 2160 km and a linear density of 144 000 dtex, consisting of 18 000 individual filaments.

The length of the spinning shafts is determined by the need not only to ensure that the filaments are cooled below 70 °C but also to prevent the moving individual filaments from sticking together. The shafts are generally 5 m long but, with a suitable quench, they may be shorter [53].

Finish is applied to the filament bundle at the lower end of the shaft to ensure trouble-free packaging of the as-spun material. The spin finish is also used to impart surface characteristics to the fibers needed downstream during manufacturing and textile processing [54–56]. This is more economical and protects the environment better, but some compromises with respect to processability during tow drawing and textile processing are unavoidable.

After the finish application, strands coming down from the spinning units are turned horizontally and combined into a tow, which is drawn off and deposited in a spinning can. Depending on the installation, these cans hold 0.5 – 2 t of tow, all of which should have the same length.

The fibrous as-spun product is preoriented; in newer spinning units with very effective quench, for example, it is characterized by a birefringence of $(8 - 14) \times 10^{-3}$ or by a natural draw ratio of ca. 1:2.5.

High-speed spinning at ca. 3000 m/min, which is advantageous for textile filament yarns, has been attempted for production of PET staple fibers [57]. Problems still exist in developing a reliable process for depositing the tow in the spinning can [58]. A sheath – core effect in the filaments also presents difficulties.

As is customary in the production of staple fibers and tows from melt- or dry-spun synthetic polymers, the as-spun tows are combined and further processed continuously as a tow band. The tow band (up to ca. 1.20 m wide) is first immersed in a warm bath where the stresses in the individual strands are equalized; the tow is thoroughly wetted, and if necessary, additional finish is added. From the immersion bath, the tow enters the draw zone between two sets of rolls [54].

During drawing, the draw points or draw zones of all filaments in the band must be as close together as possible and must not wander [54]. A number of drawing processes are available for this [59]. If the tow is cold when it enters the draw zone, the yield stress must be lowered by sudden heating, e.g., via a steam jet, so that drawing can occur. In this process, the draw ratio is limited, and if necessary, a second drawing step must be provided.

If the tow is heated on hot feed rolls, drawing begins on the last or next-to-last feed roll and can even be facilitated, if necessary, by an immersion bath under the third roll from the end. It is also usual to pass the tow through an additional hot zone in the draw stand. With this process, reaching higher draws with one drawing is possible.

Drawing in water is a compromise in which only the last feed roll is heated and dipped into the hot water draw bath. Drawing begins at that point.

If postdrawing is to be accomplished in a separate draw zone, the draw rolls of the first stage are heated because they represent the feed rolls of the second draw, which is then carried out in a heating device.

The stress – strain behavior of the end product can be preselected by the draw ratio but is more critically affected by the type and place of heat-setting. Thus, fibers that are to exhibit a steep stress – strain curve with high initial modulus, similar to cotton, are relatively highly drawn, e.g., 1:4.5 to 1:6, depending on the as-spun yarn. After drawing, the tow is heat-set under tension, usually at constant length. The heat-setting temperature is between 160 and 230 °C, depending on the shrinkage desired. After setting, the tow traverses a cooling zone under tension and then enters the crimper. To facilitate crimping, it is first slightly moistened or steamed. The tow must not become too hot in the crimper; otherwise it relaxes and textile properties deteriorate. After crimping, finish can again be applied if necessary, in which case the tow must again be carefully dried [59].

Fibers that are to have a flat stress – strain curve similar to wool do not need to be so highly drawn; a draw ratio range of ca. 1:2.5 to 1:3 will suffice. After drawing, the tow is sent immediately to the crimper via a short steam zone. The crimp is then heat-set without tension, often on traveling grate machines. The heat-setting temperature, ca. 120 – 180 °C, is selected according to the amount of shrinkage desired in the end product. The flat stress – strain curve is formed by the tensionless setting, and the crimp becomes highly stable.

Finally, the crimped and, if necessary, shrinkage-stabilized tow is packaged. Either it is compressed into a bale and sold as endless tow, or it passes through a cutter and is cut into staple fibers, which are then baled. The usual mass of a bale can range up to 500 kg.

Staple fiber draw lines are up to 80 m long and produce from 20 to 250 t/d, the latter, of course, only for high-volume products. Delivery speeds range from 150 to 300 m/min, with tow sizes up to 600 ktex and more [60]. Investment and manufacturing costs per tonne per day are reduced considerably with increasing productivity of these draw lines [58].

Completely continuous installations with capacities of 12 – 15 t/d produce smaller lots. They are supposed to be superior to the usual tow band installations in terms of investment and manufacturing costs, but they produce fibers with three-dimensional crimp. Whether such fibers can be spun in blends with natural fibers and whether fabrics produced from such yarns will be acceptable in the marketplace remain open questions [58].

Types of Fibers, Properties, and Uses. Polyester staple fibers encompass the broadest product spectrum of any fiber. They can be found in all areas of application [4, 61–63]. They are used in apparel for overcoats, jackets, leisure and sportswear, ladies' outerwear, men's suiting, work and protective clothing, children's wear, underwear, and sleepwear. In home furnishings, they range from drapery and curtain fabrics, through furniture coverings, pillows and pillow stuffing, table and bed linen, to wall and floor coverings. They have a whole host of industrial end uses along with filament yarns, spunbonded products, and monofilaments. A few examples of applications are in filtration, automobile interiors, geotextiles, and material for the sewing trade.

Yarns made from PET fibers can be processed without reservation in weaving and knitting as well as in tufting. The fibers are completely suitable for processing as unblended

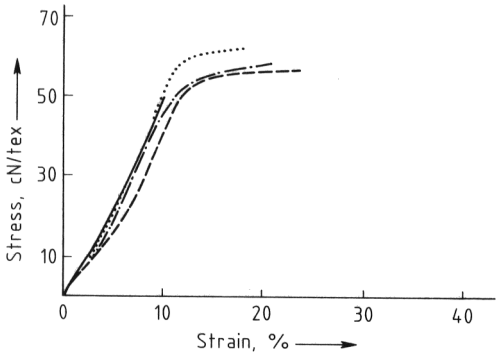


Figure 4. Stress – strain curves of PET cotton type staple fibers
———————— Cotton
— — — — — — PET cotton type (normal shrinkage)
–·–·– PET cotton type (low shrinkage)
····· PET sewing thread type

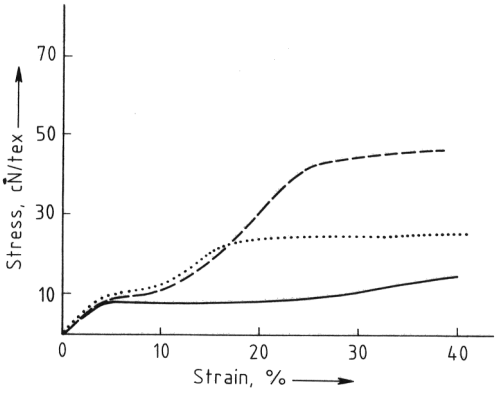


Figure 5. Stress – strain curves of PET wool types
——— Wool
– – – – PET wool type (normal)
····· PET wool type (low pilling)

yarns (100 % PET), as well as in blends with cotton, wool, silk, cellulosic man-made fibers, acrylic fibers, and many more.

Of all polyester fibers, *cotton types* have the largest market share. These are processed into blended yarns, and these in turn into blended articles. These contain cotton, viscose, or modal fibers in what are today considered the "classical" blend ratios of 65:35 or 1:1 (PET to cotton) and in other ratios.

The stress – strain curve of cotton types is shown in Figure 4. Its initial slope corresponds approximately to that of cotton. Their finenesses of 0.4, 0.9, 1.3, and 2.4 dtex, and the major one of 1.7 dtex, at cut lengths of 30 and 38 mm are matched to cotton.

Fibers with normal high shrinkage and others with reduced shrinkage are available and used to vary the hand and appearance of textile fabrics over a wide range. With the additional possibilities offered by the choice of fineness and weave construction, the textile processor can exert a major influence on the permeability of, for example, tent, overcoat, shirt, and blouse fabrics. In comparison to wool types of polyester fiber, dyeing of highly oriented cotton types is somewhat slower but, like the former, presents no problems.

Special cotton-type fibers, which are also offered as continuous tow for processing on stretch – breaking converters, are intended for sewing. These fibers are especially highly drawn and, therefore, have the highest moduli (resistance to elongation) and tenacities.

Wool types are intended primarily for processing in blends with wool. The major blend ratio is 55:45 (PET to wool). The stress – strain curves of these fibers are matched to that of wool (see Fig. 5) by tensionless heat-setting during fiber manufacture, as described in Section 1.4. Shrinkage is therefore low, and dyeability is optimum. The spectrum of fineness and cut length ranges from 1.7 dtex (38 mm) to 6.7 dtex (120 mm). Wool types are also available as continuous tow for processing on cutter – converters.

The so-called pilling phenomenon, which occurs in blends with wool, has been responsible for considerable developmental cost. Small balls or pills are formed on the surface of textile fabrics during use. Suitable fibers have been developed to solve this problem [27, 62]. Their special structure eventually causes the fibers anchoring the pill to break. In this manner, the pill disappears soon after it is formed.

A third group consists of the *fiberfill types* commercially available as staple fibers but also as continuous tow. These fibers are used both in apparel (primarily for heat insulation) and in home furnishings (primarily in pillows, cushions, and bedding). Their crimp is two- or three-dimensional. To improve the hand of fiberfill, such fibers are often provided with a special finish, based primarily on silicone. The range of

linear densities of these fibers is between 1.5 and 14 dtex at a cut length of 30 – 80 mm (most common length, 60 mm). This group also contains high-shrinkage fibers with a shrinkage at the boil of 50 %.

In home furnishings and automobile interiors, *polyester carpet types* are used. These also include poly(tetramethylene terephthalate) fibers, see Section 4.1. Carpet fibers based on PET are used as both normal and high-shrinkage types in home furnishings and in needle-punched felt. Such fibers are also made with various cross sections; their finenesses and cut lengths range from 6.7 dtex (135 mm) to 20 dtex (150 mm). An essential characteristic of polyester floor coverings is that their mechanical properties are unaffected by moisture.

Special types of PET staple fibers have secured a place in the market. Some can be dyed in an open vessel without carrier to deep shades [37]. Such staple fibers and tows meet special requirements of environmental protection where wool blends have to be used (carriers) and HT dyeing is therefore excluded. These fibers exist as standard types and as pill-resistant tows. Cationic dyeable staple fibers are used in relatively small amounts in the wool area and in polyester carpets.

Since the mid 1970s, *flame-retardant PET fibers* have rounded out the product spectrum [42]. These fibers are used in apparel and, especially, in home furnishings. They meet legal requirements and even exceed them in some cases. For these, PET copolymers with phosphorus compounds have proved particularly useful. Fibers of this type combine the comfort expected of unmodified PET fibers with modern safety requirements. They are distinguished by deep dyeability with disperse dyes. Because of their diverse applications, these fiber types are available in finenesses and cut lengths from 1.7 dtex (38 mm) to 13 dtex (150 mm).

3.2. Continuous-Filament Yarns for Apparel and Home Furnishings

Special Features of the Manufacturing Process. Poly(ethylene terephthalate) that is to be spun into continuous-filament yarn for apparel generally exhibits an intrinsic viscosity [η] of 0.70 – 0.75 [4]. It must be highly purified, especially when used in high-speed spinning, which is often the case. The polymer must also be dried carefully to $< 0.01\ \%\ H_2O$.

As in staple fiber units, the spinning positions of a spinning machine are aligned in a row. Quenching is mostly done by a transverse air flow with several spinnerets in a single shaft so that all filament bundles are affected uniformly. At the lower end of the spinning shafts, the filament bundles are individually combined into yarns while finish is applied to them. Finishing with a perforated yarn guide has been generally adopted. Below the spinning shafts, the yarns are usually drawn off by godets, the circumference and revolutions of which determine the spinning speed; the yarns are then wound individually on bobbins [4].

Originally, spinning speeds were 500 – 1500 m/min. The as-spun yarn was amorphous and characterized by an orientation birefringence Δn of $(3 - 10) \times 10^{-3}$, a so-called *low orientation yarn* (*LOY*) [20, 62]. The as-spun yarn was drawn by passing it, with friction, over heated pins in the draw zone and then additionally, with surface contact, over a hot plate. This process was replaced by drawing on heated rolls with several wraps [4]. For heat-setting, the delivery roll of the set of draw rolls was also heated but at considerably higher temperature. Final drawoff was by a third pair of rolls. The drawn yarn was wound on a twister (draw twisting) or on a winder (draw winding); frequently it was then twisted, heat-set, and rewound. Such units, which involve slow spinning and separate drawing, are still operating but are probably no longer being built.

Improvements in winding frames for drawn yarn led to the next development, spin drawing . In this process, a set of draw rolls is mounted below each spinning shaft. The as-spun yarn is drawn down at ca. 700 m/min and finally wound at ca. 3000 m/min. Winders developed for high-speed spinning in 1983 permit drawing down at speeds up to ca. 4000 m/min with final windup speeds up to 6000 m/min [56]. This process is highly cost-effective, and product quality is good.

In a variant of the spin-drawing process, the draw rolls are mounted near the spinneret at the

point where the filaments have just attained their final fineness and are still warm [65]. This process, too, is rated highly for cost and quality of product.

Spinning speeds have gradually been raised to 2800 – 4500 m/min to increase productivity of the spinning units. The result has been production of *partially oriented yarn (POY)* [20, 64]. These yarns are less sensitive because of their inherent slight crystallinity and require less drawing. Drawing can now be combined with texturing into a single process, with considerable savings in investment and operating costs [66].

Drawoff rolls or godets are not required in high-speed spinning, and drawing-off can be left to the winder; however, special measures must be taken to match the spinning tension to the optimum (mostly lower) windup tension [56].

Yarn spun at higher speed and then drawn takes up dye more readily; because it is more highly oriented, postdrawing is lower and entails less additional crystallinity. Material spun at very high speed is, moreover, said to have an especially loose structure, with fewer large crystalline regions, even after drawing [20].

Commercial high-speed spinning has become possible only through the development of suitable winders, which can also be used for as-spun yarn. They can go as high as 6000 m/min and, for experimental purposes, up to 10 000 m/min [67].

In the speed range of 3000 – 4000 m/min, productivity no longer increases substantially with spinning speed. Hence, yarn spun at 2800 – 4000 m/min has been adopted as the starting material for draw texturing [64]. Therefore, additional investment in increased spinning speed is probably not worthwhile [68]. Efforts have been directed at reducing spin orientation and thus increasing draw ratio and productivity. For example, a heating tube below the spinneret reduces spin orientation [69], as do minor additions to the polymer of low-viscosity polymers [70] or components with slight cross-linking action [71].

The drawing process is combined with texturing in draw texturing to produce textured yarns from material spun at high speed. In this process, the yarn is drawn in the texturing zone on the first heater of the texturing unit, i.e., between the delivery rolls and the twister. This places stringent requirements on the as-spun yarn. Its structural properties, such as orientation and crystallinity, must be uniform to ensure uniform dyeability of the end product. In addition, the as-spun yarn must not have any defects such as broken filaments. In most cases, the yarn is additionally heat-set on a second heater in the texturing unit with a 7 – 14 % contraction in length. This setting process reduces the crimp elasticity of the yarn, which is then dimensionally stable.

The major problem in the manufacture of textured PET yarns is uniform dyeability. The many process steps and, hence, variables require special attention during manufacture. Total testing costs are high.

A smaller fraction of PET filament yarns for apparel is processed without texturing. Flat yarns are obtained by the old process of separate spinning and drawing mentioned previously, as well as by spin drawing. More recently, flat yarns have also been spun at high speed [15, 20]. Several processes, such as high-speed spin drawing and warp drawing [72, 73], can accomplish this economically and with high product quality.

Because PET yarns spun at 6000 m/min still have flat stress – strain curves, they cannot be used as is [64]. Thermal treatment in the spinning shaft, e.g., a heating zone in the shaft, helps increase their orientation and crystallinity [74, 75]. The stress – strain behavior of this *highly oriented yarn (HOY)* then suffices for several special applications. At still higher spinning speed, the sheath – core effect of orientation and crystallinity can exert a negative influence [20, 76].

Types of Continuous-Filament Yarn, Properties, and Uses. Continuous-filament yarns are products of the man-made fiber industry that can be converted directly to textile fabrics, i.e., without intermediate processing. Whereas staple fibers are produced by first cutting crimped filaments which then must be spun into a yarn, possibly in mixtures with other fibers, in a relatively expensive process, filament yarn is available immediately.

Filament yarn is offered flat, i.e., with silk-like, or variously crimped textures; thus, it provides opportunities to change the hand, bulk, and optical appearance of downstream goods and to accommodate styling requirements

in apparel and home furnishings, which far exceed the range attainable with natural fibers [4, 61–63].

Partially oriented yarns (POY) have, since the introduction of high-speed spinning technology (see Section 1.2), led to successful intermediates for internal fiber production as well as to salable products. These filament yarns are spun and wound at speeds of ca. 3000 – 4500 m/min. They are precursors for pirn drawing (cops drawing), warp drawing, as well as warp drawing – sizing or draw texturing. Most POY products with a fineness of 300 dtex and 32, 34, or 36 filaments per yarn (dtex 300 f 32, etc.) are produced for draw texturing, which is the largest end use.

Flat Yarns. For direct textile processing in weaving and knitting, suitable flat *fully oriented yarns (FOY)* are available on pirns, bobbins, or as warp beams. They are sold with round, trilobal, triangular, or even octalobal cross sections with an individual filament fineness of 2 – 5 dtex and a yarn fineness of 22 – 167 dtex.

Pirn (cops) material intended for weaving and warp knitting is produced "classically" with twist from LOY or from POY. Material in bobbins, on the other hand, is used exclusively in weaving and comes primarily from one-step processes such as spin drawing or high-speed spinning (4000 – 6000 m/min) (see Section 1.2). The fineness of individual filaments made by this latter process ranges from 0.6 to 3 dtex. These HOY yarns are distinguished by uniform dyeability. A stress – strain curve, which, in contrast to standard yarn, exhibits higher tensile elongation, is shown in Figure 6. Warp beams, finally, are produced by the warp-drawing process from POY exclusively for warp knitting. For weaving, the warp draw – sizing process is used.

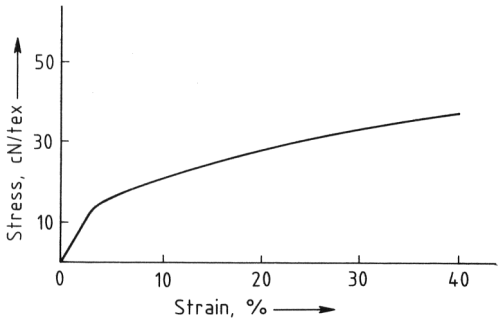


Figure 6. Stress – strain curve of highly oriented filament yarns (HOY)

Textured Yarns. The major application for textured yarn, primarily false-twist textured, is in knitting and weaving for apparel. Air-textured yarn, on the other hand, is used predominantly in home furnishings and is processed by weaving.

False-twist textured yarns are draw-textured, starting with POY, mostly by the friction process, but in some cases by the spindle process. Their linear density is 50 – 200 dtex (singles yarn), with an individual filament fineness of 1.25 – 5 dtex. The round cross section of POY filaments is distorted by draw texturing. However, special yarn types are produced with a triangular profile, which is preserved during draw texturing. This type of individual filament cross section imparts a special luster, almost a glitter, to textile fabrics. The linear density of most false-twist textured yarns now used in knitting and weaving is ca. 167 dtex. Fine yarn down to 50 dtex/40 filaments is used in ladies' blouses, for example.

Air-textured yarn can be made from either POY or FOY. With POY, a drawing step precedes air texturing on the texturing machine, whereas FOY is textured directly. In this process the filament cross section, usually round, is preserved. The linear density of such yarn is 200 – 3000 dtex for single yarn, which is appropriate for its primary use in home furnishings. The fineness of individual filaments is 2 – 3 dtex.

Special Types. The extensive product line of continuous-filament yarns includes many special types. Examples are filament yarns with staple yarn character, i.e., filament yarns with the less regular and bulkier structure of staple yarns, which is achieved by the type and arrangement of individual filaments. In some cases, free fiber ends even protrude from the yarn.

A large variety of properties is possible today. Among the most important are yarns with high bulk character, which is achieved by differential shrinkage of individual filaments. The properties of such yarns, however, are closer to flat yarns. Other yarns are formed by cotexturing different types of individual

filaments. These approach staple yarns, even with regard to the comfort of clothing made from them.

Extremely low fineness filaments with individual counts down to 0.1 dtex (produced by splitting thicker filaments) or 0.6 dtex (spun directly) are used in textiles with the appearance and feel of buckskin.

In differential dyeing cationic dyeable yarns are used in addition to normal disperse dyeable filament yarns. When yarns are made from blends of disperse dyeable individual filaments and cationic dyeable ones, they may be dyed in different colors.

Flame retardancy in home furnishings, especially in drapes and curtain fabrics, is achieved with filament yarns that consist of modified PET. By inserting a phosphorus compound into the fiber molecule, the flame retardancy of such yarns is permanent and cannot be removed in washing or dry cleaning.

Finally, filament yarns with permanent antistatic properties are available. In general, however, the surface conductivity required for processing and for some end uses is achieved by applying finishes.

3.3. Continuous-Filament Yarns for Industrial Applications

Special Features of the Manufacturing Process. Filament yarns for industrial use are generally spun from higher molecular mass PET, which is the only way to achieve high strength. For low-fineness, high-tenacity yarn (final fineness < 1000 dtex) PET with an intrinsic viscosity [η] of 0.75 – 0.80 is used; for coarse, high-tenacity yarns (final fineness $\geq$ 1000 dtex), the intrinsic viscosity [η] of PET is 0.95 – 1.05. Such molecular masses are achieved either by continuous polycondensation with direct spinning or, preferably, by postcondensation in the solid state [4].

During condensation in the melt, COOH end groups, which catalyze hydrolytic degradation of PET in the melt, are formed in the polymer and can disarrange the structure in the final product. These end groups can be protected with carbodiimides [39] or similarly acting substances, which are added to the polymer in small amounts prior to spinning. No COOH groups are formed if solid-state condensation is carried out in a vacuum or under a protective gas and at temperatures below the melting point. Care must be taken, however, that the polymer does not absorb water during storage or during transportation from the condensation to the melting equipment.

Polymer with a high viscosity requires a rather high spinning temperature, e.g., ca. 290 °C for fine yarn and ca. 310 °C for coarse yarn [4]. To minimize thermal degradation of the melt, the lines carrying melt from extruder to spinneret must be as short as possible. Also, the melt in the distribution lines after the extruder is kept relatively "cold" and warmed to the higher spinning temperature only in the spinning pack [77].

Fine, high-tenacity yarn has a linear density similar to that of textile yarn. For this reason, it is spun on a similar machine. The yarn is either spun and drawn in separate process steps or spin-drawn continuously. The spinning speed for fine high-tenacity yarn in the two-step process is approximately 1000 m/min and 500 m/min and higher during spin drawing. The draw ratio is ca. 5; the yarn is usually allowed to shrink ca. 10 % during heat-setting at a hot roll temperature of ca. 240 °C. The delivery speed of the drawing machines is ca. 700 m/min, but during spin drawing, it is substantially higher (ca. 2500 – 3000 m/min).

A special, high-volume variant of fine, high-tenacity yarn is sewing yarn. By plying, twisting, and renewed heat-setting, throwsters turn this yarn into sewing thread, whose most important characteristic is the sewing length achievable. The goal is sewing yarn that needs no further plying and twisting to make it comparable in processability to sewing thread of staple fiber.

During spinning of particularly viscous polymers for coarse industrial yarn, very high drawing forces develop in the filaments. These forces can be relieved by delaying filament cooling with the aid of a heating tube directly below the spinneret, which reduces spin orientation and equalizes the structure of the filaments [69, 78]. In this way, noticeably higher final strength can be attained [79].

Coarse high-tenacity PET yarn is produced either in one step by spin drawing or in two steps by spinning and further treatment as a warp.

During spin drawing, the spinning speed is ca. 700 m/min; when spun on bobbins for warp processing, it is ca. 700 – 1000 m/min. Yarn has been spun at much higher speed, in which case the disturbing influences mentioned previously are compensated in other ways [80].

The spin-draw machines for coarse high-tenacity yarn resemble those for fine high-tenacity yarn except that some parts are even more massive [63]. Because of the high operating speed (up to 4000 m/min) the residence time on heat setting rolls and beyond is short. Therefore, preparing low-shrinkage material by spin drawing is difficult; however, the strength that can be achieved is considerable.

In the draw-line process, a warp of yarn is drawn in two steps and then heat-set. After the last set of rolls, which determines the setting shrinkage, the yarn is wound on individual bobbins. The delivery speed of such draw lines is 120 – 300 m/min, with a productivity of 4 – 10 t/d.

The ability of the end product to shrink and its shrinkage force can be reduced, both in spin drawing and in warp processing, by permitting shrinkage in the heat-setting step. This increases elongation of the yarn at loads important in practical applications. The much higher residence time of the yarn in postdrawing and setting in the warp process leads to lower residual shrinkage at equal relative elongation of the end product (relative elongation being the elongation at a given load). Inversely, at equal residual shrinkage, the relative elongation of the product from the warp process is lower. These relationships are influenced further by the polymer used, the spinning process, and the drawing conditions.

In certain end uses, coarse industrial PET yarn must exhibit good adhesion to rubber. For this purpose, an appropriate adhesive finish is applied during spinning or in warp processing prior to heat-setting. This finish may contain epoxy compounds (Epikote) or similarly acting material.

Industrial Yarns, Properties, and Uses. Of the three product forms used industrially, i.e., high-tenacity filament yarns, spunbonded products, and monofilaments, the filament yarns have by far the broadest application [4, 61–63]. This ranges from the building industry through machine and motor vehicle construction, chemistry, mining, agriculture and forestry, transportation, sporting goods, protection of the workplace and the environment, to apparel and home furnishings. Such yarns are offered on the market in three major categories: sewing yarn, fine yarn, and coarse yarn. Depending on end use, these yarns are employed either as normal-shrinkage or low-shrinkage types. In addition to fine and coarse white yarns, spun-dyed black types are also available. The extraordinarily broad product line is rounded out by plied fineness of coarse filament yarns. For an overview see Table 1.

Sewing Yarns. The value of sewn textiles, particularly their appearance and durability, depends to a large extent on seam performance. To best complement textile design and construction, the seam must meet many requirements, the most important of which are neat appearance, high tenacity and abrasion resistance, high lightfastness (especially to ultraviolet radiation), resistance to chemicals, and washfastness. In addition, good sewability is significant for the sewing yarns; this is defined as achieving a high sewing length at high sewing speeds without yarn breakage. All these requirements are met or exceeded by fine denier, high-tenacity PET filament yarns. They have performed well alongside PET staple yarns and PET stretch-broken yarns in 100 % PET sewing yarns as well as in core-spun yarns.

Sewing Yarns with Normal Shrinkage. Filament yarns with normal shrinkage are suitable for 100 % PET sewing yarns, which must be heatset (Table 1). Sewing threads prepared from them are used especially in high-performance areas, e.g., safety belts, cushions, leather shoes, luggage, and handbags.

Sewing Yarns with Low Shrinkage. Low-shrinkage filament yarns are offered in a broad range of finenesses (Table 1). The largest end use is in core-spun yarns. By spinning a sheath of cotton, viscose, or other polymeric staple fiber around a PET filament core, the properties of both fiber types are combined. The sheath assures sewability; the core, mechanical efficiency. Such yarns meet high requirements of aesthetics, dyeability, and temperature resistance.

Table 1. Filament yarns for industrial end uses

Types	Shrinkage in hot air at 200°C, %	Fineness, dtex	Number of filaments	Filament fineness, dtex	Tenacity, cN/tex	Elongation, %
Yarns for sewing threads, normal shrinkage	17 – 18	74 – 455	24 – 96	3.1 – 4.7	68 – 70	12 – 13
Yarns for sewing threads, low shrinkage	7	49 – 940	16 – 200	2.5 – 4.7	68 – 70	16 – 17
Fine yarns, normal shrinkage	18 – 19	280 – 940	48 – 200	3.3 – 5.8	65 – 70	12 – 14.5
Fine yarns, normal shrinkage (spun-dyed black)	19 – 22	550 – 940	50 – 100	9.4 – 11	66 – 69	19 – 22
Fine yarns, low shrinkage	4 – 14	140 – 550	24 – 96	5.8	60	21
Coarse yarns, normal shrinkage	15.5 – 22	1100 – 1670	100 – 200	5.5 – 11	72 – 73	13 – 15.5
Coarse yarns, normal shrinkage (spun-dyed black)	15.5 – 22	1100 – 1670	100 – 200	8.4 – 11	66 – 72	12.5 – 13.5
Coarse yarns, low shrinkage	3.5 – 5.0 (7.5 – 8.5)*	1100 – 1670	200	5.5 – 8.4	72 (73 – 75)*	16.5 – 17.5 (11.5 – 12.5)*
Coarse yarns for tire cord	10 – 18	1100 – 1400	200	5.5 – 7	75	12
Coarse yarns (plied fineness)	22	2200 – 11 000	400 – 2000	5.5	other values depend on single yarn	

* With adhesive finish.

Fine Filament Yarns. Both normal- and low-shrinkage fine filament yarns are available for general use. Filament yarns with normal shrinkage are offered as white or spun-dyed black types. Both types are preferred in lashing straps, tapes, belts, ropes, nets, and fire hoses.

Low-shrinkage fine filament yarns are offered only in white (Table 1). They have a wide range of applications, extending from base fabrics for PVC or rubber coating for tarpaulins, membranes, containers, awnings, and tent roofs, through conveyor belts, V-belts, hoses, filter fabrics, and drying screens for paper making to sailcloth. Its use in sailcloth demonstrates the ability of PET to meet the requirements of low mass, high tenacity, and uniformity, as well as resistance to UV light, chemicals, water, and mildew.

Coarse Filament Yarns. Coarse yarns, like fine yarns, are offered with either normal or low shrinkage (Table 1). Yarns with normal shrinkage are available in white or spun-dyed black versions. White yarns, analogous to the corresponding fine yarns, are intended for lashing straps, belts, ropes, nets, hoses (especially pressure hoses), and safety belts. The situation is quite similar with respect to the black types, which are used primarily in safety belts and lashing straps.

Low-shrinkage coarse filament yarns, which are offered exclusively in white, have equally wide-ranging applications, such as base fabrics for PVC or rubber coating for tarpaulins, membranes, containers, awnings and tent roofs, hoses, filter fabrics, belts, conveyor belts, V-belts, and drying.

An especially interesting end use for low-shrinkage, high-tenacity, adhesively finished filament yarns is in automobile tires. The properties of such yarns make them highly suitable for the carcass of radial tires. Tires with these yarns no longer exhibit the disturbing phenomenon of flat spotting, observed in nylon-reinforced tires. (Flat spotting is the formation of an elliptical footprint in the tire during standing, resulting from molecular deformation of nylon because of its low glass transition temperature. It causes a bumpy ride until the tire warms up.) Since the early 1960s, much effort

has been expended to solve the problems of PET tire-cord material. In addition to rubber adhesion, these included the hydrolytic stability of PET. High-tenacity filament yarns for tires are rather low in shrinkage. They have high moduli, exhibit high flexural strength, and thus produce little heat during mechanical loading. They, therefore, have all the prerequisites to utilize fully the high chemical stability (resistance to hydrolysis) provided by extremely low concentrations of COOH groups. Solid-phase polycondensation combined with chemical capping of the majority of any still-existing COOH groups (see Section 2.1) makes possible the high stability of the tire cord.

The high-tenacity, coarse-filament single yarns discussed so far are complemented for many end uses by a series of plied yarns. These include some that are adhesively finished for use with rubber, others that have low-shrinkage like the single yarns, and still others that have normal shrinkage. Their finenesses extend up to 11 000 dtex. These yarns are intended for use in the coating sector as well as in straps, belts, ropes, nets, and hoses.

3.4. Spunbonds

Special Features of the Manufacturing Process. Spunbonded products are consolidated random layers of 2- to 10-dtex continuous filaments [81]. They are produced as continuous sheets up to 5 m wide in a continuous process from polymers of average intrinsic viscosity ([η] ca. 0.7). Their unit weights range from 20 to 500 g/cm^2 (→ Fibers, 3. General Production Technology).

A spunbond production line usually consists of several rows of spinnerets with mutually displaced spinning packs. Each filament bundle is accelerated by a draw tube under the spinneret to a final speed of ≥ 5000 m/min and thus is drawn [82]. Spreading devices open the filament bundle and lay the filaments down on a moving belt in overlapping random patterns. Various designs are known for these spreading devices; i.e., mechanical, pneumatic, and electrostatic [81].

Properties of the filaments are the same as those of filament yarns spun at high speed: tenacity ca. 3.5 cN/dtex, break elongation ca. 70 %, and shrinkage at 200 °C ca. 3 %. The orientation is characterized by a birefringence Δn of ca. 100×10^{-3}, and the degree of crystallinity is ca. 40 %.

The loose filament web, laid down as uniformly as possible, is then consolidated by using various processes singly or in combination, such as needle punching, calendering, and bonding. For certain applications, the web must be made thermally stable by additional heat-setting.

Spunbonded Products, Properties, and Uses. Polyester spunbonds are available in unit weights of 20 – 500 g/m^2 and in widths of 1 – 5 m. The consolidation discussed in the preceding section via needle punching, bonding, or calendering requires, in addition to PET and suitable binders, the use of polyesters of lower melting point or even of PET fibers with a sheath of a different polymer.

Lightweight webs (20 – 50 g/m^2) are available with individual filament counts of 2 – 3 dtex. They are used as cover webs in sanitary products and in horticulture.

Nonwoven products (50 – 130 g/m^2) have filaments with individual finenesses of 4 – 5 dtex. Their end uses are in construction and in shoe caps.

Materials with unit weights of 130 – 500 g/m^2 and individual filament finenesses up to 10 dtex are intended especially for use in construction (e.g., carriers for asphalt sheets for roofing), needle felts, embossed PVC coatings, underground construction, hydraulic engineering, and road building.

In addition to their large use in construction, polyester spunbonds are already being used successfully in automobiles (e.g., trunk linings) as well as in protective clothing and for environmental protection (covering of storage basins).

Web properties depend predominantly on the often different technologies for web production (laydown and bonding). No systematic data exist up to now that relate web structure to various end uses. However, in general, needle-punched webs are bulky, whereas thermally bonded webs are thin. Web strengths are ca. 2 – 4 N g^{-1} m^{-2} throughout (measured on strips 5 cm wide). Break elongations are 60 – 100 % for needle-punched webs, 20 – 60 % for bonded and needled webs, and generally < 30 % for thermally bonded webs.

3.5. Monofilaments

Special Features of the Manufacturing Process. In the production of PET monofilaments, polymers with intrinsic viscosities [η] of 0.7 – 0.9 are used. Polymers of higher viscosity are often brought to their required value by solid-phase condensation. Because these polymers then have a lower content of COOH groups, they have advantages for use in hydrolysis-resistant monofilaments with increased hot – wet durability. Occasionally, the COOH end groups of the polymers are also protected chemically.

Monofilaments with final thicknesses of 0.03 – 2 mm are spun in air, cooled immediately in water, then drawn, heat-set, and packaged on a directly connected draw line [83]. Each extruder usually has its own spinning head and, accordingly, its own draw line. Various designs are recommended for spinning heads and spinnerets, such as circular spinnerets and spinnerets with straight rows of holes [84]. Feed for each spinneret hole should be the same. A few centimeters below the spinneret, the filaments enter a water bath, whose temperature is above the glass transition temperature of PET (70 °C). The filaments are cooled but remain soft. In the bath, they change direction, are brought out of the bath as a warp sheet, and are drawn off by a set of rolls at a rate of less than 100 m/min. The filaments have no spin orientation.

The first draw almost always takes place in water at 90 – 95 °C; the second draw, also takes place in a water bath, a higher boiling liquid, or a heater tunnel. Die plates are sometimes used for more accurate adjustment of the thickness. Heat-setting occurs in a heater tunnel, usually at 130 – 180 °C. Depending on the type desired, more or less shrinkage is permitted and the total draw ratio (ca. 1 : 4 to 1 : 6) is selected. At the end of the roll train, the monofilaments are taken up on individual bobbins on a creel.

In almost all applications of PET monofilaments a uniform diameter is the most important mark of quality. Tolerance of ± 3 % is required; if the process is carefully controlled, it will often be less. Additional quality requirements are smooth surface and, if necessary, uniform cross section. Textile properties of a given type must always remain constant, especially shrinkage tension and shrinkage. In monofilaments with improved resistance to hydrolysis, the residual strength after prolonged use should be preserved uniformly.

Types of Monofilaments, Properties, and Uses. Monofilaments are produced with diameters of 0.034 – 2.00 mm These are thick filaments (the finenesses corresponding to these diameters are 12.5 – 43 000 dtex) and are, therefore, often called wires. A broad spectrum of types of PET monofilaments is found commercially in woven fabrics and zippers. These end uses place strict requirements on uniformity of diameter and properties, and especially on stress – strain behavior and shrinkage. The mechanical properties of typical PET monofilaments are evident from the stress – strain curves in Figure 7.

Monofilaments for weaving are used in the building industry in interior construction and interior installation. Other, often large, areas of application are paper machine sieves, safety belts, filter and screening fabrics, as well as conveyor belts. Fish nets, cordage, fishing lines, and medical applications all require the special properties of monofilaments for weaving.

The finest monofilaments, with diameters of 0.034 – 0.055 mm, have high elongation (see Fig. 7) and, at the same time, high shrinkage. Coarser wires range from 0.080 – 2.00. In addition, some wires have a rectangular cross section with diameters from 0.25 and 0.50 mm to 0.57 and 0.88 mm.

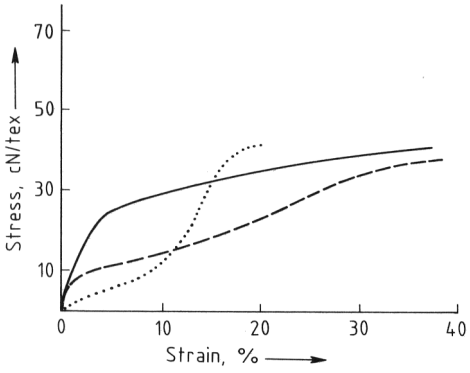


Figure 7. Stress – strain curves of typical PET monofilaments
———— Finest monofilament (0.055 mm diameter)
– – – Monofilament for weaving (weft type)
····· Monofilament for zippers

Monofilaments for weaving, especially for paper machine sieves are available as normal, hydrolysis-resistant, and chemically stabilized types. The most important representatives have high elongation (wires for the weft) or low elongation (wires for the warp) but low shrinkage.

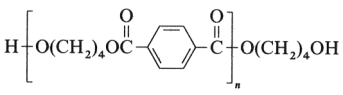
Another important group comprises *zipper monofilaments*, with a diameter of 0.40 – 1.16 mm. This competes with polyamide wire. A major advantage with PET monofilaments is that their stress – strain properties and shrinkage behavior can be varied to a great extent. Thus, zipper wires are available over a whole gamut of combinations from low, elastic extensibility with high shrinkage to high, plastic extensibility with low shrinkage. The majority of these types exhibit low, elastic extensibility and medium shrinkage at the boil.

In general, the combination of modulus and shrinkage properties of zipper wire and wires for weaving is determined by the special manufacturing process. It is chosen according to the load – time program and the thermal exposure of monofilaments during use. The ability to vary their properties so widely makes possible the adaptation of PET monofilaments to any kind of processing and to any end use.

4. Other Polyester Fibers

4.1. Poly(Tetramethylene Terephthalate)

The polyester of terephthalic acid and 1,4-butanediol [110-63-4] is a comparatively old fiber polymer [7].



Because 1,4-butanediol has always been more expensive than ethylene glycol, poly(tetramethylene terephthalate) [30965-26-5], also called poly(butylene terephthalate) or PBT, remained more or less on the sidelines. Not until the middle of the 1960s were special PBT products developed by several producers; the advantages of these products compared to PET permitted use of the more expensive 1,4-butanediol [85]. Today, these PBT products have become well-entrenched in the marketplace.

Production of PBT is similar to that of PET. Dimethyl terephthalate is transesterified and subsequently polycondensed, either batchwise or continuously. However, the catalysts used with PET promote ring closure of 1,4-butanediol, leading to the potentially explosive tetrahydrofuran. Therefore, tetraisopropyl titanate [546-68-9], for example, is used as catalyst in both process steps.

Because the aliphatic sections of the molecular chains are longer and thus more mobile, the transition temperatures of PBT, *mp* ca. 230 °C and glass transition temperature ca. 25 °C, are lower than those of PET. In addition, PBT crystallizes more readily than PET. The PBT unit cell exists in two modifications. Of these, one is more extended, ca. 11 % longer, and reverts to the shorter one when unloaded. This is responsible for the better recovery of PBT products from stretching and bending.

Like PET, PBT is spun on standard machines from the melt. Because of the lower glass transition temperature, formation of spin orientation not only occurs along the spinning path but continues into the drawoff and the windup. In addition, clearly recognizable crystallization of PBT occurs during spinning, which in turn also affects orientation. Properties of the as-spun yarn thus depend in a complicated manner on spinning conditions.

After the usual drawing and heat-setting, PBT has a flatter stress – strain behavior than PET (Fig. 8). The permanent extension of a PBT product after straining, however, is much less (Fig. 9) [85]. For example, after a strain of 15 %, the permanent extension of PET is 8.5 %; that of PBT, only 2.5 %. For this reason, PBT is particularly suited for carpet fibers, which must exhibit good recovery after loading. Unlike PET, PBT can be dyed easily to deep shades at the boil without carrier because of its lower glass transition temperature.

In addition to its elastic behavior and easy dyeability, PBT has other favorable properties. For example, it tends to swell less than PET. All these factors, taken together, make PBT an interesting raw material for textile zippers. Finally, because of their resistance to alkali,

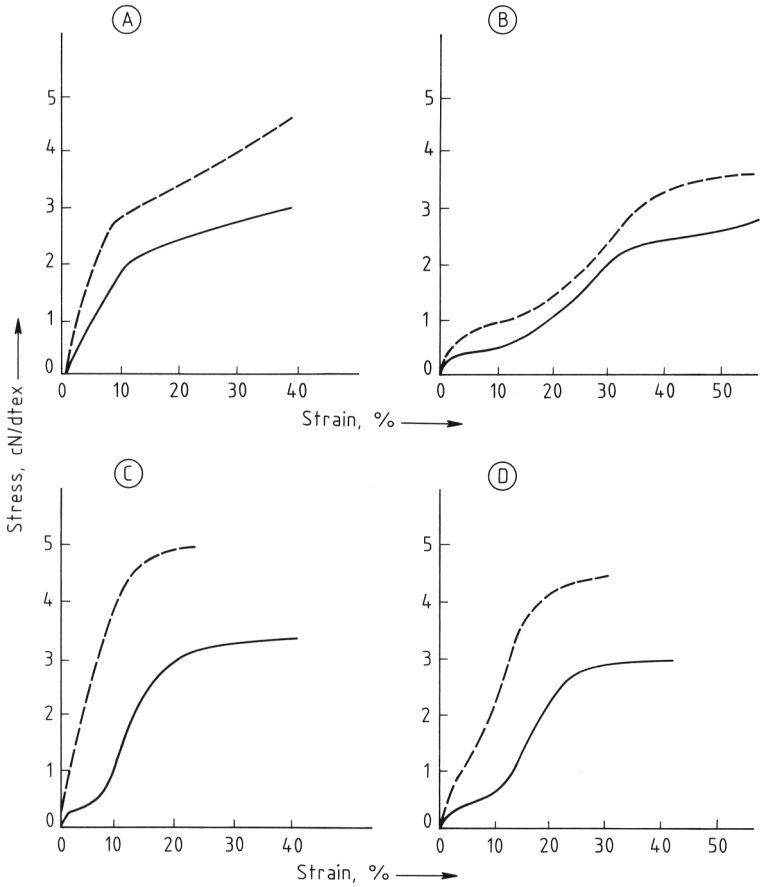


Figure 8. Stress – strain curves of drawn and heat-set PET and PBT yarns [83]
A) Drawn; B) Drawn and heat-set without clamping; C) Drawn and heat-set with clamping; D) Drawn, heat-set with clamping, plus heat-set without clamping
– – – – PET; ——— PBT

good abrasion resistance, and elastic behavior, PBT monofilaments are advantageously used in screen fabrics, which are constantly exposed to hot water or slightly alkaline media. In this way, fibers for carpets and monofilaments for zippers and screens have become products in which the more expensive polymer (PBT) pays for itself.

4.2. Poly(Trimethylene Terephthalate)

Poly (trimethylene terephthalate) (PTT) is a newly commercialized aromatic polyester fiber. Although PTT was available in commercial quantities only as recently as 1998 [88], it was one of the three high-melting-point aromatic polyesters first synthesized nearly 60 years ago [89, 90]. For a long time, the fiber industry had been aware of PTT having desirable properties for fiber applications. In a 1971 patent [91], Fiber Industries, Inc. found PTT fiber to have a lower modulus, better bending and work recoveries than PET, and was therefore more suitable than PET for making fiberfill and carpets. It was found that PTT had a better tensile elastic recovery and a lower modulus than PET and PBT [92]. These two properties are very desirable and are valued for making soft, stretch-fabrics with good hand and touch [93], and for resilient carpets [94].

In the early 1970s, the Shell Chemical Company, then a producer of 1,3-propanediol (PDO)

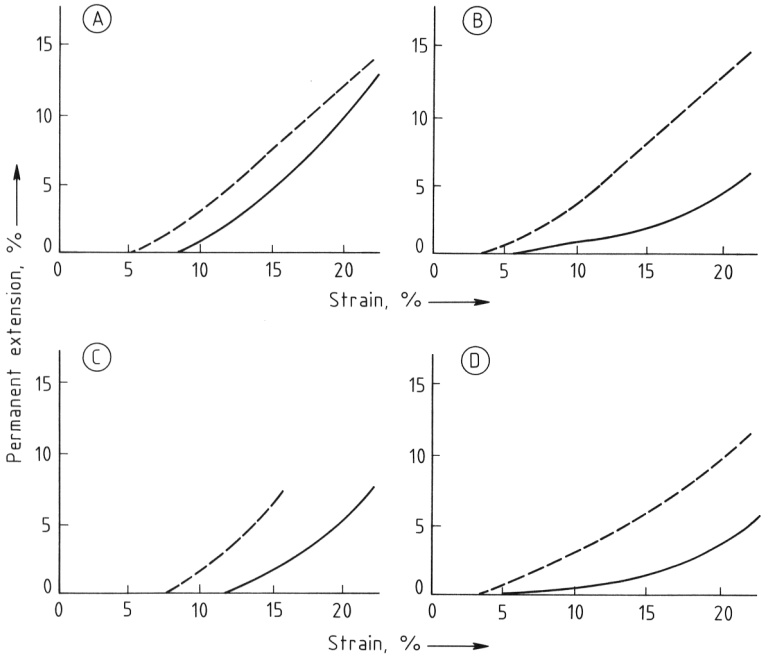


Figure 9. Permanent extension of PET and PBT yarns after strain [83]
A) Drawn; B) Drawn and heat-set without clamping; C) Drawn and heat-set with clamping; D) Drawn, heat-set with clamping, plus heat-set without clamping
– – – – PET; ——— PBT

via the acrolein route, explored the commercial potential of PDO and PTT by sampling PDO with several fiber companies. This led to a period of active research in PTT polymerization and applications [95–98].

Interest in PTT revived in the late 1980s when both Shell and Degussa made breakthroughs in two different PDO manufacturing technologies. Degussa was able to lower the cost of manufacturing PDO via the acrolein route and improve its purity to levels suitable for polymerization [99]. Shell developed an alternate synthesis route by hydroformylating ethylene oxide (EO) with a combination of CO and H_2 synthesis gas [100], leveraging their core competencies in hydroformylation technology and EO feedstock. In 1995, Shell announced the commercialization of PTT, and built a 73×10^6 t PDO plant in Geismar, Louisiana. This was followed by Du Pont announcing the retrofitting of an existing polyester plant in Kinston, North Carolina, to produce PTT using PDO obtained from Degussa. Du Pont and Genecor international collaborated to develop a potentially cheaper biological route for making PDO through glycerol fermentation. More than half a century after its synthesis, PTT finally joined PET and PBT, and became a commercial reality.

PTT is melt polymerized by either the transesterification of PDO with dimethyl terephthalate (DM) or by the direct esterification of PDO with purified terephthalic acid (PDA). The process is similar to that for PET. Because of PDO's lower reactivity, more active catalysts based on titanium and tin, which would discolor PET, are used to polymerize PTT. PTT is polymerized at much lower temperature between 250 and 275 °C. because of its higher melt degradation rate and faster crystallization rate, it requires special consideration in polymerization, pelletizing and solid-state treatment [89].

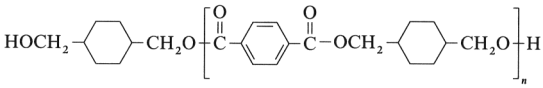
Like PET and PBT, PTT crystallizes into a triclinic structure. PTT chains appear zigzag, while PET chains are fully extended, and PBT chains look buckled. The highly contracted

crystalline chain gives PTT a good tensile elastic recovery.

Most of the PTT application developments to date have focused on textile and carpet fibers. PTT fibers and yarns have bulk, resiliency, stretch-recovery, softness, hand and drape, properties which are similar to those of nylons and much better than those of PET. Such materials are inherently resistant to most stains which are acidic in nature because they not have dye sites. They also have a lower static propensity than nylons. PTT fibers are dyed with disperse dyes but at a lower temperature than PET because of the polymer's lower T_g. The combinations of these properties are attractive to carpet and textile manufacturers in some applications where PTT could replace nylon or PET. PTT also offers the potential of creating new fiber products by using the unique combinations of these properties not found in either nylon or PET alone.

4.3. Poly(1,4-Dimethylenecyclohexane Terephthalate)

Fibers of poly(1,4-dimethylenecyclohexane terephthalate) [25135-20-0], PDCT, have been on the market since the late 1950s under the trade name Kodel II (Tennessee Eastman Company, United States).



The intermediates are DMT (Section 1.1) and 1,4-bis(hydroxymethyl)cyclohexane [105-08-8] commonly known as 1,4-cyclohexanedimethanol. This diol is produced by the two-step hydrogenation of DMT at 160 – 180 °C and high pressure in the presence of catalysts (→ Alcohols, Polyhydric, Section 2.9). The diol can exist as either the *trans* or the *cis* isomer. By appropriate choice of reaction conditions, the *trans*: *cis* ratio can be adjusted to 7:3. To prepare the polymer, DMT is transesterified with the diol and after excess diol is distilled, polycondensation takes place in a manner analogous to PET.

The polymer is transparent and amorphous. It crystallizes in the triclinic system. The crystalline density is 1.265 g/cm^3 for polymer with trans isomer and 1.303 g/cm^3 for polymer with *cis* isomer [86, 87]. Wide-angle X-ray diagrams of crystalline samples show a continuous transition of the trans crystal lattice to the *cis* crystal lattice with increasing *cis*: *trans* ratio. The fiber density is 1.22 – 1.23 g/cm^3. Small-angle X-ray investigations show a fibrillar structure with lattice layers at an angle to the fiber axis.

The glass transition temperature of the polymer is 76 °C; in drawn and crystalline fibers, it can be as high as 100 °C. The melting point is 285 – 295 °C [61].

Compared to PET, the tenacity of PDCT staple fibers is ca. 30 % less, with the same elongation at break. The abrasion resistance behaves similarly. The tensile or bending recovery of the fibers from equal deformation at room temperature, on the other hand, is greater for PDCT because of the higher glass transition temperature of the polymer [87]. The result is greater crimp stability of PDCT fibers and, hence, greater bulk of nonwovens and textile fabrics. Because of the higher glass transition temperature, however, PDCT fibers are more difficult to dye than PET fibers. Therefore, the dyeing temperature for PDCT fibers must be increased or suitable carriers and dyes chosen.

Applications of PDCT fibers are in areas such as fiberfill and carpets that require especially high crimp stability and generally high recovery forces following deformation at room temperature. These fibers are also used in blankets and synthetic furs [87].

5. Uses

The following properties are responsible for polyester fibers being used in all areas where fibers are applied:

1. The extremely broad range of mechanical properties of staple fibers and filament yarns
2. Their variable and easily adjustable shrinkage properties
3. Their ease of dyeing combined with high fastness properties
4. Their high chemical, solvent, and UV resistance

5. The low flammability of even the standard polymer, which can be further improved by modification without significantly impairing other valuable fiber properties
6. The deformability of the fibers and the fabrics made from them
7. The ability to make these deformations (e.g., crimp, creases, and pleats) permanent
8. The low moisture uptake and, hence, rapid drying
9. The fact that most soil remains on the surface where it is easily removed with water or solvents

These properties are largely insensitive to the presence of water at moderate temperature. Together, they are responsible for the dimensional stability and easy care of textiles made from polyester fibers.

Staple fibers, continuous-filament yarns, monofilaments, and spunbonds of polyester are found in all major textile markets. Among the polyesters, poly(ethylene terephthalate) is the most important polymer. Apparel, such as outerwear or sportswear, as well as work clothing and protective clothing, could not be imagined without PET fibers, either 100 % or in blends with other man-made or natural fibers. Similarly, PET fibers are widely used in an abundance of finished articles in adapted make-ups [102], e.g. home furnishings, such as drapes and curtains, furniture covers, table and bed linens, cushions, pillows, and carpets.

Polyester products have been particularly successful in industrial markets. Here, they are encountered everywhere fibers can be used. In many cases, because of their properties, especially their relatively low density (ca. 1.38 g/cm^3), they have provided elegant and, at the same time, economical solutions to problems. Examples are sewing thread, tarpaulins and awnings, safety belts, V-belts, tire cord, zippers, woven screens, geotextiles, roofing sheets, or book covers.

The extremely high performance of PET is reflected in the breadth of end uses [4, 27, 38, 61, 62]. This performance is based primarily on two properties of the fiber products: the dimensional stability of the textiles made from PET under mechanical and thermal stress, and their ease of care. Both properties are primarily determined by the glass transition temperature which, depending on the chemical structure of the polymer and the degree of orientation and order, lies between ca. 70 and 100 °C (see Section 2.1, → Fibers, 2. Structure). The fibers can be crystallized at any stage of their manufacture and during further processing. This permits production of any desired shape.

Polyester fibers are available in all possible forms in which natural and man-made fibers exist and can be processed on equipment used to manufacture yarns, woven fabrics, knit goods, and even nonwovens. Grouped broadly, the forms of PET are the following:

1. Staple fibers with a fineness of 0.4 – 20 dtex; short cut fibers, 6 mm length, fibers of 30 – 60 mm up to 150 mm; round or modified cross sections; crimped (except for flat cut fibers).
2. Textile continuous-filament yarns with a fineness of 20 – 200 dtex; individual filament fineness of 0.5 dtex (special types 0.1 dtex) to 5 dtex; flat, textured, or with staple yarn character; round or modified cross sections. The fineness of air-textured, continuous-filament yarns is 200 – 3000 dtex.
3. Fine high-tenacity continuous-filament yarns and yarns for sewing threads with a fineness of 50 – 940 dtex, with individual filaments of 3 – 10 dtex; flat with round cross sections.
4. Coarse high-tenacity continuous-filament yarns with a fineness of 1100 – 1670 dtex (plied fineness up to 11 000 dtex); individual filaments of 5 – 11 dtex; flat with round cross sections.
5. Spunbonds in widths of 1 – 5 m; unit weights of 20 – 500 g/m^2, with an individual filament fineness of 2 – 10 dtex.
6. Monofilaments with a diameter of 0.034 – ca. 2 mm; flat with round or modified cross sections.

6. Economic Aspects

Production of polyester fibers continues to grow at a faster rate than for all other fibers, both man-made and natural [101]. Thus, whereas during the 1990s, their share of world fiber production

grew from 21.4 to 35.6%, it had increased to 45.8% by the end of 2009. Tecnon OrbiChem expects the upward trend to continue during the forecast period such that by the mid-2010s, driven by developments in China and other Asian countries, particularly India, polyester is expanded to account for more than 50% of worldwide fiber production, rising to more than 60% by 2020.

During the 1st decade of the 21st century, global production of polyester filament yarn has increased by an average rate of 7.9%/a, though the rate of growth did vary from a low of 1.4% in 2005 to a high of 14.9% the following year. Based on project growth in global GDP, it is expected that production of polyester filament yarn will increase by around 7.7%/a until 2010.

In comparison, global production of polyester staple fibers during the 1st decade of the 21st century has grown at an average rate of 5.5%/a, lower than filament yarns due mainly to the effects of low cotton prices during the early part of the decade. Tecnon OrbiChem believes that until 2010 production of polyester staple will grow slightly faster than previously at around 5.8%/a, which although slower than for filament yarn is nevertheless still well above the global figure for all fibers of 4.2%.

The world situation continues to be dominated by activity in China, where production of polyester filament represented less than a third of the global total. However, by 2005 the figure had increased to more than 50%, climbing to 71% by the end of 2009. Similarly, for staple, China accounted for slightly more than 25% of total world production, rising almost 50% in 2005 and 63% in 2009. Production of both filament and staple is expected to continue growing such that by 2020, China is forecast to account for more than 85% of the total world production of polyester fiber products. Overall, production of polyester filament yarn and staple fibers in Asia during 2009 represented 92% of global total (77% in 2000), and by 2020 production of polyester fiber in Asia is expected to account for 97% of the world total.

Because domestic consumption of both polyester filament and staple has failed to keep pace with increases in production, Chinese export trade has grown rapidly in recent years. Consequently, producers in other countries have come under pressure in both domestic and export markets. Thus whereas in 2004 China was ranked 8th and 6th in the league of exporting nations for filament and staple respectively, by 2008 it was number 1 for filament exports — with more than double the volume of the second placed nation Taiwan — and number 2 behind South Korea for staple. Exports of filament and staple amounted to almost 1.2×10^6 t in 2008, around a quarter of the world total. Meanwhile, imports of polyester filament yarn have fallen by 69% in four years to 184 000 t in 2008, whilst for staple fiber the fall has been 75% to 154 000 t.

Despite the rapid increase in output, the average plant utilization rate in China was only 72% in 2008, and resulted in some planned expansions being put on hold that year. However, with recovery evident in 2009, more than 1×10^6 t/a of new polyester filament capacity came on stream, with a further 1.5×10^6 t/a scheduled for 2010, and 3×10^6 t/a in 2011. With demand expected to grow less quickly, overcapacity looks set to remain a problem for filament manufacturers in China throughout the forecast period. In contrast, because polyester staple capacity has grown at a slower rate in recent years, the average utilization rate in 2008 was around 80%, a figure that is expected to rise during the forecast period even though new plants are likely to come on stream. However, recycled material is becoming an increasingly significant proportion of staple manufacture, thought to account for as much as 50% of total fiber production in 2009.

With Asia occupying such a dominant global position, the situation elsewhere in the world is less positive. In West Europe output of polyester filament yarn has been declining at a rate of almost 9%/a since 2005, with the expectation that the downward trend will accelerate to around 12%/a through 2010. The situation concerning staple fiber production has been better in the recent past, with output falling by around 1.5%/a since 2005. However, with competition from Asia growing as production for nonwoven applications increases, output of staple in Western Europe is expected to fall at around 15%/a in the forecast years. More than 90% of polyester staple consumption in West Europe is in nonwoven applications. However, the nonwovens industry in Asia is growing as multinational companies shift their manufacturing bases to lower cost regions.

Production of polyester filament yarns in North America has been falling by around 5.3%/a for since 2005 and is expected to decline at around the same rate during the forecast period. Because the carpet market is more resistant to import penetration than others, production of polyester BCF yarns will be more secure than perhaps the forecast suggests. There has been a definite movement towards the use of polyester BCF in the production of carpets in the USA, substituting staple polyester and nylon as well as polypropylene BCF and nylon BCF as well. In 2009, consumption of polyester BCF yarn grew by 26% in a weak carpet sector.

With raw material costs rising, many polyester fiber manufacturers in Europe, North America, and Asia are turning to recycled feedstock. Demand in China for polyester bottles has been increasing, with shortages reported in Asia early in 2008, which drove up prices.

Trade names and producers of polyester fibers are listed in Table 2. World production of synthetic polyester fibers (yarn and staple) are listed in Table 3.

Table 2. Trade names and producers of polyester fibers [103]

Trade name	Type*	Manufacturer
A.C.E.	PET	Performance Fibers Inc./USA
Acelan	PET	Daehan Synthetic Fiber Co./Korea
Acelon	PET	Acelon Chemicals & Fiber Corp./Taiwan
Aliaf	PET	Terene Fibres India Ltd./India
Arachra	PET	Tongkook Corp./Korea
Asahikasei Ester	PET	Asahi Kasai Fibers Co./Japan
Bai Lu	PET	Xinxiang Bailu Chemical Fiber/China
Belira	PET	Incel/Bosnia-Herzegovina
Best	PET	Yizheng Chemical Fiber/China
Bonopoly	PET	Bongaigaon Ref. & Petrochemicals Ltd./India
Camellia	PET	Chanzhou Chemical Fiber/China
Centuron	PET	Tainan Spinning Co./Taiwan
Chiemlon	PET	Chiem Patana Synthetic Fibers Co./Thailand
CoolMax	PET	Advansa A.S./Turkey
Corterra	PTT	Setila SA/France
Dacron	PET	DAK Americas, LLC./USA
		Suzhou (Far Eastern Textiles) Polyester/China
		Advansa GmbH/Germany
		Advansa A.S./Turkey
Di Guang	PET	Human Indi Chemical Fiber/China
Diolen	PET	Diolen Industrial Fibers GmbH/Germany
		Polyenka SA/Brazil
		Enka de Colombia SA/Colombia
Dragen	PET	Jiangxi Polyester Fiber/China
DSP	PET	Performance Fibers (Kaiping) Co./China
DSP Polyester	PET	Performance Fibers SA/France
		Performance Fibers Inc./USA
Eastlene	PET	Far Eastern Textile Ltd./Taiwan
Eastlon	PET	Far Eastern Textile Ltd./Taiwan
EcoSpun	PET	Wellman, Inc./USA
Elana	PET	Elana SA/Poland
Eslon	PET	Saehan Industries Inc./Korea
Estrell	PET	Aquafil SpA/Italy
Eural	PET	Tergal Fibres SA/France
Fei Ma	PET	Foshan Polyester/China
Filwell	PET	Wellman International Ltd./Ireland
Flacron	PET	Ahmedabad & Calico Printing Co./India
Fortrel	PET	Wellman, Inc./USA
		Mantex CA/Venezuela
Futura	PET	Futura Polyesters Ltd./India
Gatron	PET	Gatron Industries Ltd./Pakistan
Grisuten	PET	Märkische Faser GmbH/Germany
Hanslon	PET	Hankook Synthetic, Inc./Korea
Heiping	PBT	Yixing Huaya Chemical Fibre/China

Hualon	PET	Hualon Corp./Taiwan
Huvis	PET	Huvis Corp./Korea
Hunvira	PET	Hung Chou Chemical Industry Ltd./Taiwan
Jailene	PET	Swadeshi Polytex Ltd./India
Jaykaylene	PET	J.K. Synthetics Ltd./India
Jekester	PET	Orissa Polyfibres Ltd./India
Jespan	PET	Hualon Corp (Malaysia) Sdn. /Malaysia
Jewelon	PET	Taiwan Spinning Co./Taiwan
Kintrel	PET	Kimex SA/Mexico
Kolon	PET	Kolon Industries Inc./Korea
Kreo	PET	Freudenberg Politex SpA/Italy
Kuraray Polyester	PET	Kuraray Co./Japan
Lalelen	PET	Sancak Tül A.S./Turkey
LSB	PET	La Seda de Barcelona SA/Spain
Luxlen	PET	Yu-Ho Fiber Industrial Corp./Taiwan
Mandal	PET	Sanghi Polyesters Ltd./India
Micrell	PET	Noyfil SA/Switzerland
		Val Lesina SpA/Italy
Mirhon	PET	Miroglio SpA/Italy
Multisoft	PET	Ledervin/Brazil
Nakron	PET	Thai Toray Synthetics Co./Thailand
Nanlon	PET	Tainan Spinning Co./Taiwan
Navilon	PET	Kum Kang Co./Korea
Neopol	PTT	Hyosung Corp./Korea
Nergis	PET	Nergis A.S./Turkey
Nirester	PET	Nirlon Ltd./India
Oplene	PET	Jeil Synth. Fibers Co./Korea
Palmylon	PET	KP Chemtec Corp./Korea
Pathom	PET	Thai Toray Synthetics Co./Thailand
Pearly Lene	PET	Tung Ho Spinning Co./Taiwan
Pentex	PEN	Performance Fibers, Inc./USA
Polymisr	PET	Misr Rayonne Co./Egypt
Pontella	PET	Setila SA/France
Rebar	PET	Chia Hsin Food & Synthetic Fiber Co./Taiwan
Recron	PET	Reliance Industries Ltd./Indien
Sadrifill	PET	DS Fibres NV/Belgium
Sadriloft	PET	DS Fibres NV/Belgium
Sadrilux	PET	DS Fibres NV/Belgium
Savar	PET	Beximco Synthetics/Bangladesh
SENS	PTT	Miroglio SpA/Spain
Serill	PET	Aquafil SpA/Italy
Setila	PET	Setila SA/France
Shinlon	PET	Shinkong Synth. Fibers Corp./Taiwan
Shreester	PET	Shree Synthetics Ltd./India
Silkiss	PET	Miroglio SpA/Italy
Silver Ring	PET	Hubei Chemical Fiber/China
Skylon	PET	Sunkyong Industries Ltd./Korea
Slotera	PET	Slovensk Hodvab a.s./SR
Softfit	PTT	Nan Ya Plastics Corp./Taiwan
Solotex	PTT	Solotex Corp./Japan
Soluna	PET	Mitsubishi Rayon Co./Japan
Sorona	PTT	Huvis Corp./Korea
		Saehan Industries, Inc./Korea
		Far Eastern TEXTILE Ltd:/Taiwan
Startex	PET	Seong-An Synthetics Co./Korea
Tairilin	PET	Nan Ya Plastics Corp./Taiwan
		Nan Ya Plastics Corp./USA
Tasinlon	PET	Chung Shing Textile Co./Taiwan
Tejin- Tetoron	PET	Teijin Ltd./Japan
		Teijin Polyester (Thailand) Ltd./Thailand
Terene	PET	Terene Fibres India Ltd./India
Tergal	PET	Tergal Fibres SA/France
Terinda	PET	Advansa A.S./Turkey
Terital	PET	Fidion Srl/Italy
Terital Eco	PET	Fidion Srl/Italy

Terlenka	PET	Enka del Colombie SA/Colombia
Tertex	PET	Inquitex SA/Spain
Terylene	PET	SANS Fibres (Pty.), Ltd./South Africa
Texlon	PET	Tongkook Corp./Korea
Thermolite	PET	Advansa A.S./Turkey
Tifico Polyester	PET	TIFICO/Indonesia
Toplon	PET	Hyosung Corp./Korea
Toray	PET	Toray Snthetic Fiber (Nantong) Co./China
Toray Tetoron	PET	Toray Industries, Inc./Japan
Torlen	PET	Elana/Poland
Toyobo Ester	PET	Toyobo Co./Japan
Trevira	PET	Hosaf Fibres (Pty) Ltd./South Africa Trevira GmbH Germany
Trevira CS	PET	Trevira GmbH/Germany
Tuntex	PET	Tuntex Fiber Corp./Taiwan
Ultrafil	PET	Pennine Fibre Industries Ltd/ United Kingdom
Unitika Ester	PET	Nippon Ester Co./Japan
Vadodora	PET	Yogi-Polyesters Ltd./India
Valena	PET	Val Lesina SpA/Italy
Vanlon	PET	Full Point Synthetic Industrial Co./Taiwan
Verde	PET	M & G Fibras e Resinas/Brazil
Wellene	PET	Wellman International Ltd./Ireland
Wolkiss	PET	Miroglio SpA/Italy
Yambolen	PET	Yambolen/Bulgaria
Zispan	PTT	Hankook Synthetic, Inc./Korea

[*] PET = poly(ethylene terephthalate), PTT = poly(trimethylene terephthalate), PBT = poly(butylene terephthalate), PEN = poly(ethylene naphthalate).

Table 3. World Production of synthetic polyester fibers (yarn and staple)

Year	Production, t
1980	5 085 000
1990	8 445 000
1995	11 958 000
2000	18 912 000
2005	24 701 000
2009	32 412 000

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Polyurethane Fibers

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ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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Following the discovery in 1937 of the diisocyanate addition polymerization process by O. Bayer and co-workers [1], this principle was applied to the production of polyurethane (PUR) fibers. Hard PUR fibers, first developed to compete with nylon 66, are no longer important. On the other hand, the same principle of synthesis was successfully applied to the manufacture of highly elastic yarns [2, 3].

Synthetic high-polymer fibers containing at least 85 wt% of segmented polyurethane are called *elasthane* [4]; the term *spandex* is used in the USA and in this article.

Spandex fibers are characterized by high elongation and elasticity. Like rubber yarns (elastodiene fibers), they belong to the class of elastomeric fibers. Spandex, produced as continuous-filament yarn, is used almost exclusively to manufacture elastic textiles and is always employed in combination with other fibers. Although spandex has gained considerable technical and economic importance, worldwide production, which amounted to 290 000 t in 2005, is relatively small compared to other textile fibers. Commercial products have distinctive raw materials bases, chemical structures, and manufacturing and spinning processes, which, in the final analysis, are responsible for the specific balance of properties [5–9].

Due to the rise in the significance of active wear in the world as compared to formal wear, spandex or PU filament consumption has been increasing [10]. Huge Chinese expansion has also led to the worldwide increase in the consumption of this filament type. It has become the first real mainstream significant usage filament from the non-melt spinning process. Dry spinning speeds of 1200 m/min have been reported, resulting in relatively mature low-cost manufacturing of this material for the applications.

The result has been widespread usage of this material for all kinds of applications – signifying how important economics are in popularizing an application development for a filament yarn product. As the product is used only as a small percentage in fabrics, popular thickness are more in the finer category. The bulk of the market consumption is in the dtex 33 – 78 range in terms of weight/volume being sold. It is significant that in recent years, the dtex 22 and dtex 17 PU products have also become important as the trend in fabrics is towards lighter close-to-the-skin products. Some recent products have been seen combined with very light dtex 33 polypropylene, resulting in extremely lightweight fabrics which are very popular in innerwear applications. A small but significant market has developed in the heavier deniers between dtex 330 and 470 for shoes, diapers, and medical applications. The growth scope in this area has leveled off recently. The major growth area for this material over the last few years has been in dtex 13 – 22 sector. Some other melt-spun stretch filaments have made an appearance but are still, in marketing terms, not significant. Here, XLA must be mentioned, which was marketed as a melt-spun stretch yarn which can be used as 100% alternative

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Table 1. Trade names and producers of polyurethane fibers

Trade name	Type	Manufacturer
Acelan	EL	Tae Kwang Industrial Co./Korea
Creora	EL	Hyosung/China
Creora	EL	Hyosung Corp./Korea
Creora	EL	Hyosung/Turkey
Dorlastan	EL	Asahi Kasei Spandex Europe GmbH/Germany Asahi Kasei Spandex America Inc./USA
Elaston	EL	Chemitex/Poland
Espa	EL	Toyobo Co./Japan
Fujibo Spandex	EL	Fujibo Kozak, Inc./Japan
Glospan	EL	Radici Spandex Corp/USA
Huastan	EL	Hualon Corp./Taiwan
Kopandex	EL	Kohap Ltd./Korea
Linel	EL	Fillatice SpA/Italy
Lycra	EL	Invista Inc./USA
Lycra	EL	Invista Brazil/Brazil
Lycra	EL	Invista (U.K.) Ltd./United Kingdom
Lycra	EL	Invista Canada Inc./Canada
Lycra	EL	Invista (China) Co./China
Lycra	EL	Fielmex SA de CV/Mexico
Lycra	EL	Invista/Mexico
Lycra	EL	Invista Singapore Fibres/Singapore
Mobilon	EL	Nisshinbo Industries, Inc./Japan
Opelon	EL	Opelontex Co./Japan
Roica	EL	Asahi Kasei Fibers Corp./Japan
Roica	EL	Thai Asahi Kasei Spandex Co./Thailand
Sheiflex	EL	Shei Heng Hsin Sheiflex Industrial Co./Taiwan
Texlon	EL	Tongkook Corp./Korea
Toplon	EL	Hyosung Corp./Korea

* EL = elastane fibers.

to the material and need not to be used as a blend percentage as in case of PU yarns. Marketing and acceptance of this filament-making material held a lot of initial potential, but the cost reductions in PU filament enabled by the increasing of dry spinning speeds and the rising sophistication of the technology and production processes in PU have stalled the progress of XLA.

Trade names and producers of polyurethane fibers are listed in Table 1. World production of polyurethane fibers is listed in Table 2.

Table 2. World Production of polyurethane fibers

Year	Production, t
1995	70 000
2005	290 000

1. Physical Properties

Spandex is highly extensible by application of an external force. When the load is removed, the material rapidly and completely reverts to its original state. This is a result of the two-phase structure of the hard and soft segments. The soft segments, which are highly mobile at the use temperature, are coiled in the unloaded state and stretched in the loaded state. The restoring force results from the increase in entropy during reversion to the coiled state (entropy elasticity). The crystalline hard segments of symmetrical aromatic urea groups form a network structure via hydrogen bonds and thus provide form stability [11–24].

Characteristic stress – strain curves of a commercial spandex are shown in Figure 1 in a cyclical loading – unloading experiment (stress – strain cycle). The mechanical properties of spandex filament yarns for the usual range of types and finenesses are listed in Table 3.

Below the glass transition temperature of the soft segments, spandex loses its elasticity. In commercial products, this temperature of 210 – 250 K is far below normal environmental temperature range. Critically important for textile processors is the behavior at high temperature (160 – 170 °C, which is the temperature during textile treatment and shaping processes).

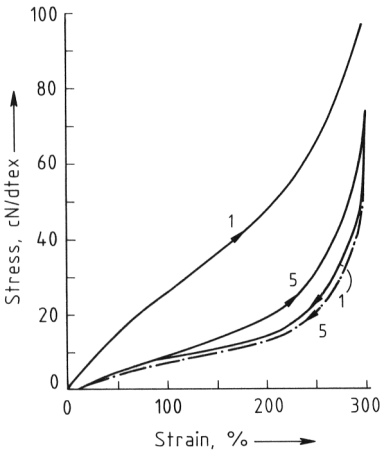


Figure 1. Stress – strain cycle of a 480-dtex spandex yarn (Dorlastan type V 400) *
* 1 is first curve; 5 is fifth curve; —— is elongation; —— is recovery.

Table 3. Mechanical properties of continuous filament spandex yarns

Property	Range of values
Fineness	20 – 5000 dtex
Elongation at maximum tensile load	
Standard-elongation types	420 – 570 %
High-elongation types	600 – 800 %
Tenacity	
Referred to original fineness	0.45 – 1.2 cN/dtex
Referred to fineness at break [a]	3 – 7 cN/dtex
Cyclic loading to 300 % elongation	
Modulus, 150 % [b]	0.04[c] – 0.1 [d] cN/dtex
Modulus, 300 % [b]	0.1[c] – 0.25 [d] cN/dtex
Residual elongation	10 – 30 %

[a] Fineness at maximum textile elongation.
[b] Referred to original fineness.
[c] High-elongation types.
[d] Standard-elongation types.

2. Chemical Properties

Compared to rubber yarns, spandex is substantially more stable to chemical influences during textile processing and subsequent use. Any possible damage manifests itself primarily in a loss of strength and an onset of yellowing. As expected, polyether spandex is more affected by oxidative processes and polyester spandex by hydrolysis. The stability of spandex subjected to various chemical treatments is given in Table 4.

Spandex-containing textiles can be cleaned chemically without problem. Sensitivity to photo-oxidative damage is increased by unsaturated fatty acids and cosmetic oils [25]. Nitrogen oxides lead to yellowing and, hence, are detrimental to white textiles that contain spandex. Compared to rubber yarns, spandex has a greater affinity for textile dyes.

3. Raw Materials

Segmented polyurethane, the raw material for spandex fibers, consists of long-chain dihydroxy compounds (macrodiols), aromatic diisocyanate compounds, and short-chain diamino or dihydroxy compounds (chain extenders). Because of their chain mobility, the long-chain diols (soft segments) are responsible for the extensibility. The urethane and urea groups, formed by aromatic diisocyanates and short-chain diols (hard segments), function as physical cross-links and are the source of yarn strength.

Macrodiols. Macrodiols suitable for the manufacture of spandex have molar masses of 1 – 3 kg/mol and melting points < 50 °C. Only polyether and polyester diol are important. The most frequently used polyether diol is poly (tetramethylene ether glycol), polymerized from tetrahydrofuran via ring opening (→ Polyoxyalkylenes, → Polyoxymethylenes). Spandex fibers with polyether soft segments are highly resistant to hydrolysis and alkali, and have excellent low-temperature properties. They are, however, sensitive to light, atmospheric oxygen, and the chlorinated water of swimming pools and must be specially protected from them.

Among the polyester diols used, adipic acid polyesters have gained great importance,

Table 4. Chemical resistance of spandex

Chemical treatment	Polyether spandex[a]	Polyester spandex[a]	Remarks
HCl 10 %, 20 °C, 24 h	low	high	
H_2SO_4 10 %, 20 °C, 24 h	low	high	
CH_3COOH 10 %, 20 °C, 24 h	none	none	
Cl_2– H_2O 20 mg/L, 20 °C, 24 h	high [b]	low	some yellowing
NaOH, followed by rinsing, suctioning, rinsing	none	none	
Cleaning in gasoline	low	low	
Xeno-test [c], 50 h	low	low	some yellowing
Xeno-test [c], 100 h	medium	low	little to moderate yellowing

[a] In the classification used, the following strength loss is to be expected: none, 0 – 5 %; low, 5 – 20 %; medium, 20 – 40 %; high, 40 – 90 %; total, 90 – 100 %.
[b] Can largely be prevented by use of ZnO as spinning additive [24].
[c] Light source: Hanau 450 (UV-emitting xenon gas lamp).

whereas polycaprolactone diols have not. For polyadipates, mixtures of C_2 – C_6 diols, e.g., 1,2-ethanediol – 2,4-butanediol and 1,6-hexanediol – 2,2-dimethyl-1,3-propanediol are used most frequently. Polyester spandex is more resistant to chlorinated water than polyether types and is insensitive to oxidative damage. Its sensitivity to hydrolysis can be reduced by the use of diols with a greater number of carbon atoms. Polyesters of mixed diols give spandex with a low tendency to crystallize during extension and with improved elastic properties.

Diisocyanates. Commercial spandex is almost exclusively produced from 4,4′-methylenebis (phenyl isocyanate) [101-68-8] → Isocyanates, Organic. Toluene diisocyanate [26471-62-5] (TDI), which was used in the early years of spandex production, is rarely employed today. Although aliphatic diisocyanates lead to polyurethanes with increased light durability, they are of little use because of increased difficulties in processing the spinning solutions. However, 1,6-diisocyanatohexane can be employed as a modifier [26].

Chain Extenders. Most spandex producers use short-chain aliphatic diamines, such as 1,2-diaminoethane or 1,2-diaminopropane, as chain extenders because they give fibers with the best thermal and hydrothermal properties. Hydrazine hydrate, carbonic acid, dicarboxylic acid dihydrazides, aminocarboxylic acid hydrazides, and semicarbazidocarboxylic acid hydrazides [27, 28] were used earlier as chain extenders, but are no longer of any significance. Occasionally, small amounts of codiamines, such as 1,3-diaminocyclohexane [29] or *N*-methylbis(3-aminopropyl)amine [30], are used in combination with ethylenediamine. This favorably affects certain properties, e.g., solubility and storage behavior. 1,4-Butanediol, frequently used in thermoplastic polyurethanes, results in spandex with unsatisfactory properties. 1,4-Bis(2-hydroxyethoxy)benzene, on the other hand, produces a melt-spun spandex with improved properties [31].

Solvents. Spandex fibers based on polyurethane – polyurea decompose during melting; therefore, they are spun from solution. Only dipolar aprotic solvents, usually dimethylacetamide and dimethylformamide, can be used.

Stabilizers and Adjuvants. Because of the use of aromatic diisocyanates, light tends to discolor spandex [32]. Spandex in which polyethers are used as soft segment is, in addition, attacked photooxidatively. The following are used as stabilizers for these processes: phenolic antioxidants, sterically hindered amines, light-protective agents (e.g., benzotriazoles), and phosphites. They must meet special requirements such as low thermal volatility and good laundering resistance.

Spandex yellows under the influence of nitrogen oxides, which are contained primarily in combustion gases. Tertiary amine compounds have proved to be effective protectors against these; in addition, the patent literature describes a whole series of protective agents, e. g., carboxylic acid hydrazides [33], esters [34, 35], and phosphites [36, 37].

Polyether spandex, which is sensitive to chlorinated water, can be protected by tertiary amine compounds; polymers or polyurethanes with basic groups are used, such as poly(*N,N*-dialkylamino)ethyl acrylates and methacrylates [29, 38]. Protective action is also obtained by inclusion of zinc oxide during spinning [23].

The dyeability of mixed articles (fabrics containing a mixture of yarns of polyamide and spandex) with acid dyes can be improved by adding basic compounds to the spandex. Alternatively, basic substituents, e.g., *N*-alkyldialkanolamines or *N*-alkyldiaminoalkylamines, can be built into the polymer molecule [39]. Previously, spandex was produced mainly as delustered yarns. Titanium dioxide was used as a delusterant, usually in concentrations of 2 – 5 %, to obtain as good a degree of whiteness as possible. Additional improvement in whiteness was obtained by adding nuancing dyes or pigments. However, nondelustered spandex types have gained greater prominence because they make possible more brilliant colors in dyed polyamide – spandex fabrics [40].

Freshly spun spandex yarn is slightly tacky. After being wound on the bobbin, cohesion between yarn layers develops with storage time. To counteract this and to improve the unwinding and processing behavior, separating and lubricating agents are used, e.g., polydimethylsiloxane and metal soaps [41].

4. Production of Polymer

The fiber raw material is produced by the two-stage prepolymer – chain extender process, frequently used in polyurethane chemistry.

Production of Isocyanate Prepolymer. In this process step, an α, ω-OH functional polymer (macrodiol) is reacted with an aromatic diisocyanate (called a polymer-analogous reaction) to yield an α,ω-NCO functional polymer (macrodiisocyanate). The reaction is carried out in the melt or in a highly polar solvent (e.g., dimethylacetamide) at 50 – 80 °C in a batchwise or a continuous process. The molar mass of the prepolymer, which subsequently plays an important role in determining the elastic properties of the spandex, can be adjusted via the molar mass of the macrodiol and the molar ratio of NCO:OH [42]. The prepolymers have number-average molar masses of 4 – 8 kg/mol, as well as NCO contents of 2 – 4 wt %, and are generally processed immediately without intermediate storage.

Chain Extension (Polymerization). In chain extension, the macrodiisocyanate is treated with a diamine in a highly polar solvent (e. g., dimethylacetamide) to give a high molar mass polyurethane – polyurea. The most frequently used short-chain aliphatic diamines react rapidly. To obtain a good polymer structure, rapid and intense mixing is, therefore, required during chain extension. Reactivity can be reduced by formation of a carbamate from the diamine and carbon dioxide prior to chain extension [43].

Both batchwise and continuous processes are used during chain extension. Spandex solutions with solids contents of ca. 20 – 35 % and viscosities of ca. 50 – 300 Pa · s (25 °C) are obtained. Molar mass is controlled during chain extension by using monoamines, e.g., diethylamine, as chain terminators. The polyurethane – ureas produced from diamines are linear polymers and, hence, soluble in the reaction media used.

With trifunctional starting components, covalently cross-linked polyurethanes are obtained, which are simultaneously chain extended and formed into a yarn [28] in the reaction-spinning process.

5. Spinning Processes

In contrast to elastic yarns based on rubber, spandex can be spun by using technologies generally known in the synthetic fiber industry. Because spandex based on polyurethane cannot be processed thermoplastically, solution-spinning processes are used to produce yarns.

Solution Spinning. Of the solution-spinning processes (dry, wet, and reaction spinning), dry spinning has become the most important because it lends itself more readily than the others to production of the fine spandex yarns that are increasingly in demand today.

Dry-Spinning Process (see Fig. 2). The high-viscosity elastomer solution is spun through multihole spinnerets (d) into heated spinning cells (e). During the process, the solvent evaporates, is absorbed by the entrained hot spin gases (air or inert gas), and is carried away. The solvent is separated by condensation and possibly scrubbing of the off-gas, distilled, and recycled. The individual filaments are cemented with the aid of a false-twisting device (j) to form a multifilament [44, 45]. Finish is applied to the

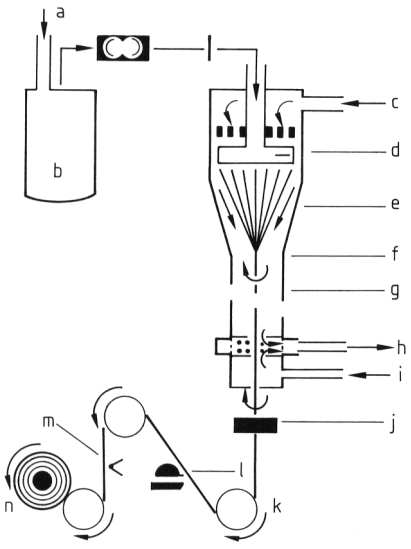


Figure 2. Dry-spinning process for spandex filament yarns [28]
a) Metering pump; b) Spinning solution; c) Hot spinning air; d) Spinneret; e) Heated spinning cell wall; f) Twisting point; g) Cell length, ca. 4 – 8 m; h) Spinning gas exhaust; i) Fresh gas; j) False-twisting device; k) Godet roll; l) Finish; m) Traverse; n) Windup device

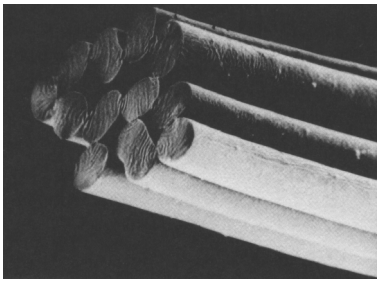


Figure 3. Dorlastan fiber cross sections, 160 dtex (12 individual capillaries) *
* ca. 50 μm.

yarn, which is wound up at a rate of 200 – 800 m/min. The drawoff speed is greater than the spinning speed (spin draw). The orientation thus produced affects yarn properties. To improve productivity, several multifilaments are spun from a single spinning cell at the same time. Figure 3 shows a cross section of a dry-spun spandex yarn.

Wet-Spinning Process (see Fig. 4). In the wet-spinning process, the elastomer solution is spun into aqueous precipitation baths (d). In the process, the water-insoluble polyurethane coagulates, and the spinning solvent is carried off by the water. As in dry spinning, the individual filaments are cemented to a multifilament. After the filament has passed through wash baths and drying cabinets, finish is applied and the filament is wound. Windup speeds are significantly lower than in dry spinning, but equipment and energy costs are lower.

Reaction-Spinning Process. In this process, chain extension of the isocyanate prepolymer by the amine and formation of the yarn occur simultaneously in the precipitation bath [46].

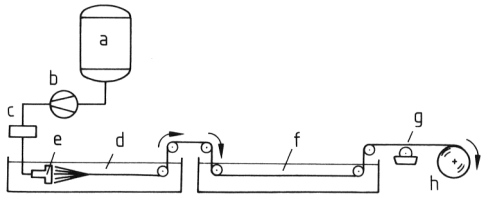


Figure 4. Schematic of a spandex wet- or reaction-spinning machine [45]
a) Spinning solution or prepolymer; b) Spinning pump; c) Filter; d) Precipitating or reaction spin bath; e) Spinneret; f) Wash or subsequent reaction bath; g) Finish; h) Windup

During spinning of the prepolymer into the reaction spin bath, a solid polymer skin forms immediately on the yarn surface and provides the stability necessary to draw off the yarn. Complete solidification is achieved in a second step. With this process, producing chemically cross-linked spandex by using trifunctional starting materials is also possible.

Melt-Spinning Process. Only elastic yarns that are exclusively based on pure polyurethane can be prepared by the high-productivity melt-spinning process. These materials do not have the properties of commercial spandex based on polyurea – polyurethane and are, therefore, of little technical significance.

6. Uses

Production of Elastic Yarns and Fabrics. Spandex fibers are processed and used exclusively in combination with hard fibers to impart high elasticity to textiles. In most cases, the spandex is used in bare form (i.e., unwrapped). Because of its rubberlike hand and poor frictional properties, spandex intended for certain end uses, such as woven elastic clothing fabrics [47], support stockings, and socks, is wrapped or core-spun with hard fibers. Of these elastic combination yarns [47], wrapped yarns are the most important. Wrapping can be carried out with one or two textile yarns. Core-spun yarns are produced on special secondary spinning machines on which staple fibers are twisted around the stretched spandex yarn. Core-spun yarns are distinguished by a remarkably soft hand. To improve the processability of the combination yarns, they can be changed by a combined stretch – steam process so that they (temporarily) lose their elastic extensibility. After being processed into fabric, the good elastic properties are restored by dyeing at the boil in the relaxed state.

The most important types of processing used to produce articles containing spandex are listed in Table 5. As can be seen, both knit (processing on circular or warp knitting machines) and woven fabrics can be produced. Articles with the highest extensibility can be prepared by the circular knitting process [48]. The elastic yarn is processed directly from the bobbin, the yarn being taken off over the end of the spool.

Table 5. End uses of spandex continuous-filament yarns

End use	Manufacturing technology	Amount of spandex, wt %	Yarn type	Fineness, density, dtex
Lingerie and lingerie bands	circular knit	5 – 12	bare, wrapped, corespun	22 – 400
	warp knit		bare, wrapped	22 – 80
Girdles	warp knit	10 – 40	bare, wrapped	22 – 800
Swim wear	warp knit	10 – 32	bare,	22 – 80
	circular knit	6 – 12	bare, wrapped	44 – 160
Hosiery bands, sock borders	circular knit	10 – 20	bare, wrapped	135 – 400
Support stockings	circular knit	10 – 60	bare, wrapped, corespun	22 – 480
Tapes	tape weaving	10 – 50	bare, wrapped	320 – 5000
Outerwear	weaving	2 – 10	rubber threads, wrapped yarns	44 – 160

To prepare warp knitwear, the elastic yarns must first be assembled [49]. To do so, up to 1500 yarns are wound parallel, side by side, under constant extension onto a warp beam. Here, processing is exclusively in the bare form. By varying the fineness, the hard fiber yarn, and the pattern notation technique, the properties and appearance of the articles can be influenced in many ways with this process and can be adapted to both functional requirements and the demands of fashion [50, 51].

Processing of elastic yarns in woven fabrics has increased substantially. End uses are suit coat and pants fabrics for articles with increased wear comfort.

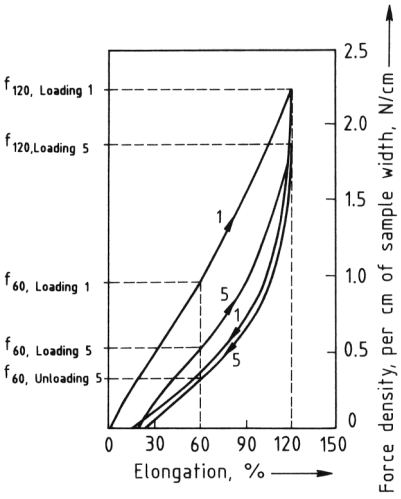


Figure 5. Curves of cyclic elongation of a tricot fabric (longitudinal direction) containing 18.5 % 45-dtex Dorlastan, unit mass 220 g/m^2, longitudinal extensibility 210 % * [45]

* 1 is first curve; 5 is fifth curve; —— is elongation; —— is recovery.

The major end uses for coarser spandex yarns and elastic wrapping yarns are tapes for various textile and engineering applications. In Western Europe, 45 % of spandex production is used in girdle and underwear manufacture, 20 % each in swim wear and hosiery, and ca. 15 % in other areas.

Textile Properties of Elastic Fabrics. The most important property of elastic fabrics is the combination of extensibility and elastic recovery. Spandex can elongate until the hard fiber construction obstructs further elongation. Extensibilities vary from ca. 25 % (woven fabrics) to > 200 % (knitwear). The elastic behavior of a warp-knitted fabric is shown in Figure 5.

By using spandex, the textile industry can fabricate elastic textiles in great variety, having given shaping and support forces, and also meeting all requirements with respect to end-use behavior, comfort, and fashion.

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Polyolefin Fibers

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ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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Polyolefin fibers, yarns, and monofilaments are usually produced by melt spinning. Film yarns and split yarns, obtained from films by uniaxial stretching, are also produced in large quantities. Polypropylene (PP) is the predominant raw material for fibers and yarns. High-modulus yarns of ultrahigh molecular mass high-density polyethylene (HDPE), commercialized in the mid 1980s, are an exception.

Both PP and HDPE are used to make film yarns and monofilaments; however, HDPE is used to a much lesser extent. Areas of application for PP fibers include carpet yarns, home furnishing fabrics, industrial fabrics, and nonwovens. Polyolefin tapes and monofilaments are used in bags, tarpaulin, industrial fabrics, carpet backing, twine, rope, and bristles. Trade names and producers of polyolefin fibers are listed in Table 1. World production of polyolefin fibers is listed in Table 2.

1. Polypropylene Fiber

Polypropylene fiber was developed in Italy by Montecatini during the second half of the 1950s [1]. Several other companies initially played an active role in its development, including Hercules, Reeves Brothers, Vectra, and Phillips in the United States; ICI in Europe; and Toray, Mitsubishi Rayon, and Toyobo in Japan. Some of them, like ICI, disappeared from the scene after the first few years; others improved their line of products and became extremely important in the market. There are many producers; in Western Europe they increased in number during the late 1970s, when the Montecatini patents expired.

1.1. Chemical and Physical Properties

Chemical Structure. Polypropylene is a hydrocarbon made up of $-CH_2CH(CH_3)-$ units. These propylene units form a stereoregular helix, with the methyl groups at an angular distance of 120 ° (isotactic polypropylene). A small percentage (ca. 2.5–5 %) is sterically random (atactic polypropylene).

Because its structure contains no polar groups, PP is resistant to most chemical agents, in particular to acids and alkalies; insensitive to water; and not dyeable with common types of dyes. Moreover, it has a low resistance to thermooxidative

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Table 1. Trade names and Producers of polyolefin (PO) fibers

Trade name	Type	Manufacturer
Arlene	PP	Aquafil SpA/Italy Aquafil USA Inc./ USA
Asota	PP/ PE	Asota GmbH/ Austria
Astra	PP	Drake Extrusion Ltd./ United Kingdom
Atlas	PP	Rheem Australia/ Australia
Bonafil	PP	Bonar Yarns & Fabrics Ltd./ United Kingdom
Charisma	PP	Drake Extrusion Ltd./ United Kingdom
Chisso Polypro	PP	Chisso Polypro Fiber Co./ Japan
Daiwabo Polypro	PP	Daiwabo Co./ Japan
Depas	PP	Depas A.S./ Turkey
Downspun	PP	PFE Ltd./ United Kingdom
Dryarn	PP	Aquafil SpA/ Italy
Duron	PP	Drake Extrusion Ltd./ United Kingdom Drake Extrusion/ USA
Dyneema	PE	DSM HPF B.V./ Netherlands DSM Dyneema LLC/ USA Nippon Dyneema Co./ Japan
Elsan	PP	Elsan A.S./ Turkey
Elustra	PP	Fiber Visions Inc./ USA
Emerlen	PP	MR 81 Srl/ Italy
Emu	PP	Boral Kinnears Pty/ Australia
ES Fiber	PP/PE	Fiber Visions A/S/ Denmark
ES Fiber	PP/PE	Chisso Corp./ Japan
Essera	PP	American Fibers and Yarns Co./ USA
Euralon	PP	Euroma SpA/ Italy
Gülsan	PP	Gülsan A.S./Turkey
Gymlene	PP	Drake Extrusion Ltd./ United Kingdom
Herculon	PP	Fiber Visions/ USA
Horizonte	PP	Fitesa/ Brazil
Hy	PP	Fiber Visions A/S/ Denmark Fiber Visions/ USA
Inhova	PP	American Fibers and Yarns Co./ USA
Istrona	PP	Istrochem/ SR
Krenit	PP	Chemfiber A/S Denmark
Kugafil	PP, PE	Fugafil – saran GmbH/ Germany
Leolene	PP	Drake Extrusion Ltd./ United Kingdom
Liplon	PP	Tai-Ray Co./ Japan
Mandal	PP	Sanghi Filaments Ltd./ India
Marquesa L	PP	American Fibers & Co./ USA
Meraklon	PP	Meraklon SpA/ Italy
Olefinesse	PP	Billermann KG/ Germany
Plasticel	PP	Plasticel SA de CV/ Mexico
Pliana	PP	Industrias Polifil, SA/ Mexico
Polyklon	PP	Meraklon SpA/ Italy
Polysilk	PP	Polysilk SA/ Spain
Polystar	PP	Nexcel Synthetics/ USA
Polysteen	PP, PE	Steen & Co. GmbH/ Germany
Prolen	PP	Chemosvit/ SR
Propilan	PP	Propilan SA/ Spain
Pylen	PP	Mitsubishi Rayon Co./ Japan
Radilene	PP	Deufil GmbH/ Germany
Reilen	PP	Reinhold GmbH/ Germany
Sasrifill	PP	DS Fibres NV/ Belgium
Salus	PP	Filament Fiber Technology Inc./ USA
Sarlon	PP	Sarlon Pty./Australia
Silver Ring	PP	Hubei Chemical Fiber/ China
Spectra	PE	Honeywell Advanced Fibers/ USA
Tecnisilk	PP	Polisilk SA/ Spain
Telar	PP	Filament Fiber Technology, Inc./ USA
Terclon	PP	Polyfil NV/ Belgium
Tiptolene	PE	Lankhorst Touwfabrieken BV /Netherlands
Toabo Polypro	PP	Toabo Material Co./ Japan
Unal Sentetik	PP	Unal Sentetik Sanayi A.S./ Turkey
Xanthi	PP	Thrace Plastics SA/ Greece

PE = polyethylene
PP = polypropylene

Table 2. World production of polyolefin fibers

Year	Production, t
1990	1 000 000
1995	3 960 000
2000	5 984 000[a]
2005	6 463 000[b]
2009	2 600 000[b]

[a]Including film fibers (tapes).
[b]Including film fibers and spunbonds.
[c]Excluding tapes.

and photooxidative degradation. The problem of nondyeability has been solved by mass dyeing techniques and the problem of degradation by the use of suitable additives. Because of the absence of polar groups, only van der Waals forces exist between macromolecules; these forces are much weaker than the hydrogen bonds found, for example, in polyamide. Because mechanical characteristics depend on these forces and on molecular entanglement, very high molecular masses (M_r from ca. 170 000 to 300 000, compared to ca. 20 000 for polyamide) must be used to obtain satisfactory strength (fiber tenacity).

Rheological Aspects [2]. Polypropylene fiber is produced by melt spinning, i.e., by extruding the molten polymer through suitable spinnerets. Therefore, the rheological behavior of the polymer melt must be considered in selecting processing conditions or even in choosing a certain polymer for specific spinning conditions. The first aspect to be considered is that isotactic PP in the molten state is highly non-Newtonian and exhibits a strong pseudoplastic character; the apparent viscosity of the melt is not constant with varying shear stress but it decreases when shear stress increases. The deviation from Newtonian behavior is markedly dependent on the relative molecular mass (M_r) and polydispersity (molecular mass distribution M_rD); for polymers of comparable polydispersity, the melt viscosity increases with increasing viscosity–average molecular mass. An extremely useful, practical indication of M_r is the melt flow index (MFI), which is a measure of flow under standard conditions (ASTM D 1238: grams extruded in 10 min through a standard orifice under a pressure of 2.16 kg/cm^2 at 230 °C); MFI is inversely proportional to melt viscosity. The MFI is measured at a shear rate close to those commonly met in usual spinning processes.

The initial MFI of PP polymers used in fiber production ranges from 2 to 35, depending on the process involved and the type of fiber produced. In addition to pseudoplasticity, PP melt exhibits appreciable signs of viscoelasticity. In a viscoelastic material the deformations undergone by the melt have not only a viscous but also an elastic component, which can therefore be recovered when the applied stress ceases, i.e., when the extruded polymer emerges from the spinneret capillary. The residual elastic energy, whose magnitude depends on the residence time in the capillary, can cause, among other phenomena, enlargement of the extrudate to a diameter larger than that of the capillary (die swell). The polymer swelling increases as the shear stress increases and as the ratio of length to capillary radius decreases.

Die swell also depends on the molecular mass distribution (M_rD): at comparable melt viscosities, die swell is larger for a polymer with broad M_rD than for a polymer with a narrow M_rD. Swelling increases as temperature decreases. All these rheological characteristics are taken into account when spinneret hole geometry, polymer type (MFI, M_rD), and extrusion conditions are being selected.

Structural Characteristics [2 pp. 327–337], [3]. The stereoregular structure of isotactic PP macromolecules makes an ordered three-dimensional configuration (i.e., a crystalline structure) possible when the molten polymer is cooled to the solid state. Under normal conditions, isotactic PP crystallizes in the monoclinic system; if cooled rapidly to room temperature, it exhibits a paracrystalline form, called smectic. In practice, PP fiber is a partially crystalline material. The crystalline structure of the fiber depends on the conditions of extrusion and quenching, the take-up speed in the spinning step, and the draw ratio and annealing conditions in the finishing step. Normally, the crystallinity of the finished fiber does not exceed 70 %; values of 40–50 % are usual. Many physical properties are influenced by crystallinity. Mechanical properties, however, are affected less by the percentage of monoclinic material than by the molecular orientation imparted during drawing; orientation is evaluated by measurement of birefringence.

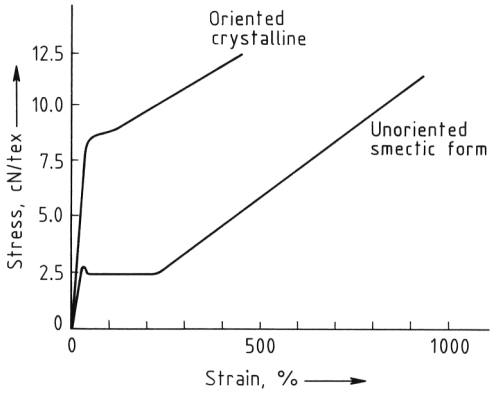


Figure 1. Stress – strain curves of as-spun polypropylene fibers

Mechanical Properties. Depending on spinning conditions (extrusion temperature, quenching, spinning speed, and rate of deformation in the molten state), the mechanical properties of as-spun PP fibers can vary widely, as shown schematically in Figure 1. The mechanical properties of drawn fibers are influenced substantially by the applied draw ratio and, consequently, also vary widely (Fig. 2).

The relationship between tenacity and draw ratio depends on the polymer used and, in particular, its polydispersity. As polydispersity decreases, the tenacity obtained at a given draw ratio increases, but the drawability of the spun fiber decreases at the same time. Therefore, polymers with narrow M_rD are not suitable for production of high-tenacity fibers; they do, however, have advantage in terms of spinning continuity at high spinning speeds.

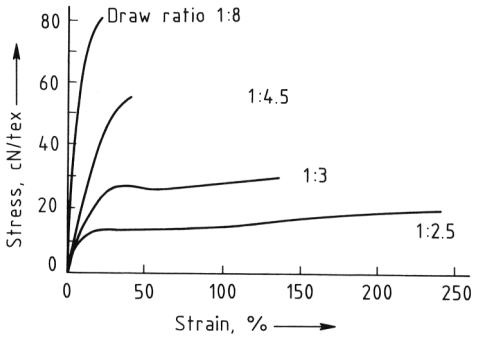


Figure 2. Stress – strain curves of drawn polypropylene fibers

1.2. Production

1.2.1. Raw Materials

Polypropylene fibers are obtained from PP homopolymer. They may also be based on PP and a propylene–ethylene random copolymer or a blend of polypropylene and polyethylene homopolymers. In the latter case, the definition "polyolefin fiber" or "olefin fiber" is more correct. However, polyolefin is also frequently used for PP homopolymer fiber.

Polypropylene is used in the production of side-by-side bicomponent polypropylene–polyethylene fibers. The Customs Cooperation Council of the European Economic Community (EEC) adopted the following definition of textile polypropylene:

Fibers composed of aliphatic saturated hydrocarbon linear macromolecules having in the chain at least 85 wt% of units with one carbon atom in two carrying a methyl side chain in an isotactic position, and without further substitution.

The availability of raw materials is not a problem, although the supply of propylene may be influenced by the demand for ethylene because ethylene and propylene are coproducts in the cracking of virgin naphtha. Other sources, of lesser importance at the moment, are liquefied refinery gases containing propylene and propane gases.

1.2.2. Staple Fiber Production Process

Polypropylene can be produced by two different processes: (1) *conventional spinning* is based on high spinning speeds and spinnerets with a rather limited number of holes; (2) *short spinning* is based on low spinning speeds and spinnerets with a large number of holes. In the first process, because of the high spinning speeds, postspinning operations are performed in a separate step; in the second process, because of the low spinning speeds, spinning and postspinning are carried out continuously. Postspinning operations are basically the same for both processes.

Conventional Spinning Process. The polymer, to which stabilizers and pigments have been added, is introduced into the extruder (a) (Fig. 3). The

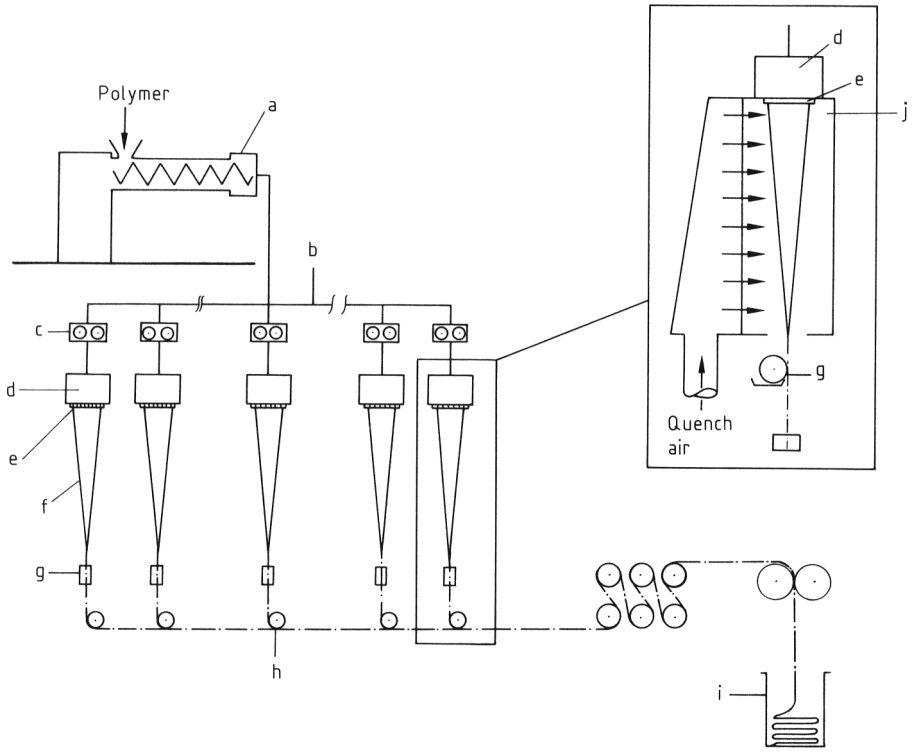


Figure 3. Conventional spinning plant
a) Extruder; b) Melt distribution; c) Metering pump; d) Spinning pack; e) Spinneret; f) Filament; g) Oiling device; h) Take-up; i) Can coiler; j) Quench box

molten material is fed to the spinnerets (e) by metering pumps (c), which control the throughput of each spinneret. The extruder is heated electrically, while the melt distribution manifold is heated by means of a diathermic fluid (e.g., Dowtherm and Diphil). Filaments (f) emerging from the spinneret are quenched with cold air (air speed 1–2 m/s) and, when solidified, collected in cans (i). An antistatic and lubricating agent is usually applied to the filaments before they come in contact with any solid surface (g).

The filament fineness depends on the throughput of the metering pump, the number of holes in the spinneret, and the take-up speed, according to the following relationship:

$$d = \frac{1000}{3.6}\frac{Q}{n \cdot v}$$

where d is the fineness, decitex; Q is the pump throughput, kilograms per hour; n is the number of holes; and v is the take-up speed, meters per second. The spinning speed of PP fiber is usually 600–1200 m/min, and the temperature of the molten polymer in the spinneret is 220–300 °C, depending on molecular mass of the polymer, spinning speed, and desired characteristics of the fiber being produced. Spinnerets used for staple production are 150–250 mm in diameter and have between 200 and 2000 holes, depending on the fineness of the fiber. In some cases, rectangular spinnerets are used to achieve higher productivity. The number of holes is limited to avoid having the filaments stick together (filament marriage). Polymers with a fairly low M_r (MFI 5–20) are used commonly in the production of standard fibers; higher M_r (MFI ca. 2) polymers are used only for high-tenacity fibers. To obtain satisfactory spinning continuity, the polymer must be filtered before reaching the spinneret; both sand filters and screen filters are used.

Postspinning Operations Drawing, crimping, heat setting, cutting, and baling are the steps that follow spinning in the production process.

Several tows coming from the spinning section are processed together to reach a total fineness of 200–300 ktex (0.2–0.3 kg/m). They are stretched between two sets of rolls; the draw ratio depends on the ratio of the roll speeds of these two sets. The draw ratio for standard fibers is between 1 : 3 and 1 : 5. To obtain uniformly drawn fibers, the tow is heated in a steam chamber located between the two sets of rolls. Alternatively, heated rolls can be used in the first set. If high-tenacity fibers are desired, the drawing operation is sometimes divided into two steps by means of a third set of rolls. Crimping is intended to impart bulk and cohesion to the fiber for subsequent conversion to final products. The fiber is compressed in the crimper (stuffer box) and subsequently dried and heat-set in a hot-air oven (100–130 °C) to stabilize crimp and reduce thermal shrinkage after drawing. A finish is usually applied to the fiber during the post-spinning operations. Staple cutting and baling operations are the final stages of production. The speed of these operations is limited by the crimping speed and is generally 150–250 m/min.

Short Spinning Process. The rheological behavior of PP is such that, when spinning speeds are fairly low (120 m/min), and the stream of quenching air blows through the filaments close to the spinneret, the filaments do not stick together even with close hole spacing (ca. 1 mm). Then, the speed of consecutive operations can be matched, and a continuous, uninterrupted, one-step process can be achieved. A consequence of the high hole density and the reduction in height of the quenching section is that plants can be made more compact for a lower cost. For this reason and reduced manpower requirements, the short spinning process has become very popular.

1.2.3. Continuous Filament Yarn Production Process

In principle, spinning continuous filament yarn is similar to spinning staple fiber; the main difference is that in the former, each yarn is collected on an individual bobbin. Drawing of the yarn (Fig. 4) is usually performed by two pairs of rolls (f), which are generally heated electrically. For some applications, continuous filament is used as it comes from the drawing machine (flat yarn), but in most cases, filament bulk must be increased by means of a texturing system. A mechanical texturing system is preferred for the very fine yarns used in the textile industry. In this case, the yarn is highly twisted, heat-set, and detwisted in a continuous false-twisting process to give each individual filament the shape of a spring. A subsequent heat-setting operation can be introduced in the detwisting zone to reduce yarn elasticity. For coarser continuous filament yarns (carpet yarns), systems based on fluid bulking jets are used. Consistent with the continuing trend toward reduced production costs, machines have been developed in which the different operations are performed continuously in a single step.

1.2.4. Stabilization

Polypropylene, although relatively stable to heat and light in the absence of oxygen, has poor

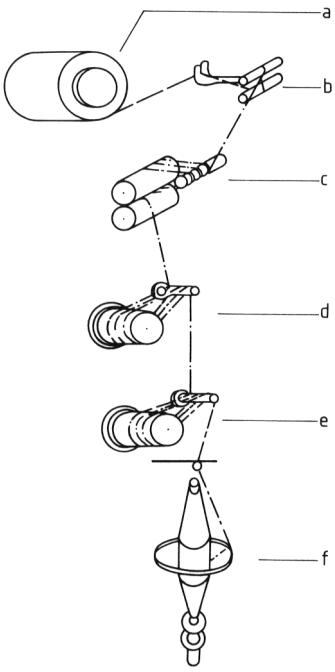


Figure 4. Draw-twisting machine
a) Spun yarn; b) Pre-tension guide; c) Pre-tension rolls and guides; d) Feed roll; e) Draw roll; f) Twisting take-up

resistance to thermooxidative and photooxidative degradation [3 pp. 38–93]. Thermooxidative degradation occurs during conversion of the polymer to a fiber. Photooxidative degradation occurs when the end product, which contains PP fiber, is exposed to direct or diffuse solar radiation in the presence of oxygen. As a hydrocarbon, PP is transparent to UV light but it is sensitive to it because of the presence of traces of oxygen-containing groups, such as hydroperoxides and ketones, which absorb at 310–330 nm. Depending on the temperature during exposure, thermooxidative degradation and photooxidative degradation often occur simultaneously. Both processes generate polymer radicals, which catalyze further molecular cleavage.

Therefore, suitable antioxidants and light stabilizers are added to protect the polymer melt at high temperature and to impart sufficient aging resistance to the finished products. (→ Antioxidants, Section 5.4). These stabilizers can be classified according to the mechanism by which they protect the polymer: (1) chain terminators or free-radical scavengers, which terminate the chain reaction by giving rise to nonreactive radicals; (2) hydroperoxide deactivators, which decompose hydroperoxides without formation of radicals; (3) UV absorbers, which screen UV radiation; and (4) quenchers, which quench the excited states of ketone groups; and (5) free-radical scavengers that trap the radicals and regenerate themselves (HALS: hindered amine light stabilizers). The following are some of the chemicals used at present:

Chain terminators	phenolic antioxidants
Peroxide decomposers	disulfides, trialkyl phosphites
UV absorbers	derivatives of hydroxybenzo phenone and benzotriazole
Energy quenchers	nickel chelate stabilizers
Free-radical scavengers	hindered amines [4]

The effectiveness of the stabilizer formulation depends on the choice of individual components. This choice must also take into account the pigments used, because they can affect heat and light stability significantly and can even interfere with stabilizers. In addition, attention must be paid to possible concomitant phenomena, such as gas fading, which is the color change caused by nitrogen oxides present in air. These oxides can react with some components of the stabilizing system, resulting in nitration of aromatic rings or addition of nitrogen oxides to double bonds. Nitrogen oxides can also react with certain finishes and cause color changes via some of the reactions mentioned previously.

The stabilizer formulation also includes antacids, typically calcium stearate, which react with the HCl formed by reaction of catalyst residue with substances containing active hydrogen. Stabilizer systems that comply with international regulations for chemicals in food contact applications are also available.

Stabilizer Evaluation. The following test methods have been developed to select the most suitable stabilizers and predict actual fiber behavior.

Oxidation Resistance. Fiber bundles, hung on a rotating frame under a small weight, are exposed in a forced-draft oven at 110 °C. Resistance to oven aging is expressed as days to failure. For operating conditions, see ASTM D 3045–74 (reapproved 1979).

Light Resistance. Accelerated tests with instruments based on a xenon lamp are preferred to those using a carbon-arc apparatus because the xenon lamp gives a spectrum similar to that of summer sunlight, whereas the carbon-arc apparatus is too high in UV radiation. Exposure conditions are selected so that the temperature is comparable to that experienced in use because the rate of photooxidation is a function of temperature. For indoor uses, such as carpets and wall coverings, fiber bundles are exposed in a Xenotest or Weatherometer according to ASTM G 26–84, DIN 54 004, ISO B 02. The resistance to artificial light is expressed as residual tenacity after exposure. Fiber exposed to combined heat and light, e.g., on rear window shelves in cars, is tested in the Xenotest at high temperature.

Gas-Fading Resistance. The fiber specimen is exposed to nitrogen oxide containing gases derived from the combustion of butane. Color variation is assessed by comparing the exposed and original samples after four exposure cycles of controlled duration.

1.2.5. Pigmentation

Polypropylene cannot be dyed by conventional methods because it lacks polar groups that can provide suitable sites for dyes. The techniques proposed thus far for making PP dyeable by traditional acid or disperse dye systems do not have near- or medium-term commercial potential, either because of the relatively high cost of additives involved or because of the as yet insufficient colorfastness. Only nickel-modified fibers are used commercially for space dyeing or printing.

For these reasons, PP fiber is colored by blending the polymer with suitable pigments prior to extrusion; this system is known as "melt dyeing" or "mass dyeing." Because of various requirements, such as thermal stability at high temperature, the range of pigments that can be used is limited; however, mass-dyed PP fibers are characterized by high colorfastness to light, heat, rubbing, and washing. Colorfastness may, of course, be affected by stabilizer–pigment interaction or by additives that facilitate extraction of the pigments. The main classes of pigments used are the following:

Inorganic:	titanium dioxide (rutile or anatase)
	iron oxides
Organic:	insoluble azo pigments
	copper phthalocyanines
	vat pigments
	carbazole dioxyazine
	carbon black

1.3. Uses

Types of Fibers Produced. Polypropylene fiber is produced in a wide range of finenesses, both as staple and continuous filament. Staple fibers range from ca. 1 to 250 dtex per filament. The fiber cross section is primarily circular; the fineness range of continuous-filament yarn is 70–12 000 dtex. The filament cross section is predominantly circular in the low to medium fineness for apparel, upholstery, and industrial uses, and triangular or trilobal for the fibers used in floor covering. For the latter application, the basic fineness range is 1300–4000 dtex; higher fineness up to 12 000 dtex is obtained by comingling.

Commercial Mass. The International Bureau for the Standardization of Man-Made Fibers (BISFA) has agreed on the following definition of commercial mass: "the commercial mass shall be obtained by adding to the oven-dry mass, i.e., after removal of finish, etc., the mass corresponding to the conventional allowance" where "the conventional allowance for polypropylene staple fiber, sliver or top and tow is 2.0 %."

Properties. Polypropylene fiber has physical, chemical, and mechanical properties that make it suitable for a wide range of applications. These properties can be divided into the following groups:

Good

Relative density
Resistance to acid and alkali
Abrasion resistance
Moisture absorption
Mechanical properties under dry and wet conditions
Dimensional stability
Stain and soil removal
Easy washing
Quick drying
Static buildup in carpets
Resistance to mildew, microorganisms, and insects
Thermal bondability
Colorfastness of suitably pigmented fibers
Light resistance of suitably stabilized fibers

Fair

Flammability
Frictional characteristics
Oil-based soil removal

Poor

Dyeability with common dyeing methods (need for pigmentation)
Heat and light resistance (need for stabilization)
Resistance to dry-cleaning solvents
Behavior during ironing

Some properties are inherent in the component material; others are imparted or enhanced

by the production process or by suitable additives. A brief survey of the major properties follows, with an indication of their effect on fiber application.

Relative density (0.91) is the lowest of all commercial textile fibers; this is an advantage in all applications because it means lightness and high cover (especially in nonwoven construction).

Chemical resistance, especially to acid and alkali, is outstanding. Polypropylene fiber was treated at 20 °C with the following chemicals; the residual tenacity after 96 h is given (in percent):

Nitric acid (66 %)	80–87
Sulfuric acid (95 %)	95–100
Formic acid (75 %)	100
Sodium hydroxide (40 %)	100
Concentrated aqueous ammonia	95–100
Trichloroethylene	80
Perchloroethylene	80
Xylene	80
Toluene	90
Benzene	90
Acetone	100
Sodium hypochlorite (5 % active chlorine)	85
Hydrogen peroxide (12 parts)	90

Hot halogenated solvents swell PP fiber, with subsequent shrinkage on drying (trichloroethylene), or even dissolve it (boiling perchloroethylene). Moreover, some boiling aromatic solvents dissolve the fiber (e.g., xylene, decahydronaphthalene), and strong oxidizing agents attack it. In the last case, however, the fiber can be improved considerably by suitable stabilizer formulations. The high chemical resistance is exploited in industrial filtration.

Abrasion resistance is comparable to that of polyamide. It increases with increasing crystallinity and molecular mass and is influenced by frictional properties. The high abrasion resistance is exploited in floor covering, upholstery, hosiery, and industrial applications.

Moisture regain is virtually nil (0.05 % at 65 % R.H. and 21 °C). The insensitivity of PP fiber to water brings about the following advantages: dimensional stability, fabric dryness in contact with the skin, quick drying, and no variation in mechanical properties under wet conditions.

Temperature Behavior. Polypropylene fiber does not distort when exposed to temperatures of 120–130 °C during conversion processes; however, it is sensitive to pressure at elevated temperature, so ironing can cause the fabric to stiffen. The softening point is 150 °C, and melting occurs at 168 °C. The relatively low melting point is exploited in thermal bonding, which has become important in hygienic and medical applications (calender bonding is generally used, but flow-through bonding with hot air can also be applied). High-temperature tentering treatment is used to produce dense nonwovens suitable as coating substrates.

Dyeability. Because PP fiber is not dyeable by common dyeing methods, pigmentation is used. Although a nickel-modified fiber is available for printing or space dyeing with chelatable dyes, its use is limited. The absence of polar groups in the PP molecule makes for easy stain removal; on the other hand, PP is more easily soiled by oil-based stains than other synthetic fibers.

Resistance to Mildew, Microorganisms, and Insects. Polypropylene fiber is neither attacked by mildew and molds nor damaged by insects.

Static Buildup. Limited charges are separated when a person walks on a PP carpet and, consequently, a low body voltage is generated, lower than that at which uncomfortable shocks can be felt.

Flammability. Application of a flame causes PP to shrink, melt, and burn if contact with the flame is sufficiently prolonged. Polypropylene burns slowly and drips like a candle. Burning can continue even if the flame is withdrawn because the limiting oxygen index of PP is 18.5. The self-ignition temperature is 570 °C.

Frictional Characteristics. The coefficient of friction of PP fiber, both fiber-to-fiber and fiber-to-metal, is fairly high. Suitable lubricants are applied to keep it low so as to allow conversion by textile processing. Cotton spinning is one of the most critical processes.

Electrical Properties. Polypropylene is a good insulator and exhibits an extremely low power loss, even at high frequencies. The dielectric constant is 2.1 at 60 Hz and 2.2 at 1 MHz; the

power loss factor is 0.0002 at 60 Hz and 0.0003 at 1 MHz; volume resistivity is 4.9×10^{14} Ω cm.

Thermal Properties. The thermal conductivity of PP fiber is the lowest among commercial fibers (0.138 W m^{-1} K^{-1}). This contributes to high thermal insulation in textiles, although the major contribution comes from air trapped in the structure.

Allergic Phenomena and Nontoxicity. Polypropylene itself does not cause skin irritation or sensitization and is not toxic; surface finishes must be selected correctly to retain these advantages.

Applications. The three major fields of application are in industrial, home textile, and apparel end uses.

Industrial applications include rope, twine, conveyor belts, industrial sewing thread, filter cloth, paper reinforcement, geotextiles, coating substrates, and carpet backing. Diaper facing is an example of a hygienic–medical product in which PP has made rapid inroads.

Home textile applications include floor covering (tufted, woven, and needle punched), upholstery fabric, wall covering, fiberfill, blankets, warp yarns in woven carpets, and yarns for secondary backing for tufted carpets. Floor coverings constitute the most important outlet for PP fiber, in both bulked continuous filament (BCF) and staple.

The *apparel uses* of PP are limited by lack of dyeability, difficulty in ironing, and inability to be dry-cleaned. However, the fiber is established in knitwear, especially sportswear. Staple and textured continuous filament yarns are used. Other applications include fleece fabrics, hosiery, and hand knitting yarns.

1.4. Economic Aspects [5]

The Oerlikon Textile report "The Fiber Year 2009/2010" estimated the world PP market for 2006 at 2.6×10^6 t. In the USA, slow demand for carpet yarn and increasing substitution by polyester BCF yarn have put additional pressure on the industry. While staple fiber applications increased by 3.5% to 1.1×10^6 t, output of filament yarn declined by 12.7% to 1.5×10^6 t.

2. Polyolefin Film Yarns and Split Yarns

The production of polyolefin film yarns and split yarns involves production of a primary film, which is subsequently cut, stretched, and possibly fibrillated mechanically. This method had been developed and patented by the end of the 1930s [6] but was not exploited industrially on a broader basis until the 1960s.

In principle, other thermoplastics can also be produced by this means. However, it is important only for polypropylene and for high-density polyethylene (HDPE).

The usual size of individual PP film ribbons is between 300 and 2500 dtex; split yarns often have sizes up to 10 000 dtex. The smallest size attainable by special processes is ca. 10 dtex.

The literature on PP film yarns and split yarns has been reviewed [7–11].

2.1. Raw Materials

The choice of raw materials depends not only on what is required of the finished product but also on the processing properties. Basically, raw materials with higher molecular masses (lower melt flow indices) are used to produce film yarns and monofilaments than to produce melt-spun multifilaments. The choice between PP and HDPE is governed by the following properties:

1. Polypropylene has higher strength, i.e., greater tenacity, than HDPE (see Fig. 5) [12, 13]. In addition, PP exhibits less "cold flow"; i.e., products of PP have lower

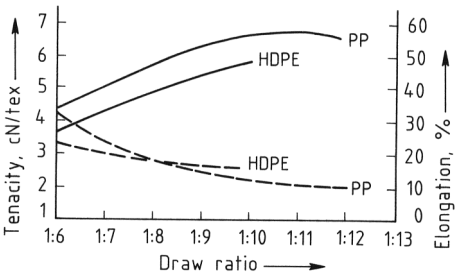


Figure 5. Tenacity (———) and break elongation (– – – –) of film yarn of polypropylene (PP) and high-density polyethylene (HDPE) as a function of draw ratio [12]

elongation under continuous mechanical loading than those of HDPE.

2. Tapes and monofilaments of HDPE are more flexible than those of PP and give finished products with a softer hand.
3. Polypropylene can withstand a higher thermal load because of its higher melting temperature (ca. 160 °C vs. ca. 130 °C for HDPE).
4. On the other hand, HDPE has better resistance to cold. Although stretching substantially improves the resistance of PP to cold, HDPE is at present preferred for applications below freezing temperature because it offers a greater margin of safety.
5. Tapes and monofilaments of HDPE have lower coefficients of sliding friction than those of PP. Consequently, they are better suited for processes in which good sliding ability is needed (for example, processing on knitting machines).
6. The tendency of HDPE tapes to split is much lower than that of PP. Depending on end use, this can be an advantage or a disadvantage.
7. The UV stability of HDPE is inherently better than that of PP. Nevertheless, very good weathering resistance has now been achieved with PP tapes and monofilaments by using high-efficiency UV stabilizers of the hindered amine light stabilizer (HALS) type.

The HDPE types used have densities between 0.945 and 0.960 g/cm^3 and melt flow index values (MFI 190/2.16, i.e., MFI measured at 190 °C under a load of 2.16 kg/cm^2) between 0.3 and 0.7 g/10 min; a broad molecular mass distribution is preferable.

Polypropylene tapes are produced almost exclusively from homopolymers. Depending on the process employed and end uses envisioned, melt flow indices (MFI 230/2.16) between 1.5 and 6 g/10 min, and preferably between 2.5 and 4 g/10 min, are common. If the process involves cooling via a water bath, PP types with low water pickup (carry over) are required.

Coloration is achieved by pigment compounds; to minimize splitting and assist in weaving PP ribbons, inorganic fillers (e.g., chalk) are used.

In special cases, copolymers (i.e., blends with other polymers) or coextrudates can be used to achieve certain properties. Coextruded films permit the production of crimped tapes and yarns [14–16].

2.2. Production of Tapes and Split Yarns

The stretching process in which the film strips are drawn to many times their original length (in most cases, six to ten times) is the central processing step. It leads to high molecular orientation in the longitudinal direction and to substantial increase in strength with simultaneous decrease in break elongation. However, strength in the transverse direction clearly decreases. At high draw ratios, this effect can cause the tape to "split," i.e., to fibrillate even at low mechanical stress. This phenomenon, which is more pronounced for PP than for HDPE tapes, is undesirable in some cases, e. g., for bagging and packaging fabrics. In other cases, it is exploited and reinforced intentionally (e.g., by profiling the ribbons or by using fibrillators) to arrive at products with lower fineness and more textilelike properties (split yarns and fibers).

Figure 6 is a generalized scheme for the production of film ribbons and split yarns. The processing steps follow.

Production of Film. In general, extruders (a) with screw diameters of 90 or 120 mm and screw lengths $\geq$ 25 times the diameter are used. Screws with a compression ratio of ca. 1:3, with a shear and mixing section, have proved useful. Cooled groove boxes in the feed section lead to more uniform granulate feed and higher throughput. In this case, flat cut screws with combined high-efficiency mixing and shearing sections can be used. The type of film production as well as the conditions of cooling and extrusion affect processing and properties of the end product [12, 17, 18]. Tapes of HDPE are usually produced from tubular films (b_1), and PP tapes preferably from cast films. The cast film can be cooled in a water bath (b_2) at 15–40 °C. This type of cooling is particularly effective because it permits high operating speed, leads to the formation of small

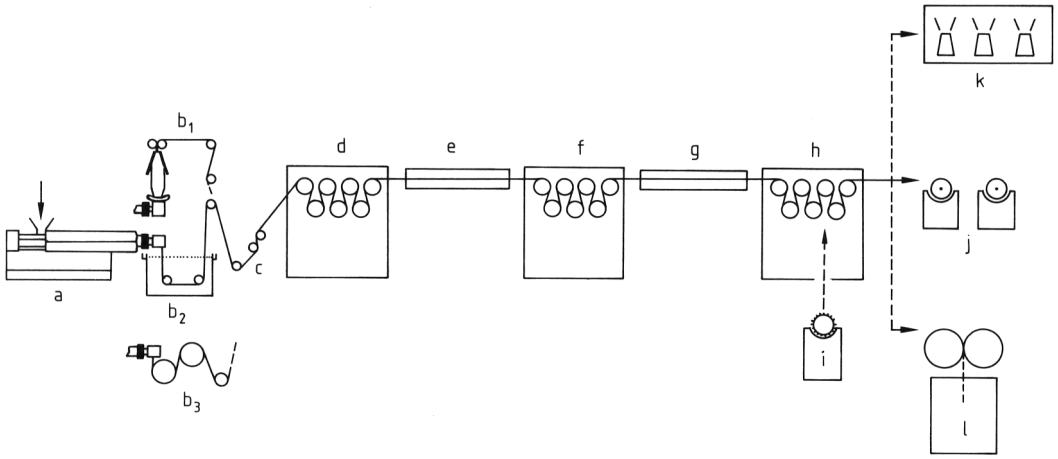


Figure 6. Production of film yarns and split fibers
a) Extruder; b_1) Tubular film (air cooled); b_2) Cast film (water quenched); b_3) Cast film (chill roll quenched); c) Knife beam; d) First godet stand; e) Stretching oven; f) Second godet stand; g) Setting oven; h) Third godet stand; i) Fibrillator (optional, only used for split fiber production); j) Windup; k) Twister; l) Staple cutter

crystallites, and is advantageous with respect to stretching behavior and strength of the tapes obtained. Raw materials with low water carry over must be chosen, and wiping, suctioning, and squeezing devices must be provided so that no water is entrained in the stretching section or the edge strip return. Film production by the chill roll process (b_3) is used only when exceptionally close thickness tolerance and high tape uniformity are required. Throughput is normally lower in tubular film installations than in cast film units because of lower cooling intensity; in addition, larger variations in film thickness are to be expected.

Cutting. Normally the film is cut prior to stretching. This is accomplished with blades arranged at the desired distance on a knife beam (c). In principle, it is also possible to stretch the whole film and cut it only after stretching and setting. The high splitting tendency of PP makes it difficult to obtain a cut completely free of nicks, so only HDPE is processed this way [19, 20].

Stretching. Stretching is accomplished by guiding the film strips over mechanically driven cantilevered feed rolls. The stretching unit is made up of two sets of godets (d) and (f) usually consisting of seven godets each. The second set runs at a higher speed than the first; the draw ratio is determined by the difference in speeds. Draw ratios from 1:6 to 1:8 are used to produce tape for weaving and warp knitting; for rope, cable, and twine, draw ratios are ca. 1:9 to 1:10. Operating speeds are $\leq$ 300 m/min.

Stretching in the short gap between rolls occurs mainly through reduction in thickness without appreciable loss in width. This leads to some orientation in the transverse direction and, hence, a reduction in splitting tendency. Stretching is generally carried out in hot air ovens (e) or on heated plates.

The overall stretching process is exothermic. However, heat must be supplied to initiate it and to assure uniformity at the high speeds required. The required temperature depends on the raw material, the operating speed, and the desired tape properties; for the most part, it is between 130 and 180 °C. Whereas the temperature of the tape itself cannot be measured, the uniformity of stretching conditions can be checked by measuring yarn tension [21].

Setting. After stretching, setting (g), i.e., controlled shrinkage, is accomplished between the second and third godet stand by again supplying heat (in a hot-air oven or with the aid of heated rolls). In this annealing process, the orientation stresses introduced during

stretching are relieved. In so doing, subsequent undesired and uncontrolled shrinkage is reduced or prevented.

The setting temperature is either equal to the stretching temperature or 10–20 °C below it. A higher setting temperature leads to less shrinkage but adversely affects tape strength. Setting shrinkage results from the difference in drawoff speeds between the second and third godet stand. For most applications, adjusting the setting shrinkage to ca. 5 % is sufficient. For end uses in which particularly high dimensional stability is required (e.g., carpet backing), a higher setting shrinkage (10–15 %) must be selected.

Splitting and Fibrillating. Polypropylene tape has a relatively high tendency to split, and the propensity for fibrillation increases with increasing degree of stretching. The spontaneous splitting tendency is occasionally exploited in the production of twine and packaging yarns. The tapes split even during twisting (k) and give a fibrous, textilelike end product. The splitting tendency can be reinforced by adding other polymers [22].

Fibrillated yarns or fibers with still lower individual fineness and greater softness are obtained by special fibrillation processes. Stretched film strips are generally guided over a needle roll revolving at controlled speed (i); the direction of rotation of the roll coincides with the running direction of the tapes. The tapes are split into a networklike multiplicity of fibrils (Fig. 7). Depending on the number, fineness, and arrangement of the needles, as well as the speed of rotation of the roll, various fibrillar structures can be obtained [22–26].

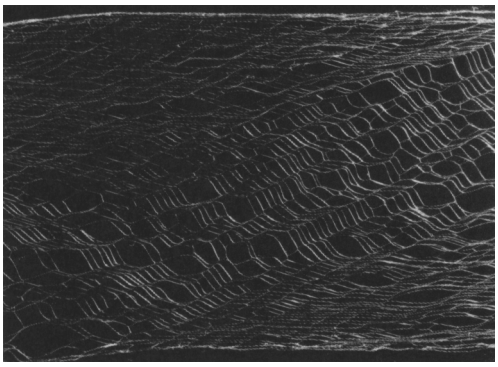


Figure 7. Networklike fibrillated yarn of propylene

Strongly fibrillated tape yarn can also be obtained without needle roll from profiled primary film. Profiling is produced either by a comblike jet lip (Barfilex process [27]) during extrusion or by roll embossing [28, 29]. In both cases, the impressed longitudinal grooves act as preset break points, which tear at the high draw ratios used (ca. 1:10). However, these processes are of minor practical importance compared to needle roll fibrillation.

Split fibers are obtained by cutting the fibrillated tapes in staple cutters (l). This process, however, is used rarely because of the development of short spinning technology to produce PP spun fibers of appropriate deniers at a reasonable cost.

End use for fibrillated tapes (split yarns) include twine, rope, reinforcement and weft yarn in woven carpets, and coarse yarn for geotextiles.

Coloration and Finishing. Tapes and split yarns are almost exclusively bulk-dyed with the aid of pigment concentrates, which are added prior to extrusion. The problem of coloring polyolefins by bath dyeing has not yet been solved satisfactorily.

Inorganic compounds such as chalk are added to reduce splitting and facilitate weaving. Ultraviolet stabilizers, required for many areas, are often provided by the manufacturer of the raw material, but the processor can also blend in concentrates. In general, UV stabilizers of the HALS type are used. They also impart good weathering resistance to PP ribbons [30]. However, HALS stabilizers may interact with certain pigments.

Antistatic agents and incorporated lubricants are generally not effective for ribbons and monofilaments. In addition, they can cause problems during film and ribbon production (e.g., plate out and water carry over). Subsequent external application (finishing) gives better results.

2.3. Uses

Tapes and split yarns of polyolefins are used in textile products that require high strength; low weight; chemical, moisture, and abrasion

resistance; as well as other properties. Because of the ease of processing and the low volume cost compared to other fiber raw materials, their use is especially economical in many cases.

To a large extent, PP and HDPE tapes have replaced jute, hemp, sisal, and other natural fibers. Film yarns and split yarns (tenacities commonly 4–6 cN/dtex) are used particularly in the manufacture of bags, flexible bulk containers and other packaging fabrics and knits; industrial fabric (e.g., tarpaulin, geotextiles, filter fabrics); carpet backing; netting (protection against hail, birds, solar radiation, etc.); awnings; camouflage shields; twine; rope and cable.

Packaging and Industrial Fabrics. Wide width fabrics are usually produced on flat looms [31]. Circular looms are useful for bagging, because in addition to simpler preparation for weaving (no beaming; weaving directly from the reel), elimination of the side seam gives better bag strength and saves labor as well as material [32].

By subsequent extrusion coating, mostly with LDPE or PP, water- and dustproof fabrics are obtained. In addition, the coating prevents ribbon slippage and loosening of the fabric.

Carpet Backing. Because of the relatively high thermal stress during carpet manufacture (dispersion coating and drying), only PP ribbon can be used. The major application is as primary backing in the manufacture of tufted carpets; to a lesser extent, PP is used as secondary backing and as binding warp yarns in conventional woven carpets. The splitting behavior must be precisely controlled, especially in primary backings, and shrinkage must be low (<1 % at 132 °C, 20 s, European Association for Textile Polyolefins method) [18]. Too little splitting leads to deflection of the tufting needles and, hence, defects in the carpet as well as breakage of individual tapes. Too much splitting also affects fabric strength adversely. Tenter setting, previously used to minimize shrinkage of the entire fabric, is employed only occasionally.

Knit Goods. Cloth for bagging or for shade, camouflage, and hail protection can be made on warp knitting machines as well as on looms [19, 33]. In most cases, netlike, coarse-stitch products, e.g., bags and pouches for fruit, vegetables, and other crops, are made.

The raw material is almost exclusively HDPE, frequently via the split-knitting process [19, 20]. Polypropylene tapes are difficult to fabricate on knitting machines because of poor sliding properties and tendency to split and break.

Twine, String, and Rope. Twine and string for packaging are obtained from highly stretched, spontaneously splitting, or fibrillated tapes of PP, by twisting and plying. For high-strength ropes and cables, fibrillated ribbons, PP monofilaments, and long staple fibers are used [34].

Floor Covering. Split fibers can, like other fibers, be processed into needle felts, which are used as floor or wall coverings. The use of split fibers in these areas has, however, decreased considerably and given way to spun fibers.

3. Monofilaments

3.1. Production

Monofilaments of PP or HDPE usually have a round or elliptical cross section, with a diameter of 0.1–3 mm (mostly 0.1–0.5 mm).

The steps in monofilament production are, for the most part, identical to those in tape manufacture. Monofilament machines consist of extruder, spinning unit (spinning head with spinning pump and spinneret), cooling bath, roll stretching units (usually two sets of seven rolls and one set of three rolls), hot-air ovens or a hot-water bath (for HDPE), and windups [10, 35]. Raw materials are generally propylene homopolymers with melt flow indices between ca. 2 and 6 g/10 min (MFI 230/2.16). If improved abrasion and rubbing resistance as well as better cold toughness are required, propylene copolymers are also used. Among the HDPE types, those with densities of 0.950–0.960 g/cm^3, MFI 190/2.16 values between 0.4 and 1.0 g/10 min, and narrow molecular mass distribution have been found to perform best.

Extruder–Spinneret. Extruders with a screw diameter of 45–90 mm are used for the production of monofilaments. Spinneret holes are arranged in concentric circles on the plate. Depending on the size of the unit and the

diameter of the monofilaments, ca. 50–100 monofilaments are extruded through one spinneret. In general, the spinneret hole diameter for polyolefins is three to four times the final diameter.

Cooling Bath. Monofilaments are produced exclusively with water bath cooling; the water temperature is 20–60 °C, depending on working material and thickness of the monofilaments.

Stretching. Stretching of PP monofilaments occurs in hot-air ovens between two stretching units with seven rolls each. The usual draw ratio is 1:8 to 1:12, and the temperature is 120–160 °C. Because of their lower softening range, HDPE monofilaments can be stretched in water baths at, or slightly below, 100 °C. Compared to stretching in hot-air ovens, this method has the advantage of better and more uniform heat transfer. Stretch ratios are generally between 1:8 and 1:11.

Setting. As in tape production, setting occurs in hot air after stretching. It is also done under tension, which is controlled by suitable adjustment of drawoff roll speed. Setting temperature is in the range of stretching temperature; setting shrinkage is usually adjusted to 4–8 %.

Windup. in contrast to film yarns (which are wound on packages with traverse laydown), monofilaments are usually wound in parallel on flanged disk spools. Windup speed is ca. 100–180 m/min. Monofilaments for bristles are wound on large-diameter reels or wheels to avoid too high a curvature.

Coloration and Finish. Coloring and finishing are similar to the process steps for tapes. However, addition of mineral fillers to reduce splitting is not required for monofilaments. To avoid fibrillation of the outer layers, surface finishes are applied (e.g., during twisting) to improve lubricity.

3.2. Uses

Monofilaments of PP and HDPE are processed into fabrics, knit goods, rope, and cable on the same machines used for film ribbons and split yarns.

Areas of application include fishing nets (HDPE); nets for protection from hail, birds, etc.; packaging nets; sieves and filter fabrics; rope and cable; bristles; reinforcing grids for construction sheeting; and tarpaulin.

Bristles for sweepers, road brooms, and the like are sometimes mechanically split at the ends. Because sufficient weathering resistance can be obtained with little or no UV stabilizer, HDPE is often used for protective netting.

4. High-Modulus Polyolefin Yarns

Conventional processes for producing polyolefin tapes, monofilaments, and fibers give a structure that consists of more or less oriented crystals as well as amorphous regions. Considerably higher values of the modulus of elasticity and tensile strength are to be expected if chain folding can be avoided, and as many molecular chains as possible can be oriented in the direction in which the load is applied. This ideal case can be approximated most closely with HDPE. Based on its relatively high packing density in the crystal lattice, HDPE should give the highest theoretical stiffness and strength value [36]. On the other hand, HDPE can be relatively easily prepared with very high molecular mass, so the number of chain ends and defects in the crystal can be minimized. The theoretically attainable stiffness and strength values of polypropylene are lower because of its helical structure. However, PP is also of interest because of its higher heat resistance.

The necessary "ultrahigh" orientation of the molecular chains can be achieved essentially in two ways with high molecular mass polyolefins: (1) drawing in the solid state (at a temperature clearly below the melting range) [37–40], and (2) spinning of highly viscous solutions (gel spinning) and subsequent one- or two-stage drawing [41, 42].

Higher modulus and strength are attainable by drawing in solution than by drawing in the solid state because products with higher molecular mass can be used, and a higher degree of orientation can be achieved.

4.1. Production

Two technologies are available; both are still in the process of commercialization. Drawing in

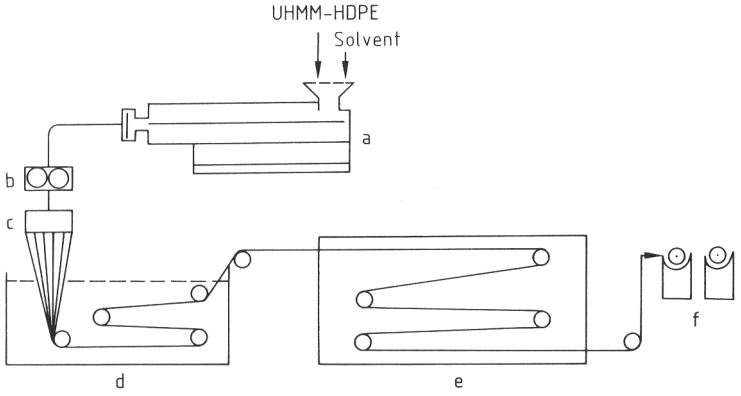


Figure 8. Gel-spinning process for the production of high-modulus UHMM HDPE * yarns
a) Extruder; b) Spinning pump; c) Spinneret; d) Precipitating bath – extraction; e) Heating – drawing; f) Windup
* Ultrahigh molecular mass high-density polyethylene.

the solid state is accomplished in draw jets at ca. 100 °C [43]. At draw ratios up to 1:30, moduli of ca. 50 GPa are attained for HDPE and ca. 20 GPa for PP. This process is being commercialized by the British Petroleum (BP) and Celanese companies.

In gel spinning (Fig. 8), a highly viscous solution in decalin, paraffin oil, or paraffin wax is first prepared in a kneading or stirring unit [44]. It is then extruded through a spinneret (c) into a precipitating bath (d). After entering the precipitating and cooling bath, the filaments are in a gel state in which the molecules remain largely disentangled. For orientation in the fiber direction and subsequent crystallization with final removal of solvent, a single- or multiple-step drawing process follows (e). Drawing occurs under heat and with a stretch factor $\geq$30. Preferably, HDPE with a molecular mass of ca. 2×10^6 is used (UHMMPE). The yarns can subsequently be cross-linked using radiation.

4.2. Properties and Uses

By gel spinning, HDPE yarns with moduli of elasticity of 50–100 GPa, and tenacities of $\leq$ 35 cN/dtex can be produced [45]. Because of their low density (0.97 g/cm^3), these yarns have an extremely high specific strength and are very abrasion, light, chemical, and moisture resistant. In addition, they exhibit high energy absorption and knot strength as well as good resistance to cold. Limitations in use include a relatively high tendency to creep and a relatively low melting temperature (ca. 150 °C). Radiation cross-linking increases heat resistance and reduces the tendency to creep.

End-use possibilities are extremely high-strength rope and cable, fabric for sails, industrial filters, bulletproof vests, and reinforcing layers for composites.

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Polyacrylonitrile Fibers

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ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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" Polyacrylonitrile fibers" is a collective name for all fibers that contain at least 85% polymerized acrylonitrile [107-13-1]. These fibers are also referred to as "acrylic fibers." Most polyacrylonitrile [25014-41-9] (PAC) fibers consist of ternary copolymers with 89–95% acrylonitrile, 4–10% of a nonionogenic comonomer, and 0.5–1% of an iogenic comonomer containing a sulfo ($-SO_3H$) or sulfonate ($-OSO_3H$) group. Fibers of 100% acrylonitrile are also produced for industrial use [1]. Because polyacrylonitrile decomposes before melting, it cannot be spun from the melt but only from solution.

History. In the early 1930s, H. Rein at I.G. Farbenindustrie carried out experiments to produce fibers from polyacrylonitrile. Because of polyacrylonitrile's insolubility in organic solvents, its nonmelting properties, and its high softening point, advantageous fiber properties were expected. Patents for the use of dimethylformamide (DMF) as a solvent for acrylonitrile polymerization were filed in Germany in 1942 by I.G. Farben and in the United States in 1944 by Du Pont. DMF was the first industrially useful solvent for the production of polyacrylonitrile fibers. Soon thereafter, dimethylacetamide (DMA) was also found to be a solvent. Technology for dissolving the polymer in aqueous solutions of certain organic salts was also developed. The first acrylic fiber was commercialized by Du Pont in 1948. In the Federal Republic of Germany, production of acrylic fibers began in 1954 [2].

The composition of the copolymer determines the dyeing behavior of the fibers. The nonionogenic comonomer serves as an internal plasticizer and increases the rate of dye uptake. The sulfonate group of the ionogenic comonomer makes possible chemically bonding ionogenic dyes, whose color-imparting ion is a cation (basic dyes). The amount of ionogenic comonomer determines the saturation value, i.e., the maximum amount of dye that can be chemically bonded by the fibers. Acidic ionogenic comonomers are replaced by basic comonomers if use of acid dyes is desirable.

Basic-dyeable acrylic fibers are the major type of fiber consumed; those made of 100% acrylonitrile and those dyeable with acid dyes lag far behind.

The term "modacrylic" designates all fibers that contain 50–85% of bound polyacrylonitrile. Fibers with 40–60% copolymerized vinyl chloride and fibers with 30–45% copolymerized vinylidene chloride are important because of their flame-retardant properties.

Polyacrylonitrile fibers are wool-like in nature. An important step in their development was the improvement in dyeability by modification with suitable comonomers. Their wool-like nature and good dyeability have established a secure place for acrylic fibers in the textile market along with polyester and polyamide fibers.

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1. Physical Properties

Articles of acrylic fibers have a wool-like hand. Lower fineness fibers produce a softer hand; higher fineness makes it harsher. The high bulk and low density (compared to natural fibers) make possible light, airy textiles with good recovery, warmth retention, and covering power. Because acrylic fibers do not swell, articles made from them remain permeable to air even when wet. The tensile strength of acrylic fibers and the abrasion resistance of articles made from them are greater than those of natural fibers.

Commercial fibers have different dye affinities and dye uptake rates. For light shades, dispersion and basic dyes are used; for dark shades, only basic dyes. Dyeing temperature is generally ca. 100°C. Dyeings are distinguished by brilliance and fastnesses. The degree of luster is determined by the type, brilliant or delustered.

Articles of acrylic fibers fall into the easy-care category. They absorb little moisture, can be washed at moderate temperature, and dry rapidly. They are resistant to many organic solvents, and stains can be removed easily. They do not felt. Weathering and lightfastness are excellent and unsurpassed by any natural or synthetic fiber. This makes the fiber especially suitable for outdoor uses such as awnings. The fiber is not attacked by bacteria, mildew, or insects, and does not rot.

2. Chemical Properties [3]

Good chemical resistance of the homopolymer to hydrolysis permits industrial applications up to 140°C in a humid atmosphere, e.g., for filter fabrics. The resistance of acrylic fibers to industrial gases, smoke, and soot is very good. Acrylic fibers are resistant to moderate concentrations of mineral acids and to oxidizing agents. They are soluble in concentrated sulfuric acid and concentrated nitric acid. Resistance to weak alkali is sufficient. Acrylic fibers are insoluble in most organic solvents, e.g., benzene, mineral oil, carbon tetrachloride, aliphatic hydrocarbons, aliphatic alcohols (e.g., ethanol), aliphatic esters, and aliphatic ketones (e.g., acetone).

In the burn test, the fibers melt, ignite, and burn with a yellow, sooty flame; a dark, hard, and brittle residue remains. In contrast, modacrylic fibers melt in the flame to dark, hard lumps; burn partially; but extinguish again if the flame is removed.

3. Production

Production of polyacrylonitrile fibers includes the following processing steps (Fig. 1) [4]:

1. Polymerization (Section 3.1)
2. Dissolving (Section 3.2)
3. Spinning (Section 3.3)
4. Aftertreatment (Section 3.4)

3.1. Polymerization

The fiber raw materials for acrylic or modacrylic fibers are produced by polymerization or copolymerization of acrylonitrile (→ Acrylonitrile). For further details concerning reactivity and material constants see [5].

Polyacrylonitrile can be made by anionic or radical polymerization. Although polymer solutions can be produced in high space–time yields by anionic polymerization, radical-initiated polymerization or copolymerization of acrylonitrile is generally the method of choice in the manufacture of raw materials for acrylic or modacrylic fibers. Either solution polymerization or precipitation polymerization is used.

Like all vinyl monomers, acrylonitrile can polymerize with the formation of isotactic as well as syndiotactic sequences. The processes used to produce acrylonitrile polymers give about equal amounts of isotactic and syndiotactic sequences [6].

For commercially useful acrylic fibers or yarns, homo- or copolymers of acrylonitrile are used as raw materials. The raw materials for acrylic fibers in *textile applications* are acrylonitrile terpolymers.

The same initiator systems and similar reaction conditions can be used for the industrial homopolymerization of acrylonitrile as are used to produce acrylonitrile copolymers, the raw materials for the usual acrylic fibers in textile applications.

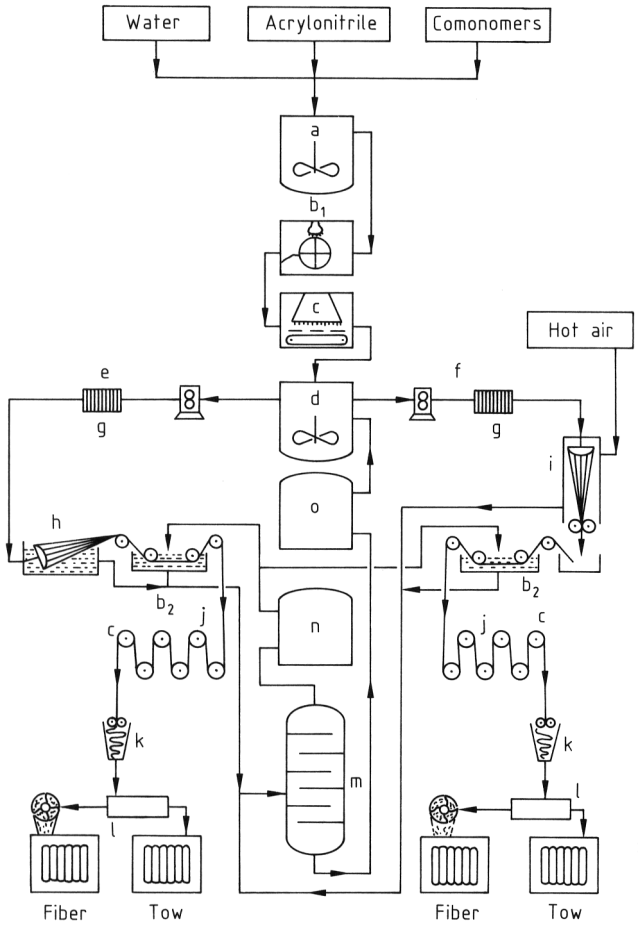


Figure 1. Manufacture of acrylic fiber* [4]
a) Polymerization; b_1) Washing and filtering of polymer; b_2) Washing of filaments; c) Drying; d) Dissolving; e) Wet-spinning process; f) Dry-spinning process; g) Filter; h) Spinning bath; i) Spinning shaft; j) Drawing, drying; k) Crimping; l) Steaming; m) Distillation; n) Water; o) Solvent
* Wet spinning—lower left; dry spinning—lower right.

Interest has developed in very high molecular mass acrylonitrile copolymers that contain small amounts of comonomers. These materials are used to produce high-strength acrylic yarns [7].

To obtain the desired properties in acrylic fibers for textile applications, acrylonitrile terpolymers are used as raw materials. These polymers contain 4–10% comonomers, are free of ionic groups, and are particularly suited for statistical copolymerization with acrylonitrile. Examples are the methyl esters of acrylic or methacrylic acid, vinyl acetate, or acrylamide. Depending on the need for raw materials for cationically or anionically dyeable acrylic fibers, an acidic or basic comonomer is used as an additional component. Monomers containing sulfonic acid groups have proved particularly useful as acidic or anionic comonomers, e.g., methallyl sulfonic acid, styrene sulfonic acid, and 2-methyl-2-sulfopropylacrylamide, or soluble salts of these sulfonic acids, respectively. Examples of basic comonomers are dialkyl aminoalkyl methacrylates or vinylpyridines.

Although the processing technology of the terpolymerization reaction is largely independent of monomer composition, special attention must be given to the structure of the dyeing

comonomer when selecting the initiator or initiator system.

Precipitation Polymerization. In the precipitation polymerization of acrylonitrile in water to produce acrylic fiber raw materials, use is made of the relatively good water solubility of the monomer. To introduce end groups into the fiber raw material, which can be utilized to adjust dyeability properties, initiator systems are used. The polymerization is initiated with water-soluble peroxodisulfate redox systems, such as potassium, ammonium, or sodium peroxodisulfate, combined with water-soluble salts of sulfur (IV) or derivatives of sulfur (II). Especially useful in the production of raw materials for cationically dyeable acrylic fibers is the initiator system peroxodisulfate–hydrogen sulfite. The decomposition reaction of this redox system has been thoroughly studied [8].

The relationship between dyeability and the number of different end groups in the copolymers is known [9]. The type and concentration of polymer end groups of the fiber raw material have a major influence not only on the coloring properties but also on the resistance to thermally induced yellowing and the degree of whiteness of the resulting acrylic fibers.

To obtain cationic dyeable acrylic fibers, precipitation polymerization is carried out at 40–70°C and at a pH of <6. Peroxodisulfate–hydrogensulfite is used as initiator of polymerization with a several-fold molar excess of hydrogensulfite relative to peroxodisulfate. To purify and demonomerize the polymer completely and gently, a compact polymer granulate, which can be dried after washing and filtering, is produced.

In the synthesis of fiber raw materials for acrylic fibers that are to be dyed with anionic dyes, redox systems, e.g., H_2O_2–thioglycerine [10], that do not result in anionic end groups are used.

A detailed description of redox polymerization of acrylonitrile and a comprehensive review of the use of redox systems can be found in handbooks [11]. The constancy of distribution of molecular mass, chemical composition, and degree of whiteness is particularly significant to the final properties of acrylic fibers.

Solution Polymerization. The copolymerization of acrylonitrile in solution results in polymer solutions that can be spun without additional process steps after the elimination of residual monomers. The polymerization reaction conditions must be optimized so that monomer conversion is almost complete; low molecular mass fractions that could adversely affect the mechanical and thermal properties of the resulting acrylic fibers must be avoided as much as possible. Examples of suitable solvents are dimethylformamide, dimethyl sulfoxide, nitric acid, and concentrated aqueous solutions of ammonium thiocyanate or zinc chloride. In radical polymerization, these solvents—but especially the polymer solutions—are effective chain-transfer agents. For that reason, specially selected initiator systems and special reactors are used for the large-scale commercial solution polymerization of acrylonitrile [12].

The choice of precipitation polymerization or solution polymerization often depends on the prior history of the acrylic fiber producer. Both processes have advantages and disadvantages, and economics—size of installation, type of spinning process in use and raw material situation—is often the deciding factor.

3.2. Dissolving

The solvents used in dry and wet spinning are listed in Table 1.

Commercial Process. A dough, which is as free of clumps as possible in order to avoid long dissolution times, is prepared from the powdery polymer and the solvent by growing a compact polymer granulate; intimate mixing of polymer and solvent stream, e.g., in screw mixers, turbines, or paddle mixers; and, providing low solvent temperature, which initially produces a suspension with good distribution of polymer in the solvent.

A two-step process is used for dissolution in aqueous salt solutions. The polymer is first suspended in a salt solution that does not dissolve the polymer; then the salt concentration is increased to the amount necessary for dissolution. This process takes place in agitating pans, either batchwise or continuously. The batchwise process requires several hours to produce dimethylformamide solutions. The dissolving

Table 1. Distribution of installed capacity by solvents, 1985

Solvent	CAS registry number	Formula	Spinning process	Percent of total capacity
N,N-Dimethylformamide (DMF)	[*68-12-2*]	$HCON(CH_3)_2$	dry wet	15 17
Sodium thiocyanate*	[*540-72-7*]	NaSCN	wet	24
N,N-Dimethylacetamide (DMA)	[*127-19-5*]	$CH_3CON(CH_3)_2$	wet	24
Nitric acid	[*7697-37-2*]	HNO_3	wet	12
Zinc chloride*	[*7646-85-7*]	$ZnCl_2$	wet	3
Dimethyl sulfoxide (DMSO)	[*67-68-5*]	$(CH_3)_2SO$	wet	2
Ethylene carbonate	[*96-49-1*]		wet	3

* Aqueous solution.

temperature is between 60 and 100°C. In the continuous process, the holdup time in the agitating pan is shorter (e.g., 5–30 min), but the temperature of dissolution is correspondingly higher (e.g., up to 120°C) and the intensity of agitation is greater [13]. The solution can then be treated thermally in heat exchangers or exposed to shearing forces in screws or turbines.

The concentration of the spinning solutions is higher for dry spinning than for wet spinning. When dimethylformamide is the solvent, 25–30% solutions are normally used for dry spinning and 20–25% solutions for wet spinning. Concentration and viscosity of the spinning solution are monitored constantly.

To keep the spinning solutions free of gel particles or other impurities, which is a prerequisite for long spinneret life, they are filtered in filter presses. Heat, amines, oxygen, and ions of heavy metals (especially iron) damage initial color (degree of whiteness). Therefore, an inert atmosphere, acid, and reducing and complexing stabilizers are needed [14, 15]. Additives have also been developed to protect against saltlike clouding of the solutions (in dimethylformamide) because of the polymerization catalyst [16, 17].

Stable viscosity is desirable so that spinning remains a steady-state process; it is obtained by optimizing the temperature of dissolution (ca. 70–100°C) or by using suitable additives [18, 19].

Gelation occurs at low temperature via secondary valence forces and at high temperature via cross-linking reactions. The higher the viscosity of the solution and the molecular mass of the polymer, the greater is the tendency to gel; more uniform polymers have less tendency to gel [20].

Aqueous zinc chloride solutions and solutions in dimethyl sulfoxide and ethylene carbonate also tend to gel. Because partial hydrolysis of the nitrile groups occurs when nitric acid is used as the solvent, these spinning solutions should not be heated above 5°C.

3.3. Spinning

The polymer contained in the spinning solution is shaped into a yarn by either wet or dry spinning. In both processes, the spinning solution is pressed through small holes in the spinneret, thus giving the polymer its threadlike shape. The processes differ in the state of aggregation of the medium that the spinning solution enters on leaving the spinneret. In wet spinning, a precipitating bath of water and the solvent is involved; in dry spinning, hot air or a hot inert gas.

Wet Spinning. The 10–25% polymer solutions are deaerated, filtered, and pumped through the 10 000–80 000-hole spinnerets into the precipitating bath, where the solution thread line is coagulated to a highly swollen gel yarn by the exchange of solvent in the yarn for water. Coagulation conditions determine the strength of the sheath–core structure of the yarn, as well as its porosity and cross-sectional shape. Wet-spun yarns are aftertreated immediately without intermediate storage.

Dry-Jet Process. In a variation of the wet-spinning process, the solution thread line leaving the spinneret is first passed through air before entering the precipitating bath. Fibers with higher strength and elongation, smoother surface, and greater uniformity can be made by this process [21].

Dry Spinning. The only solvent used in dry spinning of polyacrylonitrile fibers is dimethylformamide having the following properties:

bp (101.2 kPa)	153°C
Heat of vaporization	571.24 kJ/kg
Water	<0.3%
Amines	<0.01% dimethylamine
Iron	<0.05 ppm

The pH of a 20% aqueous solution at 25°C should be 6.5–9.

The degassed and filtered spinning solution is heated to 100–150°C and spun into vertical spinning shafts through spinnerets (200–2000 spinneret holes; hole diameter, 0.1–0.5 mm). Several spinning shafts make up a spinning machine. The walls of the shafts are heated to 150–220°C; hot air or a hot inert gas (200–240°C), passes through the shaft in the same direction as the yarn. The oxygen and water content of the spinning gas should be as low as possible to avoid discoloration of the spun yarn and decomposition of dimethylformamide. Dimethylformamide evaporates in the spinning shaft and is exhausted together with the spinning gas at the bottom of the shaft. The performance of a spinning shaft is, in the final analysis, determined by the geometry of the engineering apparatus and by the amount of heat transferred to the spinning threads via the hot gas and radiation from the heated walls of the shaft. Of special significance for the quality and performance of the spun material is the air guidance in the immediate vicinity of the spinneret [22–24].

Solidified, dried spun yarns are drawn off at a rate of 200–500 m/min. Spun yarns from the shafts of one spinning machine are collected and deposited in a can. (In the manufacture of continuous filaments, spinnerets with a maximum of 200 holes are used. In this case, an oily finish is applied to the spun material below the spinning shaft, and it is wound up on bobbins.)

The dimethylformamide that has evaporated is condensed, distilled, and recycled. The spun material still contains 7–30% DMF, which is leached out during aftertreatment and recovered by distillation.

The spinning conditions (temperature of solution, temperature of shaft, temperature and amount of spinning gas, and drawoff speed) greatly affect both further processing of the spun yarns (e.g., drawability) and properties of the end product (e.g., strength and elongation).

Melt Spinning. Mixtures of polyacrylonitrile and water (ca. 13–33% relative to the polymer), in contrast to anhydrous polyacrylonitrile, can form a molten, single-phase system without decomposition of the polymer. Fibers from a polyacrylonitrile–water mixture were prepared as early as 1948 and again around 1970–1971 [1, p. 260 ff]. The advantage of such a process could be the absence of solvent and lower costs. However, many of research and development have not yet resulted in a commercial process. Possible reasons for this are the high viscosities of the melts and the difficulty of preventing the melt from becoming two-phase at any point in the process.

3.4. After treatment

The aftertreatment steps are as follows:

1. Washing
2. Drawing
3. Finish application
4. Crimping
5. Drying
6. Cutting
7. Steaming
8. Packaging

Cutting is omitted in the production of tow.

During aftertreatment, the spun material acquires the necessary physical properties, such as strength, modulus, elongation, shrinkage, crimp, and crimp stability. Large-scale aftertreatment units are capable of processing tow up to 770 ktex (770 g/m) at rates up to 120 m/min in dry spinning and up to 80 m/min in wet spinning.

Washing. Washing removes residual solvent and salts by leaching with hot water (e.g., 80°C) in multilayer or drum washing machines. A closed construction is used to protect the environment. The washing machine consists of many individual zones. The wash water travels in a direction opposite to the direction of travel of the yarn tow. The wash water is distilled or otherwise processed to recover the solvent. Washing usually precedes drawing because of the longer holdup time in the washing baths resulting from the relatively low tow speeds prior to drawing, which makes the washing process correspondingly more intense.

Drawing. Drawing imparts the required strength to the yarn and occurs in two or more steps in drawing tanks between drawing units. The preferred drawing medium is water just below the boil (e.g., 99°C). The draw ratio is between 1 : 2 and 1 : 10. Wet-spun yarns must be drawn more (because of the absence of preorientation) than dry-spun yarns to attain the same strength. The rule "the higher the draw, the higher are the strength and modulus and the lower is the break elongation" applies to both processes.

After being drawn, the yarns have a boil-off shrinkage, which, depending on the draw ratio, is between 15 and 45%. Shrinkage increases as draw temperature decreases and passes through a maximum with decreasing draw ratio. This behavior is applied to production of shrinkable fibers. Fibers already shrunk can be made shrinkable by a postdrawing treatment.

In addition to water drawing, steam drawing or drawing on feed wheels is also possible.

Finishing. Finish application occurs in an immersion bath. Most commonly, active anionic compounds are applied to the fibers from an aqueous medium. Examples are ethoxylated fatty acids, salts of ethoxylated sulfonic acids, or phosphoric acid esters of long-chain aliphatic alcohols. Finish application prevents the buildup of static charges during further processing of the fibers and imparts the proper degree of adhesion and smoothness to the surface. The finish content of the finished fiber is 0.2–0.4%. It can be determined by extracting with ether or a mixture of methanol–benzene, evaporating the solvent, and weighing.

Crimping. In general, crimping is carried out in a stuffer box after drying (stuffer box crimping). A steaming zone, in which saturated steam condenses on the tow, heats the tow and makes it more formable. Two crimping rolls, kept at constant temperature by circulating cooling water, pull tow bands of up to 3×10^6 dtex into the crimping chamber, stuff them, and push them continuously from the chamber at a predetermined pressure. In certain crimping units, steam can be introduced into the stuffer box to shrink the tow and increase the crimp stability (setting).

The type of crimp is important in processing fibers because of its effect on cohesion and on the hand of the yarns produced from the fibers. Crimp is determined by the conditions of crimping (temperature and stuffing box pressure), the percentage of comonomer in the polymer, and other factors that affect the thermal plasticity or friction, e.g., moisture content or type of finish.

Drying. Screen drum dryers, screen belt dryers, or calenders are used for drying. Drying temperatures of 120–170°C are common.

During tensionless drying, i.e., drying loosely laid tow bands or cut fibers, the shrinkage built into the fiber in the drawing process is released and removed. This process can be enhanced by steaming. When dried under tension, the fibers must subsequently be relaxed, usually by steaming. Drying reduces the moisture content of the fibers to 1–2% and increases their density.

Although polyacrylonitrile does not crystallize like polyamide or polyester, an improvement or increase in regions of near-order by drying or annealing can, nevertheless, be demonstrated by X-ray analysis. Because of the consolidating effect of drying, uniform drying is especially important for uniform dyeability of the fibers.

Steaming. Steaming generally occurs in screen belt steamers or in autoclaves. Steaming with saturated steam shrinks the fibers and increases the crimp stability. To ensure that the shrinking process is complete, a high and uniform steam atmosphere (>95% steam) is required.

Steaming increases the elongation of the fibers and slightly reduces their strength.

Steaming under pressure is especially effective in increasing the rate of dye uptake.

Cutting and Packaging. In the production of endless tow for processing on stretch–break machines, the crimped and dried tow bands are packaged in cartons or bales. The mass of such tows ranges from 50 to 110 g/m. The bundle mass is 100 kg per carton and up to 800 kg per bale.

In the production of staple fibers, the crimped and dried tow bands are cut into staple fibers with slotted wheels or rotary cutters. The usual cut lengths are 40, 60, 80, 100, or 150 mm, depending on end use. Cut fibers are compressed and packaged into bales of ca. 200–300 kg in packing presses.

The aftertreatment of *filament yarns* of polyacrylonitrile involves processes similar to those for tow and fibers: drawing and setting. Equipment is tailored to the particular filament count of the product. In addition, the filaments are twisted to tighten the yarn and packaged on cones, which are shipped at a mass of 1.5–2.0 kg. Commercial counts of industrial filaments are 220 dtex/96 filaments, 440 dtex/192 filaments, or 890 dtex/384 filaments.

3.5. Special Processes

Continuous Dry Spinning Process. Continuous dry spinning and aftertreatment processes have eliminated storage following the dry-spinning process [25].

Because of the relatively high spinning speed (compared with wet spinning), the tow speed after drawing must be 500–2000 m/min. A vibrating trough is used to transport the spun tow during washing. Drawing is carried out in steam; crimping, in an aerodynamic crimper with a gaseous medium (at 1.5–1.6 MPa and 50–210°C). Finish application can occur before, during, or after crimping. The steaming process is carried out in a vibrating trough in a steamer; drying, in a belt dryer.

In this process, products of uniform quality are obtained; solvent emission and waste are reduced; and manufacturing costs are lower [25].

In one variant of this process, washing is also eliminated [26].

Producer Coloring. The manufacture of colored fibers is of economic interest if large amounts of one color are to be produced. Fiber producers can make colored fibers in the following ways:

1. Spin dyeing,
2. Gel dyeing,
3. Dyeing of spun material

Spin Dyeing [27]. Dyes, either cationic or pigment dyes, are added to the spinning solution prior to spinning.

The dyes are free of adulterants. They are soluble in the solvent used and should be insoluble in water (the subsequent washing medium). Dye solutions also contain polymer to adjust their viscosity to that of the spinning solution. In general, combinations of dye solutions are metered into the polymer solution to achieve a given color; they are homogenized by means of statically or mechanically operating mixers.

Ionic bonding of the color-imparting cation to the sulfite or sulfate groups of the polyacrylonitrile polymer is rapid and quantitative. Uniformly dyed tows with brilliant color and good textile fastness are obtained by both the dry-spinning and the wet-spinning processes.

Organic pigments are used when especially high lightfastness is required, e.g., in textiles used outdoors. The pigments are dispersed in a dilute solution of polymer. In so doing, stabilizers are added to prevent coagulation of the dispersed dyes. This is followed by metering into the spinning solution as with cationic dyes.

Gel Dyeing. Dyeing during aftertreatment generally occurs while yarns are in the gel state after wet spinning. Dyeing is possible because cationic dyes rapidly diffuse into the highly swollen yarn. Dyeing can occur in the precipitating bath, the drawing tank, or a separate bath. It must be carried out prior to drying, which collapses the structure of the swollen yarn.

Dyeing by both the extraction method and the padding method has been patented. Important variables are temperature, concentration of dye, and time in the dye bath; these determine the amount of dye required and the wash- and lightfastness of the dyed material [28]. The

choice of dyes is also important in the quality of dyeing [29].

Gel dyeing has the following advantages [30]:

1. Good dye uniformity within the batch and from batch to batch
2. Same tow quality as with undyed fibers because all physical perturbations are avoided
3. Economical batch size (≥5 t) because hardly any material is wasted during dye change

Dyeing of Spun Material. Dry-spun yarns can also be dyed during aftertreatment, but the rate of dye uptake must be increased by suitable measures [31].

Uses. Fibers dyed in the course of fiber manufacture are used in clothing, home furnishings, and outdoor textiles. Yarns, pigment-colored during spinning, are recommended for outdoor textiles (awnings, sunshades, camping and terrace furniture, camping tents, and boat covers).

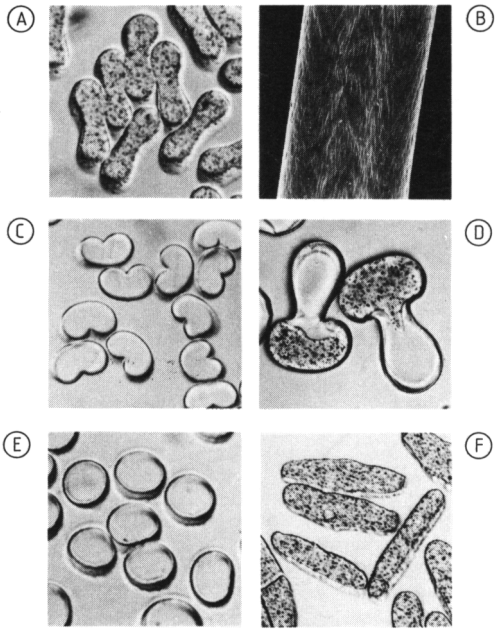


Figure 2. Acrylic fibers, cross sections and surfaces
A) Dry spun, delustered; B) Surface of A; C) Wet spun; D) Bifilar, dry spun, single component, delustered; E) Modacrylic, dry spun; F) Modacrylic, wet spun, delustered

4. Analysis

Cross Section (Fig. 2). The cross-sectional structure of polyacrylonitrile fibers and modacrylic fibers is determined by the composition of the polymer, the spinning process, and spinning conditions. The shape of the cross section determines the luster, moisture regain, and mechanical properties of the fiber [32].

Stress–Strain [1, pp. 73, 208]. The stress–strain curve of acrylic fibers (Fig. 3) is characterized below their glass transition temperature (50–95°C with decreasing moisture content) by a steep initial region A, followed by zone B, where small changes in stress result in large changes in elongation. Above the glass transition temperature, A no longer exists; the fiber is more extensible, with slowly increasing resistance until a yield stress σ_c, at which structurally determined resistance to plastic sliding processes are overcome, is attained.

The stress–strain curve is affected by the type and amount of comonomer, the molecular mass and molecular mass distribution and the conditions of spinning and aftertreatment. Figure 4 shows the effect of the draw ratio.

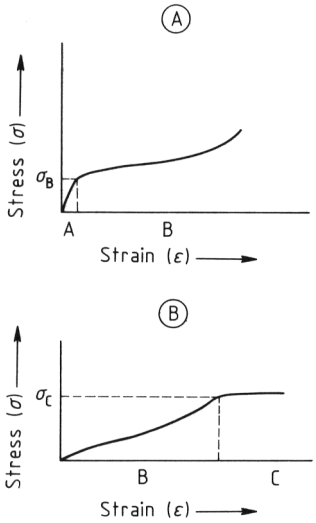


Figure 3. Stress–strain diagram of polyacrylonitrile (PAC) fibers [1]
A) Yield points below glass transition temperature $T < T_e$; B) Yield points above glass transition temperature $T > T_e$ T_e = second order transition temperature; σ_B and σ_C = points at which small increases in stress result in large changes in elongation

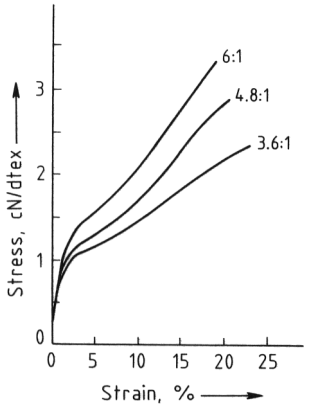


Figure 4. Effect of three different draw ratios on elongation and stress

Thermomechanical Analysis [1, pp. 77, 209]. In thermomechanical analysis (TMA), the change in length of a fiber under a constant preload is observed at a constant rate of heating. From the changes in length of fibers under low load, conclusions can be drawn concerning their degree of heat-setting. In Figure 5, brands 1 and 2 were more intensively heat-set during manufacture than brand 3, in which extension of the yarns above 110°C is prevented, principally by release of shrinkage tension.

Analytical Procedure. The *cross section* of the fiber material provides a good indication that an acrylic fiber is present. Dumbbell-shaped cross sections indicate a dry-spun acrylic fiber; beanshaped cross sections, a wet spun fiber (cf. Fig. 2).

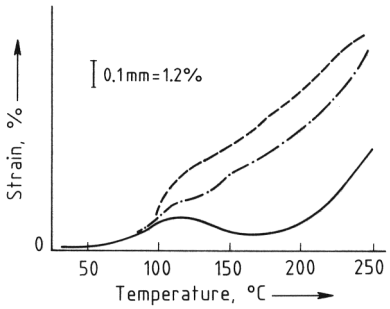


Figure 5. Thermomechanical deformation of acrylic fiber tow of three different brands* [1]
—— Brand 1; – · – Brand 2; ——— Brand 3
* Pretension 0.015 cN/dtex; rate of heating 10°C/min.

Type reactions can be used to recognize and distinguish an acrylic fiber from other synthetic fibers. Each of these reactions, must be carried out on a freshly prepared sample; acrylic fibers should be [4]:

1. Soluble in concentrated nitric acid at room temperature
2. Insoluble in concentrated formic acid at room temperature
3. Insoluble in boiling cyclohexanone

Analysis of *polymer composition* is carried out by IR spectroscopy [33]. A first indication of the composition of the copolymer is obtained from analysis of the acrylonitrile content. To determine the brand, the exact composition of the polymer is required. The major neutral comonomers are vinyl acetate, methyl methacrylate, and methyl acrylate. Major ionogenic comonomers are styrene sulfonate, methallyl sulfonate, and itaconate, or in acid-dyeable types, cyclic or aliphatic amines. In addition, the following are present in flame resistant types (modacrylic fibers): vinyl bromide, vinyl chloride, and vinylidene chloride [34].

The number of ionogenic groups can be determined titrimetrically. Acid groups can be determined potentiometrically in DMF solution with 0.1 M NaOH [35]; basic groups, in nitromethane with perchloric acid in dioxane solution [36]. The quantitative determination of sulfur-containing polymer building blocks can also be accomplished by ignition in an oxygen flask and determination of the sulfate formed or by determining the sulfur with X-ray fluorescence analysis [37]. Indications of the "physical history" of an acrylic fiber are obtained by physical methods, e.g., thermomechanical analysis (previously discussed) or by determining the degree of relaxation with a solubility test [38].

The percentage of acrylic or modacrylic fibers in fiber blends can be determined by selective dissolution in DMF or DMA [39]. For comprehensive information on analysis, see [1 pp. 379–423].

5. Types of Fibers [40]

Classification. The multiplicity of acrylic fibers can be classified by various systems.

Chemical composition determines certain properties that are used in classification; fibers can be

1. Basic dyeable
2. Dark dyeable
3. Acid dyeable
4. Self-crimping
5. Flame retardant

Characteristic descriptions, such as brilliant, delustered, bright, and spun-dyed, are also used.

Subdivision into spun fiber and tow accounts for various processing possibilities: (1) spun fiber for woolen, cotton, worsted, and open-end (rotor) spinning processes; and (2) tow for processing on stretch–break machines followed by spinning. Classification can be by fineness (denier) range (in decitex):

1. Finest: 0.4, 0.6, 0.9
2. Fine: 1.6, 2.2, 2.6
3. Medium: 3.3, 5.0, 6.7
4. Coarse: 11.0, 15.0, 17.0

Cut lengths are 28, 40, 50, 60, 100, 120, and 150 mm.

Physical modifications important to the quality of the goods are also used in classification. The following distinctions are made with respect to fiber shrinkage:

N-fiber	0–2% shrinkage
S-fiber	ca. 20% shrinkage
HS-fiber	ca. 40% shrinkage

The type of crimp is another criterion that affects the quality of the goods. Qualitative data on crimp and crimp stability (low, medium, or high) serve as characterization parameters.

The range of finenesses for tow for stretch-breaking is 1.5–17 dtex. Tow can be bright, delustered, or spun-dyed.

The number of combinations of various characteristics for basic dyeable fibers alone runs into several hundred. Some inkling of the extraordinary diversity of possible applications of the most important synthetic staple fiber can be obtained by considering that the processor has available more than 20 different brands with varying properties, that polyacrylonitrile fiber types can be blended with each other or with other synthetic or natural fibers to achieve certain properties, and that the quality of the goods is substantially affected by the many possible yarn and fabric constructions.

Industrial Fibers. Fibers for industrial use consist mostly of 100% or almost 100% acrylonitrile. Molecular mass is made as high as processibility will permit because the higher the molecular mass, the higher the strength. The fibers absorb very little moisture and, therefore, do not swell. They are resistant to hydrolysis, especially in acid medium, and are heat resistant up to 140°C.

Fibers are used in filter hoses and filter pockets in dry filtration, e.g., in the separation of fly ash in coal-fired power stations. Another end use is in dryer felts in paper machines, which absorb water that could not be squeezed out of the paper sheets. Fibers of 100% acrylonitrile are also used as asbestos replacement. For this end use, particularly high modulus and strength are required [41]. Nonmelting fibers that are nonflammable in air are obtained by heat-treating acrylic fibers in an oxidizing atmosphere at 300°C. These fibers can also replace asbestos [42]. Filaments of 100% polymerized acrylonitrile are good starting materials for high-strength carbon fibers [43].

Dyeing Modifications. Dyeability is generally achieved in polyacrylonitrile fibers by inclusion of a neutral, plasticizing comonomer (5–10%) and an ionogenic comonomer (e.g., methallyl sulfonic, 0.5–1.0%) that has an affinity for dyes. By increasing the amount of comonomer with dye affinity to 3–4%, fibers are obtained with a four- to fivefold increase in rate of dye uptake. Such fibers can be dyed at a temperature as low as 85°C rather than at the boil. Dye migration is especially good in such fibers, and the time required to fix dyes is markedly reduced. Use of a rapidly absorbing fiber is based on the differential dyeing effect, which occurs when the fiber is dyed with a conventional fiber. Special-effect yarns can be produced from homogeneous or inhomogeneous blends of fibers or rovings, e.g., yarns of mixed colors, slub yarns, and flake twist yarns. Combinations of yarns result in twisted yarns with multicolor effects.

Another dye modification is represented by acid-dyeable fibers that contain 5–15% of a basic comonomer with affinity for acid dyes. Possible comonomers are the vinylpyridines, e. g., 2-methyl-5-vinylpyridine [29994-42-1], or even aliphatic amines, e.g., 2-(dimethylamino) ethyl methacrylate [2867-47-2]. Yarns of acid-dyeable acrylic fibers are processed and dyed together with yarns of basic-dyeable acrylic fibers. Dyeing is carried out in the same dye bath containing both acid and basic dyes. In this way, interesting color effects can be achieved such as two-color effects or tone-on-tone effects. If an undyed–colored combination is desired, only acid dyes are used, to which a conventional acrylic yarn is relatively insensitive.

Modacrylic Fibers [44]. Modacrylic fibers contain 50–80% bound acrylonitrile. The comonomer that makes up the difference is essentially a halogen-containing monomer. Vinyl chloride [75-01-4] and vinylidene chloride [75-35-4] are the most frequently used halogen-containing comonomers. The main advantage of modacrylic fibers is their reduced flammability. Whereas polyacrylonitrile fibers melt in the flame, ignite, and continue to burn after removal of the flame, modacrylic fibers are self-extinguishing once the flame is removed. In addition, they do not exhibit an undesirable dripping of molten fiber. The burnt residue is solid and black. In case of fire a disadvantage is the formation of hydrogen chloride. Fibers containing vinyl chloride exhibit even less flammability than vinylidene chloride fibers.

Bromine-containing monomers, e.g., vinyl bromide or vinylidene bromide, are also used. The development of polymerizable phosphorus compounds has become known as well.

In addition to acrylonitrile and halogen-containing comonomers, modacrylic fibers generally contain other comonomers that are intended to improve the dyeability of the fibers. These are mostly monomers with acid groups, e.g., sodium styrene sulfonate [2695-37-6] or sodium methallyl sulfonate [149-44-0]. Neutral comonomers, e.g., alkyl acrylamides, which improve dyeability by loosening fiber structure, can also be included. The manufacture of modacrylic fibers in essence follows the same process steps as the manufacture of polyacrylonitrile fibers.

Because of the type and high percentage of comonomer, modacrylic fibers exhibit higher plasticity, which is expressed as lower sticking temperature or higher shrinkage. Attempts were made to eliminate this disadvantage by reducing the halogen content of the polymer and including additives in the spinning solution that act synergistically to reduce flammability. Such additives are antimony trioxide, organic antimony compounds, or halogen compounds of antimony or tin. Halogen compounds can form the oxide and can be dispersed in the fiber so finely that they do not act as delusterants. Even metal compounds (e.g., barium titanate) or phosphorus compounds (e.g., derivatives of phosphorus acids) serve as flame retardants.

Modacrylic fibers tend to lose their luster under hot–wet treatment, even during dyeing. Salts are added to the dye bath or dyeing is done at lower temperature to prevent this. However, the best route is to reluster the dyed fibers with dry heat. Luster stability has been improved by changes in spinning and aftertreatment technology, by specific changes in polymer composition, and by the addition of luster stabilizers.

Reduced flammability favors the use of modacrylic fibers wherever there are fire hazards or where the danger in case of fire is particularly severe. This includes such uses as children's sleepwear; home furnishings, especially drapes; wall coverings in public buildings; and automobile upholstery. A large area of application is in pile fabrics, carpets, and imitation furs. Modacrylics are also used in wigs.

Modacrylic fibers are processed by themselves or in blends with other fibers, e.g., acrylic fibers, polyester fibers, or poly(vinyl chloride) fibers. By blending and proper construction of the finished article, special processing requirements, as well as the requirements of flammability tests, can be met.

Absorbent Fibers [1]. To produce fibers with greater wear comfort, special attention has been paid to developing moisture-absorbent fibers. Such fibers must be able to absorb moisture from the air and from water, either by virtue of their ability to swell or by means of a system of pores in the interior of each fiber. With acrylic

fibers, the formation of a pore system is especially significant.

The system of pores must be protected by a sheath of proper thickness to ensure that the fiber can be processed without problem. The sheath must have a multiplicity of fine channels that can conduct water into the porous interior of the fiber. The properties of such a fiber include high adsorptivity, no swelling, high threshold of clammy feel, rapid transport of water, rapid evaporation, and low density [45].

The manufacture of absorptive fibers by both dry- and wet-spinning processes has been described. In dry spinning, an appropriate precipitant can be added to the spinning solution. This results in the formation of a sheath around the filament and an internal system of pores during spinning [46]. In wet spinning, highly swollen yarns with many pores are first formed during coagulation in the precipitating bath [47]. By skillful tuning of processing conditions, these pores can be retained in the final product. Water-soluble substances can also be allowed to diffuse into the swollen filaments, which are then dried. By subsequent leaching of water-soluble compounds, a system of pores is created.

Fibers with high swellability can be produced by the inclusion of comonomers with hydrophilic groups. Examples of such comonomers are acrylic acid, methacrylic acid, or 2-(dimethylamino)ethyl methacrylate. The saponification of comonomers on the fiber produces hydrophilic carboxyl groups. A popular route to the production of water-absorbent fibers is the spinning of mixtures of polyacrylonitrile and other polymers. Addition of cellulose acetate favors pore formation. Addition of hydrophilic polymers, e.g., saponified acrylonitrile, favors water absorption.

Bicomponent Fibers. The side-by-side type of bicomponent fibers in which both components are placed eccentrically in the cross section and run along the entire length of the fiber, is commercially important (see Fig. 2D). Differential shrinkage of the components forming the fiber produces three-dimensional crimp when the shrinkage is released. The differential shrinkage of the two components is achieved by a difference in the amount of comonomers. If the concentration of hydrophilic, usually ionic, groups differs in the two components, reversible crimp results. This refers to a crimp that can be removed by washing and regenerated by drying. If the concentration of hydrophilic groups of the two components is essentially equal, the crimp is irreversible, i.e., permanent. The shrinkage of the fiber, and hence the crimp, can be released during fiber manufacture by drying or steaming or during subsequent processing, e.g., dyeing of the fiber or yarn.

Bicomponent fibers are produced both as staple fibers and as tow. Knit fabrics of these yarns are distinguished by good volume, pleasant, wool-like hand, and good stitch definition. Bicomponent fibers are also used in carpets because of covering power [48, 49]. The market for these fibers is primarily in Japan and the United States.

Shrinkable Fibers. Shrinkable fibers can be produced from tow by processing on stretch-break machines. In general, the fiber shrinkage produced on these machines is 15–24%. If suitable measures are taken during tow production and stretch-breaking, fiber shrinkages of 24–40% are attainable.

Shrinkable staple fibers are generally offered at two levels of shrinkage: (1) shrinkable fibers with ca. 20% shrinkage and (2) high-shrink fibers with 35–40% shrinkage. The desired level of shrinkage can be obtained most easily during the manufacture of shrinkable fibers by suitable choice of draw ratio and draw temperature with subsequent mild drying. Care must be taken, however, to produce a shrinkable fiber free of voids so that no electrostatic problems occur in further processing and no changes in coloration or luster occur in the processed fiber. Good technical properties are also desirable. Criteria for a void-free structure are negative birefringence and density >1.180 g/cm^3 [50].

Shrinkable fibers are processed in blends with nonshrinkable fibers to give high-bulk yarns, which are distinguished by their high volume. High-shrinkage fibers are also used in imitation furs as bottom hair, in the production of multistep plushes, and in felts. Manufacturing methods are described in detail in many patents [1]. Important measures are consolidation of the yarn by removal of solvent, drying, and heat treatment in water or steam, partly prior to drawing and partly between two

drawing steps. The rate of drawing is also important.

6. Economic Aspects

At its peak in 1983, polyacrylonitrile fibers accounted for 7.1% of total world fiber production, but since then share has been falling such that by 2009 the figure was 2.9% [51]. The downward trend is expected to continue in the future, with Tecnon OrbiChem forecasting that by 2020 acrylic fiber production will account for around 1.7% of the global total. Although share has been falling annually, total worldwide production of polyacrylonitrile staple remained in the range of 2.0 to 2.7×10^6 t for almost 30 years before falling by more than 20% in 2007 to around 1.9×10^6 t. However, despite continuing competition from polyester and other fibers as well as rising raw material costs, Tecnon OrbiChem believes that global demand for polyacrylonitrile fiber will stabilize in the future with recent increases in production in parts of Asia and the Middle East/Africa balancing out the continuing decline in Europe, the Americas, and Northeast Asia. Thus by 2020 global production of polyacrylonitrile fibers is expected to be similar to the present level though the regional balance will have changed in favor of Asia.

Output of polyacrylonitrile fibers in China has grown by around 4%/a during the past 10 years, such that since 2003 it has been the largest polyacrylonitrile fiber producing region in the world. In 2009, Chinese output accounted for 32% of the world total, a figure that is expected to rise through to 2020. Fastest growth is expected in South and Southeast Asia and the Middle East, where output is forecast to rise by around 2.5%/a.

Demand in China is expected to rise faster than production, thereby ensuring future opportunities for polyacrylonitrile fiber exports. Western Europe is a region that relies heavily on exports, particularly to China, to maintain utilization levels. China continues to be the biggest importer of polyacrylonitrile staple, accounting for almost a quarter of the global total. Compared with the previous year, the volume in 2008 was down by almost 50% following a similar decrease (40%) the year before. Some recovery was evident in 2009. Turkey continues to be the second largest market for exporters, with Indonesia, the USA, and Iran all importing significant volumes. Together, these five countries account for 50% of world trade in 2008.

Trade names and producers of polyacrylonitrile fibers are listed in Table 2. World production of synthetic polyester fibers (yarn and staple) are listed in Table 3.

Table 2. Trade names and Producers of polyacrylic fibers

Trade name	Types	Manufacturer
Acelan	PAN	Tae Kwang Industrial Co./Korea
Aksacryl	PAN	AKSA AS/Turkey
Beslon	PAN	Toho Tenax Co./Japan
Bulana	PAN	Bulana/Bulgaria
Crumeron	PAN	Zoltek Magyar Viscosa RT/Hungary
Dolan	PAN	Dolan GmbH/Germany
Dolanit	PAN	Dolan GmbH/Germany
Dralon	PAN	Dralon GmbH/Germany
Drytex	PAN	Sudamericana de Fibras SA/Peru
Exlan	PAN	Japan Exlan Co./Japan
Fisivon	PAN	FISIPE SA/Portugal
Hanilon	PAN	Hanil Synthetic Fiber Industrial Co./Korea
Jayacrylic	PAN	J.K. Synthetics Ltd./India
Kanecaron	MAC	Kaneka Corp./Japan
Kanekalon	MAC	Kaneka Corp./Japan
Leacril	PAN	Montefibre SpA/Italy
Leacril	PAN	Montefibre Hispania SA/Spain
Mavilon	PAN	Zoltek Magyar Viscosa RT/Hungary
Myoliss	PAN	Montefibre SpA/Italy
Nitron-M	MAC	Polymir/Belarus
Protex	MAC	Kanebo Corp./Japan
Recrylic	PAN	Reliance Industries Ltd./India
Recrylon	PAN	Reliance Industries Ltd./India
Ricem	PAN	Montefibre SpA/Italy
Silpalon	PAN	Mitsubishi Rayon Co./Japan
Tairylan	PAN	Formosa Plastics Corp./Taiwan
Texlan	PAN	Thai Acrylic Fiber Co./Thailand
Toraylon	PAN	Toray Industries, Inc./Japan
Vonnel	PAN	Mitsubishi Rayon Co./Japan
Vonnel	PAN	FISIPE Sarl/Portugal
Yalova	PAN/MAC	Yalova Eliat AS/Turkey

PAN = acrylic fibers
MAC = modacrylic fibers

Table 3. World Production of synthetic polyacrylonitrile fibers

Year	Production, t
1980	2 060 000
1990	2 270 000
1995	2 420 000
2000	2 669 000
2005	2 632 000
2009	2 005 000*

* Staple fibers.

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Polyvinyl Fibers

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ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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1. Poly(Vinyl Chloride) and Poly (Vinylidene Chloride) Fibers

According to standard ISO terminology, the generic name for poly(vinyl chloride) [9002-86-2] (PVC) and poly(vinylidene chloride) [9002-85-1] (PVDC) fiber is *chlorofiber*; this designates products containing at least 50% vinyl chloride or vinylidene chloride units. In the United States, the Textile Fiber Products Identification Act defines any fiber containing at least 85 wt% of vinyl chloride units as *vinyon* and any fiber composed of at least 80 wt% of vinylidene chloride as *saran*.

In terms of comfort, flame retardancy, chemical resistance, and shrinkability, these fibers may be considered specialty items, essentially having the properties of the homopolymer, e.g., chemical composition, low crystallinity, high dipole moment, and low moisture regain. The obstacles to commercial development of these fibers result mainly from the low softening point, which leads to poor dimensional stability at elevated temperature and poor downstream processability compared to other synthetic fibers.

1.1. Fibers from Pure Poly(Vinyl Chloride) Homopolymer

1.1.1. Fibers from Pure Atactic Homopolymer

The poly(vinyl chloride) generally employed for fiber production is simply a variant of the standard polymer used in plastic compounds. Bulk polymerization at 60–70°C is generally preferred because contamination from polymerization additives is low; this results in an atactic polymer with a molecular mass of 70 000–85 000. The melting point of pure homopolymer is close to the decomposition point. Dry or wet spinning from solution is therefore the only industrial route available to produce commercial fibers.

Dry Spinning. To avoid thermal decomposition with dehydrochlorination, the spinning temperature must be kept relatively low; therefore, the boiling point of the solvent also must be low.

Only a few common solvents are suitable for the homopolymer. Blends of equal volumes of

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carbon disulfide and acetone (*bp* 38°C) and benzene and acetone (*bp* 64.5°C) were patented and are used in production [1]. The spinning composition consists of polymer, solvent, and additives. Polymer content varies with the molecular mass of the polymer and ranges from 25 to 30 wt%. The additives have definite functions, e.g., improving heat stability, lightfastness, whiteness, and luster [2]. Certain producers of homopolymer chlorofiber overcome the difficulties in conventional dyeing caused by the low shrinkage temperature of the fiber by adding dye to the spinning dope.

Early swelling of the complex polymer grain and high dope viscosity make dope preparation difficult. The three possible ways to overcome this problem are (1) flash mixing of polymer and solvent with a short residence time in the shearing system [3], (2) premixing the polymer with a nonsolvent [4], and (3) kneading under high shearing force with long residence time.

When the solution is processed at ambient temperature, the microcrystalline regions of the polymer are not dissolved and the solution is colloidal. Dissolution at a temperature >100°C and processing the solution above the boiling point of the solvent result in a more homogeneous solution and a large decrease in viscosity, with concomitant advantages in further processing [5]. After the dope is dissolved, it is filtered in one or two steps.

The solution is heated or cooled to the spinning temperature and extruded through a 1000- to 2000-hole spinneret in a long tube with hot air moving concurrently with the filaments. The emerging filaments are cooled, wetted by an aqueous lubricant, and wound up or collected at 300–700 m/min. The spinning parameters are important because they determine characteristics of the as-spun filament, such as cross-sectional shape and specific surface.

Staple Route. After spinning, the tow is preheated at a temperature (80°C) lower than the glass transition temperature and drawn 400–800% at a temperature (85°C) higher than the glass transition temperature. The drawing medium may be hot water or low-pressure steam.

After drawing, the fiber is thermally unstable and has a strong tendency to return to its original length; the shrinkage and shrinkage stress may be as great as 70% and 0.6 cN/dtex, respectively. For this reason, the tow is annealed under tension in water or steam [6]. The residual shrinkage is removed by relaxing the fiber tension-free at the boil or slightly above.

The next steps in the production of standard fiber are oiling, drying, crimping, and cutting, by conventional technology. Some commercial interest has been shown in high-shrinkage (30–65%) chlorofibers with their attendant high shrinkage stress. Shrinkable fibers are obtained by varying the draw ratio and avoiding the annealing and relaxation steps.

Wet Spinning. At the time of writing (1987) one industrial plant (Kustanai, former States of USSR) used the wet process to produce commercial chlorofiber. Suitable common solvents are *N,N*-dimethylacetamide (DMA) and *N,N*-dimethylformamide (DMF). Special additives are required to limit discoloration of the solution. With these solvents, the rate of coagulation is high and voids appear in the coagulated gel, permanently impairing fiber performance. To exert positive control over the coagulation rate, water is added to the solvent before the solution is prepared; the solvent is then heated to improve solubility [7]. High solvent content (up to 85%) and low temperature (5–15°C) are suitable for the coagulating bath.

After the gel has coagulated, it is drawn at a low draw ratio and then washed on a multiple-stage countercurrent machine to recover the solvent as a concentrated aqueous solution. A second draw of 400–600% is carried out at boiling or intermediate temperature; the tow is then dried under tension. Annealing can be carried out during or after drying. The tow is then relaxed tension-free, oiled, cut into staple, and baled.

In wet processing, obtaining a homogeneous structure and avoiding discoloration and residual solvent are inherently difficult. The properties of the fibers are generally inferior to those produced by the dry process.

1.1.2. Fibers from Blends of Poly(Vinyl Chloride) Homopolymer

To avoid the inherent limitations of homopolymer fibers without loss of specific and

outstanding properties, spinning blends of homopolymer and minor amounts of a polymer with fibrillar structure to act as reinforcement has been proposed. Post-chlorinated PVC (CPVC) or cellulose acetate [8] can be used without modification of the process. Other blends require special processes. Dry-spun fibers, which contain ca. 80–85% PVC homopolymer and 15–20% CPVC, exhibit the structure of a matrix reinforced with fibrils and have greatly improved heat dimensional stability, mechanical properties, and creep [9]. Such fibers are produced on a commercial scale by Rhône-Poulenc. If cellulose acetate or cellulose is used to replace CPVC, the level of heat stability increases [8, 10]. Researchers in the former Soviet Union proposed wet-spinning a blend of homopolymer with 4-phenylbenzimidazoterephthalamide in dimethylacetamide [11]. In all these cases, the PVC homopolymer is the matrix.

A Japanese firm (Kohjin Co.) produces a fiber (Cordelan) in which PVC and PVC–PVA [poly(vinyl alcohol)] graft-polymer particles are dispersed in a PVA matrix. This fiber gains heat dimensional stability, with concomitant reduction in chemical resistance, thermal insulation, and flame retardancy.

1.1.3. Products, Properties, and Uses

Products. Three major grades of products are available: (1) shrinkable products with different levels of shrinkage, (2) stabilized products for tow dyeing for apparel, and (3) highly stabilized products for piece dyeing and home furnishings (matrix-fibrils). Table 19 lists the physical characteristics of these grades. The stabilized grades are available in a wide range of fineness from 2.4 to 15 dtex and of cut lengths required for cotton, woolen, or worsted spinning systems.

Chlorofiber can be spun on cotton, woolen, or worsted systems as 100% highly stabilized fiber or as blends of shrinkable and stabilized fibers. The fibers may be dyed at the boiling temperature or slightly below by use of selected disperse dyes. Only highly stabilized fibers can be yarn- or piece-dyed.

Properties and Related End Uses. The main end uses for chlorofibers are related to comfort, flame retardancy, chemical resistance, and surface processing.

Comfort. Chlorofibers exhibit high thermal and tactile comfort [12, 13]:

- High thermal resistance (0.23–0.25 m^2 K W^{-1} cm^{-1})
- Constant thermal resistance with humidity transfer
- Water transfer
- High rate of evaporation of perspiration
- Feeling of warmth
- No lag time between sweat production and evaporative heat loss

Flame Retardancy. Chlorofibers have a very high level of flame retardancy as shown by the limiting oxygen index (LOI) of 46% at 50°C and 49% at 150°C. They do not ignite and spread flame, nor do they melt and form droplets in contrast to many other synthetic fibers. They may be blended with other flammable, staple fibers, such as wool and polyester, and retain their flame retardancy over a specific range of blend ratios. They can also be blended with thermally resistant fibers, such as aramid and preoxidized acrylic fiber, and exhibit outstanding heat resistance in terms of ignition temperature (640–680°C) and ignition flux (6.4 W/cm^2).

Chemical Resistance. Homopolymer fibers withstand weathering and are resistant to most chemicals with the exception of polar organic compounds (chlorinated hydrocarbons, aromatic hydrocarbons, ketones, and a few others).

Surface Processing. Woven or nonwoven fabrics of chlorofibers may be processed by thermal molding. Under the combined action of temperature and pressure, any shape can be achieved with a woven or knitted fabric composed of chlorofibers. These fibers may be heated and welded by high-frequency heating because of their low dielectric loss factor (0.013 at 50 Hz).

Trade Names. Retractyl-Fivravyl, Thermovyl L9, and ZC, Rhovyl (Tronville-en-Barrois, France); Teviron, Teijin (Iwakuni, Japan); (Kustanai, former USSR); (Canton, Chunking, Foochow, Shanghai, Sengli, and Tientsin, all P. R. China).

1.2. Fibers from Postchlorinated Poly (vinyl chloride) (CPVC)

Poly(vinyl chloride) homopolymer (56.7% Cl) can be postchlorinated to a maximum Cl content of 73.2% by free-radical chlorination. Solubility in common solvents, especially in acetone or blends containing acetone, depends on the chlorine content of different molecular chains and the distribution of blocks of poly(vinyl chloride) and 1,2-dichloroethane in each chain.

The *solution process* is believed to be the most suitable method of obtaining concentrated spinning solutions, with maximum solubility at a Cl content of 63%. Soviet (Chlorin) and German Democratic Republic (Piviacid) fiber producers claimed a solution process using either tetrachloroethane or dichlorobenzene as solvent. The processing steps include solution preparation, chlorination, precipitation of polymer with nonsolvent, polymer washing, and solvent recovery [7].

The *quality specifications* of spinnable polymer are:

Chlorine content	63–65 wt%
Specific viscosity at 0.2% in cyclohexane	0.2
Degree of polymerization	900–1000
Ash content	0.03–0.08 wt%
Iron content	1×10^{-3} wt%

Filament or staple fiber based on CPVC is spun by the dry or wet process in acetone. In wet spinning, the coagulation bath consists of water and a small amount of acetone; the spun gel is drawn 300–700% in one or two steps.

The properties of the filament are as follows:

Linear mass	3.6–4.2–5.6 dtex
Break strength	>1.6 cN/dtex
Break elongation	>40%
Density	1.44 g/cm^3
Shrinkage in boiling water	72%
Limiting oxygen index	51.5%

Fibers of CPVC have properties similar to homofibers, with slightly higher shrinkage and flame retardancy and lower chemical resistance and ease of dehydrochlorination [14].

Some attempts have been made to improve certain limiting characteristics: (1) grafting methyl methacrylate to increase moisture regain, (2) grafting acrylonitrile to improve thermal stability, and (3) blending CPVC with cellulose acetate at a ratio of 85:15 to increase the shrinkage temperature [7].

1.3. Fibers from Vinyl Chloride Copolymers

Copolymers of PVC with a 13–15% vinyl acetate content and a viscosity index of 57–58 exhibit a lower glass transition temperature (73°C) than homopolymers, and the bondability improves at temperatures lower than the melting point.

The process used is *dry spinning*. A solution of copolymer (≤50 wt%) in acetone, containing heat stabilizers and additives, is prepared at ambient temperature, filtered, and extruded at a temperature dependent on the polymer content (50–80°C). A hot aqueous treatment without tension, crimping, or oiling, and low-temperature drying follow if the fiber is to be used in the dry-laid nonwoven process; for the wet-laid nonwoven process, crimping is omitted.

The relevant key *properties* are:

Chlorine content	46%
Break strength	0.6–0.7 cN/dtex
Break elongation	150–200%
Softening point	69°C
mp	155–160°C
Decomposition temperature	230°C
Shrinkage in water	18–28% at 80°C
Shrinkage tension	0.003 cN/dtex
Shrinkage temperature	60°C

Bonding may be carried out between 80 and 150°C or between 150 and 170°C with transformation of the fiber into melt droplets. Thermal bonding is used to produce nonwovens, blended with other natural, regenerated, or synthetic fibers at a ca. 30% maximum content.

1.4. Fibers from Poly(Vinylidene Chloride) and Copolymers [7, 15, 16]

The homopolymer of PVDC has a softening point of 185–200°C. Its two outstanding properties, high crystallinity and insolubility, make it difficult to process. Therefore, to ease

processing conditions, copolymers with small quantities of vinyl chloride are used.

The usual copolymers contain 85–90 wt% vinylidene chloride (saran). Copolymers are processed by melt spinning or extrusion. Because they are heat sensitive and have a limited thermal life at the extrusion temperature, specially designed extruders and alloys are required. Depending on end use, plasticizers, heat and light stabilizers, and colored pigments may be added to the copolymer. Monofilaments or multifilaments are extruded at 160–175°C, quenched in water at 10–15°C with a short distance between the spinneret and the level of the quenching bath, and then drawn 500–600%.

Products, Properties, and Uses. The range of *products* includes monofilaments (70–120 dtex) and multifilaments (10–78 dtex). Typical properties are:

Density	1.65–1.75 g/cm^3
Break strength	1.5–2.0 cN/dtex
Break elongation	15–25%
Initial modulus	6–10 cN/dtex
Moisture regain	>0.1%
Softening point	115–135°C
mp	170–177°C
Shrinkage temperature	70°C
Dielectric constant at 60×10^6 Hz	3–5
Dielectric loss (tan δ)	0.05

Poly(vinylidene) chloride has excellent resistance to acid, alkali (except ammonium hydroxide), and weathering but poor heat resistance. The products cannot be dyed easily; disperse dyes may be used but fastness is poor.

2. Poly(Vinyl Alcohol) Fibers

W. O. Hermann and W. Haenel applied for the first patent on poly(vinyl alcohol) [9002-89-5] (PVA) fiber in 1931. They reported that the fiber could be made from PVA by the well-known wet- and dry-spinning methods, and that the water resistance of the fiber could be improved by physical and chemical aftertreatment. However, they did not investigate further the production of a water-resistant textile fiber because their interest was limited mainly to the solubility of the fiber in water. Water-soluble PVA monofilament, made by dry spinning and called "Synthofil," was manufactured for a short time in Germany.

In 1940, I. Sakurada and his colleagues improved the hot-water resistance of wet-spun PVA fiber by heat-treating it in hot air and acetalizing it with formaldehyde; they developed the technology for production of a water-resistant textile fiber [17].

Wet-spun staple fiber based on this technology was first available commercially in Japan in 1950; the fiber was called "Vinylon." Initially, Vinylon was distinguished from other synthetic fibers by its hydrophilic properties and it was marketed as a substitute for cotton in both clothing and industrial fibers. Improved production technology led to remarkable improvement in the mechanical properties of the fiber. In 1959, high-tenacity filament produced by dry spinning, and later by wet spinning, became available. The use of Vinylon has become almost entirely industrial. In addition to the water-resistant fiber, a water-sensitive variety has been produced for water-soluble fiber and binder fiber for making paper.

The staple fiber has been also produced commercially in the Democratic People's Republic of Korea since 1961 and the People's Republic of China since 1965.

2.1. Physical and Chemical Properties

The mechanical properties of commercial PVA fibers (Vinylon) produced in Japan are shown in Table 2 [18]. The tenacity and modulus are the highest among commercial general-purpose synthetic fibers. Fiber having a tenacity of 12 cN/dtex and a modulus of 274 cN/dtex has been produced for cement reinforcement. Resistance to abrasion and fatigue is also excellent. The fiber absorbs slightly more water than polyamide fiber; and its mechanical properties in the wet state are somewhat lower. Formalization is effective in improving water resistance of the fiber but may lower the mechanical properties. The elastic recovery is slightly lower than that of acrylic fiber but better than cotton or rayon. Acetalization with benzaldehyde is an effective technique for improving the elastic recovery of PVA fibers used in clothing. The resistance of PVA fiber to various chemicals is generally superior to that of polyamide and polyester

fibers. In particular, its excellent alkali resistance is important in the reinforcement of cement products [19]. Because of its high polarity, PVA fiber adheres well to matrix materials in fiber-reinforced composites for resin, rubber, and cement. Its weather resistance is the highest of the various synthetic fibers.

The fiber is softened by heating above 230–240°C, but it has no definite melting point. Commercial fibers with sufficient hot-water resistance, and water-soluble fibers that dissolve in 20–90°C water, are produced by applying the appropriate heat or acetalization treatments. For use in wearing apparel, the formalized staple fiber, mainly blended with cotton, is dyed with direct, vat, sulfur, or metallized dyes.

2.2. Poly(Vinyl Alcohol) for Fiber

Poly(vinyl alcohol) for fiber is produced by polymerization of vinyl acetate in methanol and subsequent alkaline hydrolysis of poly (vinyl acetate). The material must have a degree of polymerization of 1200–2500 and a narrow molecular mass distribution. These properties are attained by adjusting polymerization conditions, and especially by conducting the polymerization at a lower temperature and keeping the conversion of vinyl acetate in methanol below 70%.

For the production of industrial fiber, PVA with a degree of polymerization of ca. 1700 is generally used. The amount of residual acetyl groups in PVA should be <0.1 mol% for heat treatment to produce a sufficiently water-resistant fiber.

2.2.1. Wet Spinning

Sodium Sulfate Coagulation Bath Method. Staple fiber and tow are produced by wet spinning. In ordinary wet spinning, PVA is dissolved in water to a concentration of 14–16% by heating. After filtration and deaeration, the spinning solution is kept above 70°C to avoid gelation. It is extruded through spinnerets into a coagulation bath containing a saturated solution of sodium sulfate at 40–50°C. The coagulation speed is much slower than that of viscose, and a longer residence time in the bath is necessary. For the coagulation operation to run smoothly, and to minimize floor space requirements, a vertical spinning machine is preferred [20]. The spun fiber tow is usually drawn while passing through a second hot coagulation bath and then dried.

The wet-spun and dried fiber is soluble in hot water. It is further drawn and heat-treated in hot air or by hot rollers at 210–240°C. The temperature of the heat-treatment process must be higher than that of the hot drawing process. In heat treatment, a small amount of shrinkage is usually allowed in order to stabilize fiber structure. This treatment orients and crystallizes the polymer chains in the fiber, reducing the fiber solubility in hot water.

The heat-treated fiber is further acetalized in an aqueous solution containing 1–5% formaldehyde, 10 –20% sulfuric acid, and 5–20% sodium sulfate at 50–80°C for 10–60 min to reach a degree of formalization of 25–35 mol%. Acetalization is affected not only by reaction conditions but also by conditions of the drawing and heat-treatment processes applied to the fiber. Acetalization greatly improves the boiling-water resistance of the fiber and also changes its mechanical and chemical properties to some extent.

In the production of staple fiber, the heat-treated tow is usually crimped mechanically and cut, and the cut fiber is formalized. For industrial application, the formalized tow is subjected directly to a stretch-break spinning system (Perlock or Converter system) to convert it to spun yarn. This yields spun yarn with high tenacity and high toughness.

Short-cut fiber, destined to be water-swellable binder fiber or water-resistant substrate fiber for making paper, is produced by cutting wet-spun and dried tow, or tow that has been heat-treated and sometimes formalized, to the proper length of 3–12 mm.

Alkaline Coagulation Bath Method. Fiber that has been wet-spun in a sodium sulfate coagulation bath has a cocoon-shaped cross section and skin–core of inhomogeneous structure because coagulation proceeds with rapid dehydration from the outside of the extruded jet of spinning dope. This makes it difficult to obtain a clear fiber with high tensile strength.

When PVA dope is spun into an aqueous solution of concentrated alkali, fiber with a round cross section and a homogeneous,

compact structure can be obtained [21]. The fiber is transparent and can be highly drawn to give improved tensile strength and modulus, and better water resistance. In this case, the spinning dope extruded in the coagulation bath is gelated instantaneously by contact with the alkaline coagulant, so dehydration proceeds homogeneously. This wet-spinning method is used in Japan. In commercial practice, the aqueous coagulation bath contains sodium hydroxide at a concentration >200 g/L and at a temperature of 40–50°C.

The alkaline coagulation method was modified to give more highly drawn fiber with a higher modulus by using aqueous acidic spinning dope containing a small amount of boric acid [22]. Because of the presence of boron, cross-linking appears to occur between the polymer chains of PVA during fiber formation. This suppresses entangling of the polymer chains and makes coagulation more homogeneous.

The spinning dope, containing boric acid of 0.5–2.0 wt% (relative to PVA) at pH 3–5.5, is spun into an aqueous alkaline coagulation bath containing 20–100 g/L of sodium hydroxide and 100–300 g/L of sodium sulfate at pH 13.5–14.0. After removal from the coagulation bath, the spun fibers are treated with acid, washed with water, dried, and drawn to a draw ratio >10 to give high tenacity (>9 cN/dtex) and high modulus (>177 cN/dtex).

This technology was developed initially for production of high-tenacity, high-modulus filament yarn for use in belt cord for radial tires. The yarn is modified further to produce high-modulus fiber, which can be substituted for asbestos in cement reinforcement; this fiber has a tenacity of 12 cN/dtex and a modulus of 274 cN/dtex [23].

Wet Spinning with Organic Solvent. Poly (vinyl alcohol) has a high crystalline modulus comparable to that of polyethylene. This high modulus has not been exploited extensively to date in the preparation of fiber. Various investigations have been carried out into the preparation of PVA fiber with a much higher modulus. In many cases, this has involved modified wet-spinning methods that use organic solvents.

When a hot, dilute solution of PVA in polyol is cooled slowly, highly crystallized PVA is deposited [24]. This phenomenon has been connected with gel-spinning–ultrahigh-drawing procedures. When the gel fiber from a solution of PVA in glycerin, having an ultra-high degree of polymerization of 38 000, was hot-drawn at high temperature, the resulting fiber had a tenacity of 17 cN/dtex and a modulus of 555 cN/dtex [25].

2.2.2. Dry Spinning

Dry spinning of PVA is used in the production of filament yarns. The two classifications of dry spinning are low-draft spinning [26] and high-draft spinning [27].

Low-Draft Spinning. Aqueous spinning dope, which has a concentration of 41–45% and an extremely high viscosity, is used in low-draft spinning. It is prepared by dissolving PVA granules, conditioned with water, by heating them in an extruder under pressure.

The high-viscosity spinning dope at a temperature of 130–160°C, is spun in air at ca. 50°C. The cooled and solidified filament is wound in a low-draft ratio of 0.3–1.0 based on the extrusion rate of the spinning dope from the spinneret (i.e., draft ratio = winding rate/extrusion rate), and gradually dried while the drying temperature is raised. The dried filaments have a circular cross section, a homogeneous structure, and low strain; they can be drawn to the highest draw ratio and heat-treated near the melting point. The resulting filament has adequate hot-water resistance and is used commercially without formalization.

This method is suitable for producing heavier filament for industrial applications. It was originally developed for the production of heavier monofilaments of 110–1100 dtex. It is now also applied to the production of multifilaments, such as 1330 dtex/200 filaments.

High-Draft Spinning. In high-draft spinning, aqueous spinning dope containing PVA at a concentration of 28–41% is spun at 90–95°C into a spinning tube consisting of a drafting zone at 30–80°C and 55–95% R.H., and a drying zone at >80°C and <50% R.H. While passing through the spinning tube, the filament is highly drafted, dried, and taken off at a winding speed of 200–500 m/min. The dried filaments are hot-drawn and heat-treated, and sometimes further acetalized.

This method can give finer filaments (<5 dtex) for textile applications. Some filament for apparel, made from a mixture of PVA and aminoacetalized PVA is produced commercially and can be dyed with acid dyes. This method is now used primarily to produce water-soluble filament. Filament soluble in water at 20–90°C is produced commercially by using PVA with low degrees of polymerization and saponification, and by adjusting heat-treatment conditions [28].

2.2.3. Mixed Spinning

The technology for spinning bicomponent fiber from PVA and PVC in an emulsion was developed in 1961 [29]. Vinyl chloride is emulsion-polymerized in an aqueous solution of PVA, and the emulsion is mixed with PVA to give a spinning dope containing PVC and PVA in ca. 1 : 1 mass ratio. The fiber is produced in essentially the same way as regular PVA fiber, by using the sodium sulfate coagulation bath method. The fiber is characterized by its flame retardancy and is produced commercially in Japan under the name Polychlal.

2.3. Uses

In Japan, about 90% of Vinylon fiber production, ca. 30 000 t/a, is consumed in industrial applications that require such advantages as high tenacity, excellent weather resistance, and effective reinforcing effect in matrices. The main industrial uses are fishing nets, ropes, belts, canvasses, and sewing threads. Perlock-type spun yarns from 100% Vinylon tows and filament yarns are used predominantly. The water-soluble filaments are used to produce chemical lace fabrics.

Table 1. Trade names and producers of polyvinyl fibers

Trade name	Type*	Producer
Clevyl	CLF	Rhovyl SA/France
Envilon	CLF	Denki Kagaku KK/Japan
Fibravyl	CLF	Rhovyl SA/France
Krehalon	PVDC	Kureha Gosen Co./Japan
Kugafil	PVDC	Fuagafil-saran GmbH/Germany
Kuralon	PVAL	Kuraray Co./Japan
Mewlon	PVAL	Unitika Ltd./Japan
Niti-Vilon	PVAL	Nitivy Co./Japan
Quing Wei	PVAL	Ankui Wanwei/China
Retractyl	CLF	Rhovyl SA/France
Rhovyl	CLF	Rhovyl SA/France
Saran	PVDC	Fugafil-saran GmbH/Germany
Shuang Lun	PVAL	Fujian Textil & Chemical Fibre/China
Solvron	PVAL	Nitivy Co./Japan
Teviron	CLF	Teijin Ltd./Japan
Thermovyl	CLF	Rhovyl SA/France
Toykolon	CLF	Denki Kagaku KK/Japan
Viclon	CLF	Kureha Gosen Co./Japan
Vilon	PVAL	Nitivy Co./Japan

* PVAL = poly(vinyl alcohol), CLF = chlorofibers = chlorinated polyvinyl fibers, PVC = poly(vinyl chloride), PVDC = poly(vinylidene chloride).

Table 2. Mechanical properties of Vinylon fibers [18]

	Staple and tow			Filament
Property	Regular tenacity	High tenacity	Regular tenacity	High tenacity
Tenacity, cN/dtex				
Standard	3.5–5.7	6.0–9.3	2.6–3.5	5.3–10.6
Wet	2.8–4.6	4.7–7.9	1.9–2.8	4.4–9.3
Wet–standard ratio,%	72–85	78–85	70–80	75–90
Loop tenacity, cN/dtex	2.8–4.6	4.4–5.1	4.0–5.3	6.2–11.5
Knot tenacity, cN/dtex	2.1–3.5	4.0–4.6	1.9–2.6	2.4–4.4
Elongation,%				
Standard	12–26	9–17	17–22	6–22
Wet	12–26	9–17	17–25	8–26
Young's modulus, cN/dtex	22–62	62–221	53–79	62–221
Resilience at 3% elongation,%	70–85	72–85	70–90	70–90
Relative density	1.26–1.30	1.26–1.30	1.26–1.30	1.26–1.30
Commercial regain,%	5.0	5.0	5.0	5.0
Water absorbency,%				
20°C, 20% R.H.	1.2–1.8	1.0–1.5	1.2–1.8	1.0–1.5
20°C, 65% R.H.	4.5–5.0	3.5–4.5	3.5–4.5	2.5–4.5
20°C, 95% R.H.	10.0–12.0	8.0–10.0	10.0–12.0	8.0–10.0

The development of special grades has increased the demand for Vinylon remarkably. The water-swellable, short-cut fibers are popular as binders in the production of paper and wet-laid nonwoven fabrics. Another short-cut fiber, modified to have the highest tenacity and modulus as well as a special surface structure that enhances its adhesion to matrices, is used as a substitute for asbestos to reinforce cement products. These special grades are exported to the world market.

Only 10% of Vinylon production is used domestically in Japan for apparel, mainly by blending Vinylon with cotton and other fibers. The main apparel application is work clothing that requires durability and chemical resistance.

In Korea and China, significant quantities of PVA fiber are blended with cotton and used for apparel. In these countries too, fiber applications in the future will shift gradually to industrial uses.

2.4. Trade Names and Producers

Trade names and producers of polyvinyl fibers are listed in Table 1.

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Polytetrafluoroethylene Fibers

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Polymerization technology for polytetrafluoroethylene [9002-84-0] (PTFE) has been known since 1941 and has become well established, leading to utilization of the polymer not only as a plastic but also in fiber form [1]. This is undoubtedly because it combines interesting chemical (inertness) and physical (low friction, temperature resistance, and triboelectric characteristics) properties.

Tetrafluoroethylene is polymerized under pressure in the presence of persulfate or peroxide in water; oxygen is excluded. The reaction is exothermic and increases in velocity with increased pressure. The viscosity of the polymer, as well as its molecular mass cannot be measured readily; however, indications are that the polymer chain is linear. At the normal polymerization level, molecular masses are estimated to be between a few hundred thousand and several million.

1. Physical and Chemical Properties

Some of the physical properties of polytetrafluoroethylene are as follows:

mp	327°C
Glass transition temperature	ca. 120°C
ϱ	2.1 g/cm^3
Melt viscosity (380°C)	10 GPa

These fibers are similar to the polymer (i.e., highly crystalline 93–98%) and, because of the high energy of the C-F bond, display appreciable resistance to heat and chemicals. As a result, the polymer is difficult to burn. The fibers also are distinctive because of their good light and weathering durability, and their utility at temperatures up to 290°C. Phase changes that occur below 30°C are responsible for the cold flow characteristics of the material, although the fibers are reported to be more dimensionally stable than bulk polymer because of their molecular orientation. Decomposition products are generated above 290°C at a rate of 0.0002%/h. Copolymers, containing minor amounts of other fluorinated monomers, are also available. These are melt-extrudable but, because of their high melt viscosities, only into monofils of =100 dtex. A 50–50 copolymer with ethylene (Tefzel, Du Pont) has a lower melt viscosity and can be extruded at commercially attractive speeds; however, its temperature –chemical characteristics are altered by the presence of the nonfluorinated comonomer.

2. Production

Polytetrafluoroethylene can be sintered above its melting point into a tough, viscous melt. However, melt spinning is not feasible with the homopolymer because the temperature required to overcome the viscosity leads to polymer degradation. Because economically attractive solvents for the polymer have not been found (a few fluorinated hydrocarbons dissolve several percent of polymer above 300°C), either paste extrusion below the melting point of the polymer or dispersion spinning to form fibers is used. To promote agglomeration during extrusion of plasticized (with 20 wt% kerosene) homopolymer, extrusion is done under conditions favorable to production of

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particulates in ribbon form, so that at least 30% have a width of 0.1 nm, an aspect ratio of at least 5:1, and a cross section of <0.001 nm^2. Sintering followed by drawing and heat-setting results in solid or expanded films (depending on process conditions), which are then split into filaments of ca. $\geq$100 dtex.

An alternate process is used to produce finer filaments. A 60% solid dispersion of polytetrafluoroethylene polymer, stabilized with aryl or alkyl polyglycol ethers, is blended with viscose solution (5%). The latter acts as a matrix during early phases of the process. The mixture is filtered and then extruded at room temperature through a multihole spinneret (hole diameter 0.15 mm) into a coagulating bath containing 6% sulfuric acid, 16% sodium sulfate, and 0.3% zinc sulfate. The spinning velocity is about 12 m/min.

After coagulation, the yarn is washed with water at 90°C, dried at 190°C, and then the temperature raised to 340–360°C, the temperature at which polymer particles are sintered and the viscose residue degrades and is partially burned. After a brief contact time at 360–390°C, the yarn is stretched four to eight times its original length.

The resultant continuous-filament yarn has a tenacity of 1.8 cN/dtex and an elongation of 20–30%. The filament mass is 6 dtex. The fibers are brown and can be bleached in boiling sulfuric acid containing nitric acid or by exposure for several days in an air oven. The latter must be done cautiously by raising the temperature stepwise to 350°C, to avoid exotherms because of the sudden oxidation of the viscose residues.

3. Uses

Polytetrafluoroethylene fibers are utilized in woven and nonwoven forms as filter media for aggressive liquids and gases (i.e., strong acids, bases, and oxidizing agents), including air pollution control fabrics. Fibers are also used in gaskets and pump seals because of their chemical resistance and low-friction characteristics. In electrical systems, they are utilized as insulators for wires and components, and as cleaners–wipers in xerographic devices, where their high-temperature and triboelectric characteristics are important. Because of their great chemical stability, these fibers are used as the binder component in asbestos chlor-alkali cell diaphragms. The low-friction characteristics and high length–diameter ratio of the fibers are important in their use as solid lubricants in engineering plastics. Monofils have found application in demisters in the production of mineral acids.

In addition, dispersion of fibers on woven or nonwoven substrates imparts chemical stability to the surface and results in layered composites with excellent dielectric properties and corrosion resistance for utilization in xerography.

Trade names and producers of polytetrafluoroethylene fibers are listed in Table 1.

Table 1. Trade names and producers of polytetrafluoroethylene fibers

Trade name	Type	Producer
Gore	PTFE	Gore & Ass. GmbH/Germany
Lenzing Profilen	PTFE	Lenzing Plastics GmbH/Austria
Lenzing PTFE	PTFE	Lenzing Plastics GmbH/Austria
Teflon	PTFE	Toray Fluorofibers (America) Inc./USA
Tefzel	PTFE	Albany International, Inc./USA

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High-Performance Fibers

Vlodek Gabara, Retired from E.I. Du Pont de Nemours and Company, Richmond, Va., USA

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1. Introduction

1.1. Definition and Classification

Although a strict definition of high-performance fibers does not exist, the term generally denotes fibers that can perform under severe conditions of temperature, chemical attack, mechanical stress as well as flame or offer an unusual functionality e.g., conductivity or magnetic properties. It commonly refers to fibers with some characteristics that differentiate them from commodity fibers such as nylon, polyester, and acrylic fibers. Synonyms are advanced fibers, specialty fibers and, in some cases, high-functional fibers. High-performance fibers can be classified broadly into three categories according to their unique characteristics:

1. Heat-resistant fibers
2. High-strength and high-modulus fibers
3. Other specialty fibers

The unique characteristics of the materials are closely linked with their composition. Thus, it is expected that fibers from ceramic materials have outstanding thermal and compressive properties; many metallic fibers are conductive while unique structure of carbon fiber offers an excellent combination of compressive and tensile properties. This article focuses on how to derive these unique characteristics using organic polymers (both aromatic and aliphatic) based on chemistry of carbon and thus in general less thermally stable. Information on inorganic fibers like carbon, alumina, and boron, can be found in (→ Fibers, 11. Inorganic Fibers; → Fibers, 13. Ceramic Fibers; → Fibers, 15. Carbon Fibers). Testing methods are described

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in (→ Fibers 16, Testing and Analysis) while some uses of high performance fibers are discussed in (→ Composite Materials).

Organic High-performance fibers can be also classified on the basis of the processes that are used in their production. Obviously the unusual characteristics of these fibers makes the processing conditions very demanding. Most of them do not melt and thus have to be shaped by spinning from solution (*solution spinning*). Solution can be spun into a hot gas to evaporate some of the solvent before coagulation (*dry spinning*) or directly into a coagulating liquid (*wet spinning*). A few examples of polymers which do melt can be spun in that form at very high temperature (*melt spinning*) (→ Fibers, 3. General Production Technology).

As described in greater detail in this article, the commercial examples of wholly aromatic polymers include polyamides, polyesters, and polyketones. They can be classified as *meta*- or *para*-oriented, depending on their chemical structure. Fibers from *meta*-oriented polymers are useful as heat-resistant fibers while *para*-oriented polymers are useful not only as heat-resistant fibers, but also as high-strength (HS) and high-modulus (HM) fibers.

1.2. Historical Overview

In the late 1940s, DuPont defined a broad direction for its future research. Substitution of existing materials as an organizing principle led to the search for fibers with high temperature resistance, high strength, high elasticity, etc. In the area of high-performance fibers, *meta*-oriented wholly aromatic polyamide [poly(*m*-phenyleneisophthalamide) – PMIA] was the first example developed in the 1950s. The commercial version of the product was called Nomex. Continuing development in understanding factors that govern high-temperature resistance of polymer shifted the focus on polymers with *para* orientation. This lead to the development of poly(phenyleneterephthalamide) (PPTA) which when properly shaped into fiber (Section 3.1 para-Oriented Aromatic Polyamide Fibers) exhibited not only the expected high temperature performance but also very unique high strength and stiffness. In 1972, the commercial version of this fiber was introduced as Kevlar.

The pioneering nature of this work not only lead to the development of useful commercial products but provided also fundamental underpinning to a development of advanced fibers based on different chemical structure and through very different shaping processes. More than 50 years of research in this field identified a large number of compositions. More than 100 compositions of polymers belonging to this class of materials were already identified by 1989 [1], and the number has increased significantly since then. Most of them were based on aromatic polyamides but other chemistries, such as aromatic polyesters, aromatic polyketones and aromatic polyethers were also investigated and some are being produced on a commercial scale albeit significantly smaller than polyamides. The fundamental understanding of structural requirements for very high strength and stiffness developed during work on Kevlar led to the development of very high strength and stiffness fibers based on chemistry as different from *p*-aramids as aliphatic polyethylene (1980s).

Some of these developments are described below, but it seems useful to stress the rapid development in the field, which allowed to approach in a macroscopic form and on a commercial scale, fiber properties of the same order of magnitude as those of the chemical bonds in just 25 years.

2. Heat Resistant Fibers

Early research on resistance of organic polymers to high temperatures focused on their thermal degradation [2, 3] which was linked with the strength of chemical bonds, especially those in the main chain. The bond dissociation energies for aromatic or heterocyclic compounds are higher than those for aliphatic ones. This suggests that aromatic polymers possess better thermal stability than aliphatic polymers (see Table 1). Thus DuPont's early research on heat resistant fibers was focused on aromatic polymers.

The use of fibers under high temperature brings into focus not only polymer decomposition, but also the retention of physical properties under these conditions. Fundamental understanding at the time led scientists to

Table 1. Bond dissociation energies

Bond	Bond dissociation energies, kJ/mol	
	Aromatic or heterocyclic	Aliphatic
C–C	410	347
C–H	427	406
C–O	448	389
C–N	460	343

concentrate on compositions with high glass transition temperature (T_g) and high melting point (T_m), which in turn lead to compositions with relatively high chain rigidity and strong interchain interactions due to dipolar forces or hydrogen bonding. Thus it is not surprising that the first commercial products coming from DuPont (late 1950s and early 1960s) were aromatic polyamides [4–6]. They are still the largest volume commercial products serving thermal and flame protection applications.

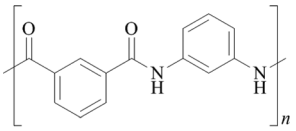
Other compositions that found applications in this area include aromatic polymers with different groups linking the rings, such as polyoxadiazole (POD), polyimide (PI), poly(phenylene sulfide) (PPS), and polyetheretherketone (PEEK).

Continuing research in the area of aromatic polymers led to the development of aromatic polyesters while further search for very rigid polymers led to polyazole fibers. The latter, while possessing high temperature properties, were designed primarily for high strength and high stiffness applications and are discussed in Section 3.2 Polyazole Fibers and Section 3.3 Fibers from Thermotropic Polymers.

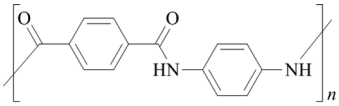
2.1. *meta*-Oriented Aromatic Polyamide Fibers

The unique characteristics of fibers based on aromatic polyamides, which differ significantly from the class of fibers known as polyamides (see → Fibers, 4. Polyamide Fibers), led the US Federal Trade Commission to define the term *aramid* for fibers based on aromatic polyamides in which at least 85% of the amide linkages are attached directly to two aromatic rings. A very detailed description of preparation, properties, and applications of aramids is beyond the scope of this article but is provided in [7].

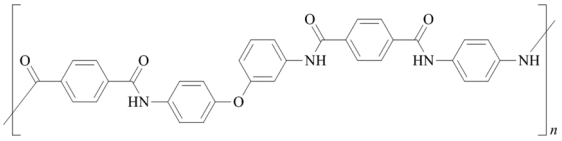
In spite of the very large amount of work and exploration of countless aramid compositions only three of them reached commercial significance. Poly(*m*-phenyleneisophthalamide) (PMIA) [24938-60-1] is the basis for most of today's commercial aromatic polyamide fibers used in thermal and flame protection. Poly(*p*-phenyleneterephthalamide) (PPTA, **2**) [24938-64-5] and copoly(*p*-phenylene/3,4-diphenyl ether terephthalamide) (POP, **3**) are most often used in applications requiring high strength and stiffness. The fundamentals of their preparation and uses are discussed in Section 3.1 para-Oriented Aromatic Polyamide Fibers.



1



2



3

The importance of PMIA in heat and flame protection applications is best illustrated by the number of commercial products introduced so far. The unique properties of aromatic polyamides result also in unique difficulties in their synthesis and processing. Technological difficulties lead frequently to subpar fiber quality or too high manufacturing costs and resulted in abandoning production by some of the producers. The trade names and producers are listed below.

Trade name of PMIA products	Producers
Nomex	DuPont
Tejinconex	Teijin
Newstat	Yantai
Chinfunex	Charming
X-Fiper	SRO
The following products are no longer produced:	
Fenilon	Kazakhstan
Apyeil	Unitika
KM-21	Mitsui-Toatsu

Potential solutions to these difficulties in all phases of the manufacturing process are illustrated below.

2.1.1. Solution Polymerization

A typical synthesis of aliphatic polyamides by a reaction of diamines with diacid in a melt and removal of water to shift the equilibrium of the reaction towards polymer formation (see → Fibers, 4. Polyamide Fibers) is not applicable to aromatic polyamides. Their very high glass transition (275°C for PMIA) and melting temperature (435°C for PMIA), combined with proximity to the decomposition temperature (450°C for PMIA) [8], make polymerization in melt impossible. The lower reactivity of aromatic amines requires also change from diacids to their more reactive derivatives. The most commonly used process involves solution polymerization but interfacial polymerization or its modifications have also been used. Acid chlorides are most frequently used as diacid derivatives. Both solution and interfacial polymerizations for polyamides in general have been described and their fundamental characteristics have been analyzed [9]. The solution polymerization process for aromatic polyamides is described in [10].

Synthesis of these polymers is based on the Schotten–Baumann reaction. Several unique characteristics of these reactions necessitated creative engineering solutions to produce polymers with high molecular mass in commercial facilities. The high molecular mass is a prerequisite for good physical properties of fibers. These reactions are extremely fast (50% conversion can be achieved in a matter of milliseconds even at very low temperatures) and highly exothermic. The byproduct of the reaction, hydrochloric acid, blocks unreacted amine groups making them nonreactive thus limiting the conversion and molecular mass, leading to formation of oligomeric species only. Limited solubility represents an additional challenge for solvent selection as well as polymerization conditions.

Traditional acid acceptors can be used to reduce the limiting effect of HCl. The effect of different acid acceptors and criteria for selection has been investigated in great detail [9]. High molecular mass aromatic polyamide can be obtained when using tertiary amines as acid acceptors [11]. A basic solvent can be both an acid acceptor and a solvent. Examples of such solvents include dimethylacetamide [*127-19-5*] (DMA) and *N*-methyl-2-pyrrolidone (NMP) [872-50-4] [12]. However, when a separate acid acceptor is used, its amount has to be close to stoichiometric quantities of HCl generated. This frequently requires large quantities of an additional ingredient in the process which is often undesirable. Thus the use of a basic solvent is usually a better option.

The reaction mechanism and kinetics are complex. Contrary to standard melt polymerization the reaction using diamines and diacid chlorides is irreversible. General theoretical considerations for these type reactions are given in [13] and kinetics for the aramids polymerization process is described in [14]. The reaction is divided into two phases: A free amine phase (less than 50% conversion, Eq. 1), and a hydrochloride phase (above 50%, Eq. 2 and Eq. 3). During the free amine phase the reaction is extremely fast (milliseconds) but as unreacted amine groups are blocked by HCl the rate of reaction is controlled by the rate of exchange of amine hydrochloride end groups with the solvent (sol.), which in this case acts as an acid acceptor.

$$2 - NH_2 + -COCl \rightarrow -NHCO- + -NH_2 \cdot HCl \quad (1)$$

$$-NH_2 \cdot HCl + \text{sol.} \rightleftarrows \text{sol.} \cdot HCl + -NH_2 \quad (2)$$

$$-NH_2 + -COCl \rightarrow -NHCO- + \text{sol.} \cdot HCl \quad (3)$$

This very fast reaction, when combined with high heat of reaction, presents significant technological challenges in designing appropriate approaches to minimize temperature rise

because high temperature can lead to side reactions of highly reactive species, i.e., acid chloride groups and HCl. These side reactions can produce nonreactive end-groups and thus decrease the attainable molecular mass of the polymer. Selection of the solvent is critical for these systems. The solvent has to dissolve the intermediates but also dissolve or at least swell the growing polymer [9]. The solvent acts as a heat sink and thus limits adiabatic temperature rise. It needs to be stable under reaction conditions. Purity of the solvent plays a key role as several impurities can react with highly reactive ends in this polymerization system. The most common impurity is water. The ratio of monomers in this system plays an as import role in defining molecular mass as in traditional melt polymerization processes.

In general, after polymerization, the polymer remains dissolved in the reaction medium, and the solution can be used directly for fiber spinning. While it is not absolutely necessary, in commercial processes HCl produced during polymerization is usually neutralized [5] to prevent excessive corrosion of the equipment. Calcium hydroxide is one of the possible bases used and the formed calcium chloride remains dissolved in the polymer solution. The presence of salts like $CaCl_2$ improves polymer solution stability [15]. Another approach to neutralization involves the use of liquid ammonia and the formed insoluble NH_4Cl is filtered off, producing a solution without or with a low salt concentration [6].

2.1.2. Interfacial Polymerization

Similarly to solution polymerization, interfacial polymerization requires very fast reactions and thus uses the same highly reactive ingredients. Monomers are dissolved in two immiscible liquids, and the solutions are brought into contact. In general, the two layers are mixed vigorously to maximize the contact area. In this process the diamines are dissolved in water whereas diacid chlorides are dissolved in solvents, such as dichloromethane, xylene, or hexane [10, 16, 17]. The reaction occurs close to the interface but in general in the organic layer. Amines are somewhat soluble in the organic solvents used whereas acid chlorides have almost no affinity to the water phase. The reaction of acid chlorides with water has to be significantly slower than that with diamines, and the generated HCl needs to be neutralized to obtain a high molecular mass polymer. In general, an inorganic base (e.g., sodium carbonate) is included as a neutralizing agent in the water phase. Polymerization is carried out at a relatively low temperature since an increase in temperature lowers the molecular mass of the polymer by the increasing rate of side reactions e.g., with water. The molecular mass of the polymer produced via interfacial polymerization is less sensitive to the ratio of monomers than in the solution polymerization because locally their ratio is controlled by diffusion into the reaction zone.

In a modified interfacial polymerization process [18–20], the reaction begins in a homogenous phase with both diacid chlorides and diamine dissolved in tetrahydrofuran (THF). As in other systems, polymerization cannot proceed beyond 50% conversion (no acid acceptor), and it stops at the stage of oligomers. The oligomers are either in solution or in suspension. Addition of a water phase with a dissolved base (e.g., sodium carbonate) allows polymerization to proceed to completion with the polymer precipitating as fine particles, which are washed and dried for further use.

In general, the heterogeneous nature of the interfacial polymerization process results in a polymer with significantly broader molecular mass distribution than the one produced in solution polymerization.

2.1.3. Fiber Formation

Fibers based on aromatic polyamides are spun from solution because their very high melting points are too close to their decomposition temperatures to allow for melt spinning. The limited solubility of these polymers requires highly polar solvents, which are frequently used in conjunction with salts [15]. Two fiber spinning processes are used to commercially produce these fibers, i.e., dry spinning and wet spinning. Both of these processes include extrusion of a viscous polymer solution through a spinneret and coagulation (precipitation of the polymer) through contact with a nonsolvent. The main difference between the two is that in dry spinning a fraction of the solvent is

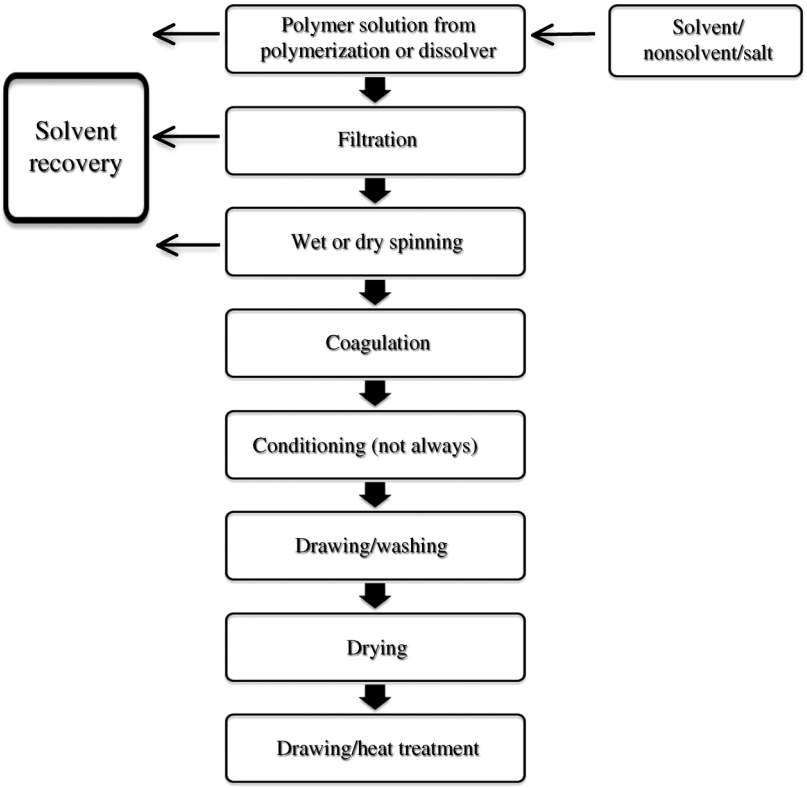


Figure 1. A typical fiber formation process [21].

evaporated in a heated column and thus the coagulation occurs at a higher polymer concentration in the "liquid" filament than in wet spinning where the solution is extruded directly into the nonsolvent. A good example of a fiber formation process is shown in Figure 1 with potential variants of the process.

Dry Spinning. A version of the dry spinning process useful for PMIA solutions has been developed [10, 22]. In this process the polymer solution is extruded at high temperature through a spinneret into a column of hot inert gas. For dry spinning it is advantageous to use a spinning solution containing salts (e.g., $CaCl_2$) to improve solution stability at elevated temperatures [22]. As the fiber moves through the column, the solvent is evaporated. In general, for *m*-aramids solutions, solvent evaporation during spinning is not complete and complete removal is not necessary when the spinning is followed by a wet drawing process. As the solution is extruded into a gas, a low drag environment, the spinning process can be reasonably fast, in the order of a hundred meters per minute.

Wet Spinning. In the wet spinning process, the solution is extruded directly into a coagulating bath. The coagulation process is critical for producing good fiber. During coagulation the polymer solution undergoes spinodal decomposition (separation into polymer rich and polymer poor phases), which, if not controlled well, can lead to a highly voided fiber structure that is unsuitable for the subsequent drawing process. Factors affecting this include solution composition (polymer concentration, presence of salts), coagulation bath composition, and temperature. In general, this process requires that the polymer spinning solution contains little or no salt and high salt concentration is needed in the

coagulation medium [23]. A wet spinning process has been developed that allows the use of a spinning solution with a relatively high salt concentration [21]. As in wet spinning the solution is extruded into a liquid (water solutions), which is a relatively high drag environment; the process has to be slow, in the order of ten meters per minute.

2.1.4. Washing, Drawing, Heat Treatment

To obtain good mechanical properties, fibers spun via either of these processes need to be oriented. Orientation is accomplished in a drawing process in which the spun fiber is extended several times in its original length. The process is carried out above glass transition temperature. If the drawing is to be done in wet form, i.e., in water, the addition of a plasticizer (in general the solvent from which the fiber was spun) is required to lower the glass transition temperature below the boiling point of water. The drawing process is combined with washing of the fiber to remove the residual solvent before drying. As these polymers are very thermally stable, the fiber can be drawn in a dry state as well but at temperatures significantly above T_g. This drawing process may be linked with the heat treatment process above the glass transition temperature if higher crystallinity of the final fiber is desired.

2.1.5. Fiber Properties

PMIA-based fibers can be produced at a substantial level of crystallinity. The unit cell is triclinic with a calculated density of 1.45 g/cm^3 (observed for heat treated fibers is 1.38 g/cm^3) [24]. Both density and crystallinity vary with fiber orientation and heat treatment conditions. Hydrogen bonding and relative chain rigidity are responsible for the high glass transition (275°C) and high melting point of the crystalline phase (435°C) whereas high bond dissociation energy leads to a high decomposition temperature (450°C). This combination of properties results in good dimensional stability (low shrinkage) when exposed to high temperature as well as very good retention of mechanical properties at elevated temperatures. The high degree of aromaticity is responsible for the limiting oxygen index (LOI), which is a measure of flame retardance and represents the percent concentration of oxygen needed for self-supporting combustion. PMIA-based fibers reach a LOI of ~ 30%. However, the aromatic structure is also responsible for UV absorption leading to color change and, at longer exposure, to a decrease of mechanical properties.

Fiber structure is also responsible for the good chemical resistance of these fibers. They are only soluble in very aggressive solvents (e.g., NMP, DMA, DMF, strong acids like H_2SO_4 or HF). The chemistry of the chain (amide groups) is responsible for susceptibility to hydrolytic attack in the presence of acids or bases as well as to oxidation by strong oxidizing agents. Amide groups are also the cause of relatively high water absorption (5–7% depending on the humidity).

Table 2 summarizes fiber properties of some commercial PMIA fibers.

2.1.6. Uses

The unusual properties of these fibers open a very broad range of applications. This breadth of uses is predicated on understanding how these fibers work in final structures and on developing special ways to use them. To maximize the value of these fibers it was necessary to create a special field of research, i.e., application research.

Protection. The best-known application of *m*-aramid fibers is in protective garments designed to protect workers from the hazards of flame and heat. These include industrial workers in the oil industry, electrical workers, and firemen. The

Table 2. Selected properties of commercial PMIA fibers [25, 26]

Property	Nomex 430	Teijinconex std
Density, g/m^3	1.38	1.38
Equilibrium moist content, %	5.2	5.2
Tensile strength, GPa		
at rt*	0.59	0.61–0.68
at 200°C	0.39	0.41
at 250°C	0.32	0.35
Tensile modulus, GPa		
at rt*	11.5	7.9–9.8
at 200°C	9.9	6.1
at 250°C	9.4	4.3
Tensile elongation at rt, %	31	35–45
LOI, %	28	29–32

* rt = room temperature

first two are designed to protect people in case of a rare event whereas the latter is designed to protect people who actually go into a flame environment. Low shrinkage of fabrics is critical in this application. The shrinkage forces are high enough to "break open" a garment when exposed to flame and destroy the protective barrier. While *m*-aramids exhibit low shrinkage under most usage conditions, to meet the requirement of fire-protection it is important to further reduce shrinkage at flame temperatures. This can be accomplished by blending the fibers with *p*-aramid fibers [27]. Conditions of use of these garments are obviously aggressive and thus, in addition to inherent flame retardency, good durability of the fibers is critical.

In addition to the functional requirements of protection, it is important to be able to produce garments in a broad range of colors. Some of the products available on the market can be "piece" dyed (dyeing of the textile fabric), others are based on producer dyed fibers (by including pigments in the spinning solution). The first one offers a broader range of colors while the second one has better light fastness. In this application most of the fibers are used as cut fiber (staple products), which are processed into yarns on equipment used for cotton or wool. Only some use continuous filament yarns, e.g., car racer or pilot suits.

Industrial Applications. In addition to protecting people, these fibers are used in the protection of structures. Aircraft seat covers block fire from spreading to more flammable cushions.

Industrial Materials. The combination of good chemical and thermal resistance opened a broad field of application in hot gas filtration. The durability of these fibers is an additional characteristic governing their selection for bag filters.

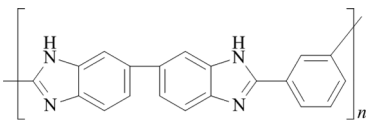
Very good fatigue properties allow the use of the continuous filament yarns as mechanical reinforcement of elastomeric hoses and belts in automotive applications.

A very unique application is in the preparation of aramid papers. In these structures short fibers are combined with an *m*-aramid binder (small high surface particles called "fibrids"). The papers are used as electrical insulation with a constant use temperature of 220°C. More detailed description of their properties and applications can be found in DuPont product literature [28]. The papers are also used in the production of honeycomb structures, which combine high stiffness and low mass with *m*-aramid flame retardant characteristics and thus are ideal for aerospace and aircraft applications [29].

2.2. Fibers from Heterocyclic Polymers

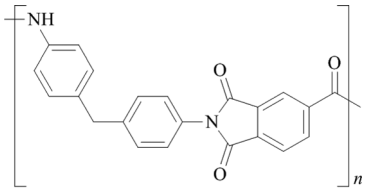
Fibers from heterocyclic polymers are based on different chemistries but share a common characteristic; in spite of a good and at times excellent level of some properties, their applications are limited primarily because of high cost or a very specific deficiency. The group includes polybenzimidazole fiber (PBI, produced by PBI Performance Products Inc.); polyamide-imide fiber Kermel (developed by Rhône-Poulenc and now owned by Kermel); polyimide fiber P84 (produced by Evonik Industries); Arimid, a polyimide fiber (produced by a Russian company that has been shut down); and polyoxadiazoles fibers (Oxalon and Arselon produced in Belarus and Podlon in China).

Polybenzimidazole Fiber (PBI, **4**) [25734-65-0] polymer is produced by reaction of diphenylisophthalate with 3,3′,4,4′ tetraaminobiphenyl. The details of its manufacturing process are given in [30]: Whereas the polymerization is carried out in solid state, the fiber is formed by dry spinning from a DMA solution. The final step of the process involves treatment with sulfuric acid to improve thermal dimensional stability. The fiber was developed in response to the Apollo 1 fire. Today it is used primarily for personal protection in the fire service industry. In comparison to other high temperature resistant fibers PBI is characterized by a high LOI of 41% and a high moisture regain of 15% (at 65% relative humidity) but relatively low strength (tenacity of 2.7 g/d) [31]. PBI is frequently used in blends with other fibers (most often with *m*-aramids or *p*-aramids) at less than 50% to both improve fabric strength and lower its cost.

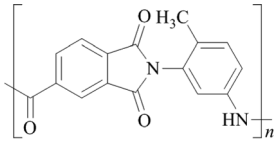


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Polyamide-Imide Fiber. Kermel fiber is currently available in two basic grades: Kermel (**5**) and Kermel Tech (**6**) [32]. Although both are produced by reaction of diisocyanates and diamines and by a similar process (solution polymerization and wet spinning [33]), they differ in the amine used. Kermel is used mainly in protective apparel whereas Kermel Tech is used in industrial applications (hot gas filtration).

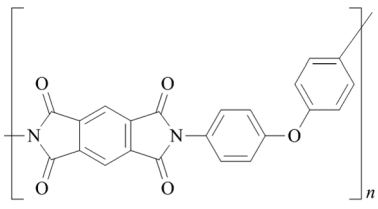


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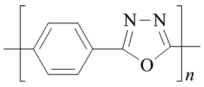
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Polyimide Fiber P84 (**7**) [65328-60-1], developed by Lenzing in Austria, is based on a polyimide copolymer (3,3′,4,4′benzophenone tetracarboxylic dianhydride with 20% of methylphenylenediamine and 80% toluenediamine) [34] and is shaped by dry spinning with DMA as a solvent [35]. Like most polyimides, it has very good high temperature resistance leading to its main application in hot gas filtration. The fiber has a trilobal cross-section which the producers claim is helpful in this application.



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Polyoxadiazoles Fibers (POD, **8**). The literature on POD is very rich, even though the volume of the product in the market place is small. The commercial (actually semi-commercial) products include Oxalon and Arselon from Belarus and Podlon from China. The polymer chemistry goes back to early work at DuPont and later Monsanto. A good summary of reactions used to produce these polymers is given in [36]. The most frequently used process on the commercial scale involves the reaction of hydrazine sulfate with diacids (most often aromatic) in oleum. Oleum acts as a solvent as well as dehydration agent. A critical fact is that the cyclization rate is much faster than the rate of polymerization [37]. Therefore, the yield of cyclization is very high (97–98%) [37]. POD fibers possess good thermal properties but UV stabilization needs to be provided [38]. The relatively low LOI (∼ 21%) of unmodified fibers is a disadvantage. All commercial spinning processes use wet spinning for fiber production. The spinning process as well as fiber morphology and properties are described in [39].

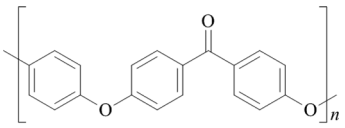


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2.3. Fibers from Melt-Processable Polymers

The performance of melt-processable polymers is less desirable for protective apparel applications than that of aramids or heterocyclic fibers. Melting is not desirable because molten droplets are likely to add to injury severity and lead, in an extreme case, to the elimination of a protective barrier. Most of these fibers are also very difficult to dye which further decreases their utility in this application. This directs their use to industrial application, such as flame barriers and hot gas filtration.

The group includes fibers based on polymers like PEEK (**9**) [31694-16-3] and poly(phenylene sulfide) (PPS) [9016-75-5].



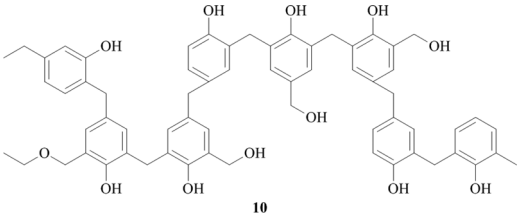
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For both polymers, engineering resins applications are the main market. Use as industrial fibers constitutes only a very small fraction of their production. Vitrex produces PEEK polymer whereas Zyex produces the fiber. PEEK has good thermal properties although a T_g of 143°C and T_m of 334°C are significantly below those of *m*-aramid. High melting temperature and processing of high molecular mass polymer required for fiber applications result in filaments with higher dtex numbers (usually above 3) as thinner fibers are too difficult to produce. This further points toward industrial applications as high filament diameter decreases the comfort of the fabric (higher stiffness). Chemical composition and spinning process are responsible for a very low moisture regain and good chemical stability (oxidative stability may be the exception). The relationship between fiber spinning conditions, structure and properties of these fibers are described in [40]. A higher molecular mass allows for higher maximum draw ratio and thus better mechanical properties [41].

As for PEEK, fiber applications of PPS are only a very small fraction of its uses. Phillips [42] was the original developer of the polymer, which is now also produced by Ticona and Toray. Of these Toray produces also fibers and films. More recently a substantial manufacturing capacity of PPS (both polymer and fiber) has been created in China. In general the polymer is produced by reaction of dichlorobenzene with sodium disulfide in a solvent [43]. The fibers are formed by a melt spinning process (see → Fibers, 3. General Production Technology). The largest application of these fibers is hot gas filtration because of their very good chemical resistance to acids. Again, the weak point is its relatively low resistance to oxidation at high temperature.

2.4. Cross-linked Fibers

In the scope of this article it is not possible to describe all thermally stable fibers. The last group of fibers worth mentioning is based on cross-linked phenol-formaldehyde resin (Kynol) and melamine-formaldehyde resin (Basofil). Kynol (**10**) [9003-55-8] [44] is melt spun as novolak and cross-linked by reaction with formaldehyde.



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Basofil [45] is spun via centrifugal spinning, which produces short fibers of variable diameter and variable length. Basofil is easy to dye while the deep color of Kynol makes dyeing difficult. Both are used in very limited (mostly in personal protection) volumes as they are relatively brittle and weak. As a result to be commercially usable they have to be processed in blends with other fibers.

3. High-Strength and High-Modulus Fibers

Realization that almost perfect orientation and full chain extension of the polymer are critical to approaching theoretical bond strength and stiffness in practical fibers goes as far back as the 1930s [46, 47]. Calculations of modulus based on bond force constants [48] and of strength using the weakest link theory [49] showed values significantly higher than those observed. For example, theoretical modulus of 240 GPa has been calculated for polyethylene whereas the measured modulus is in the range of 1–4 GPa. The issue faced by this field of science was whether one could achieve in a practical environment the level of orientation and chain extension required to obtain these properties.

Theoretical work on solution properties of rigid polymers for relatively low polymer concentration [50] and for a full range of concentrations [51] showed that above a critical concentration the solutions separate into two phases, i.e., anisotropic (locally organized) and isotropic (not organized). The materials where the change from isotropic to anisotropic phase occurs as a result of change of polymer concentration in solution are called lyotropic. In thermotropic materials this change occurs in a melt as a result of change of temperature. The phenomenon is based on packing considerations

for the rigid particles. The effect of polymer concentration and the molecular mass of the polymer on the critical point of phase separation for lyotropic systems was calculated in [51]. In the domains of anisotropic phase the local orientation of chains is very good. This then makes it easier to obtain near perfect global orientation in the fiber.

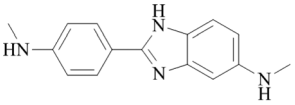
The initial interest in aromatic polyamides was due to the higher bond strength and expected better thermostability. DuPont's success with work on *m*-aramids, culminating in commercial introduction of Nomex fiber, focused further work in this basic area of polymers. The chemistry indicated that movement from *meta*- to *para*-configuration would further improve fiber thermal properties. The science developed during work on *m*-aramids was fully applicable to *p*-aramids, but clearly additional advances were needed to deal with even less tractable polymers. The work on solution polymerization [12] and on polymer solutions [15] was critical for these more difficult to dissolve polymers. While the work began as normative extension of the *m*-aramid effort to improve thermal stability, it led to the unexpected result of producing a fiber now known as Kevlar, with very high strength and stiffness.

This was a clear breakthrough not only because of the utility of these properties, but also because it demonstrated that properties approaching theoretical ones can be achieved. It spawned research on other aramid and nonaramid chemistries yielding not only a family of products with very impressive properties but also a new field in fiber science. Chemistry developments moved towards super rigid molecules of polyazoles whereas processing work led to drawable systems of semirigid polymers. The final step was the development of gel spinning, which allowed transformation of flexible molecules into oriented and chain extended configurations.

3.1. *para*-Oriented Aromatic Polyamide Fibers

Scientific literature contains hundreds of compositions studied but only three have reached commercial reality and only poly(*p*-phenyleneterephthalamide), (PPTA, **2**) has reached a very large scale of operation with more than one producer.

PPTA fibers are based on spinning a lytropic solution while fibers based on polyamides from 2-(4-aminophenyl)-1*H*-benzimidazol-6-amine (DAPBI, **11**) and copoly(*p*-phenylene/3,4'-diphenyletherterephthalamide) (POP, **3**) are based on spinning isotropic solutions followed by fiber drawing to achieve desired orientation. The breakthrough began with KWOLEK spinning an organic solvent solution of poly(1,4-benzamide) which is more tractable than PPTA (compare nylon 6 with nylon 6,6) [52, 53]. A more complex monomer synthesis, the need to block the amine groups before polymerization (usually with HCl), and the need for an additional acid acceptor were the major reasons for higher costs. They became the driver for future transition to PPTA.



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3.1.1. Fibers from Lytropic Solutions

There are several producers offering fibers based on PPTA: The original producer DuPont (Kevlar), Teijin (Twaron; developed by AKZO), and Kolon (Heracron). Several very small producers in China are at early development stages.

Typical polymerization and fiber preparation processes are shown in Figure 2 [54]. In all cases, the process is split between polymerization and fiber formation, because the polymer is not soluble in the polymerization mixture.

Polymerization. The chemistry of the polymerization process of PPTA is the same as for PMIA, but it starts with the *para* monomers. The technological solutions for production of the polymer are significantly different because the polymer is much less tractable. It is not soluble in the reaction mixture. Hence, the best possible solvent is required to obtain high molecular mass polymer. Even with the best solvent, the polymer molecular mass is a result of competition between the rate of

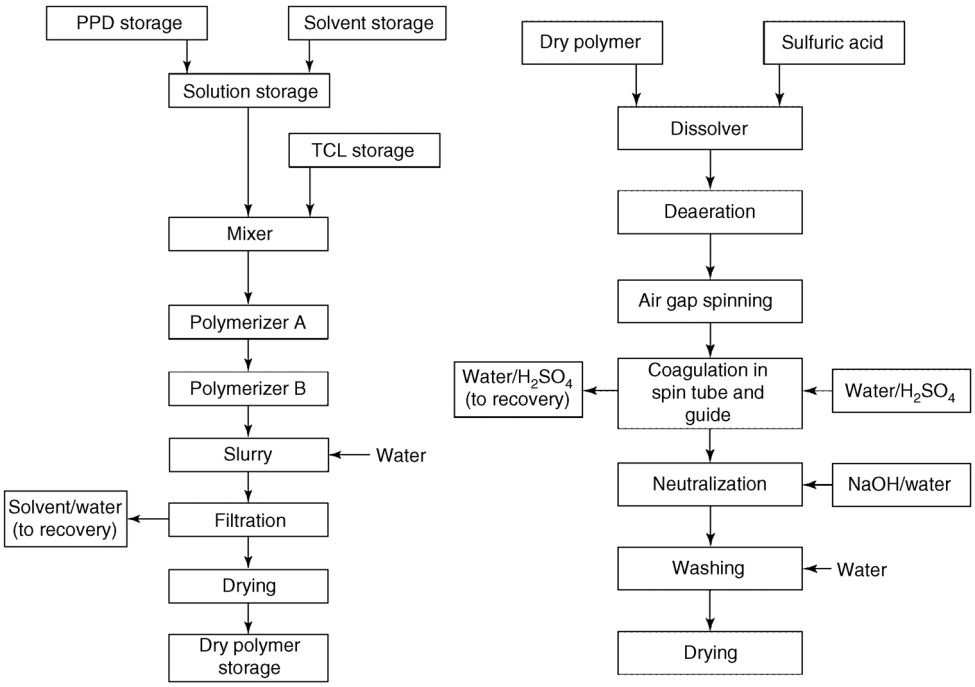


Figure 2. Polymerization (A) and spinning (B) of PPTA fibers [54].

polymerization and the rate of precipitation. Original work used hexamethylphosphoramide (HMPA) as a solvent, which was later abandoned due to toxicity concerns. Different solvent systems have been explored. Most of them are based on using some salts (e.g., $CaCl_2$, LiCl) to improve polymer solubility in amide solvents [15]. DMA was used with LiCl [55] and NMP with $CaCl_2$ [56]. Efforts to accelerate the polymerization reaction focused on the use of acid acceptors (beyond the basic solvents). Their use with DMA as solvent systems was described in [57].

A description of the polymerization process is provided in [58]. The reaction starts in a solution, but in a very short time, in the order of seconds, the materials convert into a friable gel that is broken into particles by mechanical action. This material exhibits flow behavior similar to Bingham type plastics. When the yield stress exceeds a critical value, the material begins to flow, but almost immediately solidifies when sheer stress is removed. Design of the reaction system, which can handle such a material, is not trivial. A twin-screw fully wiped extruder was proposed [58], which allow for continuous polymerization process whereas others described a batch reactor vessel [56, 59].

Solution Preparation and Spinning. The anisotropic nature of PPTA and of poly(1,4-benzamide) solutions was a critical factor in obtaining unique properties of fibers based on these polymers. This is due to the chain rigidity leading to highly extended chain configuration. The conformation of PPTA and poly(1,4-benzamide) chains is nearly as extended as in a crystal with persistence length of 175 and 500 Å, respectively [60–62]. These values are about 25–50% of the chain length of molecular mass of 20 000.

Results of viscosity measurement as a function of concentration of the PPTA polymer with moderate molecular mass in sulfuric acid solution (Fig. 3) [63] are in agreement with those calculated by FLORY [51]. This fundamental characteristic of poly(1,4-benzamide) permitted KWOLEK to spin high strength and high stiffness fibers for the first time. The second breakthrough was BLADES' use of air-gap spinning. The principles of air-gap spinning are shown on Figure 4 [64]. The concentrated spinning

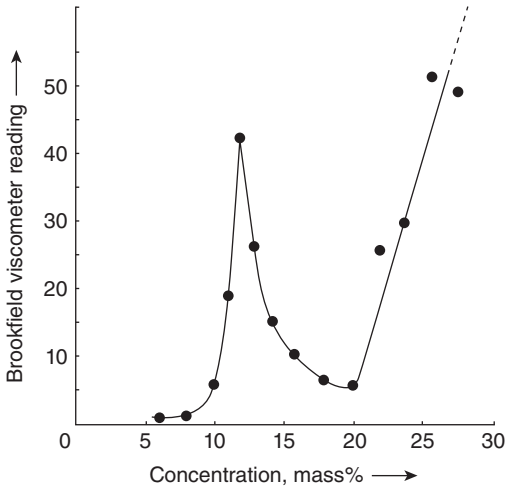


Figure 3. Viscosity versus concentration for PPTA polymers [63].

solution is extruded into a non-coagulating medium (usually air) and then exposed to a coagulating environment (usually water). This allows spinning at very high polymer concentration, which requires higher solution temperature and allows coagulation at a much lower temperature [64]. While wet spinning can be used, the air-gap allows for an orientation via

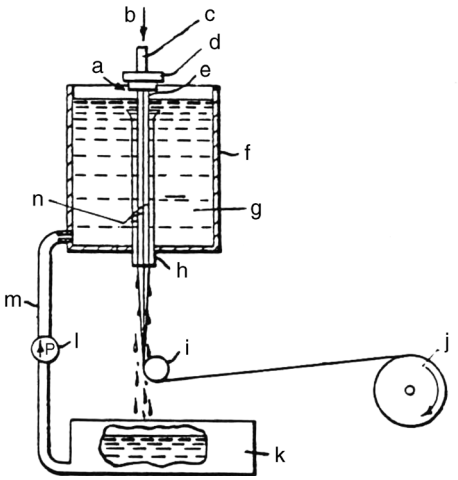


Figure 4. Air-gap spinning of lyotropic solutions [64]
a) Spinneret; b) Spin dope; c) Transfer line; d) Spinning block; e) Air gap; f) Container; g) Coagulating liquid; h) Spin tube; i) Guide; j) Rotating bobbin; k) Container; l) Pump; m) Tube; n) Filaments.

elongational flow as well as permitting higher spinning speeds because of significantly lower drag forces (similar to a difference between dry and wet spinning).

The fibers exhibited high strength (2–4 times that of wet spinning) and stiffness immediately after spinning. Further improvement of fiber modulus can be achieved by heat treatment of the fiber at high tension and high temperature [65]. Modulus of 150 GPa for Kevlar 149 obtained under commercial condition represents 80% of the theoretical value. This is a testimonial of perfection of orientation achieved under large scale production conditions. The principles of air-gap spinning are shown on Figure 4 [64].

3.1.2. Fibers from Isotropic Solutions

The best-known fiber from isotropic solution is Technora (Teijin) [66]. It is a copolymer of 3,4′-diaminodiphenyl ether and *p*-phenylenediamine (reacted with terephthaloyl chloride). Polymerization is carried out in an amide solvent (likely NMP) with $CaCl_2$. The fact that it is a copolymer improves its solubility, and the polymer remains in solution after polymerization. It is spun from the neutralized polymerization mixture. The solution is isotropic. Both wet and air-gap spinning of the fiber is possible [66]. The polymer composition and the essentially noncrystalline character of the polymer, combined with good thermal stability of aromatic material, permit it to be drawn as much as 10 times at a high temperature of the order of 500°C. Under these conditions a very good orientation with very good properties is obtained.

Another example of isotropic spinning is based on polymers and copolymers of 2-(4-aminophenyl)-1*H*-benzimidazol-6-amine (**11**) and terephthaloyl chloride [67]. The technology was developed originally in Russia and several fibers have been described (SVM, Armos, Rusar etc.) but all are at very low volume.

3.1.3. Fiber Structure

Fibers based on PPTA are highly crystalline. In general, this structure is considered as essentially 100% crystalline, with some defects, thus

Table 3. Tensile properties of *p*-aramid fibers

Property	Kevlar 29 [76]	Kevlar 49 [76]	Kevlar AP (K29) [77]	Twaron [78]	Twaron [78] HM	Technora [79]
Tenacity, GPa	3.0	3.0	3.4	2.8	2.8	3.07
Modulus, GPa	70	112	79	80	125	70
Elongation, %	3.6	2.4	-	3.3	2.0	4.4

it is difficult to talk about glass transition for this polymer. Some attempts to measure T_g on materials with relatively low crystallinity yielded values as different as 295°C and 492°C [68, 69]. The melting point of PPTA exceeds its decomposition temperature of ~ 550°C. Commercial fibers are very well oriented, e.g., Kevlar fiber shows orientation angle as measured by WAXD of 12° which decreases to 9° after heat treatment for Kevlar 49 [70]. It has been shown that Kevlar has an unusual radial orientation of hydrogen-bonded sheets (Fig. 5) [71]. The sheets exhibit regular, cooperative missorientation of ±5°, which is retained in Kevlar 49 but is absent in the product with the highest modulus (and thus the highest orientation), Kevlar 149 [72].

Aramid fibers spun from isotropic solutions, such as Technora and Armos, are copolymers and thus noncrystalline. The structure of Technora fiber (initially called HM-50) was studied [73–75]. X-ray results indicate a nematic array of copolymer chains that have completely random monomer sequences and highly extended conformations. The disagreement between predicted and observed peak profiles indicates a nonlinearity of the chain conformation. This is likely to be due to some distortion of the bond and torsion angles required to align the random sequences.

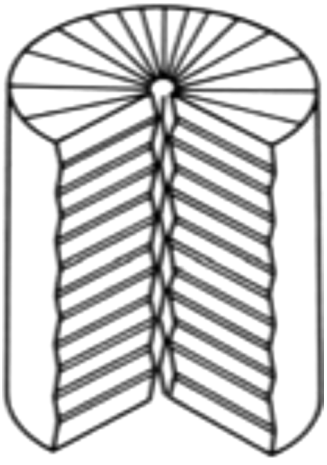


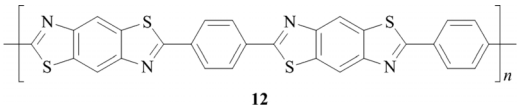
Figure 5. Radially oriented pleated sheets of Kevlar.

Comparison of mechanical properties of these fibers is given in Table 3 while a full discussion of properties and uses are described in Section 3.5 Properties and Uses of High Strength Fibers.

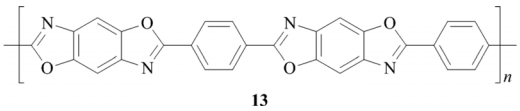
3.2. Polyazole Fibers

Continuing expansion of work on the anisotropic solution led to the synthesis of a group of rigid rod polymers, i.e., polyazoles.

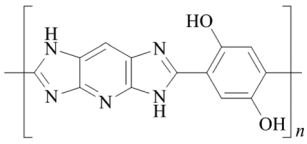
These polymers can be synthesized to a very high molecular mass [80]. Polymers synthesized in polyphosphoric acid remain in solution. The very high rigidity of these polymers and their very high molecular mass result in extremely high viscosity solutions, necessitating air-gap spinning at very high temperature. While early work concentrated on poly(*p*-phenylene benzobisthiazole) (PBZT, **12**) [69794-31-6], progress in obtaining high molecular mass of poly(*p*-phenylene-2,6-benzobisoxazole) (PBO, **13**) [60871-72-9] and its better properties redirected research to this polymer. The work was initially carried out at Dow Chemical and later at Toyobo, which commercialized the fiber under the trademark Zylon. Following a somewhat similar fundamental polymerization path, using again air-gap spinning, M5 fiber (poly(2,6,-diimidazo[4,5-b:4′,5′-e]pyridinylene-1,4,[2,5-dihydroxy]phenylene, **14**) was developed [81]. In 2006, it has been reported that Zylon fiber loses a significant fraction of its strength under atmospheric conditions at elevated temperature and high humidity. The mechanism of this unexpected phenomenon has been proposed [82].



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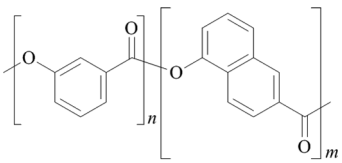
3.2.1. Fiber Structure

The PBO fiber is crystalline, with monoclinic unit cells [83]. The crystallinity of PBO improves with heat treatment, which is also accompanied by a significant improvement in fiber modulus [84]. The M5 fiber with its hydroxyl groups exhibits some unique characteristics. The as spun fiber forms a hydrate with a substantial amount of water being released upon heat treatment of the fiber. It has been proposed that during heat treatment the crystal hydrate transforms into a bidirectional hydrogen-bonded structure [85] (expected by some to improve the compressive properties of the fiber). Their mechanical properties are summarized in Table 4 while the properties and uses are discussed in Section 3.5 Properties and Uses of High Strength Fibers in more detail.

3.3. Fibers from Thermotropic Polymers

Development of liquid crystalline polyesters (LCP) followed the development of aramids. In spite of the substantial amount of work, success in the fiber field was limited. Much more successful was the development of engineering resins for injection molding where excellent flow characteristics of LCPs offer special advantages. Initial work focused on compression moldable poly-*p*-benzoate [88]. Injection molding resins based on LCP were developed soon after [89]. The path from compression molding to injection molding was made possible by improvement of tractability by copolymerization.

To produce fibers further improvements in tractability were necessary. A very large number of publications both in patent and refereed journals evaluated hundreds of compositions [90, 91] but at this point only one found commercial realization (Vectran, **15**). The typical process involves melt spinning of a polymer of relatively low molecular mass. The fiber is oriented, but has low strength because of inadequate molecular mass. To increase the fiber strength, the fiber is subjected to heat treatment at temperatures very close to the melting temperature of the polymer [92] during which a solid phase polymerization increases the molecular mass of the polymer.



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The typical properties of these fibers are given in Table 5.

3.4. High Strength Polyethylene Fibers

High-strength polyethylene (PE) fiber can be obtained via two very different technologies. The first one uses high-molecular-mass polyethylene (HMPE) that is extruded and then

Table 4. Tensile properties of polyazole fibers

Property	Zylon Regular [86]	Zylonhigh mod. [86]	M5 (2001) [87]	M5 estimated [87]
Tenacity, GPa	5.8	5.8	3.96	8.5
Modulus, GPa	180	270	271	300
Elongation, %	3.5	2.5	1.4	2.5

Table 5. Tensile properties of Vectran

Property	Vectran HT [93]
Tenacity, GPa	3.2
Modulus, GPa	75
Elongation, %	3.8

drawn in a solid state. The second one, commonly referred to as gel spinning, uses solution spinning of ultra-high-molecular-mass polyethylene (UHMWPE) and solid-state drawing. The second technology produces significantly stronger and stiffer fiber (about three times) but further developments could change that.

3.4.1. Gel Spinning

Polyethylene has a very low cross-sectional area of its chain and consequently the theoretical modulus and theoretical strength are highest among all organic high performance fibers. It is interesting that the first very high tenacity for polyethylene was reported even before work on Kevlar began. "Multifibrous strands" of polyethylene were developed by flash spinning which, when twisted, had a tenacity exceeding 2 GPa (23 gpd) [94]. Development of high strength polyethylene fiber was based on initial work on crystallization from solution and then spinning of the fiber [95, 96]. This work lead to a conclusion that fiber strength was almost linearly related to drawing stress, and the number of chain entanglements had a larger effect than the number of chain ends. The next step was the development of a gel spinning process which is solution spinning during which the fiber becomes a gel upon cooling [97].

Fundamentally, the technology is aimed at obtaining almost a perfectly oriented and fully extended chain configuration. To accomplish this with a flexible chain like polyethylene one needs to use a very high draw ratio of $\sim 40\times$ or more (semi rigid molecules like Technora are drawn up to 10 times). Thus, the morphology of as-spun fiber has to allow large extension without breaking. This is controlled by the level of entanglements in the fiber. The level of entanglement has to be small enough to allow such a degree of translational chain mobility and be large enough to maintain the integrity of the structure. This is accomplished by spinning solutions with a very low polymer concentration (few percent). In turn, for the solution to be spinnable at this low polymer content, the polymer has to be of a very high molecular mass (order of millions). Therefore the fiber is frequently referred to as based on UHMWPE (ultrahigh-molecular-mass polyethylene). This very high molecular mass also reduces structure defects by lowering the number of chain ends. The additional requirement is that the polymer has to be linear.

There are essentially two type of processes used today to gel spin UHMWPE. The first one involves dry spinning (not that different from the process described for *m*-aramids) of solution in a volatile solvent (e.g., decalin) [97]. In general, a very large fraction of the solvent is removed during that process and the fiber is quenched to below gelation temperature (most often with water). The fiber is then drawn at temperatures very close to its melting point. The draw is often accomplished in multiple stages.

In the second process, the polymer is dissolved in an essentially nonvolatile solvent (e.g., mineral oil) and is spun via a process very similar to air-gap spinning for lytropic systems [98]. The fiber is quenched below the gel point by cooling with a solvent, which is immiscible with the spinning solvent (e.g., water). The nonvolatile solvent is extracted from the solid fiber using a volatile solvent (e.g., hydrocarbon). The dry fiber is then drawn under conditions similar to the dry-spinning process. An example of an apparatus used for dry spinning and the multi stage drawing processes is given in [99]. The parameters affecting fiber drawability and properties obtained are discussed in [100]. Patent literature indicates that DSM and Toyobo produce Dyneema fiber via a process similar to that described in [100] while Honeywell uses a process to produce Spectra as described in [98]. There are number of small producers in China. Most of them use the two solvent system.

UHMWPE polymer (see → Polyethylene) is available on the open market (e.g., Ticona) and most fiber producers purchase it.

3.4.2. Extrusion Process

Understanding gained during the development of the gel spinning process for UHMWPE

fibers redirected research on processing of UHMWPE via the extrusion process. Drawing of "virgin" polyethylene films produced by direct polymerization (no melting or dissolution) was described [101]. Aggregates of molecules in these films were disentangled directly during polymerization when they formed as a solid. This allowed them to be drawn as much 60 times with resulting strength of 3.5 GPa and modulus of 116 GPa, which are similar to results obtained via gel spinning (Table 4). This work clearly demonstrated that to attain very high draw ratios, the polymer needs to be shaped directly after polymerization without melting. Other than films, precursors to high temperature draw were also evaluated. Powder rolling was studied in [102] resulting in fiber properties of 1.3 and 81 GPa for tenacity and modulus, respectively. Solid-state coextrusion of mats of polymeric powder from solution crystallization was studied in [103]. The effect of the molecular mass and its distribution on maximum draw and the resulting properties were investigated, and tensile strength approaching 5 GPa and modulus of 220 GPa have been obtained. These are just some illustrations of the very large amount of work in this area. The work led so far to three commercial products: Tensylon (DuPont), Endumax (Teijin), Dyneema Ballistic Tape (DSM), and Tsunooga (Toyobo). All of them possess middle of the range properties.

3.4.3. Fiber Structure

A very high draw ratio used in the manufacturing of UHMWPE fibers is responsible for high orientation. What clearly distinguishes it from other polyethylene fibers (see → Fibers, 7. Polyolefin Fibers) is that they are made of essentially fully extended chains. A transition from shish-kebab to fibrillar structures during fiber drawing and development of chain extended conformation is described [104] and two melting points of two different polymorphs are observed [105, 106]. The higher melting peak at 423 K is associated with the orthorhombic crystal structure. The fibrils in fully drawn fibers were composed of chain-extended orthorhombic crystallites with an average length 70 nm. They were interrupted by defect regions containing trapped entanglements or chain ends. The defect regions were approximately 4 nm long. The mechanical properties of these fibers are compared in Table 6.

Table 6. Tensile properties of UHMWPE fibers

Property	Spectra 1000 [107]	Dyneema SK 71 [108]
Tenacity, GPa	3.2	3.4
Modulus, GPa	113	119
Elongation, %	2.9	3.5

3.5. Properties and Uses of High Strength Fibers

While this group of fibers is classified as high strength and high stiffness, other properties (e.g., thermal stability, flame resistance) are also important in view of the applications in which these fibers are used. In some cases these additional characteristics become dominant, as for example in applications, which use staple fibers or pulp.

3.5.1. Fiber Properties

There is a broad range of commercially high-performance fibers currently available with excellent tensile properties (Table 3–6). The density of the different fibers varies from 0.97 g/cm^3 for Spectra and Dyneema to ~1.4 g/cm^3 for Vectran, 1.44 g/cm^3 for Kevlar and 1.55 g/cm^3 for Zylon. All of them are lower than 1.8 g/cm^3 for carbon fiber or 2.5 g/cm^3 for S-glass. However, these excellent tensile properties are not matched by compressive properties. PPTA-based fibers exhibit a yield stress at 0.5% [109]. At the yield point a significant change in the morphology of the fiber is observed. Kink bands at 45° angle to fiber direction are formed. But even at the compressive strain rate of 3% the loss of tensile properties is very small (~ 10%) [110]. The fact that compressive properties are significantly lower than tensile properties is connected to the highly anisotropic character of these materials (excellent longitudinal properties with relatively weak lateral properties). The coil test was used to determine the compressive strength of several fibers [111]. Whereas Kevlar was measured at 25.8 N/tex;

PBO fiber had strength of 13.3 N/tex and high strength polyethylene 7.5 N/tex. This sequence corresponds to the decrease of lateral properties in these fibers. Hydrogen bonding in aramids is responsible for the better lateral properties of these fibers. Consequently one would expect compressive properties for M5 fiber to be better than other polyazole fibers [112]. Fatigue measurements for these fibers show a similar picture: Tension–tension fatigue is significantly better than the compressive fatigue. Significant differences exist between these fibers as far as creep is concerned. UHMWPE fibers exhibit the highest creep. The lifetime of PPTA and UHMWPE fibers was calculated using a kinetic model of failure [113]. The results show that at a load of 50% of their breaking strength UHMWPE fiber fail after 2.5 min whereas Kevlar supports the load for 100 years.

Additional reduction of creep for PPTA fiber is achieved by improvement of its structure after heat treatment e.g., Kevlar 49 has a creep about half of that of Kevlar 29. Technora exhibits higher creep than fibers based on PPTA [114] whereas the creep of Zylon HM and Vectran is a little lower. This significant deficiency of UHMWPE fibers attracted a lot of work searching for improvement. One of the most frequently considered approaches was cross-linking using UV [115] and electron irradiation [116], but at this point none of them have entered commercial operation.

In addition to mechanical properties, thermal properties and flammability of these fibers control their applications. UHMWPE fiber is the worst in both areas. Its melting point is the lowest (below 150°C), and it is flammable. LOI of PPTA-based fibers is about 28%, a little lower for Technora and Vectran whereas Zylon and M5 with their highly aromatic structure have LOI above 65%. Among these high temperature performing fibers only Vectran melts. All other polymers decompose before melting. As far as thermal stability is concerned both Zylon and M5 are more thermally stable than aramids. All these fibers (except UHMWPE) retain their mechanical properties well at elevated temperatures e.g., at 300°C Kevlar still retains about 50% of its strength and 70% of its modulus when compared with room temperature data [76]. At the same temperature Zylon retains 60% of its strength and 80% of its modulus [86]. Excellent orientation and chain extension of these fibers result in a negative expansion coefficient for all of them, which is of value in some applications.

In addition to very good mechanical and thermal properties, high-performance fibers also have good chemical resistance. The chemistry of UHMWPE fiber dictates its very good chemical resistance to hydrolytic attack and many solvents (except under some conditions to hydrocarbons). The same properties are responsible for good UV stability (with use of UV stabilizers), but poor adhesion to resins [108]. Chemical properties of *p*-aramids are determined by the presence of the amide group, which is subject to hydrolytic attack. The rate of hydrolysis is influenced to some degree by the fiber morphology, with Technora having somewhat better stability than PPTA-based fibers and heat treated PPTA fibers better stability than standard varieties. Melt spinning of Vectran results in a very well consolidated morphology giving better chemical resistance than aramids. While having, in general, better chemical resistance than *p*-aramids, Zylon exhibits unusual degradation under humid and hot conditions. UV stability is reversed with PPTA-based fibers, which have better UV stability than other aromatic fibers. These properties are summarized in technical bulletins [76–79, 86, 87, 93, 107, 108].

3.5.2. Uses

When Kevlar was being developed the original expectation at DuPont was that it would be used mostly as tire cord. It seems that forecasting market developments is as difficult as forecasting breakthroughs in technology. In most cases the applications are driven by the unique combination of mechanical and thermal properties with low density. At this point, applications for high strength fibers are very diverse and development of new uses frequently requires different fiber forms beyond the continuous filament yarn envisioned in the original tire cord application. They are addressed in discussions of the specific uses. The review of applications is brief, but it should be remembered that these new materials frequently require the development of a very sophisticated understanding of the way they work in the final structures. Consequently,

design of structures is optimized specifically for these materials. One critical difference versus traditional materials like steel and concrete is the anisotropy of the properties of high-performance fibers. A more complete (but still brief) review of applications can be found elsewhere [117, 118].

Ballistic Protection. This is the most broadly known application of these materials though not the largest one by volume. Fiber strength is obviously important for this application, but it is also very important to design structures to maximize the amount of material participating in stopping a projectile. The wave propagation during the event is influenced by modulus and, as a result, the amount of material involved in the event is 3–4 times greater for Kevlar than for nylon. The vests are multilayer structures, and the number of layers depends on the threat they are designed to protect from. Fabric design plays an important role, as the transverse deflection of the fabric is responsible for a large fraction of energy absorption. In addition to woven structures, there are soft composites in which fibers within a layer are arranged unidirectionally (UD structures), and the layers are stacked so that the fibers are not oriented in the same directions. UD structures minimize some negative effects of the anisotropy of the fibers (two orders of magnitude difference of properties in the fiber direction versus that of cross direction) and decrease the importance of fiber–fiber friction. Ballistic application include helmets, spall liners, etc., in which fibers are used in the form of hard composites. In these cases interaction with the resin has to be considered (good adhesion is not always good for good protection). Many of the fibers considered here are used in this application: PPTA-based *p*-aramids, PBO, and UHMWPE fibers.

Composites. High specific strength and stiffness offered by these fibers are important values for applications as composites. The range of composite materials is very broad, from hard composites with resins, such as epoxy to soft ones e.g., reinforcement of rubber. Aerospace and aircraft are the most important applications for hard composites as here the value of mass reduction is highest. While relatively poor compressive properties limit applications in structural materials, the good impact damage tolerance opens some uses as hybrids with carbon fibers.

Rubber reinforcement includes high performance automotive tires but also tires for aircrafts, heavy duty machinery, bicycles as well as in a variety of transmission belts and hoses. Increased temperatures under the hood of automobiles increase value of these products. Tires represent a good example where anisotropic properties of the fiber affected tire design. The design has to avoid putting these fibers under compression during operation. Aramids are the only materials used in this application because processing and use temperatures are too high for polyethylene and cost is too high for other fibers.

A unique application is in honeycomb structures (see Section 2.1.6 Uses for *m*-aramid honeycombs). In this case *p*-aramid is used as a floc (short fiber) from which paper is produced for manufacturing the honeycomb composite. High stiffness, low mass and self-extinguishing characteristics drive applications in aircraft.

More information can be found in → Composite Materials.

Ropes and Cables. The high specific strength of these high-performance materials opens a substantial market in underwater applications. PPTA-based aramid fibers find use in anchoring oil rigs (especially in deep water exploration) or mooring lines for ships. Again, it is mostly *p*-aramids and LCP fibers that are used in this application as too high creep for UHMWPE is a limitation.

Reinforcement of optical cables is one of the best-known uses among the cable applications.

Protective Clothing. The use of *p*-aramid staple in blends with *m*-aramids to control fabric shrinkage and break open in flame is described in Section 2.1.6 Uses. Another area of high volume use of these fibers is cut protection. Gloves and chain saw chaps made from *p*-aramids and UHMWPE (if high temperature or flame protection is not needed) are used in various industries.

Asbestos Replacement and Other Applications. The unique morphology of *p*-aramid fibers

based on PPTA makes it possible to produce short, fibrillated particles by mechanical treatment of short fibers. The high aspect ratio of the fibers offers mechanical reinforcement. The very high surface area combined with good thermal properties allows them to be used in brake and clutch plates.

A long and growing list of smaller applications includes sport and recreation equipment: Boat sails, parachute fabrics, golf clubs, tennis rackets, etc.

Abbreviations used in this article:

DAPBI	2-(4-aminophenyl)-1*H*-benzimidazol-6-amine
DMA	dimethylacetamide
HMPA	hexamethylphosphoramide
LCP	liquid crystalline polyester
LOI	limiting oxygen index
NMP	*N*-methyl-2-pyrrolidone
PBI	polybenzimidazole
PBO	poly(*p*-phenylene-2,6-benzobisoxazole)
PBZT	poly(*p*-phenylene benzobisthiazole)
PE	polyethylene
PEEK	polyetherether ketone
PI	polyimide
PMIA	poly(*m*-phenyleneisophthalamide)
POD	polyoxadiazole
POP	copoly(*p*-phenylene/3,4-diphenyl ether terephthalamide)
PPS	poly(phenylene sulfide)
PPTA	poly(*p*-phenyleneterephthalamide)
UD	unidirectional

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Foamed Plastics

ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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1. Introduction

Foamed plastics are materials that have cells distributed throughout their entire mass. A cell is a small void formed during the manufacture of the foam; it is enclosed partly or completely by *cell walls* or *struts*. In contrast to an open cell, a closed cell is totally surrounded by its walls and, therefore, is not interconnected with other cells via the gas phase.

The apparent density of a foamed plastic depends on the fraction of the total volume occupied by the polymer phase that forms the skeleton; it is always lower than the density of the skeletal substance [12].

Structural foams consist of a light, closed-cell core that is sandwiched between solid integral skins. *Syntactic foamed plastics* are gas-filled polymers that are not, however, foamed. They contain completely closed cells that are formed by hollow spheres distributed in the polymer matrix (see Syntactic foams).

The constituents of the polymer skeleton can be produced by polymerization, polyaddition, or polycondensation.

History. The first foamed polymers were produced in the 1920s from rubber (Dunlop). These were followed in the 1930s by foamed plastics from urea resin (BASF), flexible poly (vinyl chloride) (I.G. Farben), and polyurethane

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(Bayer). Polyethylene foams (Du Pont), extruded polystyrene foams (Dow), rigid poly(vinyl chloride) foams (Lonza), and the first phenolic resin foam (Dynamit Nobel) were developed during World War II. Foams from polystyrene beads (BASF), epoxy resins (Shell), and silicones (Dow Corning) were announced in the late 1940s and early 1950s. In the 1960s, polyamide (BASF), polycarbonate (General Electric), polysulfone (Pechiney-Saint-Gobain, ICI), polyimide (Du Pont), and polymethacrylimide (Röhm) foams were described. Poly(phenylene oxide) (General Electric), and melamine resin (BASF) foams have been known since the 1970s.

2. Production (→ Plastics, Processing 1. Processing of Thermoplastics)

Production processes for individual foams are described in Chapter 4. Only a brief overview is given here.

2.1. Principles

The three key starting materials for a foam are polymer, blowing agent, and additives.

In the manufacture of *thermoplastic foams*, the starting material is generally an existing polymer. Foams are produced in both continuous and batchwise processes which frequently involve an extrusion step. Thus, boards or films as well as profiled and shaped parts with various apparent densities can be produced (e.g., Section 4.2.2).

Foamed thermoplastic beads are fused with steam to form a variety of shaped parts, including blocks (Sections 4.1.1 and 4.2.1).

In the manufacture of *thermoset foams*, the macromolecules are cross-linked during the foaming process. The foams are produced in various ways. The pourable charge is distributed on a conveyor belt where the mixture foams and hardens continuously (Sections 4.4 and 4.6). The resulting paste can also be poured into block molds (Section 4.4) or other cavities where the reaction is completed (Sections 4.7 and 4.8). Whipping (Section 4.5) and spraying (Sections 4.4 and 4.8) processes may also be used.

2.2. Blowing Agents

In almost all foamed plastics, the volume fraction of the gas phase (a function of density) is far greater than that of the skeletal substance. Thus, for example, at an apparent density of 10 kg/m^3, the gas phase accounts for ca. 99 % of the volume. The gas phase is produced by using a blowing agent.

Physical blowing agents may be compressed gases (air, nitrogen) or low-boiling hydrocarbon or chlorofluorocarbon (CFC) liquids, e.g., butane, pentane, trichlorofluoromethane (CFC 11). They do not leave undesirable decomposition products.

In the oldest method, originally developed for rubber, air is whipped mechanically into the latex [13]. The resulting froth is fixed by cross-linking. This process is commonly used for urea–formaldehyde resin foams (Section 4.5) and flexible poly(vinyl chloride) (PVC) foams (Section 4.3.2).

In an alternative method, compressed nitrogen is dissolved in a polymer melt. The cellular structure is then obtained by reducing the pressure. Examples are the batchwise production of cross-linked polyethylene foam (Section 4.1.1) and injection molding.

Incorporation of the blowing agent pentane [109-66-0] into polystyrene beads (Section 4.2.1) renders them heat-expandable.

Low-boiling chloro- and chlorofluorocarbons are incorporated into polyethylene (Section 4.1.1) or polystyrene melts (Section 4.2.2) in an extruder. Trichlorofluoromethane [75-69-4] (CFC 11) and 1,2-dichloro-11, 22-tetrafluoroethane [76-14-2] (CFC 114) are used as blowing agents for polyethylene. Methyl chloride [74-87-3], ethyl chloride [75-00-3], and trichlorofluoromethane [75-69-4] (CFC 11) are used for expandable polystyrene. The blowing agents evaporate and the polymer expands. Cooling increases the viscosity and sets the skeleton of the foam.

Thermoset foams (Sections 4.4 and 4.6) are also produced with low-boiling liquid blowing agents which are activated by the heat of the cross-linking reaction or by externally supplied energy.

The choice of blowing agent is based on a knowledge of physical and chemical properties [14].

Chemical blowing agents are solids which decompose at elevated temperature with the formation of gas. For optimum action, they must be distributed very uniformly in the substrate. Their decomposition temperature must be suitable for the processing temperature of the

polymer. Numerous organic, nitrogen-containing substances with decomposition temperatures of 100 – 250 °C [15], [16] or higher [17] are known (e.g., azo compounds, nitroso compounds, and hydrazides). The most frequently used compound is azodicarbonamide [123-77-3] which splits off nitrogen and carbon monoxide at about 200 °C. The decomposition temperature can be lowered by various additives such as zinc oxide [18].

The compounds, which contain polymers and blowing agents, are then subjected to extrusion processing.

If chemical blowing agents are used, thermoplastic foam injection molding (TFI) and thermoplastic foam extrusion (TFE) are usually employed to yield heavy, foamed plastics known as *structural* (*integral*) *foams* (Section 4.2.3). The injection mold (TFI) or the die (TFE) is cooled so that the foam collapses at the wall of the mold or die and forms a compact surface layer. The compacted surface has nearly the same density as the polymer matrix, whereas the internal layers are foamed.

Inorganic blowing agents, such as carbonates, are of minor importance. A mixture of sodium bicarbonate [144-55-8] and citric acid [77-22-9] serves as an additional, nucleating blowing agent in combination with pentane (Section 4.2.2). Sodium borohydride [16940-66-2], which splits off hydrogen in the presence of water and is adsorbed on fumed silica, has been reported to be an effective blowing agent [19].

Blowing agents can also be formed as reaction side products. For example, in certain polyurethane foams and in thermoset-modified PVC foams, carbon dioxide is formed from isocyanate and water (Section 4.3.1). Polyimide foam is blown by the alcohol (usually ethanol) formed in the imidization reaction (Section 4.9).

2.3. Additives

Nucleating agents are important additives in foam manufacture, especially in physically blown, thermoplastic foams. They are finely dispersed, often silicate-like solids but they may also be waxlike. They act as boiling chips in the polymer melt which is supersaturated with dissolved blowing gas.

Minute, nucleating gas bubbles, called hot spots, are also formed during the initial decomposition of chemical blowing agents [20]. Gaseous side products of the reaction act in the same manner.

Surfactants are required in thermosetting plastics to emulsify the liquid blowing agent. They reduce interfacial tension and thus facilitate nucleation. The surfactant also stabilizes the foam during expansion until the foam is set by the simultaneous hardening process.

Other additives include dyes, inert or reinforcing fillers and fireproofing agents. Antioxidants and UV stabilizers are sometimes needed.

3. Properties

The properties of foamed plastics are determined by their polymer substrate, apparent density, and morphology.

All three parameters, but especially apparent density, affect mechanical behavior. Resistance to elevated temperature and to chemical agents, as well as fire behavior, are primarily determined by the polymer. Morphology is responsible for the acoustical and thermal insulating properties. Both morphology and polymer substrate determine the water balance (water absorption, diffusion of water vapor).

Compressive Strength. One the basis of their compressive strengths determined in a compression test at 10 % deformation (DIN 53 421, ISO 844), foamed plastics are classified as *rigid* (> 0.08 MPa), *semirigid* (0.015 – 0.08 MPa) or *flexible* (< 0.015 MPa) [12]. The measured compressive strength depends primarily on the apparent density of the foamed plastic but also on the modulus of elasticity of the polymer [21].

Figure 1 provides an overview of the ranges of apparent density and compressive strength for individual foams. A linear relationship exists between the logarithms of the compressive strength and of the apparent density for all rigid plastic foams [15, p. 411], [22]. Polyethylene foams lie parallel to the scatter band; flexible plastic foams and some semirigid are outside it.

Cell Structure. Rigid and semirigid plastic foams generally have *closed cells* which do not interconnect via the gas phase. They can, therefore, also contain gases other than air, e.g., fluorocarbons. Flexible foams, on the other hand, are usually *open-celled* and filled with

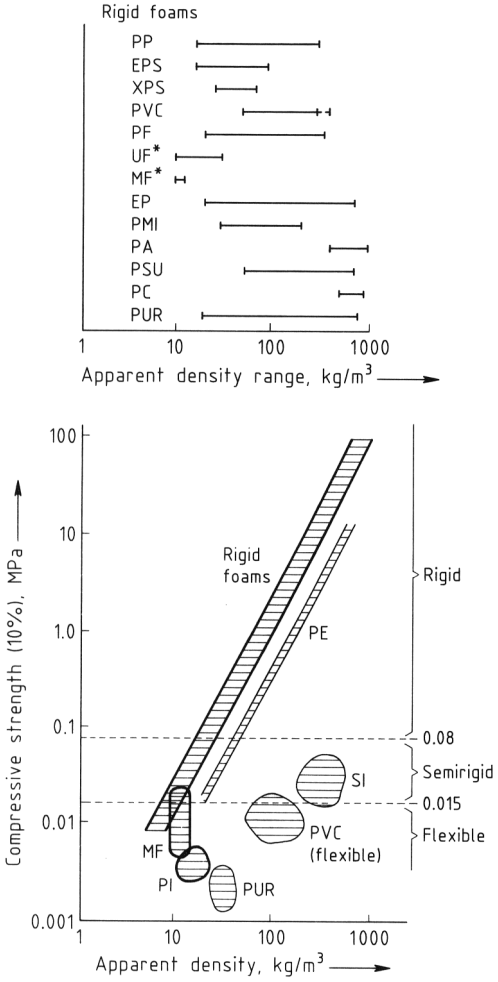


Figure 1. Compressive strength and apparent density of foamed plastics
*Also include flexible foams
Abbreviations are defined in the abbreviation list at the beginning of this article

air. Exceptions to this rule are, however, found. Figure 2 shows scanning electron micrographs of a closed-cell (A) and an open-cell (B) plastic foam.

The *cell size* of most plastic foams is 0.05 – 1 mm. Thermoset-modified PVC foams, and noncross-linked, extruded polyethylene and poly(methyl methacrylate) foams have cell sizes > 1 mm. Foams with smaller cells usually exhibit better mechanical behavior.

If the cells are oriented, e.g., stretched in the rising direction of the foam, the mechanical properties are no longer isotropic.

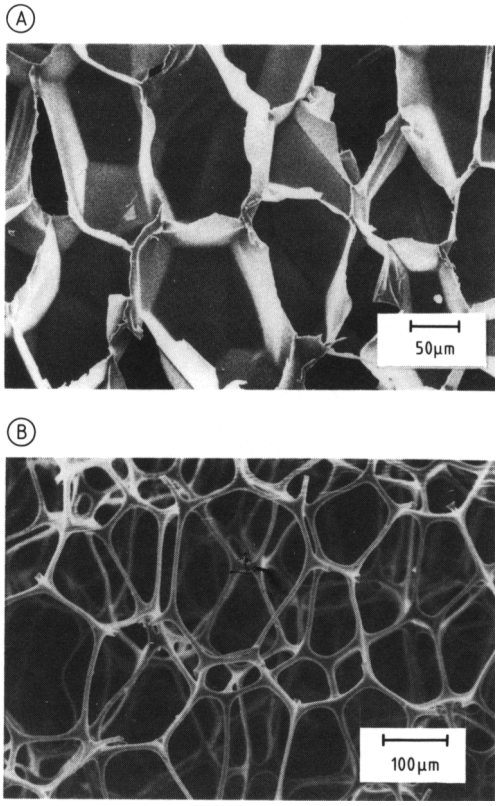


Figure 2. Scanning electron micrographs of (A) a closed-cell, extruded polystyrene foam and (B) an open-cell melamine–formaldehyde foam

The thickness of the cell wall of closed-cell foams, the strut thickness of open-cell foams, and the cell size affect the radiant fraction of thermal conductivity. Each material has an optimum value [23], [24].

Thermal Insulation. The thermal insulation of a foamed plastic depends primarily on the thermal conductivity of the filling gas, followed by the apparent density and then morphology. Foams filled with heavy chlorofluorocarbon gases, therefore, have better thermal insulation characteristics than air-filled foams. Figure 3 shows the density dependence of the thermal conductivities of several foams measured at 10 °C [25], [26].

Depending on prevailing conditions, open-cell products can absorb water and thus increase their thermal conductivity [27]. Since they are also open to diffusion, they must be provided with a barrier layer in some cases.

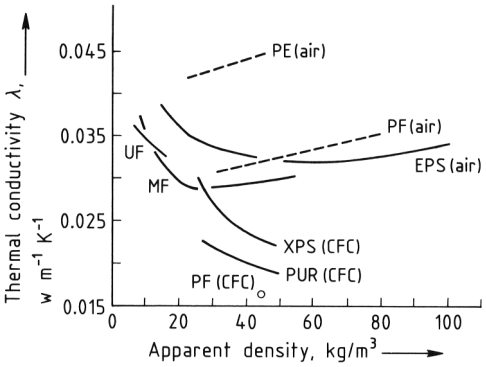


Figure 3. Thermal conductivity of foamed plastics as a function of apparent density
Values were measured at 10 °C according to DIN 52 612, ISO-DIS 8302, ASTM C 177. The gases used to fill the foams, air or a chlorofluorocarbon (CFC), are indicated in parentheses. Dashed lines indicate that values vary widely. EPS = expandable polystyrene; MF = melamine–formaldehyde resin; PE = polyethylene; PF = phenol–formaldehyde resin; PUR = polyurethane; UF = urea–formaldehyde resin; XPS = extruded polystyrene

Sound Insulation. Open-cell foams are well suited for airborne sound insulation. Closed-cell products are useful for impact sound insulation, provided they have sufficient resilience [28]. Rigid foams are less suitable for acoustic applications.

Fire Behavior. Polymer-dependent properties (i.e., maximum long-term service temperature and oxygen index) are shown in Figure 4 for the individual foams discussed in Chapter 4. Thermoplastics differ from thermosets: when exposed to a flame, thermoplastic foams sinter above their softening range and melt, whereas thermosets form a carbon skeleton.

The oxygen index provides some indication of the flammability of a polymer. It measures the minimum oxygen concentration necessary to support combustion of the material [29]. Thus, higher values are better. The oxygen index of a foamed plastic may often be only slightly higher than that of the compact polymer, exceptions are

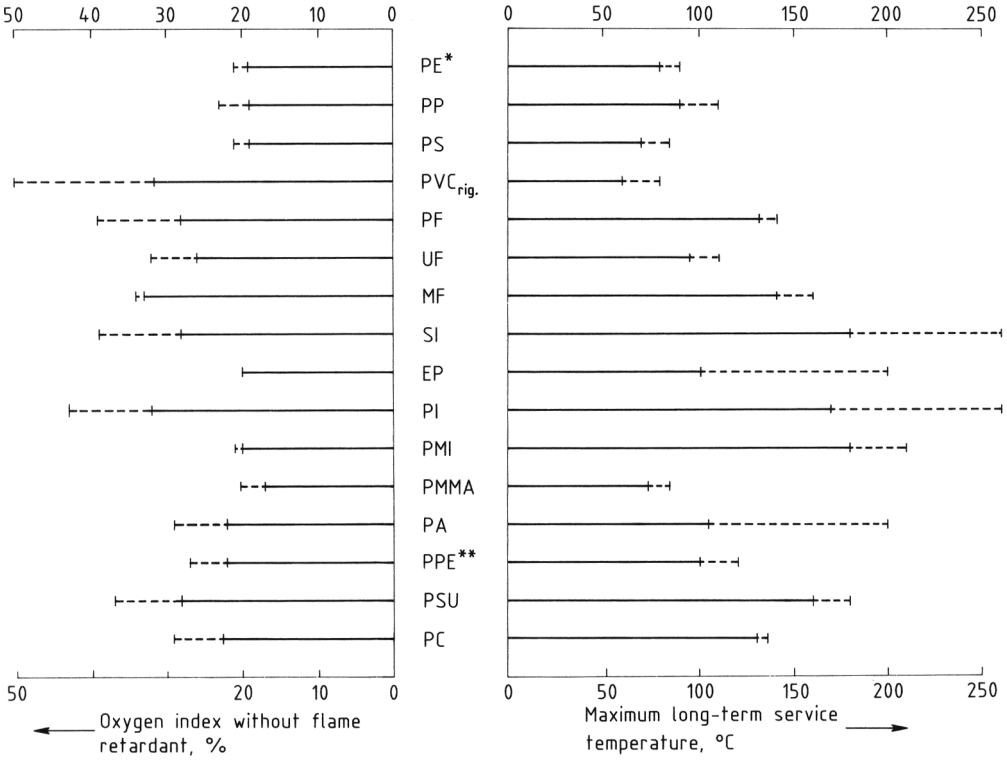


Figure 4. Oxygen index and maximum long-term service temperature of foamed plastics
The dashed lines indicate the range of variation (i.e., minimum and maximum values)
*Abbreviations are defined at the beginning of this article
**Ratio of PPE : PS = 1 : 1

urea–formaldehyde resins and poly(phenylene oxide).

Other important parameters for judging fire behavior are the smoke density and the toxicity of the combustion gases.

In compliance with the flammability requirements specified in guidelines for use in construction or transportation, some foams contain flame retardants. These are often halogen compounds, examples include chlorinated paraffins and hexabromocyclodecane for polyethylene and polystyrene, as well as boron trioxide for phenol-–formaldehyde resins (cf. Chap. 5).

4. Specific Foamed Plastics

Polyurethane (PUR) foams are treated elsewhere (→ Polyurethanes). For a description of foamed PVC coatings, see → Leather Imitates. Trade names of individual foams are listed in Table 1.

Table 1. Trade names of foamed and foamable plastics

Trade name and raw material	Producer
Polyolefin (PO)*	
Alveolit (PE)	Alveo (Switzerland)
Apro (PP)	Arco Chemical (USA)
Arpak (PE)	Arco Chemical (USA)
Eperan (PE)	Kanegafuchi Chemical Industry (Japan)
Ethafoam (PE)	Dow Chemical (USA)
Evazote (EVM)	Bakelite Xylonite Ltd. (UK)
Foam ace (PE)	Furukawa (Japan)
Frelen (PE)	Freudenberg (FRG)
Neopolen (PE)	BASF (FRG)
Opcel (PE)	Sentinel (France)
Plastazote (PE)	Bakelite Xylonite Ltd. (UK)
Softlon (PE)	Sekisui (Japan)
To-re-pepu (PE)	Toyo Rayon (Japan)
Trocellen (PE)	Dynamit Nobel (FRG)
Polystyrene (PS)	
Afcolene	Société Chimique des Charbonnages (France)
Arcel	Arco Chemical (USA)
Dylark	Arco Chemical (USA)
Dytherm	Arco Chemical (USA)
Eslen	Sekisui (Japan)
Extir	Montedison (Italy)
Kane Pearl	Kanegafuchi Chemical Industry (Japan)
Rigipore	British Petroleum (UK)
Roofmate	Dow Chemical (USA)
Styro-lite	3M (USA)
Styrocell	Shell Chemical (UK)
Styrodur	BASF (FRG)
Styrofoam	Dow Chemical (USA)
Styropor	BASF (FRG)
Vestypor	Hüls (FRG)
Poly(vinyl chloride) (PVC)	
Airex	Airex (Switzerland)
Conticell	Continental-Gummi (FRG)
Divinycell	Diab-Barracuda (Sweden)
Ensolite	Uniroyal (UK)
Foamcell	Pelf (Italy)
Klegecell	Kleber-Colombes (France)
Kömacell	Kömmerling (FRG)
Pliovic	Goodyear (USA)
PVC Foam	Shin-Etsu (Japan)
Rigicell	Goodrich (USA)
Solvic	Solvay (Belgium)
Vestolit	Hüls (FRG)
Vinoflex	BASF (FRG)
Phenol-formaldehyde (PF) resins	
Cellobond	British Petroleum (UK)
Dynapor	Dynamit Nobel (FRG)
Eurothane xtra	Recticel (Belgium)
Exeltherm xtra	Koppers (USA)
Fenomo	Isomo (Belgium)
Mosy	Compo (FRG)
Oasis	Smithers (USA)
Phenexpan	Société Chimique des Charbonnages (France)
Phenobil	Roland-Werke (FRG)
Phenocomp	Sekisui (Japan)
Phenolite	Bridgestone (Japan)
Pyrofoam	Union Carbide (USA)
Resiphen	Texaco (USA)
Urea–formaldehyde (UF) resins	
Aerolite	Ciba-Geigy (Switzerland)
Beetle UF Foam	British Industrial Plastics (UK)
Cascofoam	Borden Inc. (UK)
Hygromull	BASF (FRG)
Isoschaum	Schaumchemie (FRG)
Kobosan	Vorwerk (FRG)
Melamine–formaldehyde (MF) resins	
Basotect	BASF (FRG)
Silicones (SI)	
Cohrlastic	Connecticut Hard Rubber (USA)
Foamega	Bisco Prod. (USA)
Polyvoltac	Polyvoltac (UK)
Rau-Sik	Rehau (FRG)
Epoxy resins (EP)	
Araldit	Ciba-Geigy (Switzerland)
Scotchplay	3M (USA)
Polyimide (PI)	
Chem-Lon	Chem-Tronics (USA)
LMB 1907	Ciba-Geigy (Switzerland)
Polyimid 2080	Upjohn (USA)
Skybond	Monsanto (USA)
Solimide	International Harvester (USA)
Polymethacrylimide (PMI)	
Rohacell	Röhm (FRG)
Poly(methyl methacrylate) (PMMA)	
Isocryl	IMC Acrylguß (FRG)
Polyamide (PA)	
Maranyl	ICI (UK)
Rilsan	Société Nationale des Pétroles d'Aquitaine (France)
Poly(phenylene oxide) (PPE)	
Noryl	General Electric (USA)
Prevex	Borg-Warner (USA)
Polycarbonate (PC)	
Lexan	General Electric (USA)
Makrolon	Bayer (FRG)
Merlon	Mobay Chemical (USA)

* PE = polyethylene; PP = polypropylene; EVM = ethylene–vinyl acetate copolymer.

4.1. Polyolefin (PO) Foams

Polyolefin (PO) foams are manufactured by many producers in a variety of processes and are classified as low density (25 – 250 kg/m^3) or high density (250 – 700 kg/m^3). The market has expanded relative to other foamed plastics, especially in Japan.

Most polyolefin foams are made from low-density polyethylene [9002-88-43] (LDPE). Copolymers such as the more flexible ethylene–vinyl acetate [24937-78-8] (EVM) and, more rarely, high-density polyethylene [9002-88-4] (HDPE) are also found. Finally, foams may be produced from linear low-density polyethylene (LLDPE), a copolymer of ethylene and other olefins (1-butene to 1-octene) which is synthesized with a Ziegler catalyst. Polypropylene [9003-07-0] (PP), which is more resistant to heat deformation, stiffer, and tougher than polyethylene, was first processed into foamed sheets in the 1960s. Today, a polypropylene copolymer with a few percent ethylene is also utilized. For a detailed description of these polyolefins, see → Polyethylene, → Polypropylene. Trade names of polyolefin foams are listed in Table 1.

Fire Behavior. Like their starting materials, polyolefin foams are flammable. The smoke density is low. The combustion gases contain only carbon dioxide and, in case of oxygen deficiency, carbon monoxide.

4.1.1. Low-Density Polyolefin Foams (25 – 250 kg/m^3)

Boards, sheets, or profiled shapes are manufactured by continuous processes; boards are also produced by batch processes. In addition, beads can be made continuously or batchwise.

Continuous Process for Non-Cross-Linked Foam. Non-cross-linked LDPE foam is produced by applying the technique used for polystyrene (Styrofoam, see Section 4.2.2) which involves the gassing of a polymer melt with low-boiling halogenated hydrocarbons in an extruder. The blowing agent evaporates as it emerges from the nozzle; the melt then cools and its viscosity increases [30]. A strand of closed-cell foam (cell size 0.5 – 1.5 mm) is formed, with a thickness of 80 mm and an apparent density of 30 kg/m^3. Thin sheets of foam up to 5 mm thick are produced in the same manner or via the film blowing process (→ Films, Section 2.2.2.0.0.2.,). An example of such a film is Ethafoam produced by Dow Chemical.

Cross-Linked Foams. As shown in Figure 5, LDPE melts in a very narrow range [31]. Cross-linked LDPE exhibits a less precipitous drop in viscosity with increasing temperature. Thus, a broader temperature range for processing is obtained; in addition, the foamed plastic has smaller cells.

Cross-linking is accomplished either chemically (e.g., with dicumyl peroxide [80-43-3]) or with beams of electrons at doses up to 20 Mrad.

The gel content (degree of cross-linking) should be ca. 30 – 60 % [32]. Occasionally, divinylbenzene [1321-74-0] [33] or oximes [34] are added to the peroxide. Polyolefins grafted with silanes can be cross-linked catalytically in contact with water [35], [36]. For polypropylene, cross-linking agents with higher decomposition temperatures are used, e.g., polysulfone azides [37].

Batch Process for Molded, Cross-Linked Foam. In the in-mold, molded foam (batch) method, preformed polyethylene boards containing peroxide cross-linking agents are placed in a mold and exposed to nitrogen at ca. 38 MPa and 180 °C. After cooling and careful pressure reduction, the nitrogen remains dissolved in the melt. When heated to 100 – 130 °C, the partially cross-linked board foams to yield a foamed plastic. Its cells are very fine (0.1 mm), and

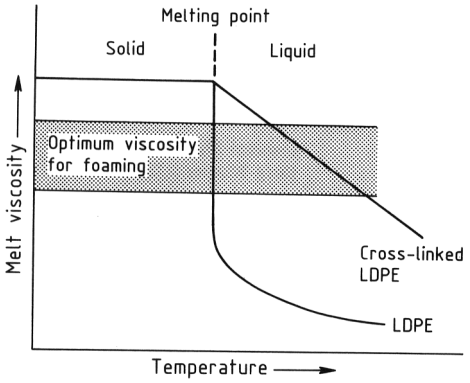


Figure 5. Melt viscosity of low-density polyethylene (LDPE) as a function of temperature

its density is 24 – 70 kg/m^3 [38], [39]. This process is used by Bakelite Xylonite Ltd. to manufacture Plastazote.

Instead of nitrogen, chemical blowing agents such as azodicarbonamide can also be used. The gel is removed from the mold rapidly while it is still hot and somewhat larger cells result.

Continuous Process for Cross-Linked Sheets. For the continuous manufacture of foam sheeting cross-linked with peroxides, the polyolefin (e.g., LDPE) is premixed carefully with up to 10 parts by weight of blowing agent (azodicarbonamide) and < 1 part by weight of cross-linking agent (dicumyl peroxide). The mixture is extruded to form a thin matrix which is then cross-linked by passing it through a heating tunnel at 180 – 230 °C. The sheet is finally foamed to a thickness of 4 – 20 mm and an apparent density of 25 – 250 kg/m^3. This process was developed by Furukawa and licensed to other companies (Bayer, Dynamit Nobel, Freudenberg) [32], [40], [41].

In a similar process, the matrix containing the blowing agent is cross-linked by irradiation with electrons. Subsequently, it is foamed in a shaft by exposure to IR heaters and hot air at 200 – 250 °C (Fig. 6). Free expansion can also be carried out in a hot fluid bath. The depth of penetration of the electron beam limits the maximum thickness of the foamed sheet to 5 mm. Apparent densities are 30 – 200 kg/m^3. This process was developed by Sekisui and Alveo, it is used to produce Alveolit [42], [42], [43].

Continuous Process Using Cross-Linked Beads. Strands of foam, produced by extruding LDPE with added butane, are comminuted to spherical beads. After the polyethylene has been cross-linked by an electron beam, the beads are fused continuously with hot air to form foam boards with thicknesses up to 120 mm and apparent densities in the range 28 – 45 kg/m^3. Cell size is about 0.5 mm. This process is used to manufacture Neopolen (BASF) [44], [45].

Batch Processes Using Beads. Pellets of weakly cross-linked LDPE, propylene–ethylene copolymers, or LLDPE in an aqueous dispersion are impregnated with low-boiling (halogenated) hydrocarbons as blowing agents. Impregnation is performed at a temperature near the softening range in the presence of a

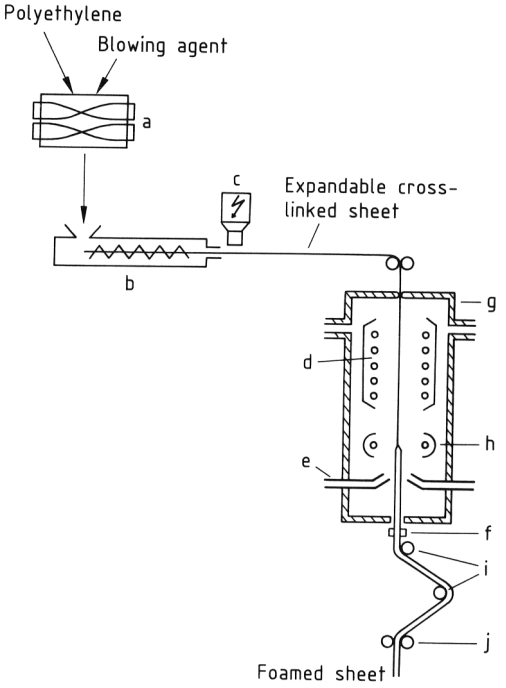


Figure 6. Production of radiation-cross-linked polyethylene by using a chemical blowing agent
a) Mixer; b) Extruder; c) Ionization irradiation unit; d) Preheater; e) Hot-air blower; f) Wrinkle-removing unit; g) Oven; h) Hot-air heater for foaming; i) Chill rolls; j) Take-up roll

suspension stabilizer (e.g., tricalcium phosphate, aluminum oxide).

When the pressure is reduced, the particles expand into foam beads with bulk densities of 20 – 70 kg/m^3, depending on the amount of blowing agent and the temperature (Fig. 7) [46], [47]. Uniform cell structure and low bulk densities can be obtained, for example, by post-treatment with nitrogen under pressure [48], [49]. To ensure that the final molded parts have a satisfactory surface, the original pellets should be small (mass, 1 mg) and the beads should have a diameter of 3 – 6 mm. The beads can be processed into molded parts without further cross-linking. This process is used by Kanegafuchi Chemical Industries, Japan Styrene Paper, and Yuka Badische [44], [47].

Processing. Polyolefin foam boards can be cut or split readily with band saws or slicers. They can also be milled, cut thermally, or punched.

By heating and subsequent pressing (hot-melt lamination), cross-linked sheets can be

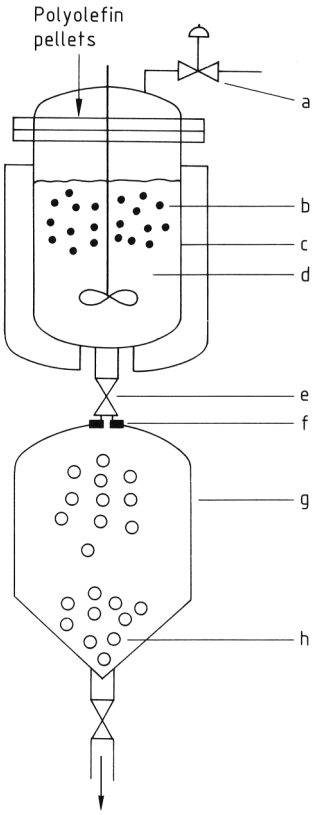


Figure 7. Production of expanded foam beads from polyolefin pellets
a) Pressure control valve; b) Polyolefin pellets; c) Pressure-resistant container; d) Water; e) Discharge valve; f) Orifice plate; g) Discharge tank; h) Expanded foam beads

fused to each other or to film, fabric, or sheet metal. They can also be cemented together with rubber-based contact adhesives or elastic melt adhesives. Thermoforming can be carried out effectively on commercial equipment [50–52].

Foam beads can be fused into parts of any desired shape, even boards, without waste by using steam or hot air; the process is similar to that used for expandable polystyrene beads (EPS) (see Section 4.2.1). Additional steps are required to completely fill the interstices between the spheres with foam:

1. In the Neopolen process for molded parts (Fig. 8), beads are placed in the mold cavity at elevated pressure and allowed to expand into the interstices by reducing the pressure. Only then are they exposed to steam, cooled, and removed from the mold [44], [53], [54].

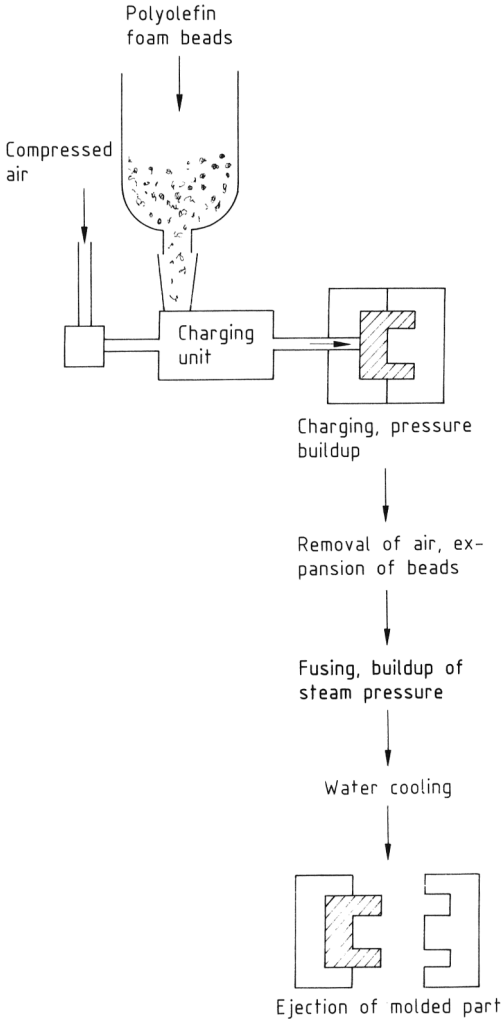


Figure 8. Manufacture of molded parts from polyolefin beads

2. The interstitial volume can also be reduced by a movable mold face which compresses the contents of the mold [55].
3. The internal pressure, and thus the expandability of the beads, can be increased immediately prior to mold foaming by using a compressed gas, e.g., nitrogen [56].

Properties and Uses. Polyolefin foams are predominantly of the closed-cell type. They become semirigid as the crystallinity of the substrate and the apparent density decrease. Because of the air trapped in the cells, PO foams display excellent shock absorption properties

which barely deteriorate under repeated impact. During prolonged loading, some of the air escapes from the cells. However, when the load is removed, air diffuses back into the cells and a slow recovery from deformation occurs, which depends on the apparent density and the load. Consequently, polyethylene foams are especially suitable for packaging impact-sensitive goods, e.g., electronic products. In packaging heavy goods, polypropylene foams can support higher loads and thus permit smaller support surfaces than the softer polyethylene foams. Polypropylene is particularly useful when greater dimensional stability under heat is required, e.g., in the automotive sector for items such as bumper cores [57].

The low moisture permeability of polyolefin foams combined with their low water absorption and relatively good weather resistance make them suitable for marine applications (e.g., ship fenders, life buoys, and life jackets) [54]. Protection against UV radiation is recommended for outdoor uses.

Because of their low thermal conductivity, which is only slightly greater than that of other foamed plastics, polyolefin foams are used as flexible pipe covers and insulating bags. More flexible types are used for impact soundproofing and resilient flooring in sports halls [50], [51], [58], [59].

4.1.2. High-Density Polyolefin Foams (250 – 700 kg/m^3)

Low-density polyethylene is foamed with chemical blowing agents (e.g., azodicarbonamide) to give apparent densities up to 450 kg/m^3. This material is used to insulate wires in telephone cables and coaxial cables; its dielectric constant is 3×10^{-4} [60].

Larger, shaped parts with apparent densities of 500 – 700 kg/m^3 can be produced from HDPE and polypropylene by the thermoplastic foam injection molding process. The integral skins of these structural foams gives a higher stiffness than is expected from their mean density [10, pp. 1 – 16].

Polypropylene is also foamed in extruders with chemical blowing agents to produce films and tapes in the density range of 400 – 700 kg/m^3. These products have high surface luster and are used in packaging [10, p. 15], [61].

4.2. Polystyrene (PS) Foams (→ Polystyrene and Styrene Copolymers)

Polystyrene [9003-53-6] (PS) foamed plastics are important because of their physical properties, their broad spectrum of applications, and their favorable price–performance relationship. They can be produced by various processes and with different apparent densities; accordingly, they differ in properties and in possible uses. Trade names of foamed and expandable polystyrene are listed in Table 1.

4.2.1. Expandable Polystyrene (EPS) Foams

Production. The techniques used for the production of expandable polystyrene (EPS) beads and their processing to expanded polystyrene foams were developed at the end of the 1940s by BASF [62] who marketed the new raw material under the trade name Styropor. Due to licensing and the expiry of patents, other raw material manufacturers and trade names have appeared (see Table 1).

Expandable polystyrene is produced by suspension polymerization of styrene with addition of blowing agents; the resulting polymer beads are then sieved into fractions with various ranges of bead size. Depending on end use different coatings may be applied (→ Plastics, Processing, 3. Machining, Bonding, Surface Treatment).

In addition to pure polystyrene, foams are also made from polystyrene copolymers (e.g., with acrylonitrile or maleic anhydride). These foams possess special properties such as increased solvent or heat resistance. Incorporation of surface coating with organobromine compounds (e.g., hexabromocyclododecane [25637-99-4], pentabromophenyl allyl ether [3555-11-1]) act as flame retardants and result in flameproofed foams, e.g., Class B 1 building materials according to DIN 4102, M 1 according to NF P 92–505 (Norme Française), or MF-1 according to UL-94 (Underwriter's Laboratories). Blowing agents include low-boiling hydrocarbons, particularly pentane, but also butane, propane, and their mixtures; EPS beads contain 4 – 7 wt % of these substances.

Two other production methods for EPS consist of impregnating standard polystyrene with

blowing agents in pressurized vessels and extrusion of EPS or standard polystyrene with added blowing agents. Cylindrical pellets are formed instead of beads.

Processing into Foam. Foam is obtained from EPS in three steps—prefoaming, intermediate storage, and final foaming (or molding) — as illustrated in Figure 9.

During *prefoaming*, the particles are heated and the polystyrene is thereby softened, the blowing agent in the polystyrene evaporates to form rapidly growing bubbles until either the heat supply is shut off or the expandability exhausted [63]. The bead diameter increases about threefold and the bead volume (bulk volume) about thirtyfold. The apparent density of the foamed product is determined by the bulk density obtained during prefoaming.

Intermediate storage is required prior to final foaming into blocks, boards, or molded parts to allow air to diffuse into the individual cells. Air is needed in subsequent molding: it acts as a supplementary blowing agent and also enables the soft cellular structure to withstand the external atmospheric pressure when the finished part is removed from the mold.

Final foaming is usually fully automated [64], [65]: perforated molds are completely filled with prefoamed beads and exposed to steam. The beads expand to fill the residual voids and are fused together. In modern installations, a vacuum is also applied. Some of the water condensed in the foam then evaporates and internal cooling reduces the pressure of the foamed plastic more rapidly, so that the parts can be quickly removed from the mold (short cycle times).

Boards are manufactured batchwise with block molds or with board molding machines; they may also be produced continuously on special moving-belt machines.

The glass transition temperature of polystyrene is reduced if pentane, which acts as a plasticizer, is used as blowing agent. The temperature range used during prefoaming and final foaming is then 85 – 120 °C. The most widely used heat-transfer medium is steam, which has a large heat capacity; it diffuses rapidly through the cell walls, and thus acts as a supplementary

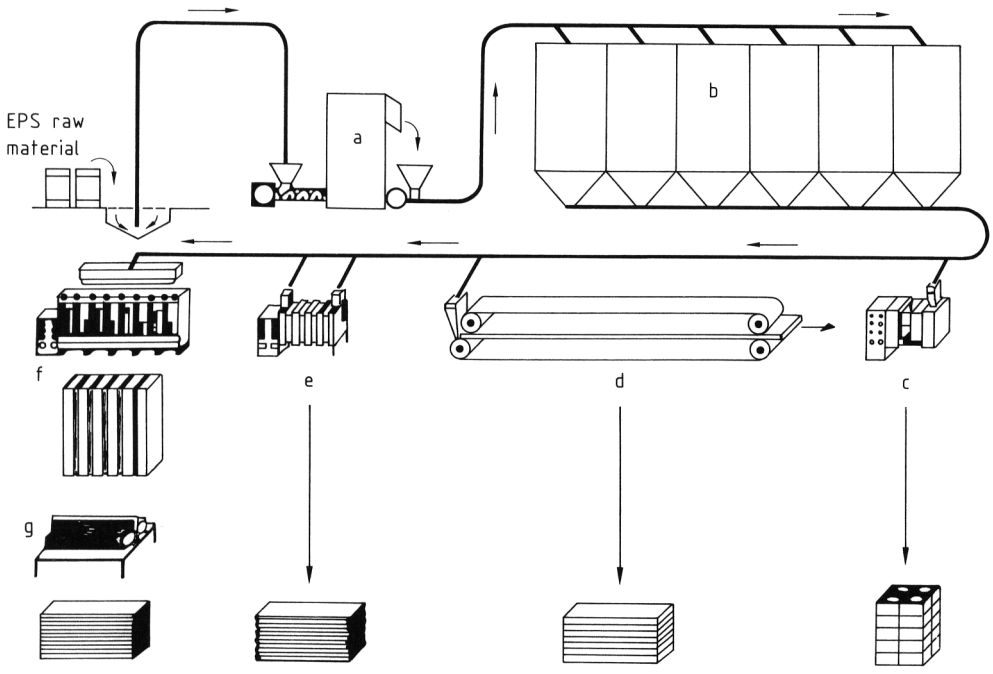


Figure 9. Processing of expandable polystyrene (EPS) foam into molded parts and insulation board
a) Prefoamer; b) Intermediate storage; c) Automatic molding machine; d) Continuous foaming unit; e) Automatic board molding machine; f) Block mold; g) Cutter

blowing agent. In some special cases, hot air is used instead of steam.

Foam boards for heat insulation are made primarily from foamed blocks 1 – 6 m^3 in volume. After stabilization for several hours to complete cooling and air uptake, the blocks are trimmed and cut into boards on cutters using electrically heated or oscillating wires. Post-treatment such as grooving or slotting is carried out on milling machines. Sheets of any desired length and 1 – 6 mm thick can be produced from special cylindrical blocks by using peeling machines with rotary blades. These peeled sheets are used under wallpaper and in packaging.

The resilience of boards for impact soundproofing is increased by briefly compressing the blocks prior to cutting or by rolling (or squeezing) the individual boards.

In a number of applications, the foamed plastic must be stored prior to use. This helps to remove internal moisture (steam condensate and residual cooling water) and to reduce post-shrinkage of the foam.

Properties. Most of the physical properties of EPS foams depend strongly on the apparent density, the most important are summarized in Table 2. Boards for thermal insulation generally have densities between 15 and 30 kg/m^3, whereas the density of boards used for impact soundproofing is ca. 12 kg/m^3. The density of shape-molded parts is generally 20 – 30 kg/m^3, for special applications it may be much higher.

The chemical resistance of the foams corresponds largely to that of polystyrene.

Uses. Expandable polystyrene foams have many applications including thermal insulation, impact soundproofing [66], and formwork elements for concrete in the building industry; insulation of cold-storage depots and cooling cells, storage and transport tanks, pipes, etc.; and molded parts for packaging [67], promotion articles, toys, and sporting goods. It is also used for producing molded articles by lost-foam casting, a process that is similar to wax molding. A molded EPS form is embedded in sand and molten metal is poured into this composite. The foam shape evaporates and is replaced by metal.

Considerable amounts of nonfused, loose beads are also used as additives in bricks; (during firing they decompose to leave uniformly distributed pores). Further uses are as additives in light-weight concrete [68] and as renderings for thermal insulation or as drainage material.

Foamed EPS waste that accumulates during processing can be recycled; it is ground, mixed with preformed beads, and reused during molding. Ground EPS foam has also proved useful for loosening soil, for drainage, and as a filling material. These foams are inert and do not harm ground water, flora, or fauna.

4.2.2. Extruded Polystyrene (XPS) Foams

Foamed polystyrene boards and films are produced in large amounts by extrusion [69].

Production. In the original DOW process [70], polystyrene and a blowing agent were fed into a

Table 2. Physical properties of expandable polystyrene (EPS) foams as a function of apparent density

Property	Testing method	Apparent density, kg/m^{3*}				
		15	20	30	60	100
Compressive stress at 10 % deformation, N/mm^2	DIN 53 421	0.06 – 0.10	0.10 – 0.14	0.18 – 0.25	0.40 – 0.65	0.8 – 1.3
Dimensional stability/ compressive creep, %	DIN 18 164	< 5	< 5	< 5		
Thermal conductivity at 10 °C, W m^{-1} K^{-1}	DIN 52 612	0.036 – 0.039	0.033 – 0.036	0.031 – 0.035	0.031 – 0.035	0.036 – 0.039
Specific heat, kJ kg^{-1} K^{-1}		1.21	1.21	1.21	1.21	1.21
Coefficient of linear thermal expansion, K^{-1}		7×10^{-5}	7×10^{-5}	7×10^{-5}	7×10^{-5}	7×10^{-5}
Water vapor transmission rate, g m^{-2} h^{-1}	DIN 53 429	1.7	1.6	0.8	0.3	0.15
Water absorption after 7 days, wt %	DIN 53 434	0.4 – 2	0.4 – 1.5	0.3 – 1.0	0.3 – 0.7	0.3 – 0.7

* Density determined according to DIN 53 420.

pressurized autoclave and melted. The molding batch was then cooled to about 100 °C; upon emerging into the atmosphere or into a mold chamber, it foamed and formed a uniform cell structure.

The melting of the polystyrene pellets and the gassing, homogenizing, and cooling of the melt were then performed in extruders [71]. The continuously emerging strand foams, is formed into a flat sheet, solidified in a cooling zone, and cut into boards.

Blowing agents are mainly halogenated hydrocarbons which increase the foam's thermal resistance (decrease thermal conductivity) because of their high molecular mass.

In addition to Styrofoam (Dow Chemical), similar XPS boards with apparent densities of ca. 25 – 60 kg/m^3 are also available, e.g. Styrodur (BASF).

Foam boards are generally dyed during extrusion and provided with flame retardants (e.g., hexabromocyclododecane).

Depending on the end use, the boards are produced with different apparent densities, thicknesses, surface textures (foam skin, milled), and edges (flat, step groove, or groove and tongue).

Properties. The most important physical properties of extruded polystyrene (XPS) foams at different densities are summarized in Table 3. The requirements for use as thermal insulation material in building applications are specified in ISO 4898. The chemical resistance corresponds to that of polystyrene.

Uses. Extruded polystyrene foam boards are expecially suitable for thermal insulation in special constructions where high compressive strength, good appearance in exposed locations, and very low water adsorption are required.

Extruded polystyrene films are produced exclusively by the film blowing process (→ Films). A tubular film is extruded from an annular spinneret. It is then expanded three- to sixfold by using a high internal gas pressure and is thus stretched transverse to the direction of drawoff. The film is then calibrated via a cooling mandrel, cut into one or more strips, flattened, and either wound or processed immediately by thermoforming or lamination.

In the past films were produced in smaller, simple extruders from expandable polystyrene containing a blowing agent. However, the growing demand for such films required the use of large, direct-gassing installations that use standard polystyrene and an added blowing agent as in the extrusion of boards [72]. Low-boiling, preferably nonflammable, hydrocarbons are usually used as blowing agents. Chemical agents (e.g., citric acid plus sodium bicarbonate) and nucleating agents are also added to achieve a uniform cell structure.

Depending on the end use, film thicknesses range from several millimeters to a fraction of a millimeter and apparent densities from 100 kg/m^3 for thick films to 200 kg/m^3 for thin ones.

During thermoforming or lamination with cardboard and other layers, the films are often postfoamed; their apparent density is thus reduced and their thickness is increased. In this way, items such as egg cartons and packaging trays for fruit and meat are obtained with apparent densities of 60 kg/m^3 or less.

Polystyrene film laminated with cardboard is being tested as a replacement for corrugated

Table 3. Physical properties of extruded polystyrene (XPS) foams as a function of apparent density

Property	Testing method	Apparent density, kg/m^3*			
		25	30	40	50
Compressive stress at 10 % deformation, N/mm^2	DIN 53 421	0.1 – 0.2	0.2 – 0.4	0.4 – 0.6	0.5 – 0.7
Compressive creep, %	DIN 18 164	< 5	< 5	< 5	< 5
Thermal conductivity at 10 °C, W m^{-1} K^{-1}	DIN 52 612	0.029 – 0.033	0.025 – 0.030	0.025 – 0.030	0.025 – 0.030
Specific heat, kJ kg^{-1} K^{-1}		1.45	1.45	1.45	1.45
Coefficient of linear thermal expansion, K^{-1}		7×10^{-5}	7×10^{-5}	7×10^{-5}	7×10^{-5}
Water absorption after 28 days, wt %	DIN 53 434	< 0.1	< 0.1	< 0.1	< 0.1

* Density determined according to DIN 53 420.

cardboard where outstanding wet strength is required. Thin films are used for decorative purposes and as nonskid interlayers.

4.2.3. Structural Polystyrene Foams

Special starting materials are available for structural foams derived from polystyrene, its copolymers, and polymer blends. They already contain chemical blowing agents and are specially formulated for thermoplastic foam injection molding (TFI) and thermoplastic foam extrusion (TFE).

Products from butadiene-modified, impact-resistant standard polystyrene and from acrylonitrile–butadiene–styrene (ABS) polymers have the highest usage, followed by structural foams produced from standard polystyrene and styrene–acrylonitrile (SAN) polymers. For a detailed description of these polymers, see → Polystyrene and Styrene Copolymers.

Production. Physical blowing agents in the form of halogenated hydrocarbons are in principle suitable for structural polystyrene foams. However, they have not been widely used because more sophisticated processing technology is required than for chemical agents and control of foam structure is more difficult.

The following chemical blowing agents are commonly used: azo compounds (especially azodicarbonamide, sometimes modified), hydrazines (e.g., benzenesulfohydrazide), and sodium bicarbonate with citric acid.

Cell structure is affected not only by the blowing agents and the processing conditions, but also by the amount and type of nucleating additives such as talc or pigments.

Thermoplastic Foam Injection (TFI) Molding. Molded TFI parts can be produced on conventional injection molding machines with shut-off nozzles. However, low-pressure TFI machines are more economical. The mold is filled in two steps: (1) injection of the melt containing the blowing agent and (2) postexpansion to fill the mold cavity. Thus, the clamping unit experiences only the expansion pressure which is about one-tenth of the injection pressure required for compact polystyrene. In this two-step process, removal of heat from the melt starts with evaporation of the blowing agent and surface streaks are created on the molded parts. Streaking can be prevented by various techniques, some of which are patented [8].

Thermoplastic Foam Extrusion (TFE). The formulations of raw materials used in TFE are similar to those used in TFI. However, since the temperature of the extrusion mass is generally lower, blowing agents with a lower decomposition temperature are used or catalysts are added to promote decomposition of the blowing agent. Although a number of patented extrusion processes exist (e.g., the Celuka process for very smooth surfaces, the Woodlite process for woodlike grain), conventional devices, profiled nozzles, and subsequent calibration are commonly employed [73]. Prior to use, the parts or profiles are frequently subjected to surface treatment such as spraying, printing, or lacquering.

Properties. The physical and chemical properties of structural polystyrene foams depend highly on the raw materials used. With their generally very high apparent densities and virtually compacted surface layers, the mechanical properties of structural foams are only slightly inferior to those of solid parts.

Uses [8]. The major end user of structural polystyrene foam is the furniture industry. The product is not used simply to imitate wood, but to construct structural parts for furniture of modern, functional design that exploits the properties of the raw material. The hi-fi and television industries are also important customers for housings and other TFI components. Significant quantities are also used in the building and transport industries, in the manufacture of sports equipment, and in the automotive sector.

4.3. Poly(Vinyl Chloride) (PVC) Foams [→ Poly(Vinyl Chloride)]

Depending on the content of plasticizers, polymer processing aids, and thermosetting binders, poly(vinyl chloride) [9002-86-2] foams can be flexible, semirigid, or even rigid. Because of their range of properties, PVC foams have numerous uses. Frequently, they form part of structurally complex, multicomponent articles such as floor coverings or window frames.

The composition of PVC foams varies widely. Some consist mainly of PVC and contain only minor amounts of additives necessary for smooth processing and trouble-free application (stabilizers, lubricants, fillers, pigments, or blowing agents and their decomposition products). Others contain larger amounts of modifiers (plasticizers, cross-linking agents, processing aids, or impact modifiers.

Dry blends, granules and fluid or paste mixtures containing blowing agents are used to manufacture PVC foam. The most important processing technologies for dry blends and granules are molding, extrusion, calendering, and injection molding. Fluid or paste mixtures are usually processed by spread coating.

The PVC molding masses are foamed with both chemical and physical blowing agents (see Section 2.2) [74]. The foaming rate can be influenced by kickers or inhibitors. Poly(vinyl chloride) foams cannot be consistently classified because of the different manufacturing processes involved and their broad spectrum of properties and uses. However, division into rigid and flexible PVC foams has proved useful. Semirigid PVC foams are classified as rigid PVC foams although they contain plasticizers.

Trade names of PVC foams are listed in Table 1.

4.3.1. Rigid Poly(Vinyl Chloride) Foams

High mechanical strength, along with resistance to moisture, rot, and chemicals, is common to all rigid PVC foams. Thermal conductivity is 0.036 – 0.040 W m^{-1} K^{-1}. These foams have a high oxygen index and their combustion gases contain carbon dioxide, carbon monoxide, and hydrogen chloride.

Most rigid PVC structural foams are produced by extrusion of PVC compound (dry blend or granules containing blowing agents) in the form of pipes, shaped parts, or boards [75–85]. Metal pipes or shapes can also be coated with foamed PVC by extrusion [86], [87]. Furthermore, rigid PVC foam shapes can be reinforced with glass fibers. Very few rigid PVC foam components are produced by injection molding [88].

In the extrusion of molded rigid PVC parts, processing conditions are adjusted so that the blowing agent foams the molding mass only after it leaves the nozzle. Foamed parts have an outer skin whose thickness and density vary depending on how the melt foams and how rapidly the boundary phase is cooled. Complex shapes and boards of PVC foam can be produced by the so-called Celuka process [89] in which appropriate machine design allows foaming to proceed "inwards".

In the coextrusion process [90], [91], a compact PVC layer (which may be stabilized and pigmented as desired) is melted onto the foam during extrusion as an outer skin. Such profiles are preferred for outdoor use, e.g., as panels.

Rigid PVC foams range from predominantly closed-cell to open-cell, depending on the type and amount of blowing agent and the process used. These foams are used in the building and furniture industries and in the do-it-yourself sector for thermal insulation and as wood substitutes.

Thermoset-modified rigid PVC foams are generally manufactured by a two-step process [92–95]. In the first, so-called high-pressure stage, a paste containing PVC, plasticizer, isocyanate cross-linking agent, stabilizers, and a chemical blowing agent is heated in closed molds to about 180 °C under high pressure. The PVC and the plasticizer then form a gel, and the blowing agent decomposes to form tiny closed cells. After about 1 h, the molds are cooled while the pressure is maintained. In the second, so-called expansion stage, the molded articles containing the blowing agent are exposed to water vapor for several hours at 90 – 100 °C and reduced pressure. The material is still thermoplastic and thus softens; the expansion pressure of the occluded blowing agent increases the volume of the molded article. Some of the isocyanate additive reacts with water to form carbon dioxide which acts as an additional blowing agent; the remainder, together with a special auxiliary system, cross-links the PVC and significantly consolidates the foam structure.

The closed-cell foams produced are used primarily as core materials of high mechanical quality for composites in automotive, ship, and airplane construction. Important manufacturers are Kleber Colombes (France), Airex (Switzerland), and Conti-Gummiwerke (Federal Republic of Germany).

Rigid thermoplastic PVC foams can be produced by the same mold foaming process used for thermoset-modified foams. They are manufactured from polymer granules without using plasticizers, isocyanate, or cross-linking agents. These foams are used as core materials for composites and, because of their closed outer skin, are also used in marine buoyancy or flotation items.

4.3.2. Flexible Poly(Vinyl Chloride) Foams

Flexible PVC foams can be manufactured by various processes, either with or without a carrier.

Flexible PVC foams without support can be manufactured in the same way as rigid PVC foams, by a two-step process using dry blends, granules, or pastes containing blowing agents. The PVC foams obtained are predominantly closed cell; their flexibility and elasticity depend on the cell structure and the plasticizer content. Flexible PVC foams can also be produced continuously but with limited cross section by paste spreading or extrusion.

Flexible foams are used for sealing and insulation in the building trade, for heat insulation and buoyancy in clothing, and for impact protection in sports equipment.

Flexible PVC foams with support are produced by spreading pastes containing blowing agents on various supporting materials. Synthetic PVC leather, for example, consists of a textile carrier, a base layer of flexible PVC, and a layer of flexible PVC foam with a thin, compact surface. The flexible foam layer imparts a soft feel to synthetic PVC leather (→ Leather Imitates).

Modern, chemically embossed, color-printed floor and wall coverings have a similar structure. Inhibitors in the printing ink retard or prevent decomposition of the chemical blowing agent and thus create an embossed pattern that matches the printed pattern [96]. These materials are especially important as floor coverings (Congoleum process) because they are pleasant to walk on (→ Floor Coverings).

A spreadable whipped foam is obtained by intensively whipping gases (nitrogen, carbon dioxide, air) into PVC pastes. This foam is used mainly to back textile or rubber floor covering with an elastic layer that contains largely open pores after gelling [97–99].

Miscellaneous Flexible PVC Foams. Other flexible PVC foam items are produced from pastes containing blowing agents. They are used predominantly as sealing materials. Thus, for example, seals in crowned cork bottle caps used for beverages are produced by gelling and foaming a small amount of PVC paste applied directly to the cap. Similarly, flexible PVC foam seals for industrial components (e.g., air filters for automobiles) can be foamed in situ.

4.4. Foams from Phenol–Formaldehyde (PF) Resins (→ Phenolic Resins)

Production. Phenolic resin foams are produced by the acid-catalyzed, exothermic hardening of a phenol–formaldehyde resin [9003-35-4] condensed under alkaline conditions [100], [101] (→ Phenolic Resins). Evaporation of an added (halogenated) hydrocarbon blowing agent by the heat of the reaction produces foaming. Surfactants emulsify the blowing agent and stabilize the expanding foam. The foam is hardened with catalysts such as sulfuric acid, phosphoric acid, or arylsulfonic acids. Hydrochloric acid is no longer used [102]. For complete and thorough hardening, heat treatment may follow [103].

Hydrogen produced by reaction of powdered aluminum with an acid catalyst can also act as a blowing agent. This method is employed in the former Soviet Union where PF foams account for about one quarter of foamed plastic production [104].

Production is predominantly a batch process in which the foaming mixture is poured into block or other cavity molds. The use of spray guns has also been reported [105].

The well-known continuous production of laminated sheets [106] is used by Koppers [108], [108] and British Petroleum Chemicals [109], [110]. Closed-cell foams are presumably created. The starting materials are special resols with a high resin solids content. The blowing agent is a mixture of trichloromonofluoromethane [75-69-4] (CFC 11) and 1,1,2-trichloro-1,2,2-trifluoroethane [76-13-1] (CFC 113). Alkoxylated silicones [108] or glycerol ricinoleates [110] are used as surfactants.

For hardening, strong organic acids such as an anhydrous mixture of tolyl- and xylylsulfonic acids [108] or 50 % sulfuric acid [110] are used. Special mixing heads have been developed for intensive mixing of components [111].

The mixture is sandwiched between two surface layers of, for example, aluminum-coated cardboard; the foaming mass is shaped and hardened, while still plastic, in a heated, double-belt press (Fig. 10). The pressure exerted in the press is reported to have an important effect on foam quality. It reduces the open-cell content [107] and void formation underneath the upper layer [109].

The resulting laminates are between 30 and 55 mm thick and have apparent densities of 35 – 60 kg/m^3.

Properties. The hard, brittle, thermoset nature of cured PF resin is shared by the foam. It is, however, less pronounced in foams with smaller cells (cell size < 80 μm) or with highly perforated cell walls [112].

All PF foams in existence at the end of the 1970s were open-cell types. Here, the cells are interconnected by holes in their walls which are several micrometers wide. Because the holes also allow communication with the surroundings, the cells are air-filled [113–115]. Like polyurethane and polystyrene foams, closed-cell PF foams can now be produced, whose cell walls are intact and free of pores [116], [117]. These cells can thus retain fluorohydrocarbon blowing agents. Because the thermal conductivity of these heavy gases is lower than that of air, the resulting foams are better insulators than air-filled foams (thermal conductivity < 0.02 W m^{-1} K^{-1} and 0.033 W m^{-1} K^{-1}, respectively).

Water absorption naturally increases with the number of open cells. Light, largely open-cell PF foams (apparent density ca. 20 kg/m^3) may even be used as floral foam in flower arrangements [118].

If the foam is only partially closed-cell, expensive water-vapor barriers may be needed as, for example, in underground long-distance heating lines insulated with PF foam having an apparent density of 100 kg/m^3 [119]. Infiltration of water would not only impair heat insulation but also initiate corrosion in combination with the acidic hardening agents. Despite the generally high acid content (up to 20 wt %), corrosion problems are seldom encountered, especially with closed-cell products. Corrosion inhibitors such as calcium carbonate can be added.

Over short periods PF foams can resist temperatures up to 180 °C and, over longer periods, up to 130 °C. They are resistant to many solvents and attacked only by concentrated acids or bases.

Compared to other organic insulators, PF foam has a favorable fire behavior primarily because of the low smoke density of its combustion gases and its low flammability. Like other thermosets, the material does not melt. When ignited, a carbon skeleton is formed. With respect to the evolution of toxic gases (carbon monoxide), however, PF foams do not have any advantage over other foamed plastics [100], [101].

The afterglow of open-cell foams (punking) can be suppressed by the addition of flame retardants such as boron trioxide [1303-86-2] or aluminum hydroxide [21645-51-2]. Closed-cell PF foams hardened with sulfuric acid do not exhibit punking; when burnt, they "pop"; due to

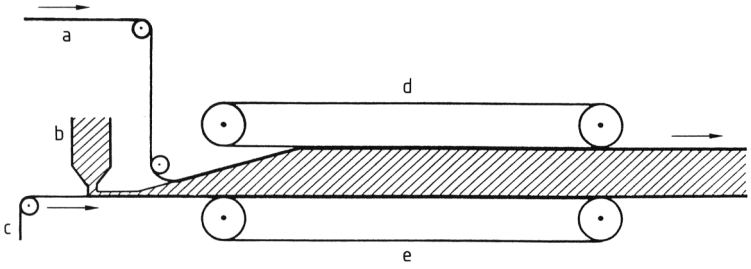


Figure 10. Production of laminated phenolic foam board
a) Upper surface layer; b) Dispenser for foamable phenolic resin; c) Lower surface layer; d) Upper conveyor belt; e) Lower conveyor belt

the noisy bursting of small particles of material [120].

Uses. In the building industry, for example, PF foam boards covered with glass-fiber webs are used as thermal insulation for flat roofs. They can be processed with hot bitumen because of their high heat resistance. When reinforced with an impregnated paper honeycomb, PF foam serves as the core of structural sandwich elements for walls and roofing, which are capable of bearing static loads. Sheet metal, polyester–glass fiber, plywood, or plaster may be used as surface layers [120–122].

Hemispheres cut from blocks are used for pipe insulation. A pour-in-place process with special molds has also been described [119].

In the former Soviet Union, PF foam is preferred for insulation in transport (motor vehicles, railroad cars, ships) as well as in aeronautic and space applications [104].

Special PF Foams. Inorganic additives (fillers) are added to PF foams to improve their mechanical strength and fire behavior. Depending on the type and amount of filler, *filled PF foams* with apparent densities of 100 – 300 kg/m^3 are obtained. Fillers include expanded silicates such as perlite [7344-61-8] [123]. Products that contain phenolic and furan resins are highly filled with materials such as aluminum hydroxide and are used as noncombustible building materials [124].

Phenolic foam with an apparent density of 20 – 30 kg/m^3, which is filled with polystyrene foam beads, can be obtained by dielectric heating [125].

Hybrid foams with good mechanical properties and low combustibility can be produced from PF resins and polyisocyanates [126].

4.5. Foams from Urea–Formaldehyde (UF) Resins (→ Amino Resins)

Production. A surfactant solution containing a hardener (e.g., phosphoric acid) is foamed with compressed air and blended with an aqueous 30 – 40 % solution of urea–formaldehyde resin [9011-05-6]. The resin is distributed throughout the surfactant foam, and cross-linking is initiated by the acidic hardener. A light, whipped-cream-like foam is formed which can be shaped easily and used to fill any cavity. The foam hardens rapidly to a water-insoluble, rot-resistant, foamed plastic without creating expansion pressure [127], [128]. A hardening time of 15 – 40 s is generally selected, which can be controlled within certain limits by changing external variables (temperature, hardener concentration).

Newly formed foam contains ca. 70 – 75 wt % of water. During drying, cracks are formed in the lamellae and the foam becomes open-celled [129]. This is accompanied by a ca. 8 % decrease in volume which can be reduced to 3 % by additives (e.g., polyols) [128], [130], [131]. Any free formaldehyde remaining is lost along with the water. Problems caused by formaldehyde release can be avoided largely by using more urea or improved resin formulations [132–134].

Stationary and portable equipment is available for foaming. Insulating layers can thus be introduced in cavities that are not easily accessible (e.g., in double walls).

Properties. Apparent densities of UF foam range from 10 to 30 kg/m^3 depending on the application. It can support little or no mechanical load and is, therefore, not used as semifinished product.

Urea–formaldehyde foam can withstand continuous exposure to temperatures up to 100 °C; at higher temperature, gradual shrinkage occurs. This material decomposes above 200 °C [128].

The thermal conductivity of UF foam (ca. 0.035 W m^{-1} K^{-1}) is in the same range as that of other air-filled insulating foams (cf. Fig. 3).

The material has a relatively favorable oxygen index (cf. Fig. 4). Although UF foam does not meet the flammability requirements of DIN 4102, it performs better in other flammability tests [ASTM D 1692–59 T, BS 2782 (1985) 508 D] [128].

Uses. The apparent density of in situ UF foam used in buildings must be at least 11 kg/m^3 (DIN 18 159). The foam serves mainly as thermal insulation in wall cavities [129], [135] and in plumbing ducts [136].

In mining, cavities (e.g., gallery roofs) are filled with UF foam to prevent accumulation of dangerous firedamp [137], [138]. The foam is also employed in the construction of airtight

dams to seal off sections of mines (e.g., abandoned shafts) [139].

In agriculture and horticulture, UF foams with apparent densities > 20 kg/m^3 and preferably in the form of flocks (e.g., Hygromull, BASF) are mixed into the soil to improve heat balance. Because of their open-cell structure, the foams also store water and dissolved nutrients.

Kindling is obtained by emulsifying liquid petroleum products with UF foam during manufacture [140].

Foamed plastic with an apparent density of ca. 30 kg/m^3, ground to a particle size of 0.1 – 6 mm and containing a surfactant and an antistatic agent, is used in carpet cleaning [141].

Urea–formaldehyde foam is suitable for cushioning impacts only if no more than one violent impact is anticipated (parachute deployment) [142]. For trade names of UF foams, see Table 1.

4.6. Foams from Melamine–Formaldehyde (MF) Resins (→ Amino Resins)

The rigid, brittle melamine–formaldehyde resin [9003-08-1] foams known until the late 1970s had no practical significance [143]. However, a flexible, elastic foam can now be produced from the same resin. This foam (Basotect, BASF) has a completely different morphology [144], [145]; it is open-celled and has slender, flexible struts (cf. Fig. 2B). The length : diameter ratio of the struts is crucial to its elastic behavior. For strut diameters from 7 to 15 μm, the ratio must exceed 10.

Production. A surfactant is used to emulsify pentane with a melamine–formaldehyde precondensate (molar ratio 1 : 3). Hardening occurs upon addition of formic acid. Controlled expansion in a continuous foaming tunnel is initiated by heating [146], [147].

Pentane and water from the reaction mixture act as blowing agents [148]. After removal of water and pentane, the foam is perfused continuously with hot air at 220 – 250 °C, and any cleavable formaldehyde is completely eliminated [149]. Flexible foams result only if the solids content exceeds 70 % [146]. Brittle products are obtained if the solids content is lower.

Properties. Density ranges from ca. 10 to 12 kg/m^3. Morphology and, hence, mechanical properties can be modified by pressing, which slightly bends the originally straight struts. The material becomes more flexible, with a negligible increase in density. For example, the compressive stress at 40 % deformation drops from 1.1 to 0.8 MPa [150]. Extreme mechanical–thermal treatment produces a highly consolidated, weblike material [151].

Because of the large proportion of IR radiation scattered by the thin struts, the thermal conductivity of the foam is in the lower range of air-filled insulators (Fig. 3).

Melamine resin foam can withstand short exposure up to 250 °C and long exposure up to 150 °C. No solvents are known for the foam; it is attacked by concentrated acids and bases.

Water absorption and diffusion properties are similar to those described in Chapter 3 for open-cell foams. The open, extremely fine structure and the flexibility of the foam result in especially favorable acoustical properties; despite the low apparent density, these properties are similar to those of open-cell polyurethane foams and mineral fibers.

The material meets the requirements of flammability class B 1 building materials, specified in DIN 4102 (“schwer entflammbar,” i.e., of low flammability), without an added flame retardant. According to the tunnel test of ASTM E 84–82 A, it is a class A material as defined in the Standard Building Codes. The smoke density of the combustion gases is low but does not reach the minimum values of PF foam. The material carbonizes during burning, without melting, and decomposes above 350 °C [145].

Uses. Thermal insulation, heat resistance, and ease of processing have opened up many applications for MF foams in industrial heat insulation (e.g., pipe insulation).

The material is used for sound insulation in the form of decorative ceiling and wall paneling, as well as for casings in automotive engines. Because of its low dynamic stiffness, MF foam is also employed for impact sound insulation. Laminates with plasterboard provide good soundproofing in addition to the desired thermal insulation.

4.7. Silicone (SI) Foams

Production. Silicone foams are produced from hot- or cold-vulcanized silicone rubber (→ Rubber, 5. Technology, → Silicones).

Heat-activated vulcanization systems contain mostly high molecular mass polysiloxanes incorporating methyl as well as vinyl groups. Additional components are chemical, heat-activated blowing agents, peroxide cross-linking agents, and silicate fillers [152]. These "single"-component blends are stable at room temperature and begin to foam when vulcanized by the action of heat.

Generally, preforms of the mixture or previously formulated dry blends are foamed in compression molds or extruders at 150 – 200 °C. The particles of silicone foam are then annealed at ca. 200 °C to remove any decomposition products derived from the cross-linking agent and to complete residual cross-linking.

Room-Temperature Vulcanization (RTV) Systems. Pourable mixtures that can be vulcanized and foamed at room temperature are required for producing molded articles and for filling cavities or coating parts with silicone foam.

Two-component systems are used in which short-chain polysiloxanes containing Si — H groups are allowed to react with low-viscosity polysiloxanes containing Si — OH groups. The reaction is performed at room temperature in the presence of a condensation catalyst:

$$\equiv Si-H + \equiv Si-OH \xrightarrow[\text{Room temp.}]{\text{Catalyst}} \equiv Si-O-Si\equiv + H_2$$

The hydrogen evolved acts as a blowing agent, but additional blowing agents may be necessary. Organotin compounds are used as catalysts [153], [154]; platinum catalysts yield products with improved heat and fire resistance [155–157].

The degree of cross-linking and the morphology of the foam can be controlled by the ratio of silanol to silane groups, especially by their functionality. Foams that range from rigid to flexible and from largely open-cell to closed-cell can be produced this way [158].

The above reaction takes only a few minutes but can be retarded by using acetylene alcohols or rhodium compounds as catalyst. The system is then stable for several hours and can be reactivated with heat [159].

Foam systems that can be cross-linked with atmospheric moisture have also been described [160].

A froth produced from a silicone emulsion can be converted to a light, elastomeric silicone foam in a microwave oven; no additional blowing agent is required [161].

Properties. Silicone foams are produced with apparent densities of 60 – 300 kg/m^3, but highly filled products are heavier. The heat distortion temperature is at least 200 °C; the material generally decomposes above 350 °C although higher limits have been recorded [162]. Thermal conductivity is reported to be 0.035 – 0.07 W m^{-1} K^{-1}.

Silicone foams display largely constant cushioning properties over a wide temperature range (– 80 to + 200 °C), and compression set is low. These materials exhibit good dielectric properties; are resistant to hydrolysis, radiation, aging, and weathering; and are physiologically inert.

The materials have a high flame resistance, with a favorable oxygen index of about 30 and a low smoke density. Combustion gases contain only carbon monoxide and carbon dioxide.

Uses [157]. Examples of the uses of silicone foams are

- sealing (shaped profiles, strings, rings) including heavy-duty applications in nuclear power plants;
- filling cracks or cavities, and sealing cable inlets and outlets in construction work;
- thermal and electrical insulation of fragile components in aerospace applications, with simultaneous vibration damping;
- production of carbonizing heat shields used in space vehicles (filled foams) [163];
- cushioning in airplane seats [162]; and
- fitting artificial limbs and producing inert implants for medical use [164].

4.8. Epoxy (EP) Foams (→ Epoxy Resins)

Production. The starting components for epoxide foams are epoxide oligomers, cross-linking agents, blowing agents, surfactants, and possibly also fillers. Silicone–glycol copolymers are described as surfactants [165]. The preferred epoxide oligomers

are reaction products of 2,2-bis(4-hydroxyphenyl) propane [80-05-7] (bisphenol A) and epichlorohydrin [106-89-8] (→ Epoxy Resins). Cross-linking agents include fast-acting aliphatic amines (e.g., diethylenetriamine [111-40-0]) or slower acting aromatic amines (e.g., 1,3-phenylenediamine [108-45-2]) that are effective only at elevated temperature. The reaction is highly exothermic and thus activates the blowing agent which is often a fluorinated hydrocarbon or a compound that splits off nitrogen (e.g., sulfonyl hydrazides). Precise temperature control during foaming is important. Too high a temperature causes cracking and deformation of the foam.

Foams with apparent densities of 20 – 40 kg/m^3 are produced from fast-acting systems by a two-component spray process. However, mold-pouring or injection processes are more common and can also be used with slow-acting systems that require external heat. The resulting foams have apparent densities of 60 – 300 kg/m^3 [166]. Trade names are listed in Table 1.

Syntactic foams (see also 1) [167] often consist of epoxy resins and, therefore, are discussed in this section. Their cells are formed by hollow spheres (microballoons) that are distributed in the polymer matrix as a filler. The hollow spheres are composed of glass or phenolic resin and have a diameter of ca. 100 μm and a wall thickness of ca. 2 μm. Larger "macrospheres" composed of epoxy resin and with a diameter of over 1 mm have also been described [168].

The hollow spheres are mixed with a low-viscosity epoxy resin in the same way as fillers. When the fraction of spheres is 40 vol % or less, mold pouring is used for further processing; extrusion or compression molding can be employed for fractions up to 67 vol %. A vacuum is applied for degassing. The products have apparent densities of 200 – 800 kg/m^3.

Phenolic resins, polyimides [169], silicones [170], and polyether sulfones are also used as matrix resins.

Properties and Uses. Epoxy foams are usually rigid and primarily closed-cell materials. They have favorable mechanical properties, absorb very little water, and are not hydrolyzable. They are resistant to many chemicals but not to ketones.

The good adhesion of EP foams to many materials makes them suitable as laminate cores. They also serve as edge seals for honeycombs made from materials such as the aramid Nomex that are used in airplane construction.

Because of their low dielectric constant (< 2), EP foams are used in protective housings for radar equipment (radomes). Materials with a higher dielectric constant are obtained by addition of metal flocks (e.g., aluminum) and are used as radar lenses.

Sensitive electronic components are protected by encapsulation in EP foam [165].

The heat distortion temperature is reported to be 100 – 200 °C. The thermal conductivity of EP foams containing heavy gases is ca. 0.02 W m^{-1} K^{-1}, whereas that of foams manufactured with other blowing agents exceeds 0.035 W m^{-1} K^{-1}, depending on the density. Therefore, these foams are also used as insulation for hot-water pipes.

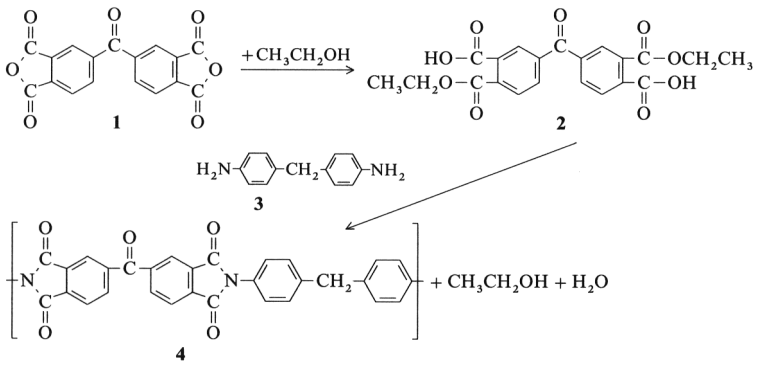
Epoxy foams that do not contain fire retardants are flammable. The oxygen index is 20.

Syntactic foams are very rigid and able to withstand very high hydrostatic pressures. They are employed in laminates for underwater vehicles, including a shuttle for deep-sea mining to a depth of 6000 m. Other uses include flotation devices with a density of 0.5 g/cm^3 for steel pipes in offshore oil exploration [168], and ablation materials for space flight.

4.9. Polyimide (PI) Foams (→ Polyimides)

The increasing importance of polyimides as temperature-resistant materials has led to the development of PI foams. Trade names are listed in Table 1.

Production. In a typical polyimide synthesis, the hemiester (**2**) is prepared from 3,3′,4,4′-benzophenonetetracarboxylic acid dianhydride [2421-28-5] (**1**) and ethanol. The polyimide (**4**) is obtained by reacting (**2**) with a diamine, in this case 4,4′-diaminodiphenylmethane [101-77-9] (**3**) (and if necessary with 2,6-diaminopyridine [141-86-6]), in the presence of suitable surfactants.



The powder obtained after spray-drying the precursor solution is foamed into large blocks in a microwave oven. The water and alcohol liberated upon imidization act as blowing agents.

Flexible, open-cell foams are formed [171]. Morphology and especially thermal properties can be modified by using other diamines containing, for example, hexafluoropropyl groups [173], [173].

Rigid panels can be produced by impregnation of fibrous webs or honeycombs with precursor solution and subsequent foaming. Syntactic PI foams (cf. Syntactic foams) and rigid PI foams [174] are also known.

Properties. The range of apparent densities of flexible PI foams is 6 – 18 kg/m^3; the thermal conductivity is ca. 0.035 – 0.040 W m^{-1} K^{-1} at 10 °C.

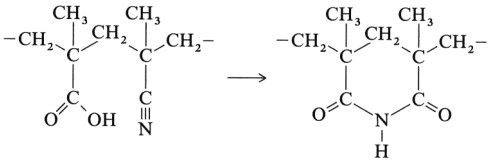
The materials are resistant to solvents. They do not undergo hydrolysis and can be used between − 195 and + 260 °C. Their fire behavior is particularly favorable: they have a very low smoke density and a high oxygen index [175–177].

Uses. Lower density PI foam is used for acoustic and thermal insulation. Its low mass and fire behavior make it highly suitable for aerospace applications [178] where material cost is not a primary concern.

Examples of uses are as a heat and vibration protection for sensitive military and aerospace electronics equipment, a lightweight fire barrier for airplane cabins, and cryogenic insulation for fuel tanks. The higher density foams can replace polyurethane foams in airplane seats because of their cushioning properties [179]. Uses in shipbuilding have also been reported.

4.10. Polymethacrylimide (PMI) Foams (→ Polyimides)

Methacrylic acid [79-41-4] and methacrylonitrile [126-98-7] are subjected to radical copolymerization after the addition of blowing agents (e.g., formamide, or 1-propanol) that will come into play later. A transparent sheet is formed which is heated in a second step to 175 – 220 °C.



Copolymer of methacrylic acid and methacrylonitrile

Polymethacrylimide [*53112-45-7*]

Heating results in imide formation and the production of a rigid, closed-cell foam (Rohacell, produced by Röhm, Federal Republic of Germany) [180–182].

Properties. The relatively rigid material has apparent density of 30 – 200 kg/m^3. The heat distortion temperature (180 °C) can be increased to ca. 205 °C by annealing, which increases the degree of imidization. While warm, the foamed plastic can be reshaped and compacted. The thermal conductivity is 0.030 – 0.034 W m^{-1} K^{-1}.

Polymethacrylimide foam is resistant to organic solvents but attacked by alkaline media. The material burns, giving off little smoke; its oxygen index is 20.

Uses. Polymethacrylimide foam serves as a core material for lightweight laminates with

high flexural rigidity which can be loaded dynamically. Because the foam is thermoplastic and can be compacted, complex forms can be produced with precision from a preform in a press. Therefore, the product frequently simplifies existing fabrication techniques. It is used in skis, tennis racquets, helicopter rotor blades, and load-bearing parts in airplanes.

Components with a large surface area (e.g., for railroad car construction) can be produced from sheet-molding compound sandwiches in short cycles at a molding pressure of ca. 1 MPa [183–185].

4.11. Poly(Methyl Methacrylate) (PMMA) Foams (→ Polymethacrylates)

Production. Monomeric methyl methacrylate [80-62-6] is subjected to radical polymerization in the form of a thin layer between glass plates. It contains trichlorofluoromethane or pentane as a blowing agent and butyl methacrylate as a plasticizer. A board is formed (typical thickness 4 mm) which is subsequently foamed at 110 °C [186].

Properties. The foamed sheets (typical thickness 16 mm) have very large closed cells (diameter 2 – 10 mm) and thus absorb very little visible light. Material with an apparent density of 30 kg/m^3 has a thermal conductivity of 0.035 – 0.044 W m^{-1} K^{-1}. It is highly weather resistant.

The maximum long-term service temperature of the PMMA foam Isocryl (IMC Acrylguß) is 80 °C.

Uses. The transparent insulating material is used for double-glazing improvements to increase the thermal insulation of windows in large buildings and greenhouses. It is also used in ceiling construction [187].

4.12. Polyamide (PA) Foams (→ Polyamides)

Production. A structural foam with only slightly lowered apparent core density (1.1 → 1.0 kg/m^3) is produced by the reaction injection molding (RIM) process. Caprolactam [105-60-2], for example, is injected into a mold with sodium lactamate [2123-24-3] as catalyst and an acyl lactam as activator [188–190]. Nitrogen serves as blowing agent [191]. Reaction injection molding permits good filling of the mold with low postshrinkage of the molded part. No sink marks are formed.

Foams with apparent densities down to ca. 400 kg/m^3 are made by conventional thermoplastic injection molding from polyamide (nylon 6) and a second batch containing blowing agents (e.g., azocarbonimide) [192], [193].

Polyamide foams with apparent densities below 200 kg/m^3 can also be obtained by alkaline lactam polymerization with low-boiling hydrocarbons as blowing agents [192–195]. However, they have no commercial significance.

Properties and Uses. Polyamide foams with higher apparent densities are used more widely than those with low densities, and their properties resemble more closely those of solid polyamides. Their toughness, rigidity, and abrasion resistance are worthy of mention. The high heat resistance, solvent resistance, and relatively favorable fire behavior are additional advantages. The inherent water absorption of polyamides can alter the mechanical and thermal behavior of the foam.

Some applications of structural PA foams are as housings for electrical apparatus, lamp sockets, furniture parts, pallets, containers, and bowling pins. Trade names are listed in Table 1.

4.13. Poly(Phenylene Oxide) (PPE) Foams [→ Poly(Phenylene Oxides)]

Blends of poly(phenylene oxide) [25667-40-7] with high-impact polystyrene are fabricated into structural foams by thermoplastic foam injection molding. Trade names are listed in Table 1.

The material is distinguished by good mechanical properties and a high heat resistance. The polystyrene content has an adverse effect on the favorable fire behavior of PPE (oxygen index = 30).

Applications in the automobile sector (crash pads) and in computer manufacture have been described [10, p. 16].

In the patent literature, the manufacture of extruded, lighter weight foams from PPE – PS blends, by using chlorinated hydrocarbons as blowing agents, is described [196].

4.14. Polysulfone (PSU) Foams (→ Specialty Plastics)

Production. In the *dough-foam process*, particles of polysulfone [25135-51-7] are allowed to swell and form a gel in a solvent such as methylene chloride or a ketone. A cold-extruded dough sheet is comminuted to dough pellets, which can then be processed into foam-molded parts by using EPS technology (cf. Section 4.2.1). The gel can also be pressed directly to give a preform which foams when heated. Heating causes the solvent or blowing agent to escape and the low glass transition temperature of the gel increases to the high polysulfone value of ca. 200 °C [197–199].

Properties and Uses. The apparent densities of PSU foams are between 40 and 500 kg/m^3, depending on the process used. Unfilled products made by the dough-foam process, for example, have apparent densities of 390 kg/m^3; fiber-reinforced foams may have apparent densities as high as 700 kg/m^3.

Polysulfone foams display high heat resistance and a favorable fire behavior.

Possible applications include self-lubricating bearings, as well as special laboratory and medical products.

Highly filled syntactic polyether sulfone foams have been proposed for radomes [200].

4.15. Polycarbonate (PC) Foams (→ Polycarbonates)

Production. Structural polycarbonate [24936-68-3] foams with apparent densities of 560 – 900 kg/m^3 are produced by low-pressure thermoplastic foam injection molding. Special chemical blowing agents [201] are admixed prior to processing which occurs at about 300 °C [202].

The manufacture of lighter weight foams by extrusion with chlorinated hydrocarbon blowing agents has also been described [203].

Properties and Uses. Polycarbonate foams, like the solid material, exhibit high impact resistance, rigidity, and heat resistance. They are flame-resistant and have a high electrical resistance. They are resistant to acid, but are attacked by bases, and by aromatic or halogenated hydrocarbons.

Examples of applications are housings for electrical apparatus, sports equipment (water skis), and furniture parts. Trade names are listed in Table 1.

5. Testing (→ Plastics, Properties and Testing)

Almost all major industrialized countries have adopted their own standards for testing foamed plastics (e.g., ASTM, United States; BS, Great Britain; DIN, Federal Republic of Germany; Association Française de Normalisation AFNOR, France). International standards (ISO) also exist. In some countries, test methods are specified in end-use-related standards. Thus, for example, foams for the building industry and their test methods are specified in ASTM C 578 "Standardized Specification for Preformed, Cellular Polystyrene Thermal Insulation."

In this overview, only the principles of the most important, generally valid test methods are described. Detailed information necessary for actual testing must be obtained by referring to the standards listed.

5.1. Mechanical Properties

Density (ASTM D 1622, ASTM C 303, ISO 845, DIN 53 420). The density is determined by using cubical test specimens or slabs; it is measured in kilograms per cubic meter.

Open- and Closed-Cell Content (ASTM D 2856). The content of open and closed cells is determined by measuring the apparent and true volumes with a special apparatus. The fraction of open or closed cells is reported in volume percent.

5.1.1. Rigid Foams

Compressive Properties (ASTM D 1621, ISO 844, DIN 53 421). The *compressive stress* is the compressive load per unit area of minimum original cross section carried by the test specimen at any given moment (Fig. 11). It is expressed in force per unit area, e.g., newtons per square meter or pascals. The *compressive strength* is the stress at the yield point (the first point on the stress–strain curve at which an

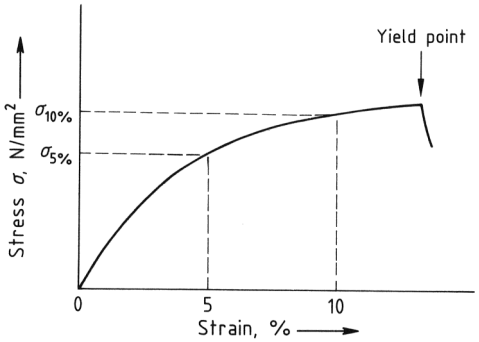


Figure 11. Typical stress–strain curve for a foamed plastic

increase in strain occurs without an increase in stress). In the absence of such a yield point, the compressive strength is the stress at 10 % deformation.

Tensile Properties (ASTM D 1623, ISO 1962, DIN 53 430). The *tensile strength* σ_B is obtained by dividing the breaking load in newtons by the original minimum cross-sectional area of the specimen in square centimeters. The *elongation* is the extension of the material at the moment of rupture expressed as a percentage of its original length measured between gauge marks. The shape of the test specimen used depends on the amount of sample available, as well as the stiffness of the material. It may be round or square and have tapered ends or rounded shoulders; length varies from 10 cm to 1 m. A typical shoulder shape is shown in Figure 12. Speed of testing strongly influences the results; a standard speed is chosen such that rupture occurs in 1 – 6 min.

Breaking Load and Flexural Properties (ASTM C 203, ISO 1209, DIN 53 423). The breaking load and flexural properties are tested by different procedures on a bar of rectangular cross section which can be loaded in two ways:

1. The bar rests on two supports and is loaded midway between the supports.
2. The bar rests on two supports and is loaded at the two quarter points.

Normally, values are measured at the maximum load or breaking point. The *flexural strength* is equal to the maximum stress in the outer layers at break; it is calculated from the load applied at the break point by means of

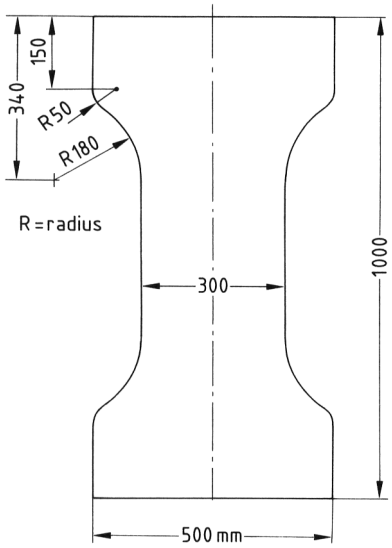


Figure 12. Specimen for tensile testing
All lengths are given in millimeters

equations that depend on the testing procedure used. Flexural properties may vary with specimen span-to-thickness ratio, temperature, difference in rate of straining, and testing procedure followed. In comparing results, these parameters must be consistent.

Dynamic Stiffness (DIN 52 214). The dynamic stiffness of elastified rigid foams is easily measured and is used to estimate their potential as impact soundproofing material. A metal plate that applies a 2 kPa (kN/m^2) load uniformly to the test specimen is affixed to it with plaster. An alternating force is applied perpendicular to the metal plate. The resonance frequency f_r of the system is measured. The dynamic stiffness s' is proportional to f_r^2.

5.1.2. Flexible Foams

Several procedures are used to test the compressive behavior of flexible foams.

Compression Load Deflection Test (ASTM D 1564, ASTM D 2406, DIN 53 577). This test involves measuring the load necessary to produce a defined compression (20, 40, or 60 %) over the entire surface area of the foam specimen. The compressive stress at the specified compression is given in pascals or newtons per

square meter. The test is also used to measure the relaxation of flexible foams after removal of the compressive load.

Indentation Load Deflection (ILD) (ASTM D 1564, ASTM D 2406, DIN 53 576). This test measures the load necessary to produce a defined indentation (e.g., 25, 65, or 70 %) in the foam product. A flat, circular indentor foot of specified diameter is connected to a load-measuring device by means of a swivel joint and is pressed into the specimen. The force in newtons required for 25 and 65 % indentation is known as the 25 and 65 % ILD value, respectively.

The ASTM tests also describe a procedure for measuring indentation on loading. These values are known as indentation residual gage load (IRGL) values. The load deflection is determined by measuring the thickness of the foam under fixed loads on a circular indentor foot.

Compression Set Test (ASTM D 1564, ASTM D 2406, DIN 53 572). This test involves compressing the foam specimen under specified conditions of time and temperature, and noting the effect on the thickness of the specimen. The compression device consists of two or more flat plates arranged so that the plates are held parallel to each other by bolts or clamps; the space between the plates can be adjusted to the required thickness by means of spacers.

Standard testing conditions are a compression of 50 or 75 %, a temperature of 70 °C for 22 h, and a relaxation time of 30 min. The constant-deflection compression set is calculated and expressed either as a percentage of the original thickness or as a percentage of the original deflection.

Tensile Properties (ASTM D 1564, ASTM D 2406, DIN 53 571). Tensile stress, tensile strength, and elongation at break are measured when a tensile load is applied to the foam. The test specimen is stamped out with a die of a specified shape (shoulder shape, see Fig. 12). The *tensile stress*, in pascals or newtons per square millimeter, at a given elongation is the load applied at this elongation divided by the original cross-sectional area of the specimen. The *tensile strength* is the tensile stress at the breaking point.

Resilience (Ball Rebound) Test (ASTM D 1564). The ball rebound test is used to evaluate the resilience of foams; a steel ball is dropped on a foam specimen, and the height of rebound is noted. Values are given as a percentage of the dropping height and are known as ball rebound resilience (BRR) values.

5.2. Thermal Properties

Dimensional Stability (ISO 2796, DIN 53 431) consists of measuring the dimensions of a test specimen at a standard test temperature (e.g., −25, 0, or +70 °C). The change in linear dimensions is expressed as a percentage of the values measured at room temperature.

Compressive Creep (ISO/TR 2799, ISO 4898, DIN 18 164) consists of measuring the change in thickness of a test specimen when it is subjected to a load at elevated temperature. The change is given as a percentage of the original thickness. Several testing procedures are used; common testing conditions follow.

t, °C	Load, kPa	Time, h
70	0	48
80	20	48
70	40	168

Deflection Temperature (ASTM D 648, DIN 53 424) consists of determining the temperature at which an arbitrary deformation occurs when a specimen is subjected to an arbitrary set of testing conditions. Either a compressive or a flexural load may be used.

Flexural Load. A bar of rectangular cross section is tested as a simple beam; the load is applied at its center, or the bar is held at one end while the load is applied at the other. The loaded specimen is immersed in a heat-transfer medium whose temperature can be increased at a constant rate (e.g., 2 °C/min or 50 °C/h). The temperature of the medium is measured when a certain deflection (e.g., 2 mm) has been reached and is recorded as the deflection temperature under flexural load.

Compressive Load. A test specimen of $50 \times 50 \times 20$ mm is loaded with 25 kPa (0.025 N/mm^2). Then, as with flexural load,

the temperature of the test specimen is raised at a constant rate (e.g., 50 °C/h). The temperature at which a certain deflection is reached is recorded as the deflection temperature under compressive load.

Thermal Conductivity (DIN 52 612, ASTM C 177, ASTM C 518, ASTM C 236). The thermal conductivity, expressed in watts per meter per kelvin, is the rate of heat flow through a unit thickness of an infinite slab of a homogeneous material in a direction perpendicular to the surface, induced by a unit temperature difference.

Thermal conductivity is one of the most important properties of foamed plastics and is generally low due to their cellular structure.

Because of the technical importance of this property and the complicated nature of the measurements, different test methods exist. In principle, a steady-state heat flux is measured through flat slabs of the specimen using a guarded hot-plate apparatus. Single-sided and double-sided modes of measurement are used. An idealized double-sided system is shown in Figure 13. The specimen is sandwiched between two isothermal cold plates and a guarded hot plate. The guard portion of the isothermal hot plate provides the power necessary to create the proper thermal conditions within the test volume.

A good review of terms, definitions, symbols, and units pertaining to thermal insulating materials is given in ASTM C 168.

Fire Behavior. The fire behavior of foamed plastics depends on many parameters. Therefore, many different tests exist, each of which emphasizes different aspects of burning, i.e. ease of ignition, flame propagation, heat release, combustion products (smoke density and toxicity). The most important tests are DIN 4102, DIN 53 438, ASTM E 84, NF P92 501, NF P92 504, NF P92 505, NF P92 506, UL 94, ASTM D 2863–77.

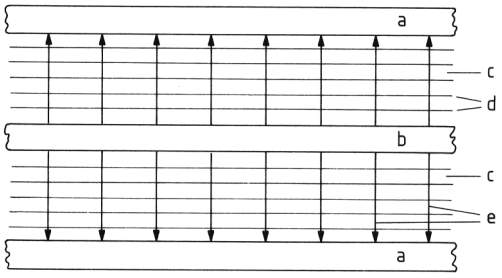


Figure 13. Schematic of the guarded hot-plate apparatus for determining thermal conductivity
a) Cold isothermal surface; b) Hot isothermal surface; c) Specimen; d) Isothermal planes; e) Heat flux lines

5.3. Miscellaneous Properties

Water absorption (ASTM D 2842, ISO 2896, DIN 53 433) of cellular plastics is determined by measuring the change in buoyancy resulting from immersion under a head of water for a certain time (2 h, 4 d, 7 d, 28 d, or longer). Water absorbed by the specimen lowers buoyancy by reducing the volume of water displaced. Water absorption may be expressed in volume percent or weight percent.

Thermal and Humid Aging (ASTM D 2126). Because of the wide variety of potential uses of cellular plastics, artificial aging tests must be based on the intended application. Normally, responses to temperature and humidity are selected. Temperature ranges from − 70 to + 200 °C and humidity ranges from ambient to 97 % are used. The specimen is examined visually; changes in density and dimensions are also measured.

Electrical properties of foamed plastics are seldom measured. Testing methods are identical with those used for standard plastics (see → Plastics, Properties and Testing).

6. Economic Aspects

Polyurethanes are the most important foams as far as consumption is concerned and are described elsewhere (→ Polyurethanes). The consumption of other major foamed plastics in Western Europe, the United States, and Japan is summarized in Table 4. The most important of these are foams derived from polystyrene beads and extruded polystyrene. Significant amounts of foam from polyolefins, poly(vinyl chloride), phenol–formaldehyde resins, and urea–formaldehyde resins are also used.

7. Toxicology and Environmental Aspects

The polymeric materials used for foamed plastic production generally do not present a

Table 4. Consumption of foamed plastics in 1986

Foamed plastics*	Consumption, 10^3 t		
	Western Europe	United States	Japan
Expanded polystyrene (EPS)	485	283	190
Extruded polystyrene (XPS)	135	293	300
Poly(vinyl chloride) (PVC)**	25	150	
Polyolefin (PO)	20	25	37
Urea–formaldehyde (UF) resin	12		
Phenol–formaldehyde (PF) resin	10	8	3

* Foamed plastics with an apparent density of < 200 kg/m^3.
** Including foams with apparent density > 200 kg/m^3.

toxicological hazard because they are not absorbed by the human body. Of greater concern are residual monomers and additives, i.e., materials of lower molecular mass. All legal requirements pertaining to such constituents must be observed. For the benefit of processors and end users, the manufacturers of synthetic foams provide pamphlets, safety bulletins, and technical information on the processing and proper handling of synthetic foams.

Foamed plastic waste is bulky and is therefore often compacted before disposal. Since toxic substances are not released on storage, contamination of ground water does not occur. After being dumped the foamed plastics are slowly degraded, the rate depending on the nature of the plastic [204]. During the controlled aerobic degradation of noncomminuted thermoplasts and thermosets (composting), soil-inhabiting Actinomycetes were shown to attack aminoplasts most effectively [205].

Although foamed plastics have a high calorific value, they do not play an important role in refuse incineration plants because of their low mass. However, thermoplastic foams must be mixed with sufficient quantities of nonmelting materials with a low calorific value.

The combustion products of most foamed plastics are carbon dioxide and steam which do not pose any environmental problems. However, chlorine-containing products release hydrogen chloride which must be removed by washing the flue gas [206].

Chlorofluorocarbons (CFCs) are used in the production of many foamed plastics. They remain enclosed within the cells of the plastic and increase the thermal insulation of air-filled foams.

The ozone depletion hypothesis [207] suggests that CFCs damage the stratospheric ozone layer that prevents shortwave UV radiation from reaching the earth. Models of stratosphere chemistry, propose as many as 200 possible reactions that involve CFCs, carbon dioxide, nitrogen oxides, and methane. Chlorine atoms seem to play an important role in initiating ozone-consuming reactions [208–210].

"Soft" CFCs (e.g., chlorodifluoromethane [75-46-6]) are being introduced as alternative blowing agents. Since they are less stable than the customery CFCs, they are reported to decompose in the troposhere and thus have a much lower ozone depletion potential [211], [212].

8. Abbreviations used in this article:

ABS	acrylonitrile–butadiene–styrene
BRR	ball rebound resilience
EP	epoxy
EPS	expandable polystyrene
EVM	ethylene–vinyl acetate copolymer
HDPE	high-density polyethylene
ILD	indentation load deflection
LDPE	low-density polyethylene
LLDPE	linear low-density polyethylene
MF	melamine–formaldehyde
NF	Norme Française
PA	polyamide
PC	polycarbonate
PE	polyethylene
PF	phenol–formaldehyde
PI	polyimide
PMMA	poly(methyl methacrylate)
PMI	polymethacrylimide
PO	polyolefin
PP	polypropylene
PPE	poly(phenylene oxide)
PS	polystyrene
PSU	polysulfone
PUR	polyurethane
PVC	poly(vinyl chloride)
RIM	reaction injection molding
RTV	room-temperature vulcanization
SAN	styrene–acrylonitrile
SI	silicone
TFE	thermoplastic foam extrusion
TFI	thermoplastic foam injection molding
UF	urea–formaldehyde
UL	Underwriter's Laboratories
XPS	extruded polystyrene

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Part 4

Resins

Ullmann's Polymers and Plastics: Products and Processes
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Alkyd Resins

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ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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1. Introduction

Alkyd resins are, literally, polyesters. They are made by condensation polymerization of three types of monomers:

1. Polyols
2. Polybasic acids
3. Fatty acids or triglyceride oils

Because of their distinctive properties, alkyds often are classified separately from other polyesters, as they are in this encyclopedia.

The largest use of alkyds is for surface coatings (paints, enamels, lacquers, and varnishes) in which the resins function as binders, forming a tough, continuous film that adheres to the object coated. Alkyds are the most versatile of coating binders, and they are used extensively in all major categories of coatings: architectural, industrial, and special purpose (see Chap. 6). Despite gradual replacement of alkyds with other types of resins, a substantial fraction of all organic coatings applied worldwide use alkyds as a primary binder or as an additive.

Alkyds are also important ink binders. Other uses include caulks, adhesives, and plasticizers.

Relative to most commercial polymers, alkyd resins often have low glass transition temperatures T_g. Consequently, they are viscous, tacky materials that are difficult to handle. Most often, the handling problems are overcome by dissolving the resins in organic solvents to give solutions that can be poured and pumped.

Because of their low T_g, most alkyds are useful as coating binders only after they are chemically cured to harden the film after the liquid coating has been applied. Curing is accomplished by cross-linking chemical reactions. Cross-linking may result from chemical reaction of the coating film with oxygen in the air or from chemical reaction with a second resin or substance. The second resin, called a cross-linker, is blended with the alkyd at the time of coating manufacture or application. Certain alkyds are added to acrylic and nitrocellulose lacquers, where their role is to plasticize the brittle thermoplastic resins. Alkyds used in this way do not cross-link.

History. Paints containing vegetable oils have been used for at least 600 years. A major goal in the early development of alkyd resins was to combine vegetable oil technology with polyester technology to make improved materials. Probably the first polyester resin was made by Berzelius [18] in 1847. It was an intractable product of glycerol and tartaric acid. In 1901 W. Smith [19] reported a brittle glycerol – phthalic anhydride polymer, and by 1910 workers at General Electric were attempting to develop more tractable materials for electrical end uses. Work was probably hampered by lack

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of an accepted theory of polymerization, but several patents were obtained.

The General Electric program eventually led to preparation in 1921 of glycerol – phthalic anhydride – fatty acid polymers. By 1926 these polymers were being used commercially as adhesives, and research on their use in coatings was underway [20]. The first account of this work was published in 1929 [21]. A U.S. patent was issued in 1933 [22] but was declared invalid in 1935. Technical progress presumably was aided by emergence of polymerization theory in the late 1920s [23], [24].

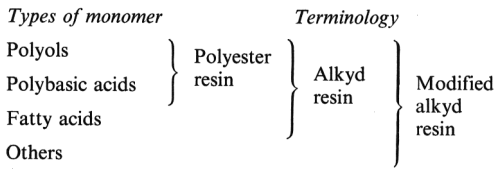
An important early development was the monoglyceride process for making alkyds directly from vegetable oils, eliminating the expense of preparing and purifying glycerine and fatty acids. In the 1930s, linseed oil was the most common binder for architectural paints, but alkyds were beginning to replace it. Alkyds offered faster drying, less yellowing, and superior protective properties. By 1940 U.S. consumption of alkyds exceeded 4×10^4 t/a.

By the early 1950s, alkyds had become the preeminent binder for coatings. U.S. consumption had reached 2×10^5 t/a and was rising. However, water-based architectural paints were being introduced. These paints generally used polyvinyl or polyacrylic emulsion resins as binders and contained little or no alkyd. During the 1950s, 1960s, and 1970s, water-based paints gradually captured most of the architectural coatings market from alkyd- and oil-based paints. The newer paints were popular because they could be cleaned up with water and were economical to produce because of low petroleum prices. Despite declining use in architectural paints, total use of alkyds continued to increase during most of this period because of rapidly growing use in a huge variety of industrial and special purpose coatings and in inks. Alkyd consumption in the USA reached a plateau at about 3×10^5 t/a in 1960 – 1980 and then began declining at a rate of about 2 %/a, reaching about 2.3×10^5 t/a in 1996 [25]. Worldwide consumption of alkyds is probably declining at a slower rate and perhaps holding steady.

Alkyd technology is being adapted to meet contemporary needs. Concern about air quality led to development of alkyds for use in high-solids and water-reducible coatings. Rising petrochemical prices have increased interest in all polymers made partly from renewable resources. Besides, alkyds are entrenched in innumerable specialized end uses, so wholesale replacement would be difficult.

Definitions and Classifications. Terminology relating to alkyd resins can be confusing because it has never been uniform and because it has changed considerably over the years. The ASTM defines an alkyd as "a synthetic resin made from polyhydric alcohols and polybasic acids; generally modified with resins, fatty oils, or fatty acids" [26]. The DIN definition is similar [27].

For this article, slightly narrower and more exact definitions have been adopted. They are conveniently represented as follows:



In this article the word "alkyd" is used as both a noun and an adjective. Therefore, "alkyd" and "alkyd resin" are synonymous. This usage is widespread, although some authors feel that only the latter usage is correct.

The scope of this article includes alkyds and modified alkyds. Polyesters are treated under separate keywords (see → Polyester Resins, Unsaturated, → Polyesters).

A brief retracing of the history of resin terminology may help clarify some of the terms that may be encountered. "Alkyd" is a respelling of "alcid", a word apparently coined at General Electric for the reaction product of polyfunctional alcohols and organic acids. Therefore, in the 1920s "alkyd" meant what is now meant by "polyester". The resins now called alkyds were called "oil-modified alkyds" during the 1930s. For a time, almost all commercial alkyds contained oil, so the phrase "oil-modified" was redundant and fell out of use. As polyester resins gained popularity in coatings, they began to be called "oil-free alkyds", a term that is now becoming obsolete. In the older literature, the term "glyptal" is found. It is synonymous with "alkyd". It was originally a General Electric trade name.

Today, the term "modified alkyd" usually refers to a resin in which a fourth type of

monomer (a modifier) is incorporated in the polymer molecules. This definition is used in this article.

Because alkyds are a large and diverse family of resins, several *subclassifications* are often used. These groupings describe the features that most strongly affect resin properties and end uses, such as the type and amount of fatty acid and the identity of other components.

Fatty Acid Type. There are two broad groupings:

1. *Drying alkyds* contain enough unsaturated fatty acids to make curing by oxygen possible.
2. *Nondrying alkyds* contain lower levels of unsaturated fatty acids and are not polymerized appreciably with oxygen.

To be more specific, the particular oil used in preparing the resins is often stated.

Fatty Acid Amount. A classification called "oil length" arbitrarily groups alkyds by the amount of oil or fatty acid present. For alkyds made directly from oils, the oil length is given by Equation (1).

$$\text{Oil length} = \frac{(\text{mass of oil used to make alkyd resin} \times 100)}{(\text{mass of reactants} - \text{mass of water evolved in process})} \quad (1)$$

For alkyds made from fatty acids, the formula is amended to correct for the extra mass of water lost (usually about 4 %) during esterification of the fatty acids, i.e., the factor of 100 in Equation (1) is replaced by 104.

Many authors classify alkyds by "oil length", a term apparently derived from terminology in varnish production in which oils were blended with other ingredients such as rosin or phenolic resins. Oil-length classifications are approximate, mainly because the ranges tabulated in Table 1 are standardized in Europe but not, apparently, in the rest of the world. Different authors assign somewhat different dividing points between short and medium, medium and long, etc. Despite being inexact, oil length classifications are used widely. The ranges used in Europe and the USA are listed in Table 1 [28].

Table 1. Percentage of oil in alkyd classes

Oil length	Europe (DIN 55 945)	Common U.S. usage
Short oil alkyds	< 40	< 45
Medium oil alkyds	40 – 60	45 – 55
Long oil alkyds	60 – 70	55 – 70
Very long oil alkyds ("alkyd oils")	>70	> 70

Other authors, however, give different ranges for the USA; in one case they are the same as Stoye gives for Europe [29]. In view of the ambiguities involved, it is safest to work with the actual oil length numbers, not the verbal ranges.

Other Constituents. When the polyol and polybasic acid are not specified in describing an alkyd, it probably contains glycerol and phthalic anhydride, the most common ingredients. Other ingredients often are mentioned in describing a resin, e.g., "an isophthalic alkyd".

Modified alkyds usually, but not always, are classified according to the generic type of modifer, e.g., "a styrenated alkyd" or "a silicone-modified alkyd".

2. Production

2.1. Raw Materials

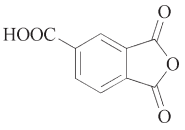
Well over one hundred raw materials are used in commercial alkyd manufacture. Each resin contains a minimum of three monomers and often five to seven. Only the most common raw materials are listed here.

Polyols (→ Alcohols, Polyhydric, → Ethylene Glycol, → Glycerol). Alkyds produced by processes that start with triglyceride oils (see Section 2.3) always contain at least some glycerol. Other polyols often are used, leading to alkyds of mixed polyol content.

Processes starting with fatty acids (see Section 2.3) allow the use of any polyol or polyol mixture to achieve the desired spectrum of properties. Glycerol [*56-81-5*] can be used, but less expensive synthetic polyols are a common choice. 1,1,1-Trimethylolpropane [*77-99-6*] is a popular synthetic alternative to glycerol. Pentaerythritol [*115-77-5*], with four hydroxyl groups per molecule, is popular because it builds highly branched polymers and because it is relatively inexpensive. Mixtures of pentaerythritol

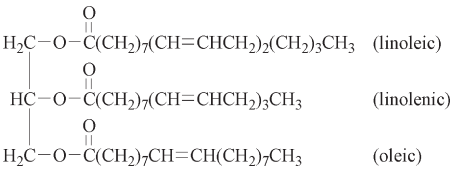
and ethylene glycol [*107-21-1*] may be used as a low-cost substitute for glycerol.

Polybasic Acids and Their Anhydrides. Phthalic anhydride [*85-44-9*] (→ Phthalic Acid and Derivatives) is used more than any other polybasic acid for reasons of economy and easy processing. Isophthalic acid [*121-91-5*] is often used where superior weatherability and corrosion resistance are required. Cycloaliphatic diacids, such as 1,4-cyclohexanedicarboxylic acid [*1076-97-7*], are also said to give better weatherability than phthalic acid.Trimellitic anhydride [*552-30-7*] (→ Carboxylic Acids, Aromatic) is used mainly in water-reducible alkyds. Many alkyds contain a small percentage of maleic anhydride [*108-31-6*] (→ Maleic and Fumaric Acids), which is said to reduce resin color and may enhance oxidative cross-linking.



1,2-Polybasic acids are never used as such. Instead, their internal cyclic anhydrides are used. The anhydrides form nominally the same polymer composition as the acids, but they are easier to handle, easier to polymerize, more stable, and less costly. In large-scale operations phthalic anhydride and maleic anhydride are kept hot and are handled in liquid form, an economy not feasible with the high-melting acids.

Triglyceride Oils and Fatty Acids (→ Fats and Fatty Oils, → Fatty Acids, → Drying Oils and Related Products). *Triglycerides* containing unsaturated and mixed fatty acids can remain liquid at temperatures well below 0 °C. For example, linseed oil contains a mixture of C_{18} fatty acids with zero, one, two, and three double bonds per C_{18} chain; it does not freeze at the very cold temperatures to which flax seeds may be exposed. A typical molecule might have the structure:



The total number of double bonds in a fatty acid, the Wijs iodine number, is measured by titration with iodine [30]. This number, however, correlates poorly with the reactivity of a triglyceride oil toward oxygen, a critical factor for coatings based on drying alkyds. Fatty acid residues containing only one double bond are almost unreactive. Those containing more than one double bond separated by a single methylene group, e.g., –CH=CHCH$_2$CH=CH–, react readily with oxygen and impart drying capablities to the oil or alkyd. Linoleic and linolenic acids have two and three such double bonds, respectively. Conjugated double bonds, e.g., –CH=CHCH=CH–, within the fatty acid are even more reactive.

Nondrying alkyds, for which reactivity with oxygen is unwanted, are made from triglyceride oils that contain a high proportion of saturated fatty acids, such as coconut oil. They can also be made from synthetic fatty acids.

While the fatty acid makeup of each type of oil is somewhat characteristic, the exact composition of the fatty acid mixture may vary widely with soil, climate, strain of plant, extraction process, and other factors. For example, the iodine number of soybean oil may vary from 103 to 151 [30]. Commercial oils are reliably within a much narrower range, for example 128 – 135 for soybean oil [31].

Usually the double bonds of the fatty acids are in the relatively unreactive *cis*, nonconjugated configuration. Certain oils, such as tung, oiticica, and dehydrated castor, contain conjugated and/or *trans* double bonds and are used to make alkyds for fast air-drying and low-bake coatings.

Some of the oils frequently used in alkyds are listed in Table 2 along with their iodine numbers and an indication of the degree of unsaturation of the fatty acids present. The numbers are averages of published data and, of course, are approximate. A wide variety of other oils is used, including tung oil, whale oil, and fish oils from various sources.

The *fatty acids* used in alkyd production are usually made by hydrolyzing (saponifying or "splitting") triglyceride oils to obtain fatty acid mixtures. Linseed oil fatty acid and soybean oil fatty acid [*68308-53-2*] are used widely. The fatty acid composition of the oil is not substantially changed by the hydrolysis process. Some

Table 2. Makeup of oils used in alkyds

Oil		Iodine no.	Typical fatty acid composition, % *				
			0	1	2	3	4 – 6
Linseed	[*8001-26-1*]	190	11	18	16	55	–
Manhaden	[*8002-50-4*]	180	37	30	2	1	30
Safflower	[*8001-23-8*]	145	10	12	78	tr.	–
Sunflower	[*8001-21-6*]	135	10	25	65	<1	–
Dehydrated castor	[*64147-40-6*]	135	<1	7	92 **	–	–
Soybean	[*8001-22-7*]	132	15	25	52	8	–
Coconut	[*8001-31-8*]	8	91	7	2	–	–

* Indicates percentage of fatty acid chains containing zero, one, two, etc., double bonds per fatty acid chain
** Contains a high proportion of conjugated double bonds

fatty acid producers offer fractionated products that are enriched in particular acids.

An important fatty acid mixture not derived from a seed oil is tall oil fatty acid [*61790-12-3*] (→ Tall Oil). It is a byproduct of kraft pulping. The name derives from the Swedish word for pine. The composition and performance are fairly similar to those of soybean oil fatty acid. The presence of about 10 % of fast-reacting conjugated double bonds compensates for its lower iodine number of about 125. Tall oil fatty acid always contains some rosin as an impurity; it is sold in grades specifying the maximum amount of rosin. The 1.5 % and 4 % grades are used widely in alkyds. Tall oil produced in Europe has a somewhat different composition than tall oil produced in North America; resin production formulas developed with one type are likely to fail if the other type is substituted.

Synthetic fatty acids are used in alkyds to a modest extent.

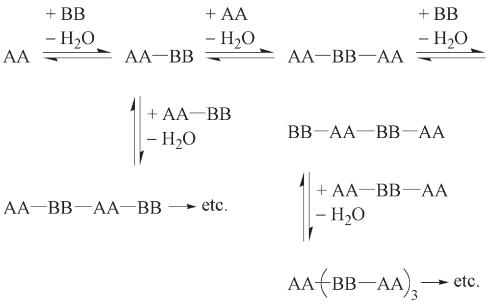
Modifiers (see Chap.).

Solvents. Immediately after production almost all alkyds are thinned in organic solvent to make them pumpable and pourable. Generally, these solvents are not removed at the time of coating manufacture, and they become part of the coating formula. Medium and long oil types usually are thinned with mineral spirits. Short oil alkyds require more polar solvents, often blends of aromatic hydrocarbon solvents. Alkyds to be used in high-solids coatings are sometimes thinned with ester or ketone solvents, which are efficient viscosity reducers. Water-reducible alkyds are thinned with water-miscible solvents such as 2-butoxyethanol or 1-propoxy-2-propanol.

Many alkyd resin and paint formulas were changed during the 1980s and 1990s to avoid solvents classified in the USA as "hazardous air pollutants" (HAPs). Similar changes were made in other countries.

2.2. Polymerization Theory

When a difunctional acid or anhydride (AA) and a difunctional alcohol (BB) are heated together, a stepwise reaction occurs that builds up linear chain molecules:



Compositions containing short chains (3 to about 20 monomer units per chain) are called "oligomers". Those containing long chains are "polymers". Under ideal conditions polymer chains containing thousands of monomer units can be made. Conditions necessary for formation of very high molecular mass chains include the following:

1. The mixture must be heated long enough to complete the reaction.
2. Equimolar quantities of AA and BB must be present.
3. No alternative reactions may be possible.
4. AA and BB must contain no monofunctional reactive impurities.

The average molecular mass can be deliberately held at lower levels by altering any of the above ideal conditions, for example:

$$9\,AA + 8\,BB \underset{}{\overset{-16\,H_2O}{\rightleftharpoons}} AA\text{—}\left(BB\text{—}AA\right)_8$$

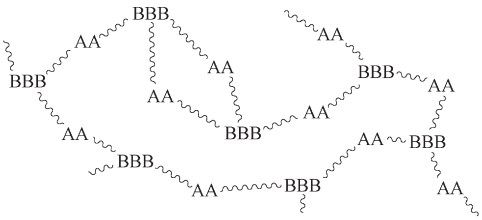
$$9\,AA + 10\,BB + 2\,A \overset{-20\,H_2O}{\rightleftharpoons} A\text{—}\left(BB\text{—}AA\right)_9\text{—}BB\text{—}A$$

where A represents a monofunctional acid. The actual products of such reactions are mixtures of various chain lengths.

If a trifunctional monomer BBB is added, chain branching occurs:

$$4\,AA + 2\,BB + BBB \xrightarrow{-6\,H_2O} AA\text{—}BBB\text{—}AA\text{—}BB\text{—}AA$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad AA\text{—}BB$$

If substantial amounts of BBB are present, continued polymerization leads to formation of a three-dimensional network, or gel:



One of the goals in alkyd resin synthesis is to prepare structures that are branched but are not quite gelled. A fairly close approach to gelation is needed to form a polymer which readily forms cross-linked networks after application as a coating. However, gelation in the reactor causes a total loss of materials and a difficult clean-up job.

Much research has been directed toward understanding polymerization and developing general principles to help the alkyd formulator achieve the desired degree of polymerization and to optimize properties. Early theories of polymerization were developed by CAROTHERS [23], [29] and by KIENLE et al. [20], [22], [24], [34], [35]. CAROTHERS hypothesized a uniform, stepwise polymerization process. In his model, gelation occurs as the polymer molecular mass approaches infinity. The condition for gelation would be

$$p_g = \frac{2}{F_{av}}$$

where

p_g is the extent of reaction at the gel point and

F_{av} is the average functionality of the monomer mixture.

According to this equation pure difunctional monomers can never gel, but a mixture of glycerol and phthalic anhydride ($F_{av} = 2.5$) would gel at $p_g = 0.8$; that is, it would gel when 80 % of the functional groups have reacted.

In practice gelation usually occurs at lower p_g than predicted by the Carothers theory. To explain this fact FLORY et al. [32], [33] proposed a probabilistic theory: gelation occurs when a relatively small proportion of the monomer molecules first becomes bonded into a three-dimensional network. FLORY's theory is satisfactory for predicting polymerizations of the chemically straightforward monomers used to make polyesters. However, alkyd formulators must deal with monomers that are far from straightforward. Complications include

- Variable starting materials
- Competing side reactions
- Reaction reversibility
- Differential reactivity of the functional groups
- Differential solubility effects
- Nonuniform process conditions

Gradual progress has been made toward a general and reliable theory of alkyd formation by several authors; see, e.g., [6], [38–44]. A completely precise theory is unlikely, mainly because alkyd polymerizations probably are not homogeneous during the late stages of reaction. Most alkyds contain small, soft gel particles as well as soluble material [44], and these gel particles are in some cases essential to the attainment of optimum properties [45], [46]. Despite this difficulty, certain alkyd polymerizations can be accurately modeled with the aid of computers and advanced statistical techniques [47]. Such theoretical methods offer considerable help and insight to the alkyd formulator. They can reduce reliance on empirical trial and error, but they will not completely eliminate it for the foreseeable future.

2.3. Formulation and Process Types; Laboratory Processing

Alkyds are made in batch processes, of which several types have evolved.

Table 3. Composition of long oil alkyd

	Equivalents COOH	OH	g	% in alkyd
Soybean fatty acids	1.246	–	349.0	60.0
Pentaerythritol	–	3.545	125.5	21.5
Phthalic anhydride	2.000	–	148.0	25.4
Totals	3.246	3.545	622.5	106.9
H_2O			−40.4	−6.9
Theoretical yield of resin			582.1	100.0

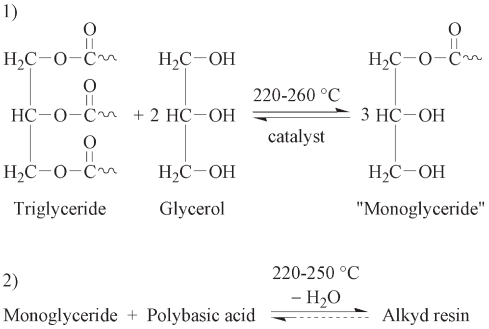
Fusion Process Using Fatty Acids. The fusion process starting with fatty acids is the oldest and most straightforward. A representative formulation is given in Table 3 [48].

Like nearly all alkyd formulations, it contains an excess of hydroxyl groups, 9.2 % in this case. This excess is essential to assure that the rate of viscosity increase will be controllable as the polymerization process approaches completion. To visualize the consequences of not using an excess of OH groups, suppose that exactly 3.246 equivalents of pentaerythritol have been used. The F_{av} would have been 2.07, and CAROTHERS' theory predicts an exponential increase in viscosity as the reaction approaches completion, ending in gelation at $p_g = 0.96$. As FLORY's theory and practical experience demonstrate, gelation would actually occur at lower p_g. Therefore in the late stages of reaction, viscosity would be increasing rapidly and exponentially. However, the 9.2 % excess of OH groups assures that the number average chain length will remain modest even when nearly all of the carboxyl groups have reacted, limiting viscosity at the desired level. Chain lengths of individual molecules in the resin will vary from the oligomer to the high-polymer range.

Viscosity could be controlled by using an excess of acid, but inferior coatings would result because of moisture sensitivity imparted by the unconverted COOH groups in the film. Unconverted OH groups impart less moisture sensitivity, and they play a useful role in certain cross-linking reactions (see Chap. 3).

To prepare the above resin on a *laboratory scale* the ingredients are placed in a round-bottom reaction flask, heated at about 240 °C, and stirred mechanically. Inert gas (N_2 or CO_2) is passed through the reaction mass to facilitate water removal; the water is condensed and measured to estimate the extent of reaction. As the reaction approaches completion (5 – 10 h), samples are removed and the acid value and/or viscosity are measured. When the desired degree of reaction has been reached, the reaction mass is cooled slightly and is diluted with about an equal volume of mineral spirits.

Fusion Process Using Triglyceride Oils. The fusion process starting from triglyceride oils is often called the *alcoholysis* or the *monoglyceride process*. It is popular because the oil provides an economical source of all of the fatty acid and part of the polyol. It is a two-stage, batch process:



The first, or alcoholysis, stage is an ester interchange reaction. Equilibrium is reached within an hour or two at sufficiently elevated temperature when the reaction is catalyzed by litharge (PbO) or by certain Li or Ca salts. Although the product is called a monoglyceride, it is actually a mixture of isomers of mono-, di-, and triglycerides and of glycerol. Polyols other than glycerol often are used and yield even more complex mixtures. In the second stage polybasic acids or anhydrides are polymerized with the monoglyceride mixture to form the resin. Other ingredients often are added during the second stage.

Procedures and equipment for laboratory preparation are generally similar to those used for the fatty acid process.

Both fusion processes suffer from several practical difficulties. To assure reasonable process rates the water of reaction must be removed by "sparging" the reaction mass with a stream of inert gas. Without sparging, process rates are slow because the esterification reaction is highly reversible. With sparging, however, the gas stream sweeps vapors of phthalic anhydride and polyol out of the reaction mass. These

materials may be lost altogether or they may condense in the upper parts of the apparatus from which they may fall back into the reactor, causing dark or nonuniform product.

Solvent Processes. To overcome these problems solvent processes are used widely, both with fatty acid and triglyceride starting materials. In these processes a few percent of unreactive, water-immiscible solvent is added to the formulation. Commercial xylene, also called xylol (mixed dimethylbenzenes and ethylbenzene, *bp* 138 – 140 °C), is used commonly. Typically a stirred alkyd polymerization mass containing 4 % xylene will boil vigorously at about 250 °C. The xylene vapors form an azeotrope with water and carry it out of the reactor. Usually the vapor stream is passed through a "partial condenser" operated at about 100 °C; this allows water vapor to escape, but it condenses most of the xylene and almost all of the monomers and returns them to the reactor. Whether or not a partial condenser is used, the vapors are condensed. Water and xylene separate into two layers, and the xylene is returned to the reactor.

Laboratory equipment for solvent processing has been described in detail [49]. Losses of xylene and of monomers can be minimized with proper operation, and uniform products can be produced.

2.4. Manufacture

A variety of equipment for alkyd production has been described [5], [8], [50]. Equipment for *solvent processing* will be described here because the trend is in that direction. However, fusion processes, which require simpler equipment, often produce satisfactory products. The fusion process is preferable for isophthalic alkyds.

Figure 1 shows a versatile configuration designed for the solvent process. The reactor typically would be constructed of no. 316 stainless steel. Capacity of commercial-scale reactors ranges from 2 to 35 m^3. A turbine agitator driven by a powerful electric motor is necessary. Heating and cooling generally are accomplished by a heat-transfer fluid flowing either through a jacket around the reactor (as shown in Figure 1) or through coils within the reactor. High-pressure steam and gas-flame heating have been used but are less satisfactory and more hazardous.

Whereas the reactor and overhead shown in Figure 1 are the heart of an alkyd plant, other equipment is needed for efficient, large-scale production. Such equipment includes the following:

1. Raw material storage and metering equipment (phthalic anhydride often handled in hot, molten form)
2. A manhole in the reactor top for adding solids and to provide access for cleaning
3. A heater for heat-transfer fluid
4. A thin tank about 2.5 times as large as the reactor, equipped with a condenser and agitator
5. Product storage tanks and drumming equipment
6. Environmental control equipment, including incinerators for gaseous and liquid waste
7. Filters
8. Safety and fire protection equipment, including rupture disks, blowout vents, and sprinklers

Automated alkyd reactors have been installed in Europe, North America, and Asia [51]. Improved safety, quality, and productivity are claimed. However, several factors have discouraged retrofitting of reactors to automate them. Although the necessary microprocessors are relatively inexpensive, automation requires costly feedback systems and servomotor driven valves. Detailed process studies are necessary to program the microprocessor to deal with all contingencies.

3. Film Formation by Coatings Based on Alkyd Resins

There are two mechanisms by which a liquid coating can be transformed into a tough, protective film after it has been applied:

1. Lacquer drying by simple solvent evaporation
2. Chemical cross-linking by reaction of the polymeric binders to form a cross-linked polymer network

Coatings based on alkyd resins often depend on both mechanisms to some degree. Chemical

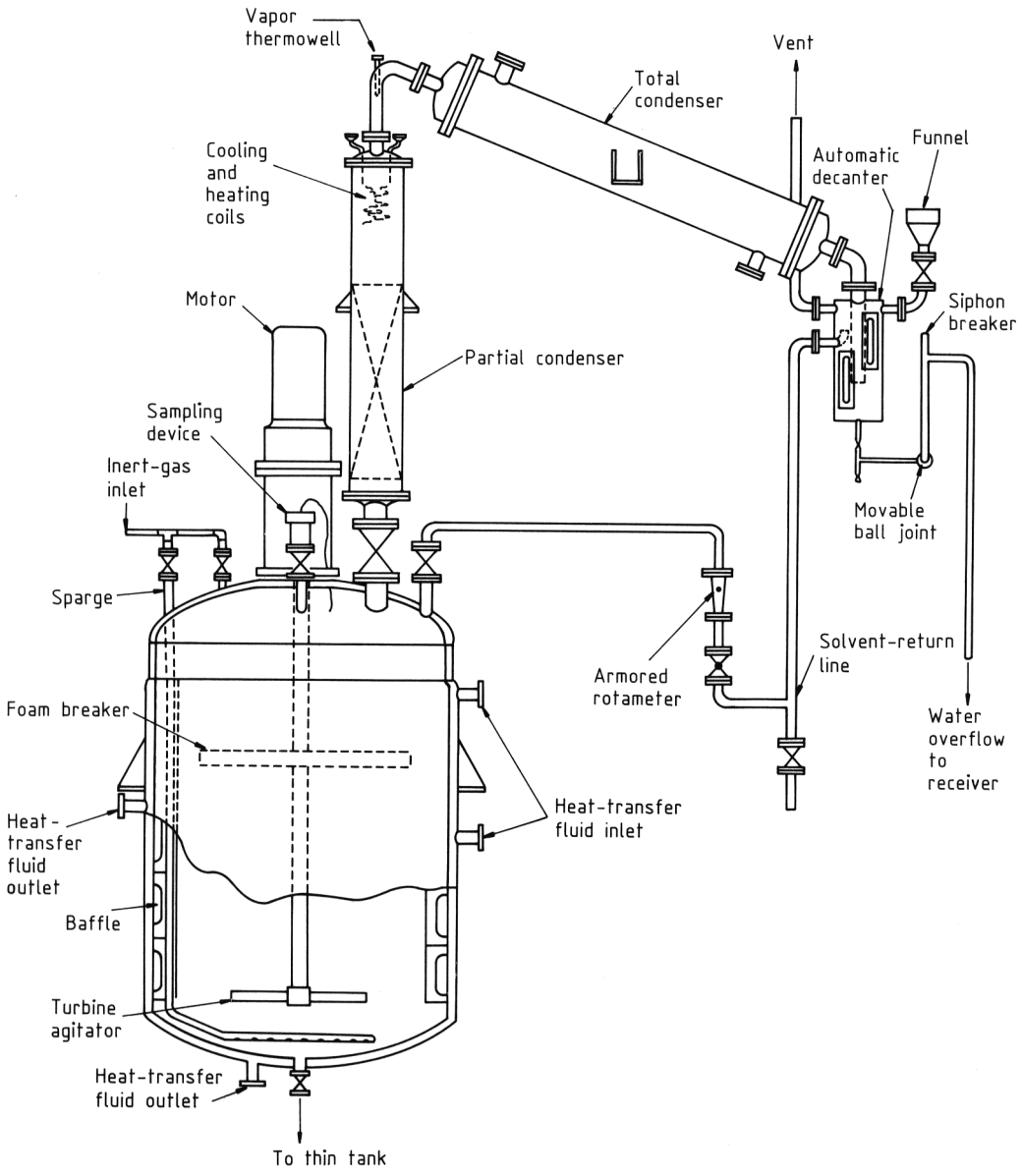
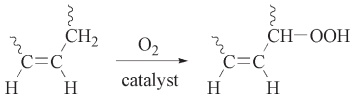


Figure 1. Alkyd solvent-processing equipment with partial condenser (adapted from [30])

cross-linking plays a vital role in converting a soft, tacky alkyd into a hard, tough film.

Drying Alkyds. The majority of alkyd coatings are designed for film formation at ambient or slightly elevated temperatures. The chemical mechanism of curing involves autoxidation of the unsaturated fatty acid residues in the resin. This chemically complex process has been studied extensively [52–58], but it is not yet completely understood. Most of the studies have involved model compounds such as monoesters of fatty acids rather than the more complex alkyd resins.

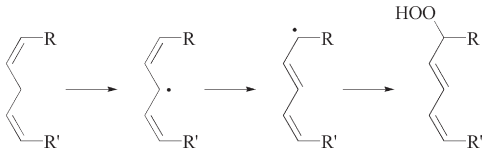
Autoxidation of alkyds is a chain reaction that proceeds by a free-radical mechanism. A key step is the formation of a hydroperoxide on an allylic methylene group:



The hydroperoxide is capable of several further reactions, some of which lead to formation of stable, covalent bonds with sites on other resin molecules. This bonding builds up a three-dimensional polymeric network, and a tough film is formed.

Small amounts of catalysts (driers) that promote autoxidation and cross-linking are added to drying-type alkyd coatings. Driers are generally mixtures of oil-soluble salts of Co, Mn, Zr, Ca or other metals [59]: soluble Pb salts are also effective but have been banned in many countries.

Fatty acid chains containing only one double bond are autoxidized slowly. Those containing allylic methylene groups activated by two double bonds react over 100 times faster. Reaction sequences probably involve rearrangement and isomerization of the double bonds, for example:



Studies on model compound [56–58] confirm the mechanism shown above for the early stages of cross-linking, but reveal that subsequent film-forming reactions are extremely complex and beyond the scope of this article.

Useful drying rates are achieved only if appreciable concentrations of polyunsaturated fatty acid residues are present. Soybean, safflower, sunflower, and tall oil alkyds are about the least unsaturated that dry well. These oils have high linoleic acid (two double bonds) content but relatively low levels of fatty acids with three or more double bonds. They are preferred for decorative coatings where resistance to yellowing is desired and moderate cross-linking is adequate.

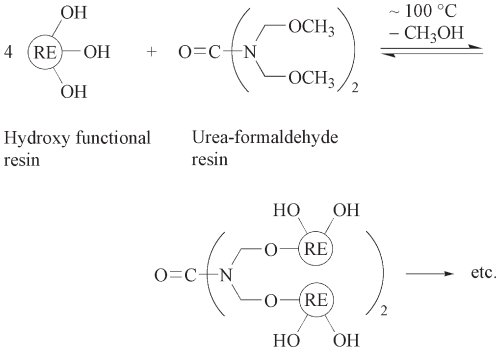
Higher levels of cross-linking and therefore better protective properties are achieved by use of fatty acids or oils with substantial contents of triply unsaturated fatty acid residues (linseed or tung) or of those containing multiple unsaturated fatty acid residues (fish oils). Blends of fatty acids or oils are used to reduce cost and sometimes to minimize premature cross-linking during alkyd manufacture.

Drying rate is often an important consideration. Oils containing two conjugated double bonds dry faster than those containing similar levels of nonconjugated double bonds. Thus, chemically modified oils and fatty acids with two conjugated double bonds (dehydrated castor oil and conjugated tall oil fatty acids) find considerable use. Fastest of all are oils that contain fatty acids with three conjugated double bonds, such as tung oil.

Rates of autoxidation are useful above about 0 °C and sharply increase with increasing temperature. A significant advantage of drying oil alkyd-based paints over latices is that they can form satisfactory films when applied at 0 °C or even a bit below.

Drawbacks of all alkyd paints paints include a tendency of the films to turn yellow and become brittle with age. Their low permeability to water can also lead to blistering when painted on wood. Use of high-linoleic, low-linolenic oils such as safflower and sunflower can minimize these problems, but can not eliminate them. Short oil alkyds are used in applications where rapid partial drying is needed. Although they have less cross-linking capability than longer oil types, they quickly develop some degree of hardness by lacquer drying as the solvent evaporates. Quick drying is desirable in many manufacturing situations, as it permits gentle handling within 15 – 30 min after coating. Film properties improve for several days or weeks as the slower cross-linking process occurs.

Nondrying Alkyds. Alkyds are used extensively in industrial coatings that are designed to be cured at elevated temperatures (baking or stoving enamels). Such enamels are usually blends of alkyds with aminoplasts, e.g., alkylated melamine – formaldehyde or urea – formaldehyde resins. Cross-linking occurs by acid-catalyzed condensation of the OH groups of the alkyd with the aminoplast:



Other chemical cross-linkers can be blended with alkyds. For example, alkyd – polyisocyanate blends are used as binders for two-package, ambient temperature curing polyurethane coatings.

Alkyds for baking enamels do not need to be autoxidizable and often are made from oils containing only saturated fatty acids, coconut, for example. Soybean and tall oil alkyds often are used in alkyd – amino enamels; such enamels cure by a mixture of condensation and autoxidative cross-linking.

Polyvalent metal alkoxides, such as Al $(OC_4H_9)_3$, can serve as trifunctional cross-linkers. They react with hydroxyl groups on the alkyd resin to form $Al(O–alkyd)_3$ structures within the film. This expedient can enhance hardness and through-cure of the paints.

Nondrying alkyds are used as plasticizers in lacquers. Their role is to soften high molecular mass thermoplastic resins that otherwise would be too hard and brittle for coatings use. Examples are nitrocellulose – alkyd blends for furniture finishes and acrylic – alkyd blends for automotive refinish lacquers. Note that in Europe the term "lacquers" is frequently applied to all types of organic coatings, while in North America the term tends to be limited to coatings made from thermoplastic, non-cross-linking binders.

4. Modified Alkyds

Roughly one-fourth of commercial alkyd usage is of modified alkyds, resins in which modifiers are at least partly interpolymerized with the usual alkyd monomers. The more important types are described in this section.

Chain-stopped alkyds contain aromatic monobasic acids (see Section 2.2), such as benzoic acid [*65-85-0*] or 4-(1,1-dimethylethyl)benzoic acid (*p-tert*-butylbenzoic acid) [*98-73-7*]. These modifiers improve lacquer-dry characteristics and harden films. However, because they do not participate in covalent cross-linking, the films tend toward brittleness.

Inclusion of monobasic acids during polymerization reduces F_{av}; to compensate, highly functional polyols such as pentaerythritol are used. Because pentaerythritol and benzoic acid are relatively inexpensive, low-cost resins with reasonably good properties are attainable. Uses are diverse, a major one being traffic-control striping. Chain-stopped alkyds are useful in high-solids coatings (see Chapter 5).

For premium-quality chain-stopped resins, 4-*tert*-butylbenzoic acid affords an excellent combination of fast dry and film plasticity. However, use of this modifier is limited by concerns about its potential for long-term health effects.

Styrenated alkyds are made in a two-stage process [54], [60]. First a drying oil alkyd is produced using a formulation designed to limit molecular mass. The resin is then thinned, usually with xylene, and styrene [*100-42-5*] is added to the solution. Addition of a free-radical initiator starts the second stage of the process, the addition polymerization of the styrene. This step is effected at higher temperature (about 140 °C) than most addition polymerizations, conditions that favor grafting of polystyrene segments onto the alkyd. The product is a mixture of graft copolymer, ungrafted alkyd, and homopolystyrene [61]. Apparently sufficient grafting occurs to "compatibilize" the mixture.

Styrene content ranges up to 60 %. The homopolystyrene ($T_g \approx 100$ °C) segments impart hardness, chemical resistance, and very fast lacquer dry characteristics. However, high levels of styrene reduce weatherability and toughness.

Acrylated alkyds are made by a similar process using acrylic or methacrylic monomers in place of styrene [62]. These monomers are more costly than styrene, but their presence improves resistance to sunlight. For example, an alkyd modified with methyl methacrylate [*80-62-6*] (homopolymer $T_g \approx 105$ °C) would be similar

in most properties to a styrenated alkyd but would be more weatherable. Alkyds modified with lower T_g acrylic or methacrylic monomers can be made readily. They are less important because they offer few advantages over unmodified alkyds.

Other olefinic monomers, such as acrylonitrile [*107-13-1*], α-methylstyrene [*98-83-9*], and mixed 3- and 4-vinyltoluene (VT), are used commercially to modify alkyds. The latter mixture affords the commercially important "VT alkyds", which lacquer dry nearly as fast as styrenated alkyds but have better film properties. Uses include fast-dry industrial enamels and aerosol paints.

Silicone alkyds are prepared by interpolymerizing hydroxyfunctional organosilicone oligomers with alkyd resins [63]. Methyl/phenyl-substituted silicones are used. The proportion of silicone ranges from 15 to 55 %. These premium quality resins have superior resistance to heat and weather. Drying oil silicone alkyds are used in heat-resistant coatings such as stove enamels and in exterior applications in which prolonged retention of properties and appearance saves substantial cost by reducing the frequency of repainting, e.g., petroleum storage tanks. Blends of nondrying silicone alkyds with melamine resins have been used in coil-applied coatings for exterior siding.

Thixotropic alkyds are modified at high temperatures with an oil-miscible polyamide resin, for example, a polymer [*51178-84-8*] of octadecadienoic acid dimer [*6144-28-1*] and 1,2-diaminoethane [*107-15-3*]. Proportions and reaction conditions must be carefully controlled [64]. Paints containing these resins are viscous, but their viscosity drops under mechanical shear and then recovers when the shear is removed. It is unclear from published information whether their behavior is simple shear thinning (near instantaneous recovery when shear is removed) or genuine thixotropy (time-delayed recovery). Regardless of methanism, the paints resist running and sagging when brushed or sprayed in thick coats. Applications include bridge and marine paints.

Uralkyds are usually air-drying compositions in which part of the polybasic acid is replaced by a polyfunctional isocyanate, most commonly toluene diisocyanate [*26471-62-5*] (→ Isocyanates, Organic) to form a polyester – polyurethane interpolymer. The resins are usually made in a two-stage process, the reactive toluene diisocyanate being added in the second stage at relatively low temperature.

An excess of OH groups is used so that all of the isocyanate reacts to form urethane linkages. Cross-linking is accomplished by the usual autoxidative mechanism. Presence of the urethane linkages imparts outstanding toughness, water resistance, and abrasion resistance; thus, urethane alkyds are used in premium-quality varnishes, for example, for gymnasium floors. A drawback is that resins containing toluene diisocyanate are brownish and yield yellowish varnishes that darken with age. This problem can be almost eliminated by use of the more costly aliphatic polyisocyanates in place of toluene diisocyanate.

A second class of uralkyds is prepared with a deficiency of OH groups so that unconverted isocyanate groups are present in the resin. After application these resins cross-link by reaction of atmospheric moisture with the isocyanate groups. They form exceptionally tough films. However, the coatings are difficult to apply and may cause skin irritation.

Epoxy esters do not fit the strict definition of alkyd resins, but they are closely related. These resins usually are formed by condensing an unsaturated fatty acid with an epoxy resin of low to intermediate molecular mass (→ Epoxy Resins). Epoxy ester coatings combine part of the toughness, adhesion, and corrosion resistance of epoxies with the easy application and cure of alkyds. They also share the main shortcomings of epoxies: surface chalking when exposed to sunlight and discoloration with age. Epoxy esters are used where their adhesion and corrosion resistance are needed and where surface weatherability is unimportant, for example, in auto body primers and in industrial maintenance paints.

Phenolic modified alkyds are used in applications in which hardness and moisture resistance are important. High-solids formulations have been developed [65].

Rosin and rosin esters (→ Resins, Natural) are used as modifiers mainly to reduce cost. Coating

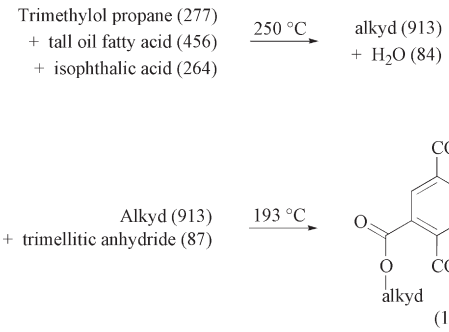
properties are similar to those of chain-stopped alkyds, but films yellow with age and have inferior weatherability. These modifiers are used in wall primers.

5. Low-Solvent Coatings

In most coating processes, the solvent in the coating evaporates into the atmosphere. Formerly the amounts were thought harmless, but by the 1960s it was recognized that the solvents used in alkyd and other coatings contribute substantially to air pollution. In this context, the solvents are called the "volatile organic content" (VOC) of the coating. In air, organic solvents react in a complex photochemical process to produce ozone, one of the most troublesome constituents of photochemical smog.

In the late 1960s and early 1970s governments in many industrial areas adopted "technology forcing" regulations designed to compel coatings users to find ways to reduce VOC emissions. These regulations stimulated research on alkyds during the 1970s and 1980s. Two major approaches were used (→ Paints and Coatings, 1. Introduction): replacing most of the solvent with water (water-borne coatings), or sharply increasing the proportion of coatings solids to solvent (high-solids coatings). It is estimated that 10 % of alkyd usage is now of the water-borne and high-solids types. The most common approach to water-borne alkyds is to make special alkyds (see below), dissolve them in water-miscible organic solvents, and then add water. These are called "water-reducible" resins. Additional approaches have been introduced more recently, such as solvent-free dispersions of alkyd resins in water. All approaches require substantial changes in conventional alkyd resin technology.

Water Reducible Resins. To make alkyd resins suitable for use in water-reducible paints, it is necessary to chemically change them so they are miscible with blends of water and limited amounts of organic solvent. This is accomplished by attaching hydrophilic sites to the polymer molecules. Numerous procedures for doing so have been published [66–68].The most common method is to place acidic carboxy groups on the molecule and then to "salt" the resin with a base, usually ammonia or an amine. A representative method uses a two-stage process involving trimellitic anhydride [69] (mass parts in parenthesis):



Reduced temperature is used in the second stage to encourage selective reaction of the anhydride group. However, there are several competing side reactions: at 193 °C the anhydride reaction is not completely selective, and acid – ester interchange reactions occur to some degree. For this reason, the process requires careful control to assure consistent product.

If enough carboxyl groups are present to give an acid value of about 45 mg of KOH per gram of resin or higher, the resin forms a transparent mixture when salted and dissolved in 20:80 solvent: water medium. Such resins are sometimes called "water-soluble" alkyds, but their abnormal solution rheology, light scattering, and other evidence indicate that they are seldom, if ever, true solutions. The terms "water-reducible", "water-thinnable", or "water-dilutable" are more descriptive.

Similar resins having acid numbers below about 45 form hazy or milky dispersions when salted and thinned with water. They are often termed "water-dispersible" as well as "water-reducible" alkyds. Such resins are gaining commercial importance because lowering the acid number seems to improve corrosion resistance of the coatings.

Most types of modified alkyds can be made in water-reducible form. For example, water-reducible acrylated [70], silicone-modified [71], and urethane-modified [72] alkyds have been developed.

A disadvantage of this approach is that the ester bond that connects trimellitic anhydride residues to the alkyd resin is more vulnerable to hydrolysis than the ester bonds in most polyesters. For this reason, stability of water-borne paints containing such resins is limited to 3 – 6

months. If a substantial fraction of the critical ester bond is hydrolyzed, the paint becomes unstable and unusable.

Numerous other approaches to formulating alkyds in aqueous media have been studied, often in efforts to improve package stability. Among the more promising are to copolymerize hydrophilic poly(ethylene oxide) segments into the resin [73], to emulsify hydrophobic alkyds with conventional surfactants [74], to prepare acrylated alkyds in which the acrylic polymer segments contain –COOH or other hydrophylic groups, and to prepare transparent microemulsions [75]. These approaches can be combined. The emulsification approach has been widely studied in recent years [76], [77], and is the basis for commercial products. Careful selection of emulsifiers, pigments, and additives is critical to assure stability and acceptable application characteristics and to avoid adverse interactions that deactivate driers [77].

High-Solids Coatings. There seems to be no standard definition of the term "high-solids coatings". The level of 70 vol% solids has been suggested as a minimum for high solids, but such a definition is arbitrary and does not conform to general usage. In this article, the term is used in a vague but useful way: a high-solids coating is one that is substantially more concentrated than similar coatings that were in general use in the 1960s. For example, an appliance finish that is sprayed at 62 vol% solids is called a high-solids coating because earlier generations were sprayed at 34%. To emphasize the relative aspect of the definition, some authors prefer the term "higher-solids coatings".

The essential technical problem in formulating high-solids coatings is to find ways to achieve low viscosity without using very much volatile organic solvent. Many formulation and application variables can be manipulated in pursuit of this goal, but the most important is resin viscosity [78]. Therefore, the challenge to the alkyd resin chemist is to reduce the resin viscosity in solution without serious adverse effect on coating properties. To accomplish this difficult task it is necessary to reduce the molecular mass of the resin while increasing its functionality for cross-linking. Especially important is reducing the proportion of soluble high molecular mass molecules in the polymer mixture. These molecules contribute disproportionately to the viscosity [79]; unfortunately, their removal may harm film properties [46]. These difficulties have, to a degree, been overcome, and high-solids alkyd coatings are gaining commercial acceptance.

In air-dry, high-solids alkyds, the most difficult problem is to attain commercially acceptable drying rates without excessive yellowing. Resins that autoxidize very rapidly can be made by use of conjugated or highly unsaturated fatty acids. However, coatings made with such resins tend to turn yellow quickly and to cure too quickly at the surface of the coating film. Surface cure creates an oxygen barrier film that unacceptably slows cure in the interior of the coating. Solutions proposed to solve this problem include use of reactive diluents [80–82], use of auxiliary cross-linkers [83], and use of special autoxidation catalysts [84]. In each case, specially tailored alkyd resins are required.

Alkyds also are used in high-solids baking enamels, where they usually are cross-linked with amino resins, and in two-package alkyd – isocyanate enamels. In both of these applications, alkyds compete with polyester and acrylic high-solids resins.

Ryer presents an overview of new alkyd chemistry and gives several specific formulas [85]. For example, a chain-stopped alkyd suitable for coatings for agricultural and heavy equipment is composed of 72.8 parts (by weight) of soya fatty acid, 44.9 parts of pentaerithritol, 40.0 parts of phthalic anhydride, and 24.4 parts of benzoic acid. Given that the water of reaction is 13.1 parts, one can use Equation (1) to calculate the oil length of this alkyd as 44.8.

Compliance Solvents. In the USA, three solvents, acetone, methyl acetate, and 4-chlorobenzotrifluoride, have been exempted from regulations limiting VOC emissions because of their very low photochemical reactivity. Exemption of one or two more solvents, including *tert*-butyl acetate, is expected. These regulatory changes are very favorable for the future of alkyds, since resourceful formulators can use them to help satisfy air-pollution regulations that limit VOC. Two chlorinated organic solvents, CH_3CCl_3 and CH_2Cl_2, were previously exempted [87] but are little used because of concerns about their safety, corrosiveness, and greenhouse effects.

Latex Modifiers. A few percent of alkyd resin is often added to water-borne architectural paints, the principal binder of which is a polyvinyl or polyacrylic emulsion resin. The alkyd improves adhesion to chalky or oily surfaces. Addition of much larger proportions of alkyd, up to 50 %, is feasible [74], but incentives to commercialize this technology have been lacking because latices have been less expensive than alkyd resins most of the time since 1970.

6. Markets and End Uses

U.S. Tariff Commission states that alkyd resin production in the USA was about $(3 - 3.5) \times 10^5$ t/a between 1960 and 1980 and then began a slow decline, reaching about 2.3×10^5 t/a by 1996 [25]. The decline is thought to be continuing at a rate of about 2 %/a. Worldwide production figures are not readily available. If the proportion of alkyd used in the rest of the world is the same as in the USA, gobal production would be roughly three times as great as the U.S. figures. The proportion appears to be higher in some major markets, and this suggests that global production may be on the order of 10^6 t/a.

A very high percentage of alkyd production is used in coatings (→ Paints and Coatings, 1. Introduction). In this market alkyds compete with many other generic types of resins. While they are gradually being displaced by other types of resins, alkyds continue to compete effectively in many end uses. The continuing popularity of alkyds seems to be based on three factors:

1. *Versatility.* Whereas alkyds cannot match the outstanding features of some competing resin types (hardness and weatherability of acrylics, corrosion resistance and adhesion of epoxies, and toughness and abrasion resistance of polyurethanes), they can be formulated to provide a satisfactory balance of properties for many purposes.
2. *Ease of Use.* Well formulated alkyd coatings tend to be easier to apply by spray, brush, or roller than other generic types. They seem less susceptible to popping, sagging, cratering, and other appearance defects. They wet oily or dirty surfaces relatively well. Alkyds are package stable and do not have to be formulated in two-package systems. Air-dry formulations dry quickly, and baking enamels cure at low temperatures. An important but often overlooked factor in the continuing popularity of alkyds is that many existing finishing facilities and procedures have been designed for alkyds, and it has proved difficult to substitute other types of coatings without expensive capital investments.
3. *Economy.* During the 1960s and early 1970s petrochemical monomers, such as acrylics and vinyls, were less costly than the mixture of petrochemical and biomass ingredients used in alkyds. By 1983 the situation had reversed; soybean oil and tall oil fatty acids were selling at less than half the price of basic acrylic monomers. The cost advantage of alkyds is diluted by the petrochemical content of alkyd resins, which averages roughly 50 %, and the need, in most cases, to use petrochemical-based solvents. Since 1983, the relative costs of alkyd resins and 100 % petrochemical-based resins have fluctuated roughly in proportion to the prices of petroleum and of vegetable oils. Soybean oil currently sell for about 0.55 $/kg in the USA, while key vinyl and acrylic monomers (including styrene) sell for 1.5 to 3.5 times as much.

A summary of where alkyds fit in each of the three major coatings market segments follows.

Trade sales, or *architectural coatings*, comprise roughly 52 % of the physical volume and 42 % of the value of coatings sold in the USA. It is estimated that 55 % of the total alkyd usage in paints is in this sector [17], [25]. Water-borne formulations based on polyacrylic and polyvinyl emulsion resins have captured over three-fourths of this market in the USA. Their chief advantages are easier cleanup, and better exterior durability. Alkyd- and alkyd – vegetable oil-based paints remain popular with many coating contractors because they can be applied faster and at lower temperatures; emulsion resin paints do not form films properly below about 5 – 8 °C, but alkyds can be used at 0 °C or even lower.

Alkyd-based paints retain a major share of certain trade sales markets, for example, stains, varnishes, high-gloss enamels, and primers. In these market segments, the hard, tough, cross-linked films of alkyds offer advantages over latices, and their superior adhesion is important.

As noted above, a few percent of alkyd is often added to acrylic emulsion paint formulations to improve adhesion.

Industrial coatings are, by definition, coatings applied at the factory to manufactured goods. They account for roughly 31 % of the volume and 36 % of the value of coatings sold in the USA About 21 % of the alkyds used in paints go into these markets [17], [25].

Alkyd – melamine automotive topcoats have been almost completely replaced by more weatherable acrylic – melamine – formaldehyde and acrylic – polyurethane topcoats. Alkyds still find uses in auto and truck production, for example, in coatings for under-hood parts.

Factory wood finishing is a large user of coatings. Alkyds are used extensively both in alkyd – aminoplast thermosetting enamels and as plasticizers for nitrocellulose lacquers.

Other large-scale manufacturing operations that use alkyds include the following:

1. Metal containers – exterior can finishes
2. Coil coatings – flexible enamels for light fixtures, siding, Venetian blinds, etc.
3. Metal office furniture – hard alkyd – aminoplast enamels
4. Farm implements – fast air-drying enamels

Alkyd coatings are popular in smaller scale factory finishing operations, often because of their ease of application. Examples are tools, fixtures, drums, toys, and shelving. These diverse operations often are called the *general industrial* coatings market; it is a substantial consumer of alkyds.

Special purpose coatings include all organic coatings that do not fit into the above categories. It is a diverse market that is often characterized by sophisticated, specialized coatings. It accounts for the remaining 17 % of the volume and 22 % of the value of U.S. coatings. About 24 % of U.S. alkyd production goes to this segment [17], [25]. Alkyds and modified alkyds share this market with polyacrylic, epoxy, and polyurethane resins. Alkyds are used wherever they are satisfactory because in most cases they are the least expensive and easiest to apply. There are many examples:

1. Highway maintenance – alkyds, thixotropic alkyds, and epoxy esters for bridges, etc.
2. Traffic-control striping – usually very fast drying chain-stopped or styrenated alkyds blended with chlorinated rubber resin; a large market
3. Auto and truck refinish – epoxy ester primers and chain-stopped alkyd topcoats; alkyds losing share to acrylics
4. Marine – alkyds used mainly above the water line; fish oil alkyds popular for rust penetration, silicone alkyds for gloss retention
5. Industrial maintenance – linseed and silicone alkyds for refineries, tanks, factories, etc.

Noncoatings uses. The ink industry is a significant user of alkyd binders, mainly of the longoil isophthalic type. Other uses include caulks, adhesives, sealants, and linoleum. At one time alkyds were used as binders in fiberglass-reinforced plastics, but they have been supplanted almost completely by unsaturated polyesters.

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Amino Resins

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1. Introduction

Amino resins are condensates formed when carbonyl compounds react with compounds containing amino, imino, or amide groups, liberating water. Before they have hardened, these products consist principally of oligomers, which are also called prepolymers.

A very large number of carbonyl- and nitrogen-containing compounds yield primarily condensates of relatively low molecular mass. Among such compounds, formaldehyde, urea, and melamine are particularly important, because of their relatively low price. The type of chemical reaction yielding these prepolymers is determined by the functional groups. The amino resins are obtained by large-scale production in modern industrial plants and offer technical advantages in many applications.

History. The history of amino resins began with the synthesis of the two main raw materials, urea and formaldehyde; the former was prepared by F. Wöhler in 1824, and the latter by A. Butlerov in 1859. However, the first investigations of urea–formaldehyde resins were not carried out until about 1880. The first reaction products were reported by B. Tollens (1884) and C. Goldschmidt (1887), and the basic chemistry of the amino resins was established about 1908 [16].

F. Pollack and K. Ripper (1921) synthesized a clear transparent material, which they called "Pollopas." This product never became commercially important, but it did give rise to a number of experiments. The first commercial products, manufactured by E. C. Rossiter of British Cyanides Co. in 1924 and 1925, led to molding materials still in use today.

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A major step forward in the industrialization of amino resins became possible by the patent of A. SCHMID and M. HIMMELHEBER (1932), in which they laid the basis for resin-bonded particle board in order to increase the yield of sawn wood for furniture production from 40–80% [17].

The melamine resins were introduced in Germany by Henkel in 1935 [18]. Their properties are similar to those of the urea–formaldehyde resins, but enable the manufacture of products of higher quality. For example, they are chemically stable after the resin has hardened and become insoluble.

An ever-increasing number of mixtures of urea–formaldehyde and melamine–formaldehyde, or of urea–melamine–formaldehyde resins are produced for the most diverse uses. Lower costs, processing advantages, and the better performance of the products made from these mixtures account for their popularity.

Amino resins find their major use as adhesives. They are used in the production of particle board, medium density fiber board (MDF), high density fiber board (HDF), plywood, waferboard, and strandboard. Other types are employed for the production of laminated beams and parquet flooring, and for furniture assembly. Amino resins are also used to strengthen paper, to produce molding compounds and the flexible backing of carpets, as leather auxiliaries and soil conditioners, and for protective surface coatings. Another important application of amino resins is to saturate decorative papers for their final use in laminate manufacture.

2. Physical Properties

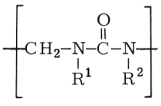
Amino resins are available commercially as concentrated solutions or solids, e.g., powders. The solutions generally contain water as a solvent, but in the surface-coating resins the solvents are alcohols. The solutions range from colorless and clear to milky and cloudy, and are tacky to the touch. Their viscosities are substantially higher than that of water, from 20–70 000 mPa · s—in general from 40–2000 mPa · s—measured at 20°C. The amino resins can be odorless, possess a characteristic smell, or, depending on the content of free formaldehyde, have a more or less sharp odor. The densities of the solutions at the commercially available concentrations of 50–80% solids are from 1.15–1.31 g/cm^3. An important property of the resins is the amount of water that can be added without precipitating solids, the so-called water tolerance or water dilutability. At relatively low temperatures, i.e., below about 20°C, pronounced cloudiness and an unusually large increase in viscosity are observed in many cases.

Some resin solutions exhibit the phenomenon of pseudoplasticity (thixotropy), which may or may not be desirable. Thixotropy means that the viscosity decreases as the shearing force increases [19, 20].

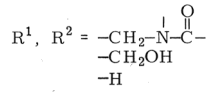
In powder form amino resins are white. In the spray-dried, commercially available form they have a particle size generally of 15–70 μm, but always < 200 μm. This particle size is a result of the spray-drying process [21]. The bulk density of the commercially available products is 0.5–0.8 kg/L. The powder resins dissolve in water to usually give milky liquids, however, in some cases clear solutions can be achieved. Flour-like additives can be mixed with some resins, which then assume the color of the additive to a greater or lesser extent.

3. Chemical Properties

Even when they are prepared from only two components, the amino resins are mixtures of various substances. For example, in the case of urea–formaldehyde resins the major components of the mixture are various hydroxymethyl compounds and oligomers composed of different combinations of basic units and substituted basic units. These oligomers differ in size. As an approximation, the basic unit can be described as methylene–urea (**1**), which can carry various substituents at the nitrogen atoms:



1



Hence, it is not possible to attribute specific chemical properties to these substances, as in the case of a pure compound.

However, some chemical properties are common to all or most amino resins.

The chemical properties given below are important with regard to processing the resins. The equations given for urea–formaldehyde also apply in principle to other reactants employed for these classes of products.

- Formaldehyde is slowly split off from hydroxymethyl compounds and undergoes addition reactions with other amino groups in accordance with the equilibrium equation [22, 23]:

$$H_2N{-}CO-NH_2 + CH_2O \rightleftharpoons H_2N-CO-NH-CH_2OH$$

- Hydroxymethyl compounds undergo slow condensation in the absence of heat or react with urea to give methylene compounds, such as methylene–diurea or methylene–oligourea:

$$H_2N-CO-NH-CH_2OH + H_2N-CO-NH_2 \rightarrow H_2N-CO-NH-CH_2-NH-CO-NH_2 + H_2O$$

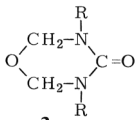
$$2\,H_2N-CO-NH-CH_2OH \rightarrow H_2N-CO-NH-CH_2-NH-CO-NH_2 + CH_2O + H_2O$$

These reactions are responsible for the gradual increase in viscosity that amino resins undergo during storage [24].

- It is known [25] that bis-methylene–urea ethers (**2**) are formed [13, p. 324, [23, 26]], but amino resin solutions contain rather small amounts of these ethers. This is due to the fact that the formation of the structural units (**1**) and (**2**) depends on the pH. (**1**) is formed in acidic media, while (**2**) is formed at both alkaline and acidic pH. Moreover, (**1**) is rather stable and basically no equilibrium with the monomers exists, while (**2**) allows a retro reaction into urea and formaldehyde. As a consequence, the amount of ether bridged diurea decreases, while the concentration of methylene bridges increases by time. Under certain production conditions cyclic ethers, so-called urones (**3**), also occur. Their formation is favored by acidic pH values (pH < 3) and at elevated temperatures (> 80 °C)

$$H_2N{-}CO{-}NH{-}CH_2{-}O{-}CH_2{-}NH{-}CO{-}NH_2$$

2



$R = -H, -CH_2OH, -CH_2OCH_3$

3

- Amino resin solutions are generally rendered slightly alkaline, i.e., pH 7.5–9, in order to stabilize them, but the pH slowly decreases as formic acid is formed. This effect is more pronounced for urea–formaldehyde resins and much less significant in melamine–formaldehyde resins.

These reactions, especially condensation with the formation of methylene bridges, are accelerated by acid catalysts and elevated temperatures. Hence, in processing amino resins, acids or acid-forming substances are important as hardeners that accelerate the condensation. Alkali-catalyzed condensation [13, pp. 331–332, 27] is of no practical importance.

The hydroxymethyl groups can be converted with alcohols into the corresponding ethers. This reaction is utilized in surface-coating resins and impregnation resins for the manufacture of paper-based edge-banding material and, to a lesser extent, in textile and paper auxiliaries.

The free formaldehyde, which is present in concentrations from 0.03% to about 2%, is of practical importance – not only because of classifications with respect to transport and storage of the resins – but in many cases because it reacts with ammonium salts of acids to give hexamethylenetetramine and the free acid, which acts as a hardener.

Resin powders also condense over time to give relatively high molecular mass products, but in this case the reaction is slower by a factor of at least five.

4. Raw Materials

The principal and most important carbonyl component is formaldehyde. Furfural and glyoxal are also employed, but these play a very minor role.

The most important amine-containing components are urea and melamine, but thiourea, guanidine, cyanamide, dicyanodiamide, and to a lesser extent acid amides, guanamines, and aniline, are also employed. Further components include the derivatives of these compounds, e.g., substituted ureas.

Relevant information on raw materials used to produce amino resins can be found in [1, pp. 3–85].

Products that are added in relatively small amounts to effect slight but often important changes in the properties are called modifiers. These include alcohols, amines, aminoalcohols, and a very large variety of other organic and inorganic substances [1, pp. 7–122].

Finally, it should also be mentioned that inert inorganic salts sometimes are added during the

production or processing of glue resins [8, p. 34, [28, 29]].

Formaldehyde [50-00-0], CH_2O, M_r 30.03, (production and properties → Formaldehyde). In the production of amino resins, formaldehyde is used either in the form of solid paraformaldehyde, in aqueous solution, or as a urea–formaldehyde precondensate that contains from 4–5 mol of formaldehyde per mole of urea. Paraformaldehyde is a mixture of hydrated polyoxymethylene molecules, with a degree of polymerization of 6–100 units. The melting point ranges from 120–170°C, depending on the molecular mass.

$$HO-[CH_2O]_n-H, \text{ where } n = 6-100$$

The most frequently used commercial form is a 30–55% aqueous solution of formaldehyde. These solutions are clear, caustic, and inflammable, have a sharp odor, and are infinitely miscible with water. Formaldehyde is present in aqueous solutions predominantly as the hydrate (HO–CH_2–OH), which is in equilibrium with its oligomers:

$$n\,CH_2(OH)_2 \rightleftharpoons HO(CH_2O)_nH + (n-1)H_2O$$

Depending on the method of production, the solutions are contaminated with a few hundredths of a percent of formic acid and from 0.4–2% of methanol. The content of formic acid and methanol increases during storage, as a result of the Cannizzaro reaction:

$$2\,CH_2O + H_2O \rightarrow HCOOH + CH_3OH$$

Moreover, on long-term storage at low temperatures, paraformaldehyde separates as a hazy suspension or a precipitate. This process is retarded by the addition of stabilizers, e.g., up to 12% of methanol or triazine derivatives.

Depending on the concentration and the methanol content, the flash point is about 50–85°C. The regulations governing flammable liquids do not apply to standard aqueous formaldehyde solutions with low methanol content.

Formaldehyde solutions can be stored and transported in containers made of stainless steel, aluminum, polyester resin, or appropriately lined iron.

Finally, aqueous solutions of urea – formaldehyde precondensates also are employed. Commercially available solutions contain from 70–85% of the active ingredients, calculated as urea and formaldehyde. The molar ratio of formaldehyde to urea ranges from 4 : 1 to 5.5 : 1, and the mass ratio is therefore 2 : 1 to 2.75 : 1. These solutions are substantially more resistant to polymer precipitation than are pure formaldehyde solutions. In the urea–formaldehyde precondensates, the major part of the formaldehyde is present in the form of urea–hydroxymethyl compounds, a smaller part as formaldehyde or its oligomers in the hydrated form, and a very small part as condensates. In this last case, the urea molecules are linked mainly by methylene bridges.

Biological Effect. Since 2000, the maximum allowable concentration (MAK value) recommended by the Senate Committee of the Deutsche Forschungsgemeinschaft (DFG) in Germany is 0.3 ppm. The corresponding values for the United States of America (given by OSHA) and Japan are 0.75 ppm (TWA 8 h) and 0.5 ppm (OEL (operational exposure limit)), respectively. At present, regulations vary from country to country (→ Formaldehyde, Chap. 10).

Other Aldehydes. Other aldehydes play a minor role. *Glyoxal* [107-22-2] is available commercially in the form of 30–40% aqueous solutions. The purity is 97–99%. Depending on the production method, the solutions contain 0.1–0.2% acid constituents. The color number should have a maximum value of 15 (APHA). Glyoxal is hydrated in the aqueous solution.

Urea [57-13-6], carbamide, diamide of carbonic acid, H_2NCONH_2, M_r 60.06 (→ Urea).

Urea is available commercially as a white crystalline product or as prills. For amino resin production, a technical-grade product is usually adequate.

It should be noted that fertilizer urea is frequently contaminated with ammonium salts, and these may act as hardeners and cause the glue mixture to solidify even in the production stage. Furthermore, the prilled urea can be mixed with sulfur or formaldehyde to keep it free flowing. Sulfur-coated urea is not recommended for resin production. The formaldehyde forms insoluble condensates on the surface of the prills, and these condensates can lead to a slight cloudiness when the prills are dissolved.

The dissolution of urea in water is an endothermic process. The enthalpy of solution (ΔH) is + 257.5 J/g, measured at 10°C in a 20-fold amount of water.

In the production of amino resins, urea is employed in solid form, in solution, or as a urea–formaldehyde precondensate.

Thiourea [62-56-6], thiocarbamide, NH_2CSNH_2, M_r 76.12 (→ Thiourea and Thiourea Derivatives).

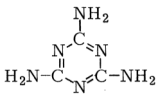
Thiourea is a relatively expensive raw material and is, therefore, not very important industrially. Apart from its use in special products, it serves only as a modifier, for example, in impregnating resins. Thiourea improves the resin properties, e.g., hardness, surface gloss, and water resistance.

The melting point of thiourea is 180°C. Its solubility in water is 9% at 100°C, substantially lower than that of urea.

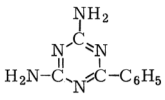
Substituted Ureas. Cyclic ethylene ureas and propylene ureas (2-oxoimidazolidine and 2-oxohexahydropyrimidine) are employed for the preparation of textile auxiliaries. Because of their high price and their limited ability to form condensates, they are not used in large amounts for any other purposes.

Melamine [108-78-1], 2,4,6-triamino-1,3,5-triazine, cyanurotriamide, M_r 126.13 (→ Melamine and Guanamines). Melamine (**4**) is a white powder that sublimes on heating. The particle diameter depends on the production process and varies from 5 to 300 μm. The rate of solubility in formaldehyde solutions depends on the particle size and is an important parameter given in the information leaflets of melamine producers. The color number of a 50% melamine–formaldehyde solution may not exceed 20 (APHA). This is important with respect to raw materials for surface coatings and to impregnating resins.

Melamine derivatives, e.g., benzoguanamine (**5**), are employed as modifiers.



4



5

Modifiers. A very large number of additives from all areas of organic and inorganic chemistry have been used to modify amino resins; most of these additives are no longer important [1, pp. 107–122]. Aliphatic alcohols, glycols, sugars, sugar alcohols, polysaccharides, and caprolactam are additives for special purposes and are still used today.

5. Production

5.1. Principle Aspects

Amino resin production consists of two stages: *hydroxymethylation* and *condensation* [30]. Depending on the reaction conditions, hydroxymethylation is accompanied to a greater or lesser extent by condensation. The following equations illustrate the process in a simple case, for example, for formaldehyde plus urea:

Hydroxymethylation:

$$NH_2CONH_2 + 2\,CH_2O \rightleftharpoons HOCH_2{-}NHCONH - CH_2OH$$

Condensation:

$$HOCH_2{-}NHCONH - CH_2OH + NH_2CONH_2 \rightarrow HOCH_2{-}NHCONH - CH_2{-}NHCONH_2 + H_2O$$

Further condensation leads to longer chains of the basic unit



Hydroxymethylation is carried out in slightly alkaline or slightly acidic media, whereas the condensation requires a more strongly acidic solution. Exceptions are the condensation conditions of melamine–formaldehyde resins, which require an alkaline pH [31], and the manufacture of melamine–urea–formaldehyde resins, which are condensed in slightly alkaline media. The process for the production of the resin is continued until the resulting product is an oligomeric mixture that is still soluble or fusible. It is protected against further condensation by rendering the medium alkaline. Condensation of the resin by means of acid catalysis, i.e., cross-linking to give a substantially infusible product, is not carried out until the resin is put to use. This process is called *curing*.

However, free hydroxymethyl groups are present even in this state.

The monomolecular and hydroxymethyl compounds with low degrees of polymerization and up to six urea–formaldehyde units are virtually all known and can be prepared in pure form [1, p. 20]. Aqueous solutions of the oligomers with low degrees of polymerization do not have a sufficiently long shelf life. Only when the concentrations of hydroxymethyl and NH_2 groups are reduced by partial condensation or when the products are present in solid form do they possess an industrially useful shelf life, i.e., of several weeks or more.

Condensations carried out in an excess of an alcohol, such as methanol or butanol, with the addition of acid and removal of water as necessary, produce curable etherified (i.e., alkylated) amino resins. These are soluble in nonaqueous solvents and can be mixed with alkyd resins, epoxy resins, etc. They are used as starting materials in the production of surface coatings.

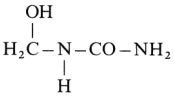
Resin glues based on urea, melamine, or both have been subjected to partial etherification to stabilize them against further condensation [32–34]. Historically, these resins have been used for the manufacture of plywood, but are practically not used any longer.

Preventing the resins from solidifying during the production process and selectively achieving certain properties – such as long shelf life, low formaldehyde content and, low formaldehyde emissions from final products, strength, and resistance to swelling of particle board after curing – are the basic difficulties encountered. Frequently, novel properties are required on short notice by the market.

5.1.1. Hydroxymethylation

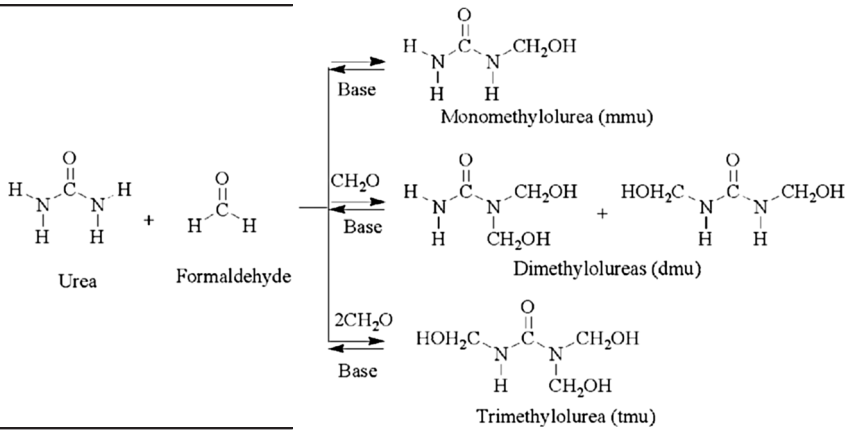
Hydroxymethylation can be carried out using either alkaline or acid catalysis, but the former is faster. The reaction mechanisms in acidic and alkaline media differ. In acids, condensation takes place at the same time. Hence, hydroxymethylation is carried out industrially in an alkaline or slightly acidic solution.

In hydroxymethylation, a semiaminal bond is formed:



Monohydroxymethylurea

This is cleaved readily, and hydroxymethylation reactions are reversible and establish an equilibrium [35]. Although mono-, di-, and trihydroxymethylurea are formed and isolated easily, tetrahydroxymethylurea is virtually nonexistent in aqueous solution.



The complete hydroxymethylation of all amino groups to form hexahydroxymethylmelamine can be carried out readily. The hydroxymethylation of urea is slightly exothermic:

$$H_2N-CO-NH_2+CH_2O \rightleftharpoons H_2N-CO-NH-CH_2OH$$

$$\Delta H = -23\ \mathrm{kJ/mol}$$

The ΔH data given in the literature fluctuate about this value by ± 5 kJ/mol. The enthalpy of hydroxymethylation of melamine, relative to the amount of formaldehyde, is – 15 kJ/mol [36, 37].

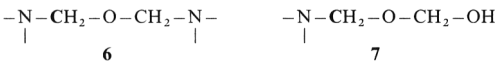
Reaction rates have been measured frequently, but they are sensitive to many parameters [22, 36].

Industrial processes produce variable mixtures of oligomers with mixed repeat units, so the overall reaction rate is also variable and cannot be defined. Moreover, the important resin properties have not been correlated with the individual reaction rates. In general, the hydroxymethylation rate increases with increased concentration, temperature, and pH. Substituents also have an effect; adjacent electron-withdrawing groups reduce the reaction rate, as do bulky substituents.

5.1.2. Condensation

The condensation is catalyzed by acids. Catalysis by strong alkalis also has been described, but the resulting amino resins are not important industrially [27]. The condensation can take place by the following routes:

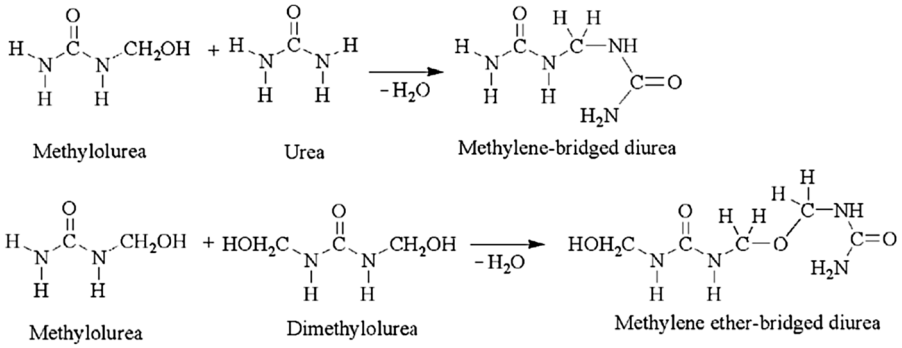
Although the presence of methylene compounds in amino resins can be established unambiguously by means of ^{13}C NMR spectroscopy, bis(ureamethylene) ethers can be detected only by an indirect procedure [38]. ^{13}C NMR spectroscopy permits the elucidation of many of the structures but does not distinguish between the **C** atoms shown in boldface in (**6**) and (**7**), although their third nearest neighbors are different.

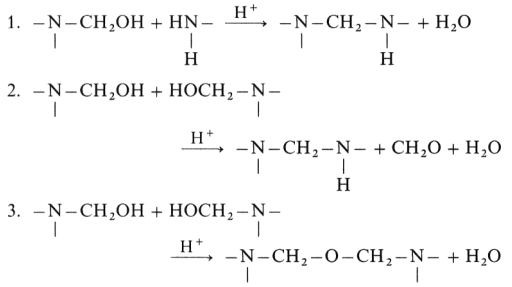


6 **7**

This problem also occurs in the case of melamine resins [39].

The methylene bonds between two urea molecules are very stable and can be hydrolyzed only by strong acids at elevated temperatures (see Chap. 8). The condensation reaction is slightly exothermic; the enthalpy is −28 kJ/mol [36].





The stability of the methylene–ether bond is between that of the hydroxymethyl bond and that of the methylene bond.

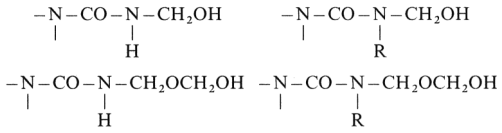
It is impossible to give a single reaction rate for the condensation process because there are many different starting materials (hydroxymethyl compounds) and many end products (methylene compounds).

The type of solvent also has an effect on the condensation rate [40]. The dependence of the reactivity of hydroxymethyl compounds on the chemical composition of the amino compounds can be interpreted on the basis of several qualitative rules [41].

5.1.3. Principal Components of an Amino Resin Solution

It is possible to identify the most important structural moieties of the oligomers in amino resin solutions by means of ^{1}H and ^{13}C NMR spectroscopy [26, 38, 42–44].

The hydrates of the formaldehyde oligomers $HO(CH_2O)_nH$, where n is about 5, can be detected along with the following hydroxymethyl structures:



Ethers, such as hydroxymethyl methyl ether, also can be identified in the spectrum by distinguishing the C atoms of the parent alcohol.

Finally, the structures (**8**) and (**9**) and ring compounds, including cyclic ethers of the urone type, also appear.



Asymmetrical **8** Symmetrical **9**

In a typical particle board glue, the ^{13}C NMR spectrum might show, for example, the following distribution of the carbon atoms of the original formaldehyde (mole fractions):

formaldehyde	0.03
hydroxymethyl compounds	0.72
methylene compounds	0.15
cyclic compounds	0.10

It is worth being mentioned that other analytical methods can be and are applied for further structure elucidation, too; for example:

- HPLC, mainly for low molecular mass constituents, like urea, monomethylolurea, *N*,*N*-dimethylolurea, *N*,*N*′-dimethylolurea, trimethylolurea, and methylene diurea
- Size exclusion chromatography, mainly for higher molecular mass species, like dimers and oligomers.

5.2. Production Processes

Amino resins usually are prepared in 5–100 m^3 batches. However, continuous processes are also employed, particularly for the production of resin glues. The patent literature describes processes where a particular stage is operated continuously while other stages are operated batchwise.

Because the reaction rate and the composition of the end product are influenced by a large number of parameters, the reaction must be controlled carefully. Important reaction parameters are:

- purity or composition of the starting materials
- molar ratio in each of the reaction stages
- type and amount of modifier
- reactant concentrations
- the pH value at each stage of the reaction
- temperature at each stage of the reaction
- type and concentration of catalyst
- amount of buffer salt
- reaction time in each stage

The large number of reaction parameters and resultant adaptations of the process lead to a very extensive body of relevant literature, particularly patent literature. Only the important processes are described here, but a comprehensive review can be found in [1, pp. 101–105].

5.2.1. Batchwise Production

The batchwise procedure is the most widely used method for the industrial production of amino resins, but it has the disadvantage of a relatively small production capacity. Nevertheless, this process permits an extensive variety of products and frequent changes of product.

The reactions are carried out in stirred kettles, in two or more stages, at 70–100°C. In the first stage, which is carried out in a slightly acidic to alkaline solution, the principal reaction

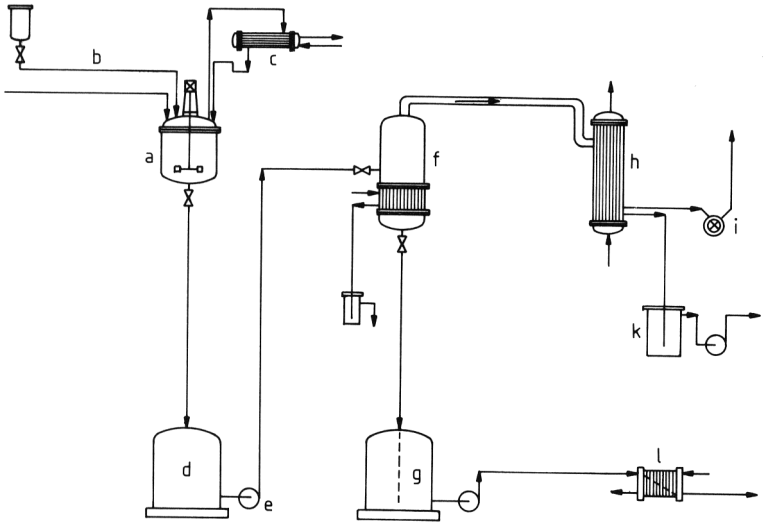


Figure 1. Plant for the batchwise production of aqueous amino resin solutions
a) Stirred kettle; b) Raw material feed; c) Reflux condenser; d) Temporary container; e) Pump; f) Vaporizer; g) Container for finished product; h) Condenser; i) Vacuum pump; k) Vessel for condensed vapors; l) Cooler

is hydroxymethylation. In subsequent stages, the condensation is carried out, water is split off, and higher molecular mass products of increasing viscosity are obtained. The duration of the condensation depends on the properties desired in the product. In general, the products are concentrated to 60–70% aqueous solutions by evaporation. The starting materials, urea or melamine, are employed in powder form. Urea can also be used in solution. Formaldehyde is employed as a 37–55% aqueous solution. In a few special cases, formaldehyde is used in the solid form, paraformaldehyde. Finally, it is possible to employ urea–formaldehyde precondensates in concentrations of not more than 80% by mass of the active ingredients.

Figure 1 shows a diagram of a plant for the batchwise production of aqueous solutions.

Aqueous Solutions. The reactor consists of a kettle equipped with heating and cooling devices, a stirrer, inlets for feeding in the raw materials and for measuring devices, a valve at the bottom for discharging the kettle, and a manhole for cleaning.

The material used is mainly stainless steel, material no. St. 1.4541 or St. 1.4571. Internal coils or external, welded-on, semicircular pipes enable heating with steam or cooling with cold water. Stirring is carried out by means of a powerful unit consisting of disk or anchor stirrers. Nozzles are welded on in order to meter in the raw materials and to permit measurement of the temperature and pH.

When the condensation is complete, the product can be evaporated. This is carried out in the stirred kettle, or more economically in a single- or multistage tubular vaporizer, with the pressure reduced to protect the resin. The quality of the resin is then compared to its specifications and it is discharged into a storage container.

The pipelines can be of aluminum or steel because the medium is slightly alkaline, the product tanks can also be of glass fiber reinforced polyester. It is advantageous to provide lined iron tanks.

A typical, simple resin glue for particle board production is made as follows [45]: 85 parts (by mass) of solid urea are introduced into 158 parts of a 50% formaldehyde solution that has been rendered neutral. The mixture is kept at 80°C for 10 min, during which time hydroxymethylation takes place. The pH is then brought to 4–5 by adding a 10% formic acid solution. The condensation causes the temperature to rise to 90–100°C within a few minutes. This temperature is maintained until a mixture of 1 part of reaction solution and 5 parts of water gives a white precipitate at a certain temperature (sharp endpoint) or a certain viscosity is achieved. The

reaction mixture is then brought to a slightly alkaline pH with a 25% sodium hydroxide solution. This terminates the condensation. A further 60 parts (by mass) of urea are then added, so that the molar ratio of formaldehyde to urea in the end product is 1.1. The resulting solution has a solids content of ~60%. The resin solution can be evaporated under reduced pressure to the commercial concentration of 66%.

This 66% solution of amino resin forms a milky solution and has a viscosity of about 500 mPa · s (at 20°C) and a density of 1.290 g/cm^3.

A typical resin for the impregnation of paper webs used in producing decorative laminates can be made as follows [12, p. 258]:

126 parts (by mass) of melamine are introduced into a stirred solution of 120 parts of a 40% formaldehyde solution and 70 parts of water at room temperature. The reaction mixture is brought to pH 9 by adding aqueous sodium hydroxide solution and is then heated very rapidly, i.e., in 20–30 min for an industrial-scale mixture, to a temperature of 100°C. After the melamine has dissolved, a process that takes place exothermally, sodium hydroxide solution is added continuously to maintain the pH value of the reaction mixture at 8.5–8.8 throughout the condensation. Condensation is carried out, with gentle refluxing and stirring, until the reaction mixture is compatible with water when mixed in the ratio 1:1.5. This is the case when a sample of the reaction mixture exhibits slight cloudiness when water, at 1.5 times the amount of solution, is added at 20°C. The reaction solution is then cooled rapidly and brought to pH 9.5–10 at room temperature by the addition of sodium hydroxide solution. The resultant impregnating resin solution has a solids content of about 55% and is usually clear.

Amino Resin Powders. In the production of amino resin powders, an aqueous resin solution is first produced (Fig. 2) and then fed into a spray drier, where it is atomized by a spray disk or nozzle. The resultant droplets are dried in the stream of hot gas produced by heating air indirectly in a heat exchanger or by mixing hot exhaust gas with air. The powder is collected in a tower and in cyclone separators or filters. It passes through a vibrating sieve into a mixing bin and then pours into sacks or drums.

Etherified Products Containing Solvent. Products of this type, which are used as starting materials for making surface coatings, can be produced in a reactor like that described in the production of aqueous solutions of amino resins (Fig. 3). The reactor must be equipped with a sufficiently large heat exchanger to vaporize the mixture of water and excess alcohol, e.g.,

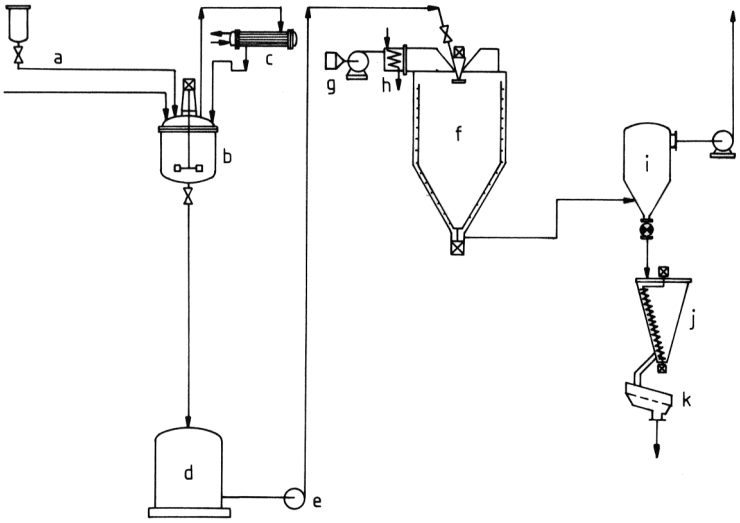


Figure 2. Plant for the production of amino resin powders by spray drying [21, p. 501]
a) Starting material feed; b) Stirred kettle; c) Reflux condenser; d) Temporary container; e) Pump; f) Spray drier; g) Blower; h) Air heater; i) Filter; j) Mixing bin; k) Vibrating sieve

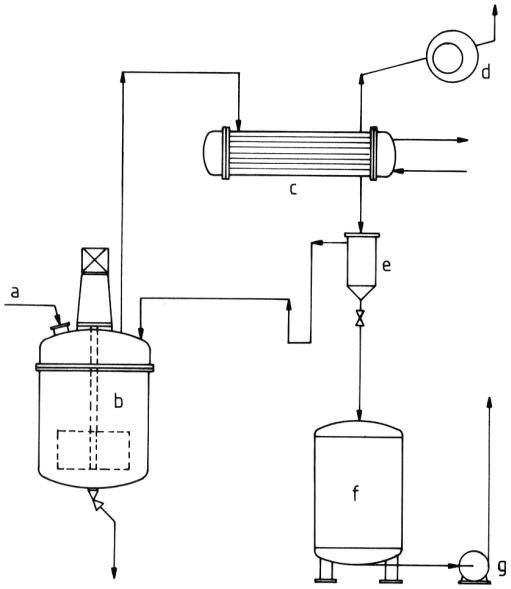


Figure 3. Plant for the batchwise production of etherified amino resins
a) Raw material feed; b) Stirred kettle; c) Condenser; d) Vacuum pump; e) Separating vessel (water separator); f) Product vessel; g) Pump

butanol. Downstream from the heat exchanger is a water separator. The separated aqueous phase still contains from 1–2% formaldehyde and 20% alcohol and, therefore, must be worked up. At the appropriate alcohol content, this solvent phase is recycled to the production process.

A butylated melamine–formaldehyde resin for surface coatings can be produced in the following way [11, p. 69]:

60 parts (by mass) of melamine, 60 parts (by mass) of formaldehyde (calculated at 100%) in the form of a 40% aqueous solution, and 220 parts (by mass) of butanol are refluxed for 30 min in a stirred kettle equipped for heating. Distillation is then carried out until water no longer evaporates. A further 20–25 parts (by mass) of anhydrous butanol are then distilled. The mixture is cooled, the resin content is determined, and the concentration is then brought to 50% with butanol.

5.2.2. Continuous Production

The continuous industrial production of amino resins was begun in order to meet rising demand. The disadvantages of continuous production are that the amount produced per unit time in a particular plant can vary only within relatively narrow limits because prolonged residence under otherwise constant conditions increases the proportion of molecules with high degrees of condensation. Changing the product is also not simple. If the plant is not cleaned out beforehand, a product having a composition between the old product and the new will be formed for a time. For this reason, the continuous production process is employed where the variety of products is restricted to a relatively narrow range. On the other hand, continuous procedures give a very uniform product quality.

The patent literature describes a large number of continuous processes. They differ only in process technology for the product flow. In general, the differences include variations in the temperature, pH, concentration, or modifiers. The process and product flow otherwise remain unchanged. In many cases the publications only describe laboratory- or pilot-scale plants that have not been scaled up for industrial use. Of the continuous processes that have been described, only those with basic differences in type are discussed here.

Aqueous Solutions. The apparatuses employed for the continuous production of aqueous amino resin solutions are tube reactors, stirred kettle cascades, or combinations of the two. The danger of incrustation by highly condensed, insoluble products is greater in the continuous process than in the batch process. In the latter, the residues are dissolved by fresh resin solutions; this is not the case in the continuous process because very little backmixing occurs.

A continuous two-reactor process was described by the Girdler Corp., United States of America, in 1943 [46]. The reactants were mixed thoroughly in the first reactor and heated to about 150°C under pressure. In the second stage, the solution under pressure was maintained at this temperature and condensation was carried out. The pressure of the reactor was then released, with the result that volatile constituents, especially water, escaped from the resin and the solution cooled.

According to a 1949 patent granted to Sherwood Paints, UK, the reaction is carried out in a

packed column [47] and water vapor is expelled by means of a countercurrent gas stream.

A process of Allied Chemical Corp., United States of America (1951), operates in a similar manner and employs a tubular coil as the reactor [48]. The resin solution is subsequently evaporated. Another process of Allied Chemical Corp. is carried out under pressure, using injected steam (1952) [49].

According to an application by Spumalit-Anstalt, Liechtenstein, the starting materials are passed over a solid catalyst (polycarbamide resin) under a pressure of 400 kPa at 140–150°C to form the resin [50].

A process of Rütgerswerke, Germany, from 1955 also uses a fixed-bed catalyst, an ion exchanger [51]. The resins obtained are used as starting materials for making molding compounds.

A Swedish application by Skanska Attifabriken AB from 1955 describes a process in which starting materials are heated separately and then sprayed into a chamber to undergo partial condensation [52]; the reaction is completed in another chamber. The advantage claimed is that none of the final products participates in the initial stages of the condensation.

An application by Du Pont, United States of America, in 1956, describes a continuous process for producing etherified formaldehyde–urea resins [53]. The stepwise reaction takes place in a cascade of two to four stirred kettles. The free alcohols (e.g., butanol, isobutanol, and others) are distilled in the last stage, and some of them are recycled.

In a Meissner process from 1966, the hydroxymethylation stage is carried out continuously and the subsequent condensation stage is operated batchwise [54]. The continuously flowing product stream from the first stage passes through a stirred kettle, which is one of a large number of kettles, so that the product flow need not be interrupted.

Other continuous processes have been worked out by Rheinpreussen AG [55] and the St. Regis Paper Co. [56], but these processes predominantly relate to phenoplasts.

A BASF process (1971) is shown diagrammatically in Figure 4 [57]. The reaction is carried out in a series of three or more stirred kettles. At the beginning of the cascade predominantly hydroxymethylation takes place. Condensation occurs later in the cascade. The reaction is terminated in the last section by

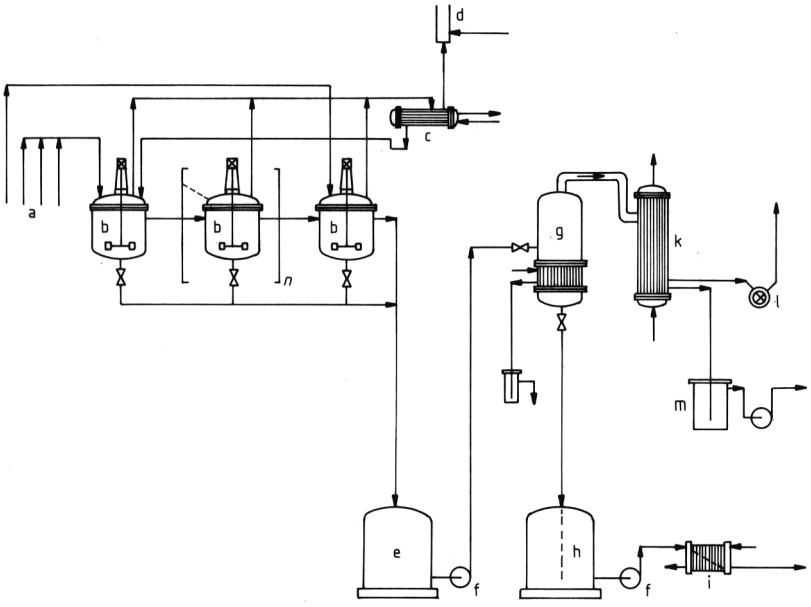


Figure 4. Plant for the continuous production of aqueous amino resin solutions [57]
a) Starting material feeds; b) Stirred kettle; c) Reflux condenser; d) Flare; e) Temporary container; f) Pump; g) Vaporizer; h) Product container; i) Cooler; k) Condenser; l) Vacuum pump; m) Container for condensed vapors

the addition of sodium hydroxide solution. The resin solution passes into a temporary container and is subsequently evaporated under reduced pressure in a single- or multi-stage vaporizer. The vapors, which contain about 2% formaldehyde, are worked up and the effluent is discharged for treatment. The end product is cooled and pumped into a tank.

Other cascade processes have been described in applications of SIR, Milano, Italy, (1972) [58] and Montedison (1980) [59].

Finally, mention should be made of the process in which formaldehyde is absorbed directly in urea solutions to produce highly concentrated, formaldehyde-rich solutions that are used as starting materials for glue resins. Examples of conventional commercial products are Kaurit-Konzentrat 244 fl. or 255 fl. (BASF), Prefere 30K180 (Dynea Austria GmbH), and Prefere 30K080 (Dynea NV, Gent, Belgium).

Stamicarbon [60] and American Cyanamid [61] have described the continuous production of concentrated, formaldehyde-rich melamine–formaldehyde solutions. These too can be used as starting materials for amino resins.

According to DSM the condensation resin is prepared in an aqueous medium at elevated temperatures (70–200°C) and pressure (0.2–20 MPa), where the monomers of the condensation resin are fed continuously to a tubular reactor provided with static mixer elements [62].

Resins in Powdered Form. Resins in powdered form also can be produced by a continuous procedure if the spray solutions, which in general are produced batchwise, are fed continuously from a temporary container into a spray tower [21].

5.2.3. Production of Special Products and Foams

In addition to impregnating resins, special products include foamed resins and resins for paper auxiliaries, label adhesives, concrete liquefiers, leather auxiliaries, carpet coatings, microcapsules, etc. Because of the relatively small individual amounts and the large variety of products, these resins are generally produced in batches. The principle of the production is the same as that for the manufacture of resin glues. The proprietary know-how relates to modifiers and small but important variations in the manner in which the process is carried out.

The foamed resins (→ Foamed Plastics) are an interesting type of amino resin. They are used to produce solid foams, which have a wide variety of applications. The production of the foamed resin solution and the end product, i.e., the foam, are discussed together.

In 1927, E. C. Bayer discovered that porous, heat-insulating materials are obtained if a foam or a foam-forming substance is added to a glue solution and the mixture is foamed and allowed to harden. In 1933, a process for the production of a foamed urea–formaldehyde resin was developed by I. G. Farbenindustrie. In this process, a foaming agent and air were used to produce a primary foam that itself contained the acid, e.g., phosphoric acid, for curing the amino resin. Curing begins after a few seconds and is complete after 12–24 h at room temperature. After drying, the foamed urea formaldehyde resins have bulk densities of 5–70 kg/m^3. More than 60% of the foam is in the form of open cells.

Whereas urea–formaldehyde foams previously could be prepared only in factories of fixed location, W. Bauer in 1953 described a transportable apparatus that permitted on-site production of the foam by means of compressed air [63]. A number of other apparatuses subsequently were developed. The state of the art is reported in [64] with respect to the design of foam-producing apparatus and a novel high-performance apparatus of this type is described. The development of foam-producing apparatuses led to much wider applications: soil conditioning in agriculture, heat insulation, sound insulation, filling of mining cavities, carrier material for cleaning fluids, and covering for landfills.

6. Environmental Protection

Effluents [66]. The condensed vapors or effluents from amino resin production may not be introduced into water without biological treatment. It should be further ensured that these effluents cannot penetrate into ground water.

Waste waters or partially hardened residues inevitably result when machines and containers are cleaned. The amount of wash water or solvent should be kept as small as possible. If the waste water contains predominantly urea or

formaldehyde, it can be reused in the production process. Otherwise, it is eliminated, for example, by incineration.

The biological treatment of industrial effluents from amino resin production is carried out primarily because of the formaldehyde, which is toxic. The usual effluents contain formaldehyde in concentrations that can be degraded readily by bacteria, which are always present. In general, a critical factor in the biological treatment of any effluent is the concentration in which the various toxic components are present.

Air. The treatment of waste gas by washing with water, catalytic combustion, or thermal combustion is used in industry. The waste gases should be very concentrated to minimize treatment costs.

Solid Wastes. Amino resins can be solidified by hardening them with ammonium chloride or phosphoric acid, or they can be absorbed in sawdust or sand. In this form, they may be deposited in a landfill in accordance with the relevant provisos and legal requirements.

7. Types of Resins and Their Properties

In addition to the simple types of resin that are produced in the largest amounts, i.e., the urea–formaldehyde and melamine–formaldehyde resins, other types of resin with different properties have been developed. These are modifications, i.e., versions of a resin obtained by use of relatively small amounts of additive or by changing the aldehyde or amino component. However, even where the composition is fixed the resin type can be varied by changing the reaction procedure. This leads to different distributions of oligomers or to different substitutions of the repeat units. The distribution of hydroxymethyl groups is the determining feature.

7.1. Urea Resins (Urea–Formaldehyde Resins)

All the urea–formaldehyde condensates [9011-05-6] containing the repeat unit **1** (see Chap. 3), from monomolecular to high molecular mass

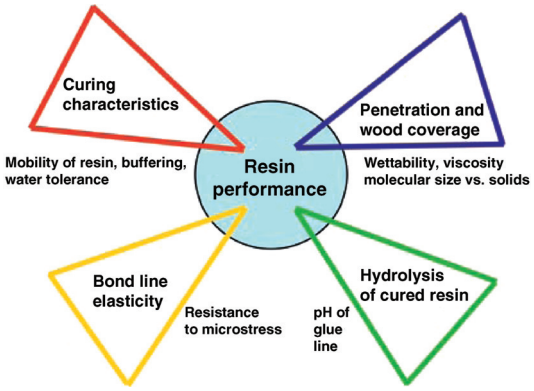


Figure 5. Interaction of resin properties

product, are useful substances. In the 1970s, a number of discoveries have been made concerning the composition of urea–formaldehyde resins. Systematic investigations into the process of condensation and the structural composition had long been impossible because of the lack of suitable analytical methods. Industrial development took place largely on an empirical basis. However, using a combination of analytical methods, e.g., ^{1}H NMR and ^{13}C NMR spectroscopy, C, H, N, O elemental analysis, determination of hydroxymethyl groups, and determination of total formaldehyde, it is possible in principle to determine the structural units and their concentrations [26]. However, the relationship between the technical properties of the amino resins or the materials produced from these resins and the distribution of the structural units is still unclear in most cases, so development is still largely empirical, but, the complexity of the interaction between substrate, resin, curing, processability, and final properties can be depicted as shown in Figure 5.

7.1.1. Pure Urea–Formaldehyde Resins

Important macroscopic parameters are the molar ratio of formaldehyde to urea, the viscosity, and the gelling time. Urea–formaldehyde condensates that have a molar formaldehyde-to-urea ratio of 1 usually give insoluble polymethylene ureas that do not possess any adhesive properties. If, however, the molar ratio is reduced from a relatively high value gradually or stepwise

during the course of the reaction, the resultant resin possesses adhesive properties. These properties improve as the molar ratio increases, but the undesirable release of formaldehyde increases simultaneously.

The highly viscous resin solutions obtainable by prolonged industrial condensation of urea and formaldehyde are low molecular mass products. They contain about six to eight urea units, as can be determined by gel chromatographic [24] and cryoscopic measurements and by endgroup determinations. This also applies to the completely insoluble powdered or glassy condensates [67]. During storage, the concentration of methylene groups increases at the expense of the hydroxymethyl groups. The viscosity also increases, initially slowly and virtually linearly, and then, after a critical time, rather steeply. Some or all of the hydroxymethyl groups generally can be blocked by etherification, and the shelf life of the amino resin is thus extended [33, 68, 69]. In principle the same reactions take place when the resin is hardened by the user, but they are substantially more rapid. However, a residual amount of hydroxymethyl groups remains after hardening [24]. Because they are susceptible to hydrolysis, even the cured urea resins are more water sensitive than the melamine or phenol resins.

The gelling time [11, p. 174] or reactivity of the resin is an important parameter for the user. This time can be determined relatively precisely, and is the time in which the resin changes from a fluid to a virtually immobile solid following the addition of a certain amount of hardener at a particular temperature. The reactivity increases with increasing molar ratio, content of hydroxymethyl groups, and content of free formaldehyde.

7.1.2. Mixed Condensates

Industrial amino resins contain mixtures of various condensates and cocondensates. Amino resin solutions are always polymeric mixtures having various degrees of condensation and differing distributions of functional groups. Resin-forming monomers employed as textile auxiliaries constitute an exception, but these in themselves are not resins. The term mixed condensates is rather loosely applied to those resins which are formed in the condensation of urea and formaldehyde when the reaction is carried out using substances that also form resins with formaldehyde. These are, for example, melamine, phenol, organic acid amides, sulfonamides, and carbamates. Therefore, in the presence of melamine or phenol, it is possible to prepare urea resins with improved strength and swelling properties for the manufacture of particle board, i.e., weather-resistant particle board. Modification with melamine gives resin glues that can be used to produce good-quality particle board even when the molar ratio of formaldehyde to urea is low.

Mixed resins with other resin formers, e.g., acrylic acid, acrylates [70, 71], acrylamide [1, p. 109] and their derivatives, are also sometimes advantageous. These are also mixtures of polymers, of cocondensates, or of homologous polymers and cocondensates.

7.1.3. Condensation of Urea with Other Aldehydes

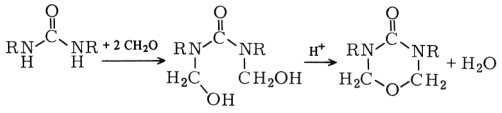
Condensation of urea with isobutyraldehyde, acetaldehyde, or crotonaldehyde is carried out industrially to obtain sparingly soluble nitrogen fertilizers, i.e., controlled release fertilizers, rather than resins [72, 73]. The condensation of urea or melamine with glyoxal gives products that can be employed as textile auxiliaries. Products obtained by the subsequent condensation of urea–formaldehyde resins with glyoxal (e.g., dimethylol dihydroxy ethylene urea, DMDHEU [1854-26-8]) also are used for textile finishing [74, 75].

7.1.4. Resins from Urea Derivatives

Condensation with urea derivatives or substitution products are well known, but these reactions are of industrial importance only for making textile and paper auxiliaries. Reactions with aldehydes can take place depending on the hydrogen atoms still present at the nitrogen, but the ability to undergo condensation decreases sharply with the size and number of substituents.

The reaction of a symmetrically disubstituted urea derivative, e.g., *N,N′*-dimethylurea or dihydroxymethylurea dimethyl ether, with

formaldehyde in an acidic medium gives cyclic urea derivatives of the urone type [76, p. 9]:



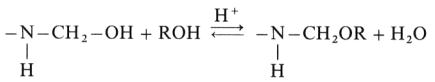
Dihydroxymethylurone dimethyl ether, bis (methoxymethyl)urone [7388-44-5] is used industrially to provide cellulose fabrics with a wrinkle-resistant finish. It has middling reactivity and stability to hydrolysis [77, pp. 164–174]. The urones do react with cellulose but form only minor amounts of self-cross-linked resins, such as the urea–formaldehyde compounds.

When S is substituted for O in urea, thiourea is obtained. The latter undergoes all of the principal condensation reactions of urea. In a weakly alkaline medium, *N*-hydroxymethyl compounds and *S*-hydroxymethyl compounds are formed. The tautomeric structure NH_2–C(SH) = NH may be assumed initially for the latter. The thiourea–formaldehyde condensates are more water resistant than the corresponding urea condensates. Some of the thiourea condensates are assumed to be cyclic compounds [78].

7.1.5. Modified Urea Resins

There is very extensive literature on the possible methods of modifying amino resins [1, pp. 95] and only the most important modifications are discussed here.

Reactions with Alcohols. The hydroxymethyl groups can be etherified with alcohols in an acidic medium [13, pp. 334].



The equilibrium constants for the etherification of monohydroxymethylurea and dihydroxymethylurea with methanol and ethanol have been measured [68]. The enthalpy of reaction, estimated from the temperature dependence of the equilibrium constant, is $\Delta H = -6$ to -8 kJ/mol. The equilibrium constants (K) differ depending on the substitution:

$K_{30\,°C,\,R=CH_3}$

$$H_2N-CO-NH-CH_2OH + ROH \rightleftharpoons H_2N-CO-NH-CH_2OR + H_2O \quad 0.6$$

$$HOCH_2-HN-CO-NH-CH_2OH + ROH \rightleftharpoons ROCH_2-HN-CO-NH-CH_2OH + H_2O \quad 7.6$$

$$ROCH_2-HN-CO-NH-CH_2OH + ROH \rightleftharpoons ROCH_2-HN-CO-NH-CH_2OR + H_2O \quad 2.0$$

$$K = \frac{[\text{Ether}] \cdot [H_2O]}{[\text{ROH}] \cdot [\text{Hydroxymethyl}]}$$

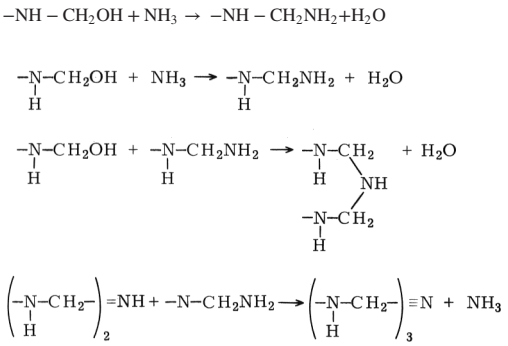
As the number of C atoms in the alcohol increases, the equilibrium is shifted to the left and the reaction rate reduced so that the etherification becomes more difficult. The ethers of the low-boiling alcohols can be transetherified with higher boiling alcohols by heating the mixture in weakly acidic solution and distilling the more volatile alcohols [13, p. 336].

Frequently only some of the hydroxymethyl groups of resin glues and impregnating resins undergo etherification with monohydric or polyhydric alcohols of less than five carbon atoms. As a result, some of the hydroxymethyl groups are protected against condensation, and the resins have a longer shelf life [1, p. 115, [79, 80]]. In the starting materials for surface coatings, 20–100% of the hydroxymethyl groups undergo etherification, depending on the type. The amino resins etherified with butyl groups are the most important for wood coatings, e.g., parquet coating. Where complete etherification takes place, the reaction is carried out using an entraining agent – the alcohol itself, toluene, or xylene – and the water is distilled azeotropically.

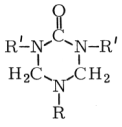
Ethers of one- to three-carbon alcohols with low molecular mass hydroxymethyl compounds of urea, ethylene urea (imidazolidinone [28906-87-8]), propylene urea (1,3-bis(hydroxymethyl) tetrahydro-2-(1*H*)-pyrimidinone [65405-39-2]), and melamine have achieved some importance in the field of textile auxiliaries [3, p. 168, [68, 77]]. These compounds are precondensates having relatively low molecular masses of about 600.

Urea resins etherified with butyl groups can be employed as starting materials for making surface coatings. However, when baked alone, they give brittle and water-sensitive films. Therefore, they cannot be used alone as binders. In combination with nitrocellulose, or with alkyd, epoxy, or acrylate resins, they give excellent baked finishes.

Reactions with Ammonia and Amines. Amines are very reactive toward hydroxymethyl compounds obtained from urea and formaldehyde. Ammonia reacts with the hydroxymethyl group to form an amino or imino group, eliminating water:



The reaction of ammonia with formaldehyde is exothermic ($\Delta H = -57$ kJ/mol) [1, p. 49] and gives hexamethylenetetramine. This reaction has been used industrially to trap formaldehyde from waste gases, for example, from particle board production [81–83]. The reaction of urea and aldehydes with primary amines gives cyclic compounds (triazines) [84] of the type **10**, where R′ can be hydroxymethyl and its methyl and ethyl ethers.



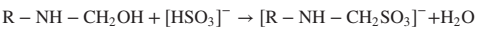
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Ammonia, primary or secondary amines, or polyamines containing two or more primary amino groups are used for the production of amino-modified resins [3, p. 206]. They are more stable towards water than the unmodified resins produced by a similar procedure.

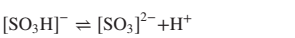
As shown in the equation above, ammonia and amines can react with the hydroxymethyl groups in urea, in a weakly acidic or alkaline medium, to give *N*-aminomethyl groups. In strongly acidic solution, these eliminate the amine substituents to form condensates. This condensation is similar to that starting with hydroxymethyl groups. Even very highly condensed urea resins are able to bind large amounts of ammonia and amines because a substantial part of the formaldehyde is still present in the form of hydroxymethyl groups. This reaction is utilized industrially, for example, to deodorize resins or particle board [81].

Condensation of the resin molecule with an amine produces a resin that has a cationic character; this increases the resin's affinity for cellulose fibers when it is used as an auxiliary for textiles or paper. These basic urea resins are therefore mainly important because they improve the wet tensile strength of paper.

Reaction with Sulfites. Just as formaldehyde hydrate reacts with a sulfite, so the hydroxymethyl groups of the amino resins react with a hydrogen or other sulfite to give an aminomethanesulfonate [1, p. 120]:



This imparts an anionic character to the resins [3, p. 206]. The pH of the solution controls its sulfite content.



To produce resins of this type, the reaction of, e.g., urea and formaldehyde is begun in a neutral or alkaline medium in order to achieve hydroxymethylation. When the desired degree of conversion has been achieved, condensation is carried out using sulfite or hydrogen sulfite in a slightly acid solution [85]. The resin can react with hydrogen sulfite because many hydroxymethyl groups are still present. Water-insoluble resins can even be rendered soluble by post-treatment with hydrogen sulfite. Although, like unmodified resins, the amino resins produced using sulfites exhibit an increase in viscosity on aging, they remain water soluble because of their hydrophilic ionic groups.

The anionic resins are of particular industrial importance in the field of water-soluble or water-dispersible adhesives. Other uses include textile auxiliaries [86], paper auxiliaries [87], leather auxiliaries, and deodorants [88] for urea–formaldehyde resins [89].

In addition to modification with sulfite, the relevant patents mention many other modifiers, such as aldehydes and triazines. The affinity of the anionic resins for cellulose (which carries a slight negative charge) is lower than that of the

cationic resins; therefore, the fibers must be posttreated with aluminum sulfate to fix the resins.

The modification of urea–formaldehyde resin glues with ligninsulfonic acid should also be mentioned [90, 91]. The products are dark resin solutions that have been used from time to time in the woodworking industry. The mechanism involved in the incorporation of the nonuniform lignin is still unclear [1, p. 120]. Lignin contains phenolic groups. Incorporation of the lignin components imparts relatively high water resistance, among other things. The lignins are of different origins and compositions, so that the production process must be adapted empirically to the different lignin varieties. This fact and the dark coloration have prevented more extensive use of lignin wastes from wood pulp production.

7.2. Melamine Resins

7.2.1. Unmodified Melamine Resins [9003-08-1]

Melamine, like urea, can react with formaldehyde [9, p. 65]. The addition of formaldehyde at the amino group is carried out at pH 9–10 and takes place very rapidly. One mole of melamine combines with 6 mol of formaldehyde to form hexahydroxymethylmelamine. Melamine in itself is only slightly soluble even in hot water [9, p. 60]. However, it dissolves readily in (alkaline) aqueous formaldehyde solutions, forming hydroxymethylmelamines. A small part of the melamine remains physically dissolved. When heated, hydroxymethylmelamines undergo cross-linking [9, p. 66] and form resins that become more insoluble the longer they are heated. Melamine condenses with formaldehyde in acid solution to form hydroxymethyl compounds. This is followed by a more rapid polycondensation, yielding cross-linked products, than in the case of urea–formaldehyde [13, p. 359]. Melamine–formaldehyde resins can be hardened thermally in the absence of a hardener or they can be hardened in the absence of heat, using a very strongly acidic hardener. The hardening processes, as in the case of the urea resins, are not entirely clear. Cross-linking takes place principally by methylene bridges, but it also has been suggested that methylene–ether bridges play a role. The melamine formaldehyde condensates possess good thermal stability, optical properties, and water resistance [13, p. 350].

7.2.2. Modified Melamine Resins

Reaction with Alcohols. Melamine hydroxymethyl compounds can be etherified with alcohols in the same manner as hydroxymethylurea compounds [13, p. 361]. The most important use of the products is as surface-coating resins, but they are also used as textile auxiliaries and even as melamine–urea–formaldehyde resins and impregnating resins. As in the case of the urea resins, etherification is carried out at relatively high temperatures with acid catalysis. Where etherification is carried out to a substantial degree, it is important to remove the water or excess alcohol from the weakly acidic solution, because cross-linking otherwise competes with etherification. The mono- to hexaalkyl ethers of the C_1 to C_4 alcohols can be prepared readily. Good conversions are obtained for higher alcohols only by means of transetherification [92].

Methyl ethers of melamine hydroxymethyl compounds are readily soluble in water even at room temperature and crystallize readily [3, p. 361]. The aqueous solutions of the methyl ethers prepared from higher hydroxymethyl compounds, i.e., those with a higher molar ratio of hydroxymethyl groups, become cloudy on heating and clarify again when cooled. Most of the methyl ethers are soluble not only in water but also in benzene and similar solvents. The products etherified with higher alcohols, e.g., butanol or benzyl alcohol, are water insoluble but are readily soluble in alcohols and some hydrocarbons. In addition to monoalcohols, polyhydric alcohols, e.g., ethylene glycol, glycerol, 3-hydroxymethyl-1,5-pentanediol, and pentaerythritol, can be employed as etherification agents. This etherification must be carried out in neutral solution because the competing cross-linking reaction otherwise takes place more rapidly and forms insoluble products.

Like the corresponding urea resins, the etherified melamine–formaldehyde resins used as starting materials for surface coatings are condensates having low molecular masses of 600–1400 [93]. These are presumably triazine structures linked by methylene bridges and contain from two to four melamine groups.

The ether groups are distributed randomly over the triazine rings.

Reaction with Amines. Amines and aminocarboxylic acids react readily with the hydroxymethyl group of hydroxymethylmelamines in the same way as with urea resins. Modification with amines or amino acids improves the hydrophilic character of the melamine resins. Condensation with amino acids gives alkali-soluble melamine resins that are used to produce impregnating or molding materials [94]. Basic products, which form salts with acids, are obtained by modification with aminoalcohols, e.g., aminoethanol [95], and are used as textile auxiliaries. These products are not of major industrial importance.

Reaction with Hydrogen Sulfite. Melamine resins, like urea resins, react with hydrogen sulfites. Industrially, the cheapest product, i.e., sodium sulfite, sodium hydrogen sulfite, or pyrosulfite is used, and the reaction is carried out in an acidic or basic medium. The products are readily water-soluble melamine resins that can be precipitated with acids. Hydrogen sulfite-modified melamine–formaldehyde resins are used industrially as concrete liquefiers in the building materials industry. In addition to sulfite, other modifiers described in the patent literature are dithionite and formaldehyde sodium sulfoxylate ($NaHSO_2 \cdot CH_2O$) [96, 97].

Other Modifiers. The modification of hydroxymethylmelamine resins with polyalcohols, sugars, toluenesulfonamides, lactams, nitriles [98–100], acrylates, and polyacrylonitrile [1, p. 109, 101] is of great importance in the production of impregnating resins. Such modifications improve the large number of laminating properties required and stabilize the resin solution against clouding and an excessively rapid increase in viscosity.

Mixed condensates and cocondensates of melamine with other compounds – e.g., phenol, urea, cyanamide, and dicyanodiamide – that react with formaldehyde have also been described in a large number of publications. For example, phenol-modified melamine–urea–formaldehyde resins are used as resin glues for weather-resistant particle board [102, 103]. These resins, too, can be modified in a large variety of ways.

7.3. Urethane Resins

Condensation of a urethane (carbamate) of the formula H_2N–COOR with an aldehyde gives a distinct compound or a resin, depending on the production conditions [8, p. 220], [13, p. 371]. In an alkaline medium, carbamates react with formaldehyde to give hydroxymethyl compounds that split back into the starting materials at higher temperatures. In an acidic medium, they cross-link to form methylene bridges and produce resins that are used to manufacture molding materials. A patent has been applied regarding the use of urethane resins derived from long-chain aliphatic alcohols as plasticizers [3, p. 220]. Urethane–urea–formaldehyde mixed resins have also been described. The reaction of cyanuric acid with polyhydric alcohols and formaldehyde gives resins that can be used as paper and textile auxiliaries and as starting materials for surface coatings.

In another procedure, urea is converted into the appropriate carbamate by heating in the presence of an alcohol and eliminating ammonia. The subsequent reaction with formaldehyde and cross-linking are carried out as described above [13, p. 374]. The resultant highly viscous solutions can be used as label adhesives and for the adhesive bonding of cardboard boxes.

The properties of urethane resins vary depending on the components and method of production. They range from oily to brittle depending on the degree of condensation. Lower aliphatic and cycloaliphatic alcohols yield hard resins, whereas higher alcohols give wax-like resins.

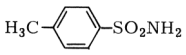
7.4. Cyanamide and Dicyanodiamide Resins

Cyanamide and dicyanodiamide react with formaldehyde both in acid and in alkaline media [8, p. 199]. Cyanamide reacts with an equimolar amount of formaldehyde at pH 6–7 to give a white precipitate, which loses water to form a crystalline compound. In general, cyanamide and dicyanodiamide are used as modifiers [1, p. 118, 13, p. 382]. Cyanamide–formaldehyde and dicyanodiamide–formaldehyde resins have been used as mixed resins for starting materials in making molding compositions, as dyeing and tanning auxiliaries, for textile

finishing, and for preserving urea–formaldehyde foams.

7.5. Sulfonamide Resins

The most commonly used basic component for this type of resins is *p*-toluenesulfonamide:



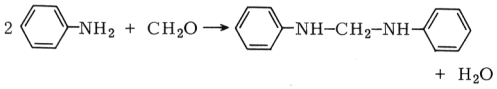
With formaldehyde, *p*-toluenesulfonamide forms resins that are fusible but not curable, whereas disulfonamides or amides possessing other groups capable of condensation give insoluble products that are infusible [104]. The special properties of *p*-toluenesulfonamide resins include compatibility with cellulose surface coatings, pale natural color (in contrast to that of phenol resins), and a low tendency to yellow.

Only the *p*-toluenesulfonamide–formaldehyde condensates have become important industrially, and these only as cocondensates or modifiers. Only the combinations with urea–melamine resins, phenol resins, and phthalate resins are of importance [105]. They also are added to melamine–formaldehyde impregnating resins as plasticizers in amounts of 3–8% [1, pp. 109].

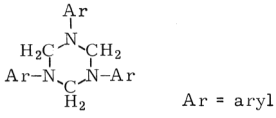
7.6. Aniline Resins

Aniline resins include the condensates of formaldehyde with aromatic amines, such as aniline [25214-70-4], toluidines, xylidines, naphthylamines, and phenylenediamines [13, p. 192].

In alkaline solution, the first stage, i.e., hydroxymethylation, leads to a simple condensate:

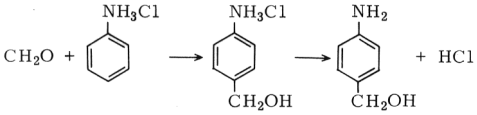


Condensation to give a cyclic product has been reported also.



Ar = aryl

The reaction with formaldehyde in an acid medium gives resins in which methylene groups link the aromatic rings directly, as in the case of the phenoplasts (→ Phenolic Resins). The para position is activated by salt formation at the amino group, so formaldehyde can add at this position to form *p*-aminobenzyl alcohol.



Polymer chains are formed and water is eliminated in this process. In the presence of an excess of formaldehyde, three-dimensional networks also form.

The amino groups have a directing function, so tertiary aromatic amines can also form resins. Unlike the phenol resins, aniline resins do not harden further. The aniline resins are therefore thermoplasts in contrast to the resins discussed above, which are duroplasts. The aniline resins are not very important industrially. They have been used in small amounts in the production of molding materials [1, p. 120] and ion-exchange resins and, because of their high resistance to tracking currents, they have been mixed with epoxy resins and used for wire enamels and insulating coatings [106].

8. Analysis

Analysis, insofar as it is used for product control during production, storage, and use, amounts to testing various types of resins for characteristic parameters or selected specifications. Complete elucidation of the chemical structure, including the sizes and amounts of the oligomers, would entail an unacceptably great expense.

Characterization of the products usually includes the following determinations [11, p. 171, [107–109]]:

- density in g/cm^3 (in the case of foams, in kg/m^3)
- solids content in % by mass
- viscosity in mPa · s, usually at 20°C
- free formaldehyde
- total formaldehyde
- free urea
- total urea

- melamine
- methoxy content
- ash content (incombustible modifiers)

The urea–formaldehyde or amino groups–formaldehyde molar ratio is calculated from the analytical data.

Further tests may be employed if special properties are required of the resins. The development of novel products and applications increases the need for analytical effort.

Solids Content. The determination of the solids content in resin solutions is a determination of the dry matter content. The value is useful only for comparison. It is determined by evaporating the volatile components at 100–130°C over a fixed period of time. This procedure removes not only the water present as a solvent and the free formaldehyde, but also the water and formaldehyde formed during the drying process in the condensation. Therefore the dry matter content is by no means to be equated with the active ingredient content. More exact data are obtained by the determination of water by the Karl Fischer method [110], by freeze drying, or, in organic solvents, by the Aufhauser method. In industry, however, the water content is estimated by the drying method detailed above because this method is simple and quick.

Formaldehyde [111–113]. The free formaldehyde can be determined directly and the total formaldehyde can be determined after the product has been hydrolyzed completely. The hydroxymethyl content can be determined by hydrolysis under relatively mild conditions. The formaldehyde bonded in the form of methylene groups is calculated by difference.

Urea. The total urea can be determined by hydrolysis and the Kjeldahl procedure. The free urea is degraded to ammonia by the enzyme urease [114]. If no other form of nitrogen is present in the resin, the urea content can be calculated from the nitrogen content, which is determined by combustion analysis. The *molar ratio* of urea to formaldehyde can be calculated from the total content of formaldehyde. This ratio provides information on the formaldehyde elimination to be expected.

Melamine in amino resins is determined by hydrolysis of the product under mild conditions followed by titration with perchloric acid. Resins having a low degree of condensation can be titrated directly using a computerized automatic apparatus.

Methanol is generally present in the form of methoxy groups bonded to hydroxymethyl groups by an ether bond; it is determined by the Zeisel's procedure.

Other components are important, particularly where the resins are used as paper or textile auxiliaries or as starting materials for making surface coatings. Some of these are maleic acid, glyoxal, phenol, amines, and sulfites. The methods of determination are discussed in textbooks on analysis or, for example, in specific articles. These substances are not determined during routine product control.

For research and development purposes, paper chromatography, thin-layer chromatography [115], column chromatography [116], gel permeation chromatography, ^{13}C NMR spectroscopy [26, 38, 42], ^{15}N NMR spectroscopy [117], ^{1}H NMR spectroscopy (using dimethyl sulfoxide as the solvent) [38, 118], and infrared spectroscopy are used.

9. Storage and Transportation

Aqueous or alcoholic solutions of amino resins are stored in steel tanks with or without internal epoxide coatings, in stainless steel tanks, or in containers made of fiberglass-reinforced polyester resin. Temperatures above 20–25°C must be avoided because they bring on rapid condensation, which increases the viscosity and soon renders the resin unprocessible. Rotary pumps or – in the case of highly viscous liquids – positive-displacement pumps, e.g., gear pumps, are employed.

Powdered amino resins are packaged in airtight, plastic-lined paper sacks that are sealed against moisture. Certain types of paper bags can withstand tropical climates. Under high pressure, the materials may solidify. Spilled product is taken to a waste dump.

Liquid resin loads of up to about 250 kg are dispatched in small polyethylene barrels,

whereas greater loads, up to about 1 t, are dispatched in polyethylene containers encased in sheet metal. Larger amounts are transported in containers, railroad tank cars, tank trucks, or marine tankers. Amino resins must be disposed of if they are damaged or become unstable during transport in tanks.

The relevant regulations governing the disposal of amino resins differ from country to country and even within some countries. A common feature of all the regulations, however, is that the resin must be hardened by the addition of acid curing agents and must be delivered to a licensed landfill. Where leakage occurs during transport, it is advisable to absorb the resin solution with any appropriate agent that is available (e.g., sand or sawdust) and then to deliver the resulting material for incineration. In the Federal Republic of Germany, amino resins are not included among substances regarded as endangering water.

10. Uses

The properties of amino resins have been adapted by industry to a very large number of applications. New uses are being developed constantly and any list is bound to be incomplete.

Uses include the following: adhesives; impregnating resins; molding materials; starting materials for making surface coatings; auxiliaries for paper, textiles, leather, and flotation; strengtheners for building materials; concrete liquefiers; binders for glass fibers and foundry sand casting; fire lighters; emery papers; flame retardant coatings; flameproofed combustible items; foamed resins for many purposes; grinding wheels; ion-exchange resins; sewage flocculants; and microcapsule production.

The largest amount of amino resins is consumed by the woodworking industry. These resins, along with the phenol resins, have largely replaced the natural glues based on proteins (glutin, casein, soybean, and blood albumin glues). Resins are used as resin glues in the particle board, MDF, HDF, plywood, and furniture industries. Impregnating resins also are used to impregnate papers for decorative laminates and for coating wood particle board.

Resin Glues for the Woodworking Industry [120]. The amino resins used as glues in the woodworking industry are available commercially predominantly in the form of 55–70% aqueous solutions or as solids, for example, powders. The powder resins entail lower transport costs but are more expensive because of the costs involved in drying them and must be dissolved by the user. Whereas the powder resins have shelf lives of one year or longer if stored correctly, the liquid products, depending on the type, have shelf lives of several weeks to six months, typically four weeks. During this period the viscosity remains within limits that permit the resin to be pumped with a conventional pump. The amino resins are more or less stable intermediates; condensation is completed by the addition of a curing agent and/or by heat treatment. A curing agent, e.g., ammonium chloride, is virtually always required for the urea resins, whereas melamine resins can be cured at 120°C. Compared to the melamine or phenol resin glues, particle board made from urea resin glue has a lower water resistance and is not resistant to boiling. If these properties are required, melamine resin glues or mixed condensates of formaldehyde, urea, melamine, and/or phenol are employed.

In addition to water resistance, the tendency to release formaldehyde is very important. If a low level of formaldehyde release is desired, the formaldehyde content of the resin glue must be correspondingly low. In some countries, and for structural applications, the glue must receive the approval of the authorities.

Since the 1980s, MDF resins have become increasingly important. The MDF resins are pure or melamine-modified urea–formaldehyde resins that have a low viscosity, about 200 mPa · s. Other modifiers may be used also. Medium-density fiberboard is used in the production of furniture with structured surfaces [1, p. 179, 119, pp. 266–275].

From an economic point of view, the urea resins are the most important amino resin glues because they are inexpensive, enable short press times, and possess technical properties adequate for most purposes.

The main use is in the production of wood particle board. These resins also play an important role as glues for plywood and blockboard and for furniture construction. The gluing of load-bearing wood components and shutter panels and the production of shaped articles are further examples of the large variety of uses of amino resin wood glues.

Impregnating Resins [121]. Urea–formaldehyde or melamine–formaldehyde impregnating resins are used to treat papers for decorative purposes. The resins themselves are brittle products and it may be necessary to modify them with a plasticizer. Because of their good properties, i.e., hardness, abrasion resistance, scratch resistance, and stability to light, the amino resins are particularly suitable for this purpose. The impregnated papers are used either to produce decorative laminates or for coating wood particle board. Papers impregnated with melamine resin are more heat stable and water resistant than those impregnated with urea resin [122].

The paper webs impregnated with the amino resin are dried in a furnace at 70–200°C and are stored under air-conditioning until they are used.

Various types of amino resin-impregnated papers are required for decorative laminates. The most important are papers that impart a decorative pattern to the board which itself consists of several layers of phenol resin-impregnated kraft paper (high pressure laminate (HPL) and, continuously pressed laminate (CPL)).

However, the major share of laminates manufactured today is produced by directly pressing amino resin-impregnated decorative papers onto a suitable substrate, such as particle board, MDF, or HDF. These laminates are abbreviated as DPL, (direct pressed laminate) or LPM (low pressure melamine).

Ground films and decorative films are likewise amino resin-impregnated papers and are used in the same way as wood veneers in the furniture industry. These films generally are produced from urea resins and to a certain extent also from melamine–urea resin mixtures.

Molding Materials. Molding materials consist of a filler, e.g., cellulose or sawdust, and a binder, which can be a urea resin or a melamine resin. The molding materials obtained from melamine resins are superior to those obtained from urea resins because of their better hardening properties, higher mechanical strength, and greater resistance to tracking currents and moisture [3, pp. 68–100].

The molding materials are employed for objects in daily use; e.g., white electrical plugs, switches, covers, telephone accessories, and buttons are made from urea resin. Melamine resin is used for camping, hospital, and canteen tableware, and for junction boxes and insulating components. Mixed resins that combine some of the properties of the individual resins are also used.

Raw Materials for Surface Coatings. Pure amino resins are not very useful as surface coatings. The majority of the commercially available amino resins used as starting materials for surface coatings are etherified with butanol or isobutanol and dissolved therein [3, pp. 124–148]. Special brands are also modified with methanol, ethanol, or propanols.

Because the surface coatings obtained using amino resins are too brittle, these resins cannot be used alone as binders. However, they are very useful in combination with other binders. Urea resins and melamine resins are the most important cross-linking components for alkyd resins.

Physically drying finishes are obtained by adding amino resins to nitrocellulose finishes. The addition of these resins improves the hardness, body, and stability to light. The principal field of use is in furniture finishing.

Acid-curable finishes are obtained by adding alkyd resins or saturated polyester resins. These finishes can be hardened by adding an acid, e.g., hydrochloric acid, *p*-toluenesulfonic acid, or a phosphoric acid derivative, at an elevated temperature. The resulting coatings are very hard and resistant to scratches, solvents, and the effects of light [3, p. 130]. Urea resins are more important than melamine resins, particularly in furniture finishing and parquet sealing.

Coatings that can be cross-linked by heat treatment alone are obtained by combining amino resins with alkyd resins, saturated polyester resins, heat-curable acrylate resins, or epoxy resins. Because of their good mechanical properties, their gloss, and their resistance, these baked finishes are extremely important in industrial metal finishing, for example, for automobile bodywork, household appliances, metal furniture, and containers [123, p. 177].

Because they are etherified and essentially free of water, the amino resins used in the surface-coating industry have shelf lives of six months to several years at room temperature. They are dispatched in plain or galvanized sheet metal containers. Only stainless steel or aluminum tanks are used for transport by tanker trucks and railroad tank cars.

Paper Auxiliaries. In the paper industry, amino resins are used to increase the dry tensile strength

and especially the wet tensile strength of the product [3, pp. 205–209, [124, 125]]. In contrast to the procedure followed in the textile industry (see Textile Auxiliaries below), the resin components are added to the paper stock before condensation. They are adsorbed onto the fiber and then undergo condensation in an acid medium. The maximum strength of the paper is reached only after a maturing period of two to four weeks. Based on the fiber, 1–5 wt% of resin is sufficient to achieve good wet strength. The amino resins also are used for the surface finishing of papers. They impart water resistance to starch-containing paper-coating compositions.

The urea resins, which constitute the most important group, are generally hydroxymethyl compounds that have been modified by the addition of amines to give them a cationic character or by the addition of sulfites to provide an anionic character. After modification, these compounds are subjected to a condensation reaction in an acid medium. The resultant ionic resins are water soluble. The ionic character also enables them to be adsorbed onto anionic paper pulp, but anionic resins must be used with aluminum sulfate [124, p. 43].

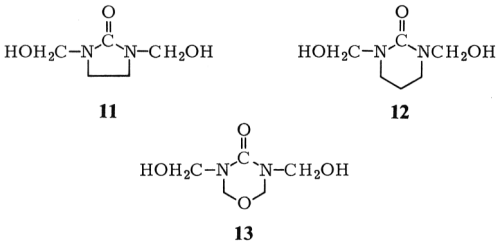
Melamine resins are also important to the wet strength of paper. In the absence of other modifiers, they react with acids to form strongly acid cationic colloids that are stabilized by an electric charge and consist of partially condensed hydroxymethyl melamines. Melamine resins modified with aminocaproic acid are also suitable substitutes, either alone or in combination with other polymers, for some or all of the colophony soaps used in the internal sizing of paper [124, p. 42].

A further field of use is the production of moisture-resistant starch pastes for the adhesive bonding of corrugated board [126].

Textile Auxiliaries (→ Textile Auxiliaries, 7. Finishing Agents). The textile auxiliaries based on derivatives of urea, melamine, and formaldehyde [3, pp. 166–181] are predominantly monomeric, and therefore should not be regarded as resins. They contain only unavoidable, small, random amounts of higher condensates. The molecules react with the primary hydroxyl groups of the cellulose on contact with the cellulose fibers. The relatively weak hydrogen bridges of the cellulose molecules are thereby supplemented by additional, stronger covalent bonds. Self-condensation takes place on the surface of synthetic fibers, which do not react with the "amino resin" monomers. This type of auxiliary is discussed here, as are others that stiffen the finish of synthetic fabrics.

The pure urea–formaldehyde adducts, mono- and dihydroxymethylurea, are water soluble and crystallize readily. In crystalline form, they possess the largest share of the market for easy-care and wrinkle-resistant finishes for cellulose textiles and mixtures of cellulose fibers with synthetics and wool. The pastes also consist principally of these basic substances, but some of them are etherified with lower alcohols and exhibit a minor amount of condensation. They are therefore used to provide wrinkle-resistant and wash-and-wear finishes as well as stiffened finishes on synthetic fabrics. The fabrics treated in this manner possess improved wash resistance. Hydroxymethyl compounds of urea that exhibit a high degree of condensation and possess a high concentration of ether groups are used to produce highly elastic stiffening effects and good wash resistance in cellulose fabrics. Because of the relatively low concentration of "amino resin" monomers (about 1 mol of resin per kg of cellulose), cross-linking between the cellulose groups is strongly favored over self-cross-linking. A disadvantage of this class of products is the relatively low stability of the acid treatment liquors in the bath, where condensation can take place easily between the hydroxymethylurea molecules.

An important group is constituted by hydroxymethyl compounds of cyclic urea derivatives; examples are dihydroxymethylethylene urea (**11**), dihydroxymethylpropylene urea (**12**), and dihydroxymethylurone (**13**).



Acyclic compounds, such as various alkyl carbamates, are also typical finishing agents. In contrast to the pure urea–formaldehyde

compounds, these exhibit little tendency to form self-cross-linked resins and react predominantly with cellulose to crosslink the fibers. The other advantages, over and above the mechanical properties, are resistance to chlorinated water, lightfastness, and shade constancy. These are closely related to the chemical structure and the resistance of the C–N and N–O bonds to hydrolysis.

Hydroxymethyl melamine derivatives and their ethers are of some importance for providing high-grade finishes, i.e., embossed finishes, Schreiner finishes, chintz finishes, and plisse finishes, but they have largely been replaced by the reactant types. The finishes obtained using hydroxymethylmelamines are more wash resistant than those made with hydroxymethylureas. Hydroxymethylmelamine compounds are preferred for embossed finishes (Everglaze) where the fabric can be damaged mechanically.

Leather Auxiliaries. Resin retannage of chrome-tanned leather is carried out using hydroxymethyl compounds of urea, thiourea, melamine, dicyanodiamide, and ethers of these [3, p. 211, 89]. Aqueous solutions of the resins should penetrate the hide before condensation begins. The acid condensation catalyst (pH 3.9–4.5) should not reduce the period of activity of the tanning liquor or damage the hide. As in the case of the paper auxiliaries, the resins are rendered cationic using amines or anionic by means of a bisulfite. The anionic resins based on melamine or dicyanodiamide make leather very strong and supple and leave the color unchanged. The hydroxymethyl groups react with the active groups of the collagen fiber, which has a high content of glycine, proline, and oxyproline.

Other Uses of Amino Resins. The number of possible uses is increasing constantly.

The importance of many uses, e.g., flameproofing agents, has declined greatly. Some applications, e.g., casting resins, have proved unsatisfactory in practice, whereas others are only at the development stage and their industrial suitability cannot yet be assessed.

11. Economic Aspects

Amino resins have become increasingly important after World War II. The most important amino resins are urea-formaldehyde, melamine-urea-formaldehyde, and melamine-formaldehyde resins [127]. The other resins mentioned in this keyword reflect only a very minor share in terms of volume and economic value. The predominant application of urea- and melamine-fortified urea-formaldehyde resins is for production of panel boards, whereas the major uses for melamine-formaldehyde resins are manufacture of impregnated paper for laminates and surface coatings.

Almost two thirds of the UF and MUF resins are consumed by particle board production; about one third by production of MDF, the rest of about 5% is used by all other end applications. For these applications, an overall European consumption of about 5.5×10^6 t can be assumed for 2004. A very small share of UF resins is also used as saturating resins in the production of laminates, for this a total volume of about 200 000 t (2009) can be estimated.

For the melamine-formaldehyde resins, the major end use is the production of laminates (HPL, CPL, DPL; about two thirds of the total volume) leaving the use of MFs as constituents of surface coatings behind (about 30%). For 2009, the total European market for MF saturating resins was about 520 000 t (2007: 525 000 t; 2003: 480 000 t).

Overall, and very simplifying, for all these aforementioned resins used in the wood based panels industry about 55% of the annual quantity is produced by the consumers themselves being backward integrated into resin production (like Kronospan Group, Sadepan Chimica, Egger, Pfleiderer, Sonae), about 45% of the annual resin consumption are covered by non-integrated resin producers (Dynea Chemicals, BASF, Hexion, Ercros, Ineos, PA Resins).

In the application of surface finishings MF resins used in melamine films clearly dominate over other surface finishing materials such as thermoplastic films [128].

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Epoxy Resins

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1. Introduction

Epoxy resins are an important class of polymeric materials, characterized by the presence of more than one three-membered ring known as the epoxy, epoxide, oxirane, or ethoxyline group.



The word "epoxy" is derived from the Greek prefix "ep," which means over and between, and "oxy," the combining form of oxygen [1]. By strict definition, epoxy resins refer only to uncross-linked monomers or oligomers containing epoxy groups. However, in practice, the term epoxy resins is loosely used to include cured epoxy systems. It should be noted that very high molecular weight epoxy resins and cured epoxy resins contain very little or no epoxide groups. The vast majority of industrially important epoxy resins are bi- or multifunctional epoxides. The monofunctional epoxides are primarily used as reactive diluents, viscosity modifiers, or adhesion promoters, but they are included here because of their relevance in the field of epoxy polymers.

Epoxies are one of the most versatile classes of polymers with diverse applications such as metal can coatings, automotive primer, printed circuit boards, semiconductor encapsulants, adhesives, and aerospace composites. Most cured epoxy resins provide amorphous thermosets with excellent mechanical strength and toughness; outstanding chemical, moisture, and corrosion resistance; good thermal, adhesive, and electrical properties; no volatiles emission and low shrinkage upon cure; and dimensional stability—a unique combination of properties generally not found in any other

plastic material. These superior performance characteristics, coupled with outstanding formulating versatility and reasonable costs, have gained epoxy resins wide acceptance as materials of choice for a multitude of bonding, structural, and protective coatings applications.

Commercial epoxy resins contain aliphatic, cycloaliphatic, or aromatic backbones and are available in a wide range of molecular weights from several hundreds to tens of thousands. The most widely used epoxies are the glycidyl ether derivatives of bisphenol A (> 75 % of resin sales volume). The capability of the highly strained epoxy ring to react with a wide variety of curing agents under diverse conditions and temperatures imparts additional versatility to the epoxies. The major industrial utility of epoxy resins is in thermosetting applications. Treatment with curing agents gives insoluble and intractable thermoset polymers. In order to facilitate processing and to modify cured resin properties, other constituents may be included in the compositions: fillers, solvents, diluents, plasticizers, catalysts, accelerators, and toughening.

Epoxy resins were first offered commercially in the late 1940s and are now used in a number of industries, often in demanding applications where their performance attributes are needed and their modestly high prices are justified. However, aromatic epoxies find limited uses in exterior applications because of their poor ultraviolet (UV) light resistance. Highly crosslinked epoxy thermosets sometimes suffer from brittleness and are often modified with toughening for improved impact resistance.

The largest use of epoxy resins is in protective coatings (> 50 %), with the remainder being in structural applications such as printed circuit board (PCB) laminates, semiconductor encapsulants, and structural composites; tooling, molding, and casting; flooring; and adhesives. New, growing applications include lithographic inks and photoresists for the electronics industry.

2. History

The patent literature indicates that the synthesis of epoxy compounds was discovered as early as the late 1890s [2]. In 1934, Schlack of I.G. Farbenindustrie AG in Germany filed a patent application for the preparation of reaction products of amines with epoxies, including one epoxy based on bisphenol A and epichlorohydrin [3]. However, the commercial possibilities for epoxy resins were only recognized a few years later, simultaneously and independently, by the DeTrey Fréres Co. in Switzerland [4] and by the DeVoe and Raynolds Co. [5] in the United States.

In 1936, Pierre Castan of DeTrey Fréres Co. produced a low melting epoxy resin from bisphenol A and epichlorohydrin that gave a thermoset composition with phthalic anhydride. Application of the hardened composition was foreseen in dental products, but initial attempts to market the resin were unsuccessful. The patents were licensed to Ciba AG of Basel, Switzerland, and in 1946 the first epoxy adhesive was shown at the Swiss Industries Fair, and samples of casting resin were offered to the electrical industry.

Immediately after World War II, Sylvan Greenlee of DeVoe and Raynolds Co. patented a series of high molecular weight (MW) epoxy resin compositions for coating applications. These resins were based on the reaction of bisphenol A and epichlorohydrin, and were marketed through the subsidiary Jones-Dabney Co. as polyhydroxy ethers used for esterification with drying oil fatty acids to produce alkyd-type epoxy ester coatings. Protective surface coatings were the first major commercial application of epoxy resins, and they remain a major outlet for epoxy resin consumption today. Concurrently, epoxidation of multifunctional olefins with peroxy acids was studied by Daniel Swern as an alternative route to epoxy resins [6]. Meanwhile, Ciba AG, under license from DeTrey Frères, further developed epoxy resins for casting, laminating, and adhesive applications, and the Ciba Products Co. was established in the United States.

In the late 1940s, two U.S. companies, Shell Chemical Co. and Union Carbide Corp. (then Bakelite Co.), began research on bisphenol A based epoxy resins. At that time, Shell was the only supplier of epichlorohydrin, and Bakelite was a leading supplier of phenolic resins and bisphenol A. In 1955, the four U.S. epoxy resin manufacturers entered into a cross-licensing agreement. Subsequently, The Dow Chemical Co. and Reichhold Chemicals, Inc. joined the patent pool and began manufacturing epoxy resins.

In the 1960s, a number of multifunctional epoxy resins were developed for higher temperature applications. Ciba Products Co. manufactured and marketed *o*-cresol epoxy novolac resins, which had been developed by Koppers Co. Dow developed the phenol novolac epoxy

resins, Shell introduced polyglycidyl ethers of tetrafunctional phenols, and Union Carbide developed a triglycidyl *p*-aminophenol resin. These products continue to find uses today in highly demanding applications such as semiconductor encapsulants and aerospace composites where their performance justifies their higher costs relative to bisphenol A based epoxies.

The peracetic acid epoxidation of olefins was developed in the 1950s by Union Carbide in the United States and by Ciba AG in Europe for cycloaliphatic structures. Ciba Products marketed cycloaliphatic epoxy resins in 1963 and licensed several multifunctional resins from Union Carbide in 1965. The ensuing years witnessed the development of general-purpose epoxy resins with improved weathering characteristics based on the five-membered hydantoin ring and also on hydrogenated bisphenol A, but their commercial success has been limited because of their higher costs. Flame-retardant epoxy resins based on tetrabromobisphenol A were developed and commercialized by Dow Chemical for electrical laminate and composite applications in the late 1960s.

In the 1970s, the development of two breakthrough waterborne coating technologies based on epoxy resins helped establish the dominant position of epoxies in these markets: PPG's cathodic electrodeposition automotive primer and ICI-Glidden's epoxy acrylic interior can coatings.

While epoxy resins are known for excellent chemical resistance properties, the development and commercialization of epoxy vinyl ester resins in the 1970s by Shell and Dow offered enhanced resistance properties for hard-to-hold, corrosive chemicals such as acids, bases, and organic solvents. In conjunction with the development of the structural composites industry, epoxy vinyl ester resin composites found applications in demanding environments such as tanks, pipes and ancillary equipment for petrochemical plants and oil refineries, automotive valve covers, and oil pans. More recently, epoxy and vinyl esters are used in the construction of windmill blades for wind energy farms. Increasing requirements in the composite industries for aerospace and defense applications in the 1980s led to the development of new, high performance multifunctional epoxy resins based on complex amine and phenolic structures. Examples of those products are the trisphenol epoxy novolacs developed by Dow Chemical and now marketed by Huntsman (formerly Ciba).

The development of the electronics and computer industries in the 1980s demanded higher performance epoxy resins. Faster speeds and more densely packed semiconductors required epoxy encapsulants with higher thermal stability, better moisture resistance, and higher device reliability. Significant advances in the manufacturing processes of epoxy resins led to the development of electronic-grade materials with lower ionic and chloride impurities and improved electrical properties. Dow Chemical introduced a number of new, high performance products such as hydrocarbon epoxy novolacs based on dicyclopentadiene. The 1980s also witnessed the development of the Japanese epoxy resin industry with focus on specialty, high performing and high purity resins for the electronics industry. These include the commercialization of crystalline resins such as biphenol diglycidyl ether.

More recently, in order to comply with more stringent environmental regulations, there has been increased attention to the development of epoxy resins for high solids, powder, and waterborne and radiation-curable coatings. Powder coatings based on epoxy–polyester and epoxy–acrylate hybrids have continued to grow in the global markets, including new applications such as primer-surfacer and topcoats for automotive coatings. Radiation-curable epoxy–acrylates and cycloaliphatic epoxies showed tremendous growth in the 1990s in radiation-curable applications. These include important and new uses of epoxy resins such as the photoresists and lithographic inks for the electronics industry. Waterborne epoxy coatings are projected to grow substantially.

The continuing trend of device miniaturization in the computer industry, and the explosive growth of portable electronics and communications devices such as wireless cellular telephones in the 1990s demanded new, high performance resins for the PCB market. This has led to the development of new epoxies and epoxy hybrid systems having lower dielectric constants (D_k), higher glass-transition temperatures (T_g), and higher thermal decomposition temperatures (T_d) for electrical laminates. Environmental pressures in the PCB industry have fueled the development of a number of new bromine-free resin systems, but their commercialization is limited because of higher costs.

Significant efforts have been directed toward performance enhancements of epoxy structural composites. Advances have been made in the

epoxy-toughening area. Epoxy nanocomposites and nanotube systems have been studied and are claimed to bring exceptional thermal, chemical, and mechanical property improvements. However, commercialization has not yet materialized.

In 1999, Dow Chemical introduced a new epoxy-based thermoplastic resin, BLOX*, for gas barrier, adhesives, and coatings applications.

3. Industry Overview

From the first commercial introduction of diglycidyl ether of bisphenol A (DGEBA) resins in the 1940s, epoxy resins have gradually established their position as an important class of industrial polymers. Epoxy resin sales increased rapidly in the 1970s and continued to rise into the 1980s as new applications were developed (annual growth rate > 10 % in the U.S. market, Table 1). More recently, the slower growth rates (3–4 %) of the U.S., Japanese, and European markets in the 1990s were made up for by the higher growth rate (5–10 %) in the Asia-Pacific markets outside of Japan, particularly in Taiwan and China. Epoxy resin growth has historically tracked well with economic developments and demands for durable goods, and so the growth of the epoxy markets in Asia-Pacific is expected to continue into the next decade.

The global market for epoxy resins is estimated at approximately 1.15 million metric tons (MT) for the year 2000 [8]. This is an increase of 5 % over 1999 demands. The North American market consumed over 330,000 MT of epoxy resins, the European market is estimated at more than 370,000 MT, and the Asian market has surpassed both the North American and European markets by consuming 400,000 MT of epoxy resins. About 50,000 MT of epoxies were consumed in the South American markets. Imports of epoxy resins from Asia into North America has steadily grown to about 120,000 MT in 2000. Epoxy resins were used with over 400,000 MT of curing agents to produce an estimated 3 million MT of formulated compounds, worth over $20 billion.

Up until the mid-1990s, the major worldwide producers of epoxy resins were Dow Chemical, Shell, and Ciba-Geigy. However, both Shell and Ciba-Geigy have recently divested their epoxy resins businesses. Shell sold their epoxy business to Apollo Management LP (based in New York City) in the year 2000 and the company was renamed Resolution Performance Products. Similarly, Ciba's epoxy business was sold in 2000 to Morgan Grenfell, a London (U.K.)-based private equity firm, and the new company name was Vantico. More recently, in June 2003, the Vantico group of companies joined Huntsman. The Vantico business units are now named Huntsman Advanced Materials. The cycloaliphatic epoxy business of Union Carbide became part of The Dow Chemical Company after their merger in the year 2001. Together, these three producers continue to dominate the world market for epoxy resins, accounting for almost 65 % of the global market. However, this is a reduction from over 70 % of market shares owned by the three largest producers in the 1980s. Smaller producers of epoxy resins for the North American markets are Reichhold (owned by Dainippon Ink and Chemicals), CVC Specialty Chemicals, Pacific Epoxy Polymers, and InChem (phenoxy thermoplastic resins). Suppliers of epoxy derivatives include Ashland Specialty Chemical, UCB Chemicals (Radcure), AOC LLC, Eastman Chemical, and Interplastic Corp.

The market in Europe is similarly dominated by the three big producers: Dow, Resolution, and Huntsman and their affiliated joint ventures. Other smaller epoxy producers include Bakelite AG, LEUNA-Harze, Solutia, SIR Industriale, and EMS-CHEMIE. Imports from Asia have become significant in recent years.

Table 1. History of U.S. epoxy resin annual production[a]

Year	Production, 10^3 MT
1955	10
1960	30
1965	55
1970	79
1975	100
1980	201
1985	347
1990	475
1994	433

[a]Data from U.S. International Trade Commission, *Synthetic Organic Chemicals*. Data include modified and unmodified epoxy resins. Modified epoxy resins include solid epoxy resin (SER), vinyl ester resins, epoxy acrylates, etc. There appear to be some discrepancies in epoxy resin production and market data as reported by different publications and organizations [7]. This is primarily due to the fact that some epoxy resins such as liquid DGEBA resins and epoxy novolacs are used as raw materials to produce modified or advanced epoxy resins, which may be further converted to end-use products. Some publications report only unmodified epoxies.

The last two decades marked the emergence of the Asian epoxy industry. In the 1980s, the Japanese epoxy industry was transformed from a number of joint venture companies with Dow, Shell, and Ciba into independent producers and the emergence of a high number of new producers. This coincides with the development of Japan as a world-class manufacturing base. The Japanese epoxy industry is known for their special focus on high performance, high purity resins for the electronics industry. According to data from the Japan Epoxy Resin Manufacturers Association, the total Japanese market demand is estimated at approximately 200,000 MT for the year 2000. The production capacity is estimated at 240,000 MT annually. Exports accounted for an estimated 40,000 MT in 2000. Major Japanese epoxy resin producers are Tohto Kasei, Japan Epoxy Resins Corp. (formerly Yuka-Shell), Asahi Kasei, Dai Nippon Ink and Chemicals, Dow Chemical Japan, Mitsui Chemicals, Nihon Kayaku, Sumitomo Chemical, and Asahi Denka Kogyo. In Japan, Tohto Kasei is a leading resin producer, with epoxy technology licensing arrangements with numerous resin producers in Asia.

Outside of Japan, there have been significant increases in epoxy market demands and capacity in the 1990s. This is due to the migration of many PCB, electronic, computer, and durable goods manufacturing plants into the region, which has considerably lower manufacturing costs. Nan Ya, a subsidiary of the Formosa Plastics Group based in Taiwan, is emerging as a major epoxy resin producer with some import presence in North America and Europe. Similarly, Kukdo of Korea also exports to the North American and European markets. The output of these two companies now account for an estimated 15 % of the world market. In China, there are numerous (more than 200) small domestic producers of epoxy resins. Recently, a number of major epoxy producers have announced joint ventures or plans to build manufacturing plants in China. These include a number of companies with integrated capacity into electrical laminates and PCB manufacturing, following the business model pioneered by the Formosa Plastics Group. Other notable Asian producers include Asia Pacific Resins, Chang Chun, and Eternal Chemical of Taiwan; Thai Epoxy of Thailand; Kumho, LG Chemical, and Pacific Epoxy Resins of Korea; and Guangdong Ciba Polymers, Sinopec Baling Petrochemical, Jiangsu Sanmu, and Wuxi DIC Epoxy Resin of China. The LG Chemical epoxy business was purchased by Bakelite in late 2002. A significant amount of resin produced in Taiwan and China is directed toward electrical laminates applications. The aggressive buildup of epoxy capacity in Asia has put significant pressures on resin prices, particularly the high volume products such as liquid epoxy resins based on bisphenol A (Table 2). But as of January 2004, the epoxy market demand in China alone has increased to more than 500,000 MT (Chinese Epoxy Industry Web site).

Table 2. Epoxy production capacity in Asia-Pacific[a] (2001)

Country	Existing capacity, 1000 MT/year	Announced capacity, 1000 MT/year
Japan	240	
Taiwan	239	70
China	100	255
Korea	180	
Thailand	30	
Malaysia	10	
Philippines	10	
Total	*809*	*325*

[a]Compilation of published data by Dow Chemical.

Estimated average prices for epoxy resin products in North America are given in Table 3. As with other petrochemical-based products, they depend on crude-oil prices. Prices of

Table 3. U.S. average epoxy resin prices and applications (2000)

Resin	$/kg	Applications
Liquid epoxy resins (Diglycidyl ether of bisphenol A, DGEBA)	2.2	coatings, castings, tooling, flooring, adhesives, composites
Solid epoxy resins (SER)	2.4	powder coating; epoxy esters for coatings; can, drum, and maintenance coatings
Bisphenol F epoxy	4.4	coatings
Multifunctional		
Phenol epoxy novolac	4.8	castings, coatings, laminates
Cresol epoxy novolac	8.8	electronics encapsulants, powder coatings, laminates
Other multifunctional epoxies	11–44	composites, adhesives, laminates, electronics
Cycloaliphatic epoxies	6.6	electrical castings, coatings, electronics
Brominated epoxies	3.3–5.5	printed wiring boards, composites
Epoxy vinyl esters	3.3	composites
Phenoxy resins	11–17	coatings, laminates, glass sizing
Epoxy diluents	4–11	

Table 4. List of some epoxy resin producers and their product trade names

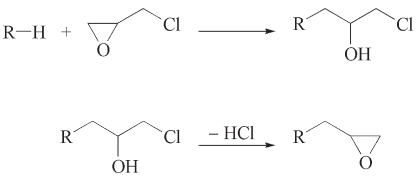
Company	Trade name
Resolution Performance Products	Epon, Eponol, Eponex, Epi-Cure, Epikote
Dow Chemical	D.E.R., D.E.N., D.E.H., Derakane, E.R.L
Hunstman Advanced Materials (formerly Ciba, Vantico)	Araldite, Aralcast
Reichhold Chemical	Epotuf
Nan Ya	NPEL, NPES
Kukdo Chemical	YD
Dainippon Ink & Chemical (DIC)	Epiclon
Tohto Kasei	Epotohto
Japan Epoxy Resin (JER)	Epikote
Asahi Kasei	A.E.R.
Mitsui Chemical	Eponik
Sumitomo Chemical	Sumiepoxy
Thai Epoxy	Epotec
Chang Chun	
InChem	Paphen
Pacific Epoxy Polymers	PEP
CVC Specialty Chemicals	Erysis, Epalloy

multifunctional resins are typically higher. They are based on more expensive raw materials than DGEBA resins and involve more complex manufacturing procedures. A listing of some major epoxy resin producers and the trade names of their products is shown in Table 4.

There are numerous suppliers of epoxy curing agents. Some of the major producers are Air Products and Chemicals, Cognis, Degussa, DSM, Huntsman, and Resolution.

4. Classes of Epoxy Resins and Manufacturing Processes

Most commercially important epoxy resins are prepared by the coupling reaction of compounds containing at least two active hydrogen atoms with epichlorohydrin followed by dehydrohalogenation:



These included polyphenolic compounds, mono and diamines, amino phenols, heterocyclic imides and amides, aliphatic diols and polyols, and dimeric fatty acids. Epoxy resins derived from epichlorohydrin are termed glycidyl-based resins.

Alternatively, epoxy resins based on epoxidized aliphatic or cycloaliphatic dienes are produced by direct epoxidation of olefins by peracids:



Approximately 75 % of the epoxy resins currently used worldwide are derived from DGEBA. This market dominance of bisphenol A based epoxy resins is a result of a combination of their relatively low cost and adequate-to-superior performance in many applications. Figure 1 shows U.S. consumption of major epoxy resin types for the year 2000.

5. Liquid Epoxy Resins (DGEBA)

The most important intermediate in epoxy resin technology is the reaction product of epichlorohydrin and bisphenol A. It is often referred to in the industry as liquid epoxy resin (LER), which can be described as the crude DGEBA where the degree of polymerization, n, is very low ($n \cong 0.2$):

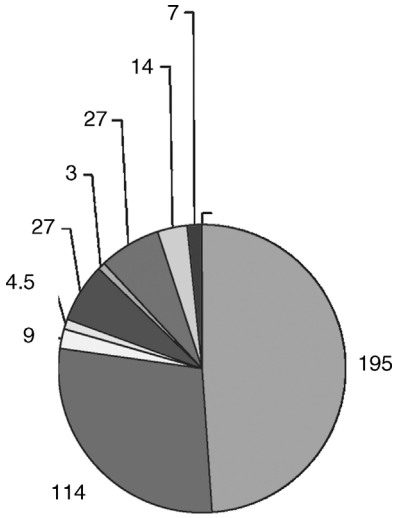
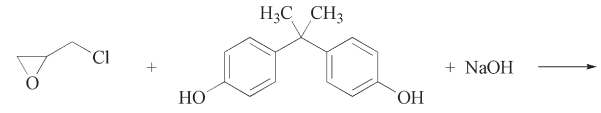
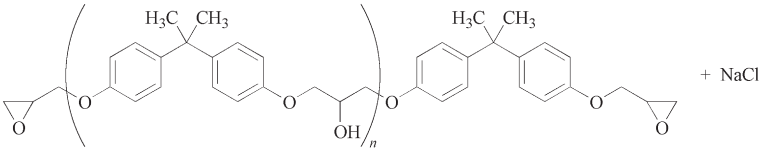


Figure 1. Major epoxy resin and derivatives markets (10^3 MT). LER; SER; epoxy novolacs; other multifunctional epoxies; brominated epoxies; cycloaliphatic; vinyl esters; and epoxy acrylates.



Epichlorohydrin Bisphenol A



DGEBA

Pure DGEBA is a crystalline solid (*mp* 43 °C) with an epoxide equivalent weight (EEW) of 170. The typical commercial unmodified liquid resins are viscous liquids with viscosities of 11,000–16,000 mPa · s (= cP) at 25 °C, and an epoxide equivalent weight of ca 188.

EEW is the weight of resin required to obtain one equivalent of epoxy functional group. It is widely used to calculate reactant stoichiometric ratios for reacting or curing epoxy resins. It is related to the epoxide content (%) of the epoxy resin through the following relationship:

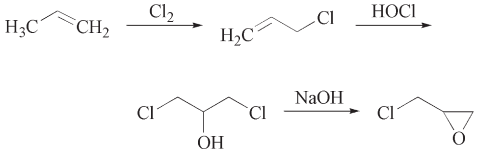
$$\text{EEW} = \frac{43.05}{\%\text{Epoxide}} \times 100 \qquad (1)$$

where 43.05 is the molecular mass of the epoxide group, $-C_2H_3O$. Other equivalent terminologies common in the industry include weight per epoxide (Wpe) or epoxide equivalent mass (EEM).

The outstanding performance characteristics of the resins are conveyed by the bisphenol A moiety (toughness, rigidity, and elevated temperature performance), the ether linkages (chemical resistance), and the hydroxyl and epoxy groups (adhesive properties and formulation latitude; reactivity with a wide variety of chemical curing agents).

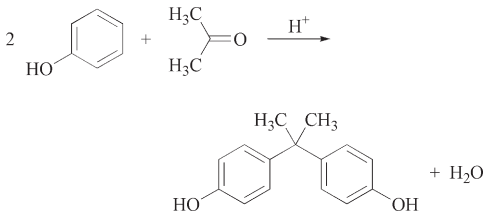
LERs are used in coatings, flooring and composites formulations where their low viscosity facilitates processing. A large majority of LERs are used as starting materials to produce higher molecular weight (MW) solid epoxy resins (SER) and brominated epoxy resins, and to convert to epoxy derivatives such as epoxy vinyl esters, epoxy acrylates, etc. The bisphenol A derived epoxy resins are most frequently cured with anhydrides, aliphatic amines, phenolics, or polyamides, depending on desired end properties. Some of the outstanding properties are superior electrical properties, chemical resistance, heat resistance, and adhesion. Cured LERs give tight cross-linked networks having good strength and hardness but have limited flexibility and toughness.

Epichlorohydrin, or 3-chloro-1,2-epoxy propane (*bp* 115 °C), is more commonly prepared from propylene by chlorination to allyl chloride, followed by treatment with hypochlorous acid. This yields glycerol dichlorohydrin, which is dehydrochlorinated by sodium hydroxide or calcium hydroxide [9].



In industrial practices, epichlorohydrin is produced by direct chlorohydroxylation of allyl chloride in chlorine and water [10–13]. Alternatively, a new epichlorohydrin process has been developed and commercialized by Showa Denko [14] in Japan in 1985. It involves the chlorination of allyl alcohol as the precursor and is claimed to be more efficient in chlorine usage.

Bisphenol A (*mp* 153 °C), or 2,2-bis(*p*-hydroxyphenyl)propane, is prepared from 2 moles of phenol and 1 mole of acetone [15, 16]

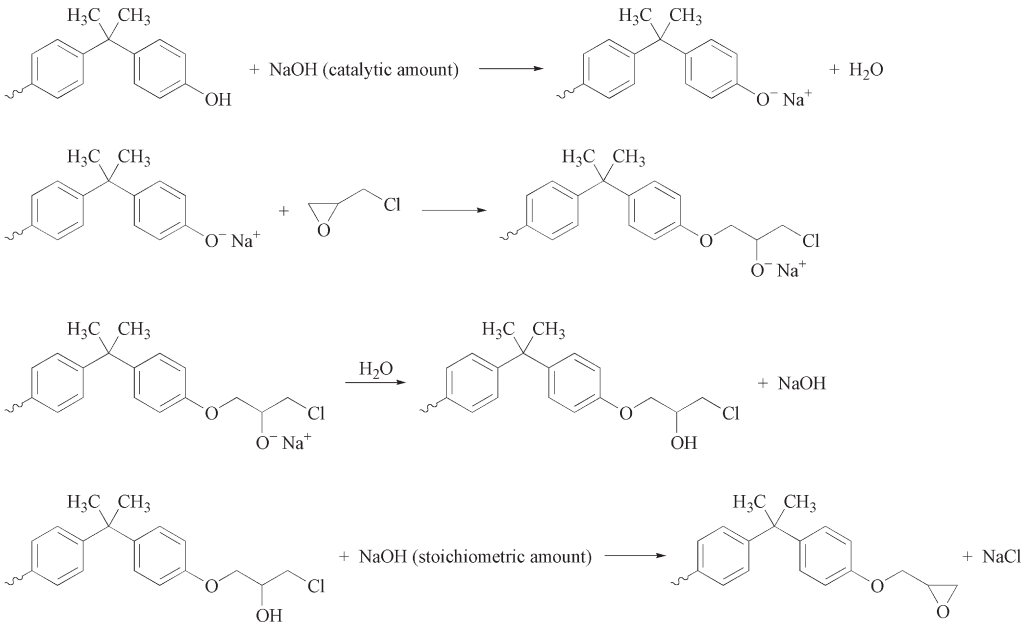


Bisphenol A based liquid epoxy resins are prepared in a two-step reaction sequence from epichlorohydrin and bisphenol A. The first step is the base-catalyzed *coupling* of bisphenol A and epichlorohydrin to yield a chlorohydrin.

Bases that may be used to catalyze this step include sodium hydroxide, lithium salts, and quaternary ammonium salts. Dehydrohalogenation of the chlorohydrin intermediate with a stoichiometric amount of base affords the glycidyl ether. Manufacturing processes can be divided into two broad categories according to the type of catalyst used to couple epichlorohydrin and bisphenol A [17, 18].

5.1. Caustic Coupling Process

In this process, caustic is used as a catalyst for the nucleophilic ring-opening (coupling reaction) of the epoxide group on the primary carbon atom of epichlorohydrin by the phenolic hydroxyl group and as a dehydrochlorinating agent for conversion of the chlorohydrin to the epoxide group:



In caustic coupling processes, caustic (20–50 % sodium hydroxide in water) is slowly added to an agitated mixture of epichlorohydrin and bisphenol A. The highly exothermic coupling reaction proceeds during the initial stages. As the coupling reaction nears completion, dehydrochlorination becomes the predominant reaction. A high ratio (usually 10:1) of epichlorohydrin/bisphenol A is charged to the reactor to maximize the yield of monomeric ($n = 0$) DGEBA. At a 10:1 level of epichlorohydrin/bisphenol A, the $n = 0$ monomer comprises $> 85\,\%$ of the reaction product mixture.

5.2. Phase-Transfer Catalyst Process

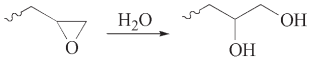
Alternatively, the coupling reaction and dehydrochlorination can be performed separately by using phase-transfer coupling catalysts, such as quaternary ammonium salts [19], which are not strong enough bases to promote dehydrochlorination. Once the coupling reaction is completed, caustic is added to carry out the dehydrochlorination step. Higher yields of the $n = 0$ monomer ($> 90\,\%$) are readily available via this method.

Many variations of these two basic processes are described in process patents [20, 21], including the use of co-solvents and azeotropic removal of water to facilitate the reactions and to minimize undesirablebyproducts such as insoluble polymers. The original batch methods have been modified to allow for continuous or

semicontinuous production. New developments have been focused on improving manufacturing yield and resin purity.

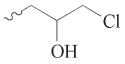
The description of liquid DGEBA resins presented so far is oversimplified. In reality, *side reactions* result in the formation of low levels of impurities that both decrease the epoxide content from the theoretical amount of 2 per molecule and affect the resins properties, both before and after curing [22]. The five common side reactions are as follows:

1. *Hydrolysis of epoxy groups.* Unavoidable hydrolysis of the epoxide ring gives a small amount (0.1–5 %) of monohydrolyzed resin (MHR) or α-glycol. It has been reported that dispersability of pigments are enhanced and rates of epoxy resin curing with diamines can be dramatically increased by higher levels of MHR [23].



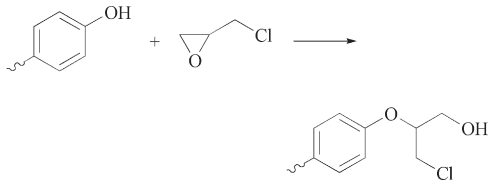
α-Glycol formation

2. *Incomplete dehydrochlorination* results in residual saponifiable or hydrolyzable chloride:

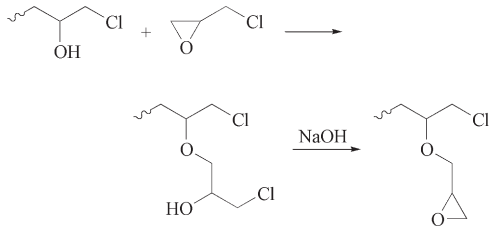


Incomplete dehydrochlorination increases the level of hydrolyzable chloride in the resin, which affects its suitablity for applications requiring superior electrical properties. In addition, hydrolyzable chlorides can affect reactivity by neutralizing basic catalysts such as tertiary amines. Many formulators adjust their formulations according to resin hydrolyzable chloride content. Typical hydrolyzable chloride contents of LERs range from < 100 ppm for electronic grade resin to 200–1000 ppm for standard grade resins.

3. *Abnormal addition of epichlorohydrin,* i.e., abnormal phenoxide attack at the central carbon of epichlorohydrin results in an end group that is more difficult to dehydrochlorinate:



4. *Formation of bound chlorides* by reaction of epichlorohydrin with hydroxy groups in the polymer backbones:



The bound chloride is not readily saponified with metal hydroxide solutions and is analyzed as part of the total chloride of the resin. Typical total chlorides values are 1000–2000 ppm.

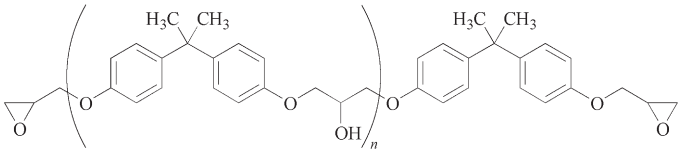
5. *Higher oligomer formation.* Reaction of a phenolic terminal group with another epoxy resin molecule instead of an epichlorohydrin molecule gives epoxy resins with broader oligomer distribution and increased viscosity ($n = 1$ and higher oligomers). Typical LERs contain 5–15 % of the higher oligomers, mostly $n = 1$ and $n = 2$ compounds.

Pure DGEBA is a solid melting at 43 °C. The unmodified commercial liquid resins are supercooled liquids with the potential for crystallization, depending on purity and storage conditions. This causes handling problems, particularly for ambient cure applications. Addition of certain reactive diluents and fillers can either accelerate or retard crystallization. Crystallization-resistant, modified resins are available. A crystallized resin can be restored to its liquid form by warming.

6. Solid Epoxy Resins Based on DGEBA

High molecular weight (MW) SERs based on DGEBA are characterized by a repeat unit

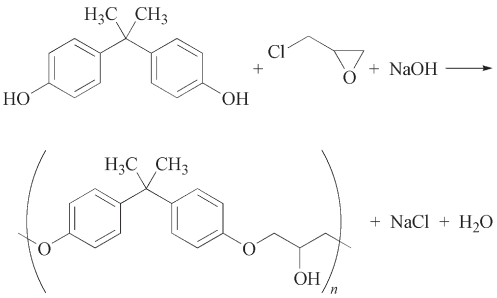
containing a secondary hydroxyl group with degrees of polymerization, i.e., *n* values ranging from 2 to about 35 in commercial resins; two terminal epoxy groups are theoretically present.



The epoxy industry has adopted a common nomenclature to describe the SERs. They are called type "1," "2" up to type "10" resins, which correspond to the increased values of *n*, the degree of polymerization, EEW, MW, and viscosity. Examples of SERs are D.E.R. 661, 662, 664, 667, 669 resins from Dow Chemical, and Epon 1001 to 1009 series from Resolution. A comparison of some key properties of LERs and SERs is shown in Table 5.

SERs based on DGEBA are widely used in the coatings industry. The longer backbones give more distance between cross-links when cross-linked through the terminal epoxy groups, resulting in improved flexibility and toughness. Furthermore, the resins can also be cured through the multiple hydroxyl groups along the backbones using cross-linkers such as phenol–formaldehyde resoles or isocyanates to create different network structures and performance.

SERs are prepared by two processes: the *taffy* process and the *advancement* or *fusion* process. The first is directly from epichlorohydrin, bisphenol A, and a stoichiometric amount of NaOH. This process is very similar to the *caustic coupling* process used to prepare liquid epoxy resins. Lower epichlorohydrin to bisphenol A ratios are used to promote formation of high MW resins. The term taffy is derived from the appearance of the advanced epoxy resin prior to its separation from water and precipitated salts.



In the taffy process, a calculated excess of epichlorohydrin governs the degree of polymerization. However, preparation of the higher molecular weight species is subject to practical limitations of handling and agitation of highly viscous materials. The effect of epichlorohydrin–bisphenol A (ECH–BPA) ratio for a series of solid resins is shown in Table 6.

In commercial practice, the *taffy* method is used to prepare lower MW solid resins, i.e., those with maximum EEW values of about 1000 (type "4"). Upon completion of the polymerization, the

Table 5. DGEBA-based epoxy resins

Resin type	*n* value[a]	EEW	Mettler softening point, °C	Molecular weight (M_w)[b]	Viscosity at 25 °C, mPa · s (= cP)
Low viscosity LER	< 0.1	172–176		~ 350	4,000–6,000
Medium viscosity LER	~ 0.1	176–185		~ 370	7,000–10,000
Standard grade LER	~ 0.2	185–195		~ 380	11,000–16,000
Type 1 SER	~ 2	450–560	70–85	~ 1,500	160–250[c]
Type 4 SER	~ 5	800–950	95–110	~ 3,000	450–600[c]
Type 7 SER	~ 15	1,600–2,500	120–140	~ 10,000	1,500–3,000[c]
Type 9 SER	~ 25	2,500–4,000	145–160	~ 15,000	3,500–10,000[c]
Type 10 SER	~ 35	4,000–6,000	150–180	~ 20,000	10,000–40,000[c]
Phenoxy resin	~ 100	> 20,000	> 200	> 40,000	

[a] *n* value is the number-average degree of polymerization which approximates the repeating units and the hydroxyl functionality of the resin.
[b] Molecular weight is weight average (M_w) measured by gel-permeation chromatography (GPC) using polystyrene standard.
[c] Viscosity of SERs is determined by kinematic method using 40 % solids in diethylene glycol monobutyl ether solution.

Table 6. Effect of epichlorohydrin–bisphenol a ratio on resin properties of taffy SERs

Mole ratio ECH/BPA	EEW	Softening point, °C
1.57:1.0	450–525	65–75
1.22:1.0	870–1025	95–105
1.15:1.0	1650–2050	125–135
1.11:1.0	2400–4000	145–155

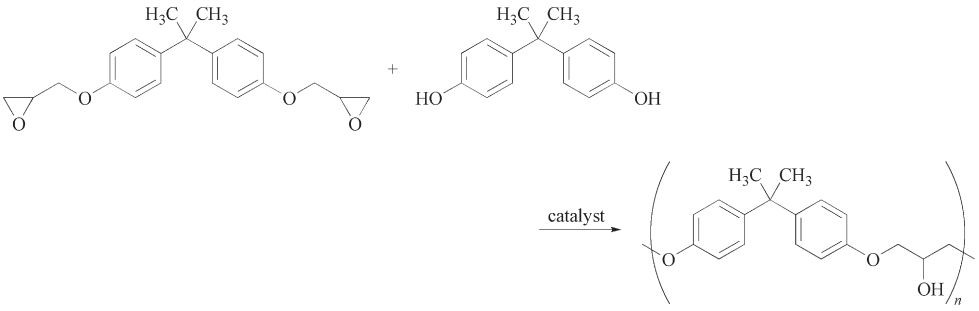
mixture consists of an alkaline brine solution and a water–resin emulsion. The product is recovered by separating the phases, washing the taffy resin with water, and removing the water under vacuum. One disadvantage of the taffy process is the formation of insoluble polymers, which create handling and disposal problems. Only a few epoxy producers currently manufacture SERs using the taffy process. A detailed description of a taffy procedure follows [24].

A mixture of bisphenol A (228 parts by weight) and 10 % aqueous sodium hydroxide solution (75 parts by weight) is introduced into a reactor equipped with a powerful agitator. The mixture is heated to ca 45 °C and epichlorohydrin (145 parts by weight) is added rapidly with agitation, giving off heat. The temperature is allowed to rise to 95 °C, where it is maintained about 80 min. for completion of the reaction. Agitation is stopped, and the mixture separates into two layers. The heavier aqueous layer is drawn off and the molten, taffy-like product is washed with hot water until the wash water is neutral. The taffy-like product is dried at 130 °C, giving a solid resin with a softening point of 70 °C and an EEW of ca. 500.

Alternatively, epichlorohydrin and water are removed by distillation at temperatures up to 180 °C under vacuum. The crude resin/salt mixture is then dissolved in a secondary solvent to facilitate water washing and salt removal. The secondary solvent is then removed via vacuum distillation to obtain the taffy–resin product.

Resins produced by this process exhibit relatively high α-glycol values, i.e., ca 0.5 eq/kg, attributable to hydrolysis of epoxy groups in the aqueous phase. Although detracting from epoxide functionality, such groups act as accelerators for amine curing. Resins produced by the taffy process exhibit *n* values of 0, 1, 2, 3, etc, whereas resins produced by the *advancement* process (described below) exhibit mostly even-numbered *n* values because a difunctional phenol is added to a diglycidyl ether of a difunctional phenol.

An alternative method is the chain-extension reaction of liquid epoxy resin (crude DGEBA) with bisphenol A, often referred to as the advancement or fusion process [25] which requires an advancement catalyst:



The advancement process is more widely used in commercial practice. Isolation of the polymerized product is simpler, since removal of copious amounts of NaCl is unnecessary. The reaction can be carried out with or without solvents. Solution advancement is widely practiced by coatings producers to facilitate handling of the high MW, high viscosity epoxy resins used in many coating formulations. The degree of polymerization is dictated by the ratio of LER to bisphenol A; an excess of the former provides epoxy terminal groups. The actual MW attained depends on the purity of the starting materials, the type of solvents used, and the catalyst. Reactive monofunctional groups can be used as chain terminators to control MW and viscosity build.

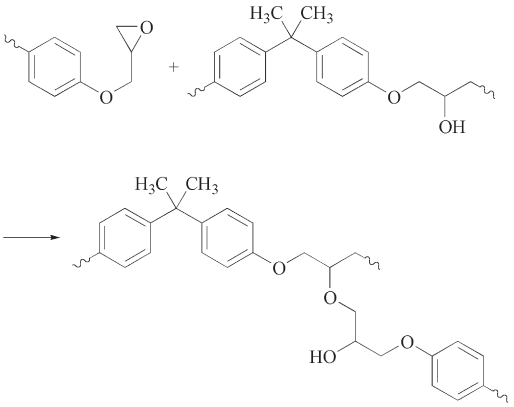
The following formula can be used to calculate the relative amount of bisphenol A that must be reacted with epoxy resin to give an advanced epoxy resin of predetermined EEW:

$$\text{Bis A} = \frac{\text{EEW}_i^{-1} - \text{EEW}_f^{-1}}{\text{EEW}_i^{-1} + \text{PEW}^{-1}}$$

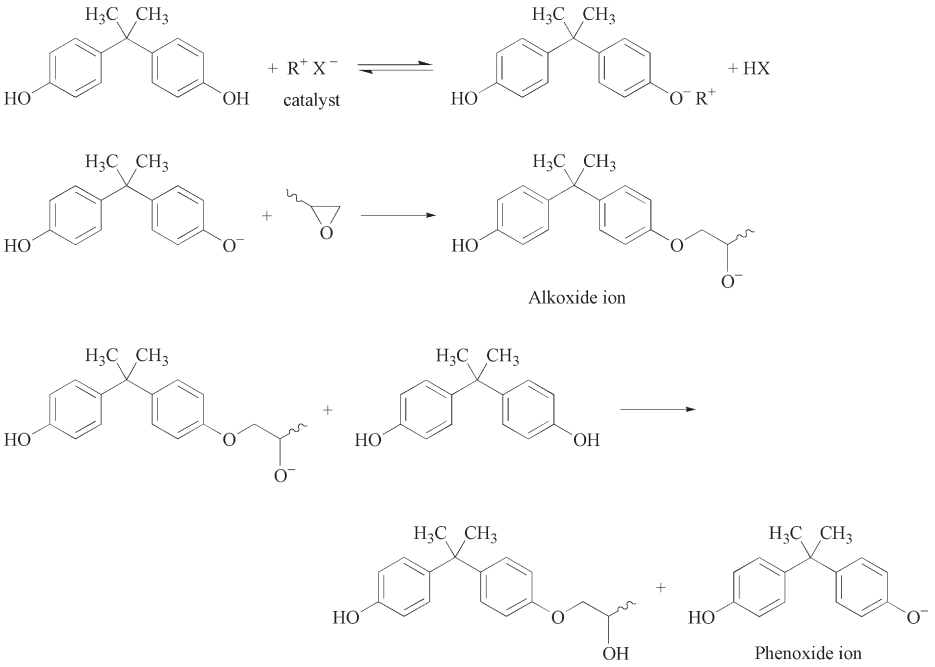
where Bis A is the mass fraction of bisphenol A in the mixture prior to advancement, EEW_i is the EEW of the epoxy resin that is to be advanced, EEW_f is the EEW of the advanced epoxy resin, and PEW is the phenol equivalent mass of the bisphenol, which is 114 g per equivalent for bisphenol A.

In a typical advancement process, bisphenol A and a liquid DGEBA resin (175–185 EEW) are heated to ca 150–190 °C in the presence of a catalyst and reacted (i.e., advanced) to form a high MW resin. The oligomerization is exothermic and proceeds rapidly to near completion. The exotherm temperatures are dependent upon the targeted EEW and the reaction mass. In the cases of higher MW resins such as type "7" and higher, exotherm temperatures of > 200 °C are routinely encountered.

Advancement reaction catalysts facilitate the rapid preparation of medium and high MW linear resins and control prominent side reactions inherent in epoxy resin preparations, e.g., chain branching due to addition of the secondary alcohol group generated in the chain-lengthening process to the epoxy group [26, 27]. Nuclear Magnetic Resonance (NMR) spectroscopy can be used to determine the extent of branching [28].



Conventional advancement catalysts include basic inorganic reagents, e.g., NaOH, KOH, Na_2CO_3, or LiOH, and amines and quaternary ammonium salts. One mechanism proposed for the basic catalysts involves proton abstraction of the phenolic compound as the initiation step:



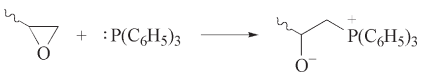
The phenoxide ion then attacks the epoxy ring, generating an alkoxide, which immediately abstracts a proton from another phenolic OH group. This is called the propagation step. Regeneration of the phenoxide ion repeats the cycle. The potential for side reactions increases after the phenolic OH groups have been consumed, particularly in melt (i.e., fusion) polymerization reactions.

One key disadvantage of catalysts based on inorganic bases and salts is the increased ionic impurities added to the resin, which is not desirable in certain applications.

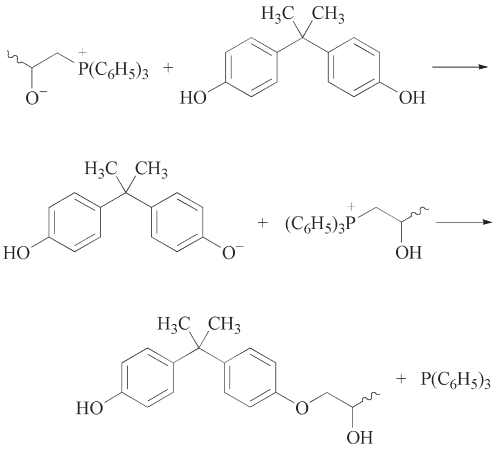
Imidazoles, substituted imidazoles, and triethanolamine have been patented as advancement catalysts [29]. However, most of the inorganic bases, salts, and amines produce resins with broad MW distribution and viscosity instability. This is due to poor catalyst selectivity and the continuing activity of the catalyst after completion of the advancement reaction.

Alternatively, a broad class of catalysts derived from aryl or alkyl phosphonium compounds were developed. Extensive patent literature claims a high order of selectivity [30, 31]. Selections of the phosphonium cation and counter ion have been shown to affect initiation rate, catalyst selectivity, catalyst lifetime, and, consequently, product quality and consistency. Some of the phosphonium salts are deactivated at high temperatures by the reaction exotherm, and are claimed to give better resin stability in terms of viscosity, EEW, and MW during the subsequent finishing steps [32–35].

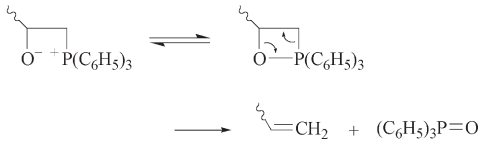
Few mechanistic studies have been published on the selectivity of phosphonium compounds, but one publication describes the role of triphenylphosphine in advancement catalysis [36]. Nucleophilic attack by triphenylphosphine opens the epoxy ring, producing a betaine:



Proton abstraction from bisphenol A yields the phenoxide anion, forming a phosphonium salt. The phenoxide reacts with the electrophilic carbon attached to the positive phosphorus regenerating the catalyst:



When the bisphenol A is consumed, the betaine decomposes into a terminal olefin and triphenylphosphine oxide:



Branched epoxies [37] are prepared by advancing LER with bisphenol A in the presence of epoxy novolac resins. Such compositions exhibit enhanced thermal and solvent resistance.

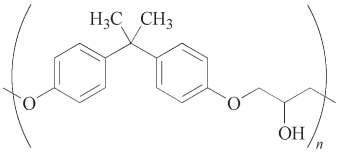
SERs are available commercially in solid form or in solution. MW distributions of SERs have been examined by means of theoretical models and compared with experimental results [38]. Taffy-processed resins were compared with advancement-processed resins by gel-permeation chromatography (GPC) and high performance liquid chromatography (HPLC) [39] in conjunction with statistical calculations. The major differences are in the higher α-glycol content and the repeating units of oligomers. Resin viscosity and softening points are also lower with taffy resins. In addition, certain formulations based on taffy resins exhibit different behavior in pigment loading, formulation rheology, reactivity, and mechanical properties compared to those based on advancement resins.

6.1. SER Continuous Advancement Process

The recent literature review indicates efforts to develop continuous advancement processes to produce SERs. Companies seek to improve process efficiencies and product quality. One of the major deficiencies of the traditional batch advancement process is the long reaction time, resulting in EEW and viscosity drift, variable product quality, and gel formation. In addition, it is difficult to batch process higher MW, higher viscosity SERs such as types "9" and "10" resins. Shell patented several versions of the continuous resin advancement processes using modified reactor designs [40]. Dow Chemical received patents covering the uses of reactive extrusion [41] (REX) to produce SERs and other epoxy thermoplastic resins [42]. The latter process makes use of a self-wiping twin-screw extruder. LER, bisphenol A, and catalyst are fed directly to the extruder to complete the resin advancement reaction in several minutes compared to the traditional several hours in a batch process. The process is claimed to be very efficient and is particularly suitable for the production of high molecular weight SERs, phenoxy resins, and epoxy thermoplastic resins. Compared to the traditional taffy processes used to produce phenoxy resins, the chemistry is salt-free, and the resins made via the REX process are fully converted in a matter of minutes, significantly reducing manufacturing costs. Additional benefits include reduced lot-to-lot variations in MW distribution, the flexibility to make small lots of varying molecular weights with minimal waste, and the ability to make custom resins with a variety of additives such as pigments and flow modifiers.

6.2. Phenoxy Resins

Phenoxy resins are thermoplastic polymers derived from bisphenol A and epichlorohydrin. Their weight-average molecular weights (M_w) are higher (i.e., > 30,000) than those of conventional SERs (i.e., 25,000 maximum). They lack terminal epoxides but have the same repeat unit as SERs and are classified as polyols or polyhydroxy ethers:



Phenoxy resins were originally developed and produced by Union Carbide (trade names PKHH, PKHC, PKHJ) using the taffy process. The process involves reaction of high purity bisphenol A with epichlorohydrin in a 1:1 mole ratio. Alternatively, phenoxy resins can be produced by the fusion process which uses high purity LER and bisphenol A in a 1:1 mole ratio. High purity monomers and high conversions are both needed to produce high MW phenoxy resins. The effects of monomer purity on phenoxy resin production are significant: monofunctional components limit MW, and functionality > 2 causes excess branching and increased polydispersity. Solution polymerization may be employed to achieve the MW and processability needed [43]. This, however, adds to the high costs of manufacturing of phenoxy resins, limiting their commercial applications.

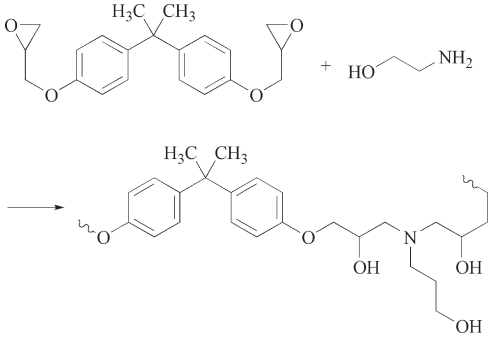
The phenoxies are offered as solids, solutions, and waterborne dispersions. The majority of phenoxy resins are used as thermoplastics, but some are used as additives in thermoset formulations. Their high MW provide improved flexibility and abrasion resistance. Their primary uses are in automotive zinc-rich primers, metal can/drum coatings, magnet wire enamels, and magnetic tape coatings. However, the zinc-rich primers are being phased out in favor of galvanized steel by the automotive industry. Smaller volumes of phenoxy resins are used as flexibility or rheology modifiers in composites and electrical laminate applications, and as composite honeycomb impregnating resins. A new, emerging application is fiber sizing, which utilizes waterborne phenoxies. Literature references indicate their potential uses as compatibilizers for thermoplastic resins such as polyesters, nylons, and polycarbonates because of their high hydroxyl contents.

Current producers of phenoxy resins include the Phenoxy Specialties division of InChem

Corp., Resolution, Huntsman, Tohto Kasei, and DIC.

6.3. Epoxy-Based Thermoplastics

Some of the new epoxy products developed in the past few years are the thermoplastic resins based on epoxy monomers. Polyhydroxy amino ether [44, 45] (PHAE) was commercialized by Dow Chemical in 1999 and trade named BLOX (Dow Chemical Co.). It is produced by the reaction of DGEBA with monoethanol amine using the reactive extrusion process. The high cohesive energy density of the resin gives it excellent gas-barrier properties against oxygen and carbon dioxide. It also possesses excellent adhesion to many substrates, optical clarity, excellent melt strength, and good mechanical properties. The product has been evaluated as a barrier resin for beer and beverage plastic bottles, as thermoplastic powder coatings, and as a toughener for starch-based foam [46]. Another epoxy thermoplastic resin under development by Dow is the polyhydroxy ester ether (PHEE). It is a reaction product of DGEBA with difunctional acids. The ester linkage makes it suitable for biodegradable applications [47].

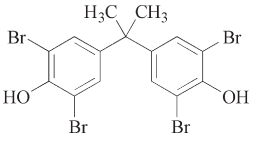


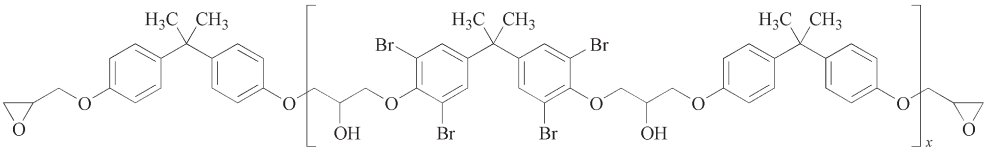
7. Halogenated Epoxy Resins

A number of halogenated epoxy resins have been developed and commercialized to meet specific application requirements. Chlorinated and brominated epoxies were evaluated for flame retardancy properties. The brominated epoxy resins were found to have the best combination of cost/performance and were commercialized by Dow Chemical in the late 1960s.

7.1. Brominated Bisphenol A Based Epoxy Resins

Many applications of epoxy resins require the system to be ignition-resistant, e.g., electrical laminates for PCBs and certain structural composites. A common method of imparting this ignition resistance is the incorporation of tetrabromobisphenol A (TBBA), 2,2-bis(3,5-dibromophenyl)propane, or the diglycidyl ether of TBBA, 2,2-bis[3,5-dibromo-4-(2,3-epoxypropoxy)phenyl]propane, into the resin formulation. The diglycidyl ether of TBBA is produced via conventional liquid epoxy resin processes. Higher MW resins can be produced by advancing LERs or diglycidyl ether of TBBA with TBBA. The lower cost, advanced brominated epoxies based on LERs and TBBA containing ca. 20 wt. % Br are extensively employed in the PCB industry. The diglycidyl ether of TBBA (ca. 50 wt. % Br) is used for critical electrical/electronic encapsulation where high flame retardancy is required. Brominated epoxies are also used to produce epoxy vinyl esters for structural applications. Very high MW versions of brominated epoxies are used as flame-retardant additives to engineering thermoplastics used in computer housings.

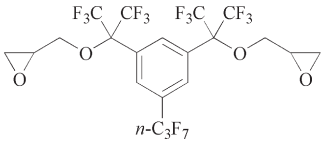




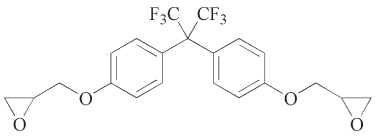
In order to meet increased requirements of the PCB industry for higher glass-transition temperature(T_g), higher thermal decomposition temperature (T_d), and lower dielectric constant (D_k) products, a number of new epoxy resins have been developed [48, 49].

7.2. Fluorinated Epoxy Resins

Fluorinated epoxy resins have been researched for a number of years for high performance end-use applications [50]. Fluorinated epoxies are highly resistant to chemical and physical abuse and should prove useful in high performance applications, including specialty coatings and composites, where their high cost may be offset by their special properties and long service life. The following fluorinated diglycidyl ether, 5-heptafluoropropyl-1,3-bis[2-(2,3-epoxypropoxy) hexafluoro-2-propyl] benzene, illustrates an example of fluoroepoxy resins [51] under development.



This resin is a viscous, colorless liquid (*bp* 118 °C at 20 Pa · s) that contains 52 wt. % fluorine. It has a low surface tension, which makes it a superior wetting agent for glass fibers. The reactivity of this resin with amine or anhydride curing agents is comparable to epoxy resins based on bisphenol A and results in a thermoset that has a low affinity for water and excellent chemical resistance. Another fluorinated epoxy resin derived from hexafluorobisphenol A was introduced to the marketplace aiming at the anticorrosion coatings market for industrial vessels and pipes. The key disadvantages of fluorinated epoxies are their relatively high costs and low T_g, which limit their commercialization [52].

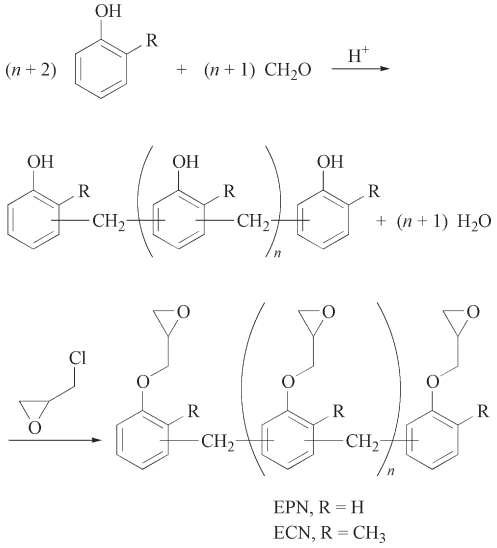


8. Multifunctional Epoxy Resins

The multifunctionality of these resins provides higher cross-linking density, leading to improved thermal and chemical resistance properties over bisphenol A epoxies.

8.1. Epoxy Novolac Resins

Epoxy novolacs are multifunctional epoxies based on phenolic formaldehyde novolacs. Both epoxy phenol novolac resins (EPN) and epoxy cresol novolac resins (ECN) have attained commercial importance [53]. The former is made by epoxidation of the phenol–formaldehyde condensates (novolacs) obtained from acid-catalyzed condensation of phenol and formaldehyde (see → Phenolic Resins). This produces random *ortho*- and *para*-methylene bridges.



An increase in the molecular weight of the novolac increases the functionality of the resin. This is accomplished by changing the phenol or cresol to formaldehyde ratio. Epoxidation with an excess of epichlorohydrin minimizes the reaction of the phenolic OH groups with epoxidized phenolic groups and prevents branching. The epoxidation is similar to the procedure described for bisphenol A. EPN resins range from a high viscosity liquid of $n = 0.2$ to a solid of $n > 3$. The epoxy functionality is between 2.2 and 3.8. Properties of epoxy phenol novolacs are given in Table 7. When cured with aromatic amines such as methylenedianiline, the heat

Table 7. Typical properties of epoxy phenol novolacs

Property	D.E.N. 431,[a] EPN 1139[b]	D.E.N. 438,[a] EPN 1138[b]	D.E.N. 439[a]
n	0.2	1.6	1.8
EEW[c]	175	178	200
Viscosity, mPa · s (= cP)	1,400[d]	35,000[d]	3,000[e]
Softening point[f]			53
Color, Gardner	1	2	2

[a]The Dow Chemical Co.
[b]Huntsman.
[c]Epoxide equivalent weight.
[d]Temperature of measurement = 52 °C.
[e]Temperature of measurement = 100 °C.
[f]Durran's mercury method.

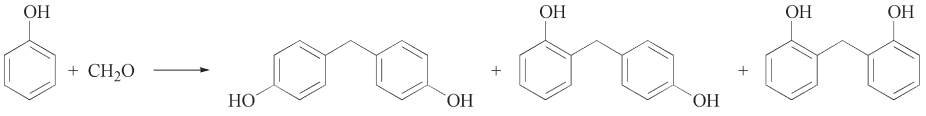
distortion temperatures (HDT) of EPN-based thermosets range from 150 °C to 200 °C, depending on cure and postcure schedules

Curing agents that give the optimum in elevated temperature properties for epoxy novolacs are those with good high temperature performance, such as aromatic amines, catalytic curing agents, phenolics, and some anhydrides. When cured with polyamide or aliphatic polyamines and their adducts, epoxy novolacs show improvement over bisphenol A epoxies, but the critical performance of each cure is limited by the performance of the curing agent.

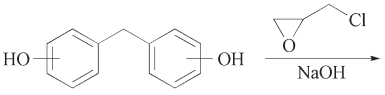
The improved thermal stability of EPN-based thermosets is useful in elevated temperature services, such as aerospace composites. Filament-wound pipe and storage tanks, liners for pumps and other chemical process equipment, and corrosion-resistant coatings are typical applications which take advantage of the chemical resistant properties of EPN resins. However, the high cross-link density of EPN-based thermosets can result in increased brittleness and reduced toughness.

8.1.1. Bisphenol F Epoxy Resin

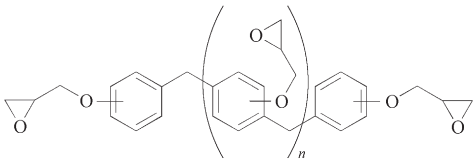
The lowest MW member of the phenol novolacs is bisphenol F, which is prepared with a large excess of phenol to formaldehyde; a mixture of *o*,*o*′, *o*,*p*′, and *p*,*p*′ isomers is obtained:



Epoxidation yields a liquid bisphenol F epoxy resin with a viscosity of 4000–6000 mPa · s (= cP), an EEW of 165, and $n \cong 0.15$.



Mixed isomers



Bisphenol F resin
(**3**)

This unmodified, low viscosity liquid resin exhibits slightly higher functionality than unmodified bisphenol A liquid resins. Crystallization, often a problem with liquid bisphenol A resins, is reduced with bisphenol F resin. Consequently, noncrystallizing LERs which are blends of DGEBA and bisphenol F epoxy are available. Epoxy resins based on bisphenol F are used primarily as functional diluents in applications requiring a low viscosity, high performance resin system (e.g., solvent-free coatings). Higher filler levels and faster bubble release are possible because of the low viscosity. The higher epoxy content and functionality of bisphenol F epoxy resins provide improved chemical resistance compared to conventional bisphenol A epoxies. Bisphenol F epoxy resins are used in high solids, high build systems such as tank and pipe linings, industrial floors, road and bridge deck toppings, structural adhesives, grouts, coatings, and electrical varnishes.

8.1.2. Cresol Epoxy Novolacs

The *o*-cresol novolac epoxy resins (ECN) are analogous to phenol novolac resins. ECNs exhibit better formulated stability and lower moisture adsorption than EPNs, but have higher costs. ECN resins are widely used as base components in high performance electronic

Table 8. Typical properties of epoxy cresol novolac resins[a]

Property	ECN 1235	ECN 1273	ECN 1280	ECN 1299
Molecular weight	540	1080	1170	1270
EEW[b]	200	225	229	235
Softening point, °C	35	73	80	99
Epoxide functionality	2.7	4.8	5.1	5.4

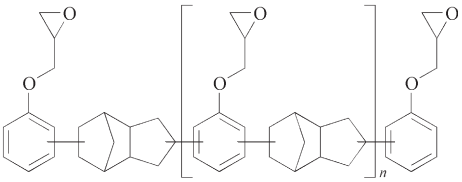
[a]Huntsman.
[b]Epoxide equivalent weight.

(semiconductors) and structural molding compounds, high temperature adhesives, castings and laminating systems, tooling, and powder coatings. Increasing demands by the semiconductor industry has led to significant advances in ECN resin manufacturing technologies to reduce impurities, mainly the ionic content, hydrolyzable chlorides, and total chlorides. The use of polar, aprotic solvents, such as dimethyl sulfoxide (DMSO), as a co-solvent to facilitate chloride reduction has been patented [54]. Typical high purity ECN resins contain < 1000 ppm total chlorides and < 50 ppm hydrolyzable chlorides.

The melt viscosity of these resins, which are solids at room temperature, decreases sharply with increasing temperature (Table 8). This affords the formulator an excellent tool for controlling the flow of molding compounds and facilitating the incorporation of ECN resins into other epoxies, e.g., for powder coatings. While Ciba-Geigy was the first producer of ECN resins, many Japanese companies (Nippon Kayaku, Sumitomo Chemical, DIC, and Tohto Kasei) supply the majority of high purity ECN resins for the semiconductor industry today. Other suppliers are based in Korea and Taiwan.

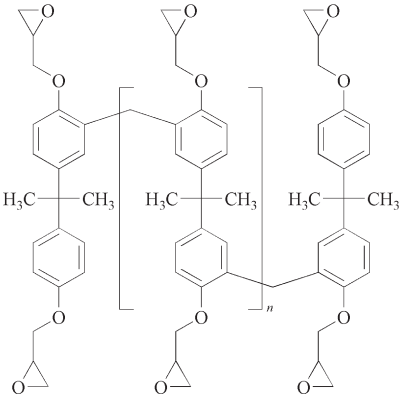
8.1.3. Glycidyl Ethers of Hydrocarbon Epoxy Novolacs

In response to the increased performance demands of the semiconductor industry, hydrocarbon epoxy novolacs (HENs) were developed by Dow Chemical in the 1980s. HENs exhibit a much lower affinity for water compared to cresol or phenol epoxy novolacs. This translates directly into increased electrical property retention, which is important in the reliability of an electronic device encapsulated in the resin. An epoxy resin that is typical of this class is based on the alkylation product of phenol and dicyclopentadiene [55] ($n = 0.1$), 2,5-bis[(2,3-epoxypropoxy) phenyl]octahydro-4,7-methano-5*H*-indene (272 EEW; softening point 85 °C; η at 150 °C 0.4 Pa · s). The product is available from Huntsman as TACTIX* 556. Similar products based on *o*-cresol are commercialized in Japan by DIC (EPICLON HP-7200L).



8.1.4. Bisphenol A Epoxy Novolacs

Bisphenol A novolacs are produced by reacting bisphenol A and formaldehyde with acid catalysts. Epoxidation of the bisphenol A novolacs gives bisphenol A epoxy novolac (BPAN) with improved thermal properties such as T_g, T_d of the epoxy-based electrical laminates.



Bisphenol A epoxy novolac

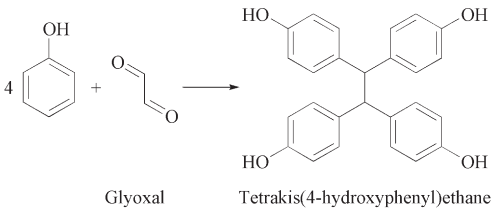
8.2. Other Polynuclear Phenol Glycidyl Ether Derived Resins

In addition to the epoxy novolacs, there are other epoxy resins derived from phenol–

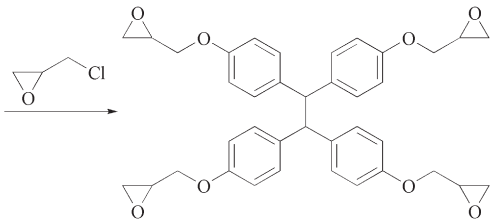
aldehyde condensation products. New applications that require increased performance from the epoxy resin, particularly in the electronics, aerospace, and military industries, have made these types of resins more attractive despite their relatively high cost.

8.2.1. Glycidyl Ether of Tetrakis(4-hydroxyphenyl)ethane

One of the first polyfunctional resins to be marketed (by Shell) is based on 1,1,2,2-tetrakis[4-(2,3-epoxypropoxy)phenyl]ethane [56]. It is used primarily as additives in standard epoxy resin formulations for electrical laminates, molding compounds, and adhesives in which increased heat distortion temperature and improved chemical resistance are desired. Tetrakis(4-hydroxyphenyl)ethane is prepared by reaction of glyoxal with phenol in the presence of HCl. The tetraglycidyl ether (*mp* ca. 80 °C, and an EEW of 185–208) possesses a theoretical epoxide functionality of 4.



Glyoxal Tetrakis(4-hydroxyphenyl)ethane

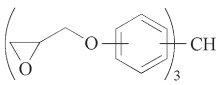


Tetraglycidyl ether of tetrakis(4-hydroxyphenyl)ethane

The commercial products Araldite 0163 (Huntsman) and Epon 1031 (Resolution) are tan-colored solids. They are widely used in high temperature resistance electrical laminates for high density PCBs and military applications. Their costs are typically higher than those of phenol and cresol epoxy novolacs.

8.2.2. Trisphenol Epoxy Novolacs

In the 1980s, new trifunctional epoxy resins based on tris[4-(2,3-epoxypropoxy)phenyl] methane isomers were introduced by Dow Chemical to help close the performance gap between phenol and cresol epoxy novolacs and high performance engineering thermoplastics [57]. These products were later sold to Ciba-Geigy and continued to be marketed under the TACTIX* 740 and XD 9053 trade names by Huntsman.



The resins are prepared via acid-catalyzed condensation of phenol and a hydroxybenzaldehyde, e.g., salicylaldehyde, to afford the trifunctional phenol, which is epoxidized with epichlorohydrin. These resins range from semisolids (162 EEW; Durran softening point 55 °C; η at 60 °C 11.5 Pa · s, at 150 °C 0.055 Pa · s) to nonsintering solids (220 EEW; Durran softening point 85 °C; η at 150 °C 0.45 Pa · s).

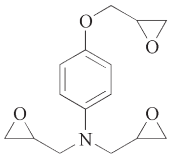
The semisolid resins are used in advanced composites and adhesives where toughness, hot-wet strength, and resistance to high temperature oxidation are required. Their purity, formulated stability, fast reactivity, and retention of electrical properties over a broad temperature range make the solid resins suitable for use in the semiconductor molding powders industry. The trisphenol-based epoxies command significant high prices ($28–48/kg), limiting their uses.

8.3. Aromatic Glycidyl Amine Resins

Among the multifunctional epoxy resins containing an aromatic amine backbone, only a few have attained commercial significance. Their higher costs limit their uses to critical applications where their costs are justified. Glycidyl amines contain internal tertiary amines in the resin backbone, hence their high reactivity. Epoxy resins with such built-in curing catalysts are less thermally stable than nitrogen-free multifunctional epoxy resins.

8.3.1. Triglycidyl Ether of *p*-Aminophenol

The triglycidyl derivative of *p*-aminophenol was originally developed by Union Carbide [58] and is currently marketed by Huntsman under the designation MY 0500 and 0510. Epoxidation of *p*-aminophenol is carried out with a large excess of epichlorohydrin under carefully controlled conditions, since the triglycidylated resin exhibits limited thermal stability and polymerizes vigorously under the influence of its tertiary amine moiety.



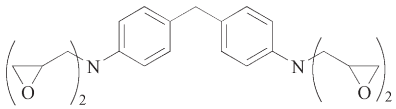
Triglycidyl-*p*-aminophenol

The resin exhibits a low viscosity, 2500–5000 mPa · s (= cP) at 25 °C, and an EEW of 105–114; a molecularly distilled version (0510) has a viscosity of 550–850 mPa · s (= cP) at 25 °C and an EEW of 95–107. It is considerably more reactive toward amines than standard bisphenol A resins. The trifunctional resin permits curing at low temperatures, i.e., 70 °C, and rapidly develops excellent elevated-temperature properties. Used as additives to increase cure speed, heat resistance, and T_g of bisphenol A epoxy resins, it has utility in such diverse applications as high temperatures adhesives, tooling compounds, and laminating systems.

8.3.2. Tetraglycidyl Methylenedianiline (MDA)

These resins are used as binders in graphite-reinforced composites and are the binders of choice for many military applications. Epoxidation of MDA is carried out with stoichiometric excess of epichlorohydrin and under carefully controlled conditions to avoid rapid polymerization side reactions.

The tetrafunctional glycidylated MDA resins range in viscosity from 5000 to 25,000 mPa · s (= cP) at 50 °C and have an EEW of 117–133; they are commercially available as Araldite MY 720 (Huntsman) and Epiclon 430 (DIC). When used in combination with the curing agent 4,4′-diaminodiphenylsulfone (DADS), it is the first system to meet the performance requirements set by the aerospace industry and is the standard against which other resin systems are judged [59]. Because of its outstanding properties, this resin is often used as the primary resin in high heat resistance formulations for military applications, despite its high costs (~ $22/kg). Among its attributes are excellent mechanical strength, high T_g, good chemical resistance, and radiation stability.



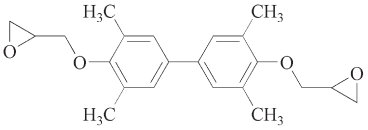
N,*N*,*N*′,*N*′-Tetraglycidyl-4,4′-diaminodiphenylmethane

Another commercially important aromatic glycidyl amine resin is triglycidyl isocyanurate (TGIC), which is discussed in the "Weatherable Epoxy Resins" section.

9. Specialty Epoxy Resins

9.1. Crystalline Epoxy Resins Development

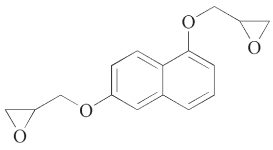
A number of new epoxy resins used in epoxy molding compounds (EMC) have been developed by Japanese resin producers in response to the increased performance requirements of the semiconductor industry. Most notable are the commercialization of crystalline epoxies based on biphenol by Yuka-Shell [60]:



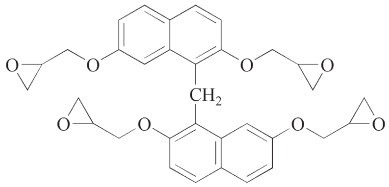
Diglycidyl ether of tetramethyl biphenol

The very low viscosity of these crystalline, solid epoxies when molten allows very high filler loading (up to 90 wt. %) for molding compounds. The high filler loading reduces the coefficient of thermal expansion (CET) and helps manage thermal shock and moisture and crack resistance of molding compounds used in new, demanding semiconductor manufacturing processes such as Surface Mount Technology (SMT). It should be noted that cured thermosets derived from these crystalline resins do not retain crystallinity.

Recently, a number of capacity expansions were announced for biphenol epoxies (sold as YX-4000 resin by Japan Epoxy Resins Corporation, formerly Yuka-Shell). DIC has developed dihydroxy naphthalene based epoxies [61] as the next generation product for this high performance market. Prices for crystalline epoxies are generally high ($22–26/kg), limiting their uses to high end applications.

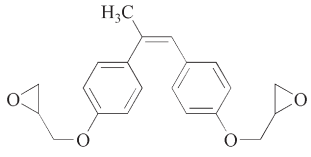


Diglycidyl ether of 1,5-dihydroxy naphthalene



Tetraglycidyl ether based on dihydroxy naphthalene

Dow Chemical developed liquid crystalline polymers (LCP) based on diglycidyl ether of 4-4′-dihydroxy-α-methylstilbene in the 1980s [62, 63]. Liquid crystal thermoplastics and thermosets based on this novel chemistry showed excellent combinations of thermal, mechanical, and chemical properties, unachievable with traditional epoxies. However, commercialization of these products has not materialized.



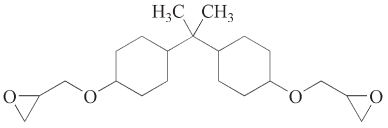
Diglycidyl ether of 4,4'-dihydroxy-α-methylstilbene

9.2. Weatherable Epoxy Resins

One of the major deficiencies of the aromatic epoxies is their poor weatherability, attributable to the aromatic ether segment of the backbone, which is highly susceptible to photoinitiated free-radical degradation. The aromatic ether of bisphenol A absorbs UV lights up to about 310 nm and undergoes photocleavage directly. This in turn produces free radicals that lead to oxidative degradation of bisphenol A epoxies, resulting in chalking. Numerous efforts have been devoted to remedy this issue, resulting in a number of new weatherable epoxy products. However, their commercial success has been limited, primarily because of higher resin costs and the fact that end users can topcoat epoxy primers with weatherable coatings based on other chemistries such as polyesters, polyurethanes, or acrylics. The following epoxy products when formulated with appropriate reactants can provide certain outdoor weatherability.

9.2.1. Hydrogenated DGEBA

In 1976, Shell Chemical Co. introduced epoxy resins based on the diglycidyl ether of hydrogenated bisphenol A, 2,2-bis[4-(2,3-epoxypropoxy)cyclohexyl]propane (232–238 EEW; η at 25 °C 2–2.5 Pa · s).

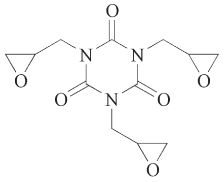


These resins resist yellowing and chalking because of their aliphatic structure. Epoxy resins based on hydrogenated bisphenol A are made by the epoxidation of the saturated diol, 2,2-bis(4-hydroxycyclohexyl)propane or 2,2-bis(4-hydroxycyclohexyl)propane with epichlorohydrin, or by the hydrogenation of a low molecular weight DGEBA resin [64]. Commercially available products include an Epalloy 5000 resin from CVC. One disadvantage is their much higher costs, and consequently, the products have not found broad acceptance in the industry. Furthermore, cross-linked networks based on hydrogenated bisphenol A epoxies lose some of the characteristic temperature and chemical resistances inherent with the bisphenol A backbone.

9.2.2. Heterocyclic Glycidyl Imides and Amides

In the 1960s, considerable work was devoted to preparing triglycidyl isocyanurate, 1,3,5-tris (2,3-epoxypropyl)-1,3,5-perhydrotriazine-2,4,6-trione [65]. The epoxidation of cyanuric acid with epichlorohydrin gives triglycidyl isocyanurate

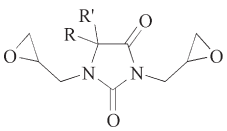
(TGIC), marketed as PT 810 by Huntsman. It is a crystalline compound (*mp* 85–110 °C) with an EEW of ca. 108. Miscibility with organic compounds is limited. Because of its excellent weatherability, TGIC is widely used in outdoor powder coatings with polyesters [66], despite its higher cost (~ $12/kg).



Triglycidyl isocyanurate

9.2.3. Hydantoin-Based Epoxy Resins

These resins were commercialized by Ciba-Geigy. Hydantoins are prepared from carbon dioxide, ammonia, hydrogen cyanide, and ketones via the Bucherer reaction and can be epoxidized with epichlorohydrin [67]. Cured and uncured resin properties depend greatly on the nature of the substituents R and R′. The hydantoin derived from acetone furnishes a low viscosity, water-dispersable epoxy resin, 5,5-dimethyl-1,3-bis(2,3-epoxypropyl)-2,4-imidazolidinedione (R = R′ = CH_3; 145 EEM; η at 25 °C 2.5 Pa · s). A nonsintering solid epoxy resin is obtained if R = R′ = $-(CH_2)_5-$.



When cured with aromatic amines or anhydrides, these resins show high heat distortion temperatures and excellent adhesion and weatherability. A variety of applications are suggested for these new resins, particularly in applications in which a non-yellowing epoxy resin is desirable.

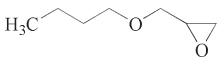
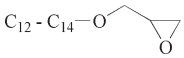
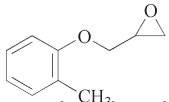
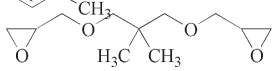
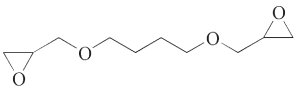
9.3. Elastomer-Modified Epoxies

Epoxy thermosets derive their thermal, chemical, and mechanical properties from the highly cross-linked networks. Consequently, toughness deficiency is an issue in certain applications. To improve the impact resistance and toughness of epoxy systems, elastomers such as BF Goodrich's CTBN rubbers (carboxyl-terminated butadiene nitrile) are often used as additives or prereacted with epoxy resins [68]. Most commonly used products are reaction adducts of liquid epoxy resins (DGEBA) with CTBN in concentrations ranging from 5 wt. % to 50 wt. %. They have been shown to give improved toughness, peel adhesion, and low temperature flexibility over unmodified epoxies. Primary applications are adhesives for aerospace and automotive and as additives to epoxy vinyl esters for structural composites. Formation of adducts of epoxy resins and CTBN is promoted by triphenylphosphine or alkyl phosphonium salts. Other elastomers used to modify epoxies include amine-terminated butadiene nitrile (ATBN), maleated polybutadiene and butadiene–styrene, epoxy-terminated urethane prepolymers, epoxy-terminated polysulfide, epoxy–acrylated urethane, and epoxidized polybutadiene.

10. Monofunctional Glycidyl Ethers and Aliphatic Glycidyl Ethers

A number of low MW monofunctional, difunctional, and mutifunctional epoxies are used as reactive diluents, viscosity reducers, flexiblizers, and adhesion promoters. Recent trends toward lower VOC, higher solids and 100 % solids epoxy formulations have resulted in increased utilization of these products. Most of these epoxies are derived from relatively compact hydroxyl-containing compounds, such as alcohols, glycols, phenols, and epichlorohydrin. Epoxidized vegetable oils, such as epoxidized linseed oils, are also used as reactive diluents. They are produced using a peroxidation process and are discussed in more detail in the cycloaliphatic epoxies and epoxidized vegetable oils section. Typically, these products have very low viscosity (1–70 cP at 20 °C) relative to LERs (11,000–16,000 cP). They are often used in the range of 7–20 wt. % to reduce viscosity of the diluted system to 1000 cP. However, the uses of reactive diluents, especially at high levels, often result in decreased chemical resistance and thermal and mechanical properties of the cured epoxies.

Table 9. Some common commercial glycidyl ether reactive diluents

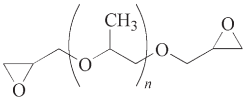
Name	Structure
n-Butyl glycidyl ether	
C12–C14 Aliphatic glycidyl ether	
o-Cresol glycidyl ether	
Neopentylglycol diglycidyl ether	
Butanediol diglycidyl ether	

Important products include butyl glycidyl ether (BGE), alkyl glycidyl ethers of C8–C10 (Epoxide 7) and C12–C14 (Epoxide 8), *o*-cresol glycidyl ether (CGE), *p-tert*-butyl glycidyl ether, resorcinol diglycidyl ether (RDGE), and neopentyl glycol diglycidyl ether (Table 9). While BGE is the most efficient viscosity reducer and has been widely used in the industry for many years, it has been losing market share because of its volatility and obnoxiousness. Phenyl glicidyl ether (PGE) is no longer used by many formulators because of its toxicity. The industry trend is moving toward longer chain epoxies such as Epoxide 8 or neopentyl glycol diglycidyl ether.

Major suppliers of these products are Resolution, Air Products, Ciba Specialty Chemicals, Huntsman, CVC Specialty Chemicals, Pacific Epoxy Polymers, and Exxon.

An example of multifunctional aliphatic epoxies is the triglycidyl ether of propoxylated glycerine (Heloxy 84) from Resolution. A similar product is based on epoxidized castor oil (Heloxy 505). These products are used primarily as viscosity reducers while increasing functionality and cross-linking density of the cured systems.

Epoxy resins based on long-chain diols, such as the diglycidyl ether of polypropylene glycol [α,ω-bis(2,3-epoxypropoxy)poly(oxypropylene)] (305–335 EEW; η at 25 °C 0.055–0.10 Pa · s), are used as flexibilizing agents to increase a thermoset's elongation and impact resistance. Because of the low reactivity of the aliphatic diols toward epichlorohydrin, these epoxies are produced by first coupling the diols with epichlorohydrin using phase-transfer catalysts such as ammonium salts or Lewis acid catalysts (boron trifluoride, stannic chloride), followed by epoxidation with caustic [69, 70]. A prominent side-reaction is the conversion of aliphatic hydroxyl groups formed by the initial reaction into chloromethyl groups by epichlorohydrin. The resultant epoxy resins are known to have lower reactivity toward conventional amine curing agents relative to bisphenol A epoxies. Dow Chemical manufactures D.E.R. 732 and D.E.R. 736 aliphatic epoxy resins. They are derived from polyglycols with different chain lengths.



Polyglycidyl ethers of sorbitol, glycerol, and pentaerythritol are used as adhesion promoters for polyester tire cords. Their high chloride content improves adhesion to rubber.

11. Cycloaliphatic Epoxy Resins and Epoxidized Vegetable Oils

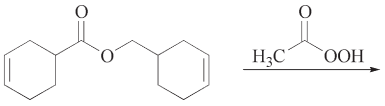
Resins based on the diepoxides of cycloaliphatic dienes were first commercialized in the 1950s by Union Carbide Corp. The combination of aliphatic backbone, high oxirane content, and no halogens gives resins with low viscosity, weatherability, low dielectric constant, and high cured T_g. This class of epoxy is popular for diverse end uses including auto topcoats, weatherable high voltage insulators, UV coatings, acid scavengers, and encapsulants for both electronics and optoelectronics. A comparison of some properties of two common aliphatic epoxies with those of LER (DGEBA) is shown in Table 10.

The preferred industrial route to cycloaliphatic epoxy resins is based on the epoxidation of cycloolefins with peracids, particularly peracetic acid [71]. Few side reactions are encountered. Some properties of various commercial products are given in Table 11. The peracid cannot be made *in situ* because the cyclic olefins are sensitive to impurities generated in this process.

Table 10. Comparative Viscosities of cycloaliphatic epoxies, epoxidized oils, and DGEBA

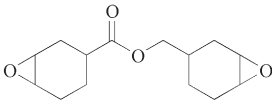
Epoxy type	Viscosity, mPa·s(= cP)	EEW
Cyclo diepoxy ERL-4221[a] (3′,4′-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate)	400	135
DGEBA	11000	190
Linseed oil epoxy	730	168

[a]Trademark of the Dow Chemical Co.



3'-Cyclohexenylmethyl 3-cyclohexenecarboxylate

An important secondary reaction is the acid-catalyzed hydrolysis of the epoxide groups. The reaction is minimized at low temperatures and strongly depends on the constituents and the reaction medium.



3',4'-Epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate

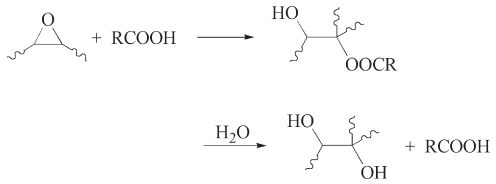
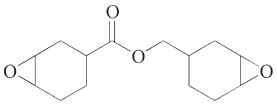
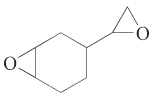
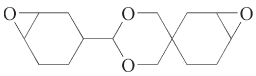
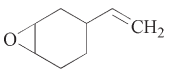
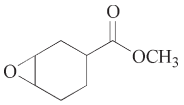
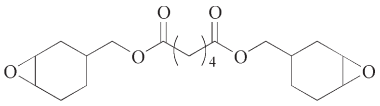


Table 11. Cycloaliphatic epoxy resins

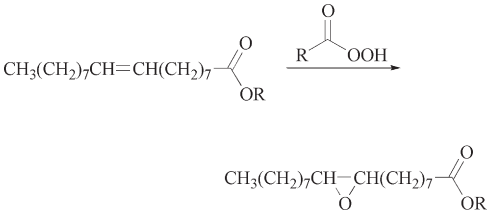
Chemical name	Structure	Commercial products	EEW[a]	Viscosity, mPa · s (= cP) at 25 °C[b]
3′,4′-Epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate		ERL-4221[c] UVR-6110	131–143	350–450
		CY-179[d]		
3,4-Epoxycyclohexyloxirane		ERL-4206[c]	70–74	15
2–(3′,4′-Epoxycyclohexyl)-5,1″-spiro-3″,4″-epoxycyclohexane-1,3-dioxane		ERL-4234[c]	133–154	7,000–17,000[e]
Vinyl cyclohexene monoxide		VCMX	124	5
3,4-Epoxycyclohexanecarboxylate methyl ester		ERL-4140	156	6
Bis(3,4-epoxycyclohexylmethyl) adipate		ERL-4299[c] UVR-6128	180–210	550–750

[a]Epoxide equivalent weight.
[b]Unless otherwise stated.
[c]Union Carbide, division of The Dow Chemical Co.
[d]Huntsman.
[e]At 38 °C.

The cycloaliphatic epoxides are more susceptible to electrophilic attack because of the lower electronegativity of the cycloaliphatic ring relative to the bisphenol A aromatic ether group in DGEBA resins. Consequently, cycloaliphatic epoxies do not react well with conventional nucleophilic epoxy curing agents such as amines. They are commonly cured via thermal or UV-initiated cationic cures. In addition, cycloaliphatic epoxy resins are low viscosity liquids that can be thermally cured with anhydrides to yield thermosets having a high heat distortion temperature. They are often used as additives to improve performance of bisphenol A epoxies. Their higher prices ($6.60–8.80/kg) have limited their commercial applications to high end products.

The largest end uses of cycloaliphatic epoxies in order of volume are electrical, electronic components encapsulation, and radiation-curable inks and coatings. A potentially large volume application is UV-curable metal can coatings for beer can exterior and ends, but the market has not been growing significantly in recent years. Other uses include acid scavengers for vinyl-based transformer fluids and lubricating oils; filament winding for aerial booms and antennas; and as viscosity modifier for bisphenol A LERs in tooling compounds. An epoxy silicone containing cycloaliphatic epoxy end groups and a silicone backbone is used as radiation-curable release coatings for pressure-sensitive products. Dow Chemical is the largest producer of cycloaliphatic epoxies. Daicel of Japan has entered the cycloaliphatic epoxy resin market.

Epoxidation of α-olefins, unsaturated fatty acid esters, and glycerol esters is affected readily by peracids including *in situ* peracids generated from hydrogen peroxide and carboxylic acids.

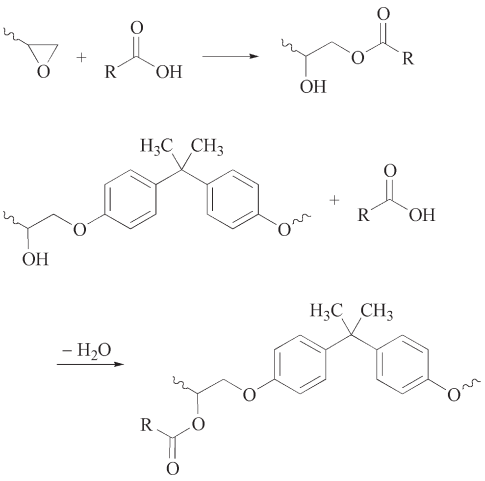


α-Olefin epoxies find utility as reactive diluents for coatings and as chemical intermediates for lubrication fluids. Larger volume epoxidized soybean and linseed oils are most frequently used as secondary plasticizers and co-stabilizers for PVC.

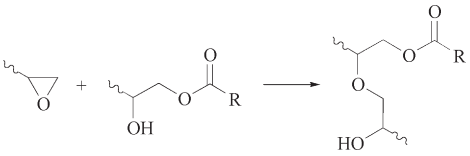
12. Epoxy Esters and Derivatives

12.1. Epoxy Esters

The esterification of epoxy resins with commercial fatty acids is a well-known process that has been employed for industrial coatings for many years. The carboxylic acids are esterified with the terminal epoxy groups or the pendant hydroxyls on the polymer chain.



A wide variety of saturated and unsaturated fatty acids are utilized to confer properties useful in air-dried, protective, and decorative coatings. Typical fatty acids include tall oil fatty acids, linseed oil fatty acid, soya oil fatty acid and castor oil fatty acid. A medium molecular weight SER, a so-called 4-type, is commonly used. Catalysts such as alkaline metal salts (Na_2CO_3) or ammonium salts are essential to prevent chain branching and gelation caused by etherification of the epoxy groups.

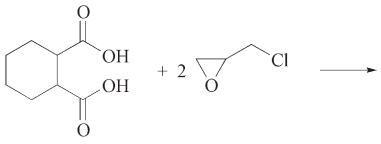


Esterification is generally conducted in an inert atmosphere at 225–260 °C, with sparging to removebyproduct water. The course of the reaction is monitored by acid number to a specified end point and by viscosity. The product is then dissolved in a solvent [72].

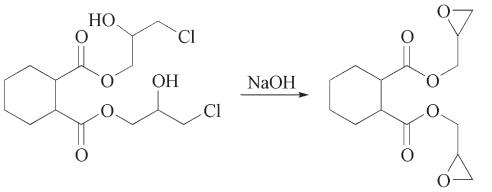
Metallic driers are incorporated in unsaturated ester solutions to promote cure via air-drying, i.e., oxidative polymerization of the double bonds of the fatty acids. Chemical resistance is generally lower than that of unmodified epoxy resins cured at ambient temperatures with amine hardeners. Epoxy esters are also used to produce anodic electrodeposition (AED) coatings by further reaction with maleic anhydride followed by neutralization with amines to produce water-dispersable coatings. Epoxy esters were widely used as automotive primer-surfacer and metal can ends coatings for many years, but are being replaced by other technologies. Their high viscosity limited their uses in low solids, solventborne coatings. Waterborne epoxy esters are now available and are used in flexographic inks for milk cartons.

12.2. Glycidyl Esters

Glycidyl esters are prepared by the reaction of carboxylic acids with epichlorohydrin followed by dehydrochlorination with caustic:



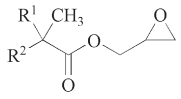
Hexahydrophthalic acid



Diglycidyl ester of hexahydrophthalic acid

The viscosity of these esters is low, i.e., ca. 500 mPa · s (= cP), and their reactivity resembles that of bisphenol A resins. Similar epoxy resin derived from dimerized linoleic acid is also commercially available. They are often used as flexiblizing agents instead of epoxidized long-chain diols.

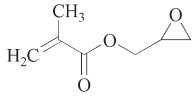
The *glycidyl ester of versatic acid* or neodecanoic acid is an example of high MW monoglycidyl aliphatic epoxy. The molecule is highly branched, thus providing steric effects to protect it from hydrolysis, resulting in good weatherability and water resistance. On the other hand, it suffers from high viscosity, and therefore it is not an effective diluent. It is often used to improve scrubability, chemical resistance, and weatherability of coatings. The product is commercially available from Resolution (Cardura E-10) and Exxon (Glydexx N-10).



R^1, R^2 = alkyl or substituted alkyl

Glycidyl ester of versatic acid

A commercially important glycidyl ester is *glycidyl methacrylate (GMA)*, a dual functionality monomer, containing both a terminal epoxy and an acrylic C=C bond. It is produced by the reaction of methacrylic acid with epichlorohydrin. The dual functionality of GMA brings together desirable properties of both epoxies and acrylics, e.g., the weatherability of acrylics and chemical resistance of epoxies, in one product. GMA is useful as a comonomer in the synthesis of epoxy-containing polymers via free-radical polymerization. The resultant epoxy-containing polymers can be further cross-linked. An example of such polymers is GMA acrylic, which is an acrylic copolymer, containing about 10–35 % by weight of GMA. Cure is by reaction with dodecanedioic acid. Its primary uses are in automotive powder coatings. GMA-containing polymers are also used as compatiblizers for engineering thermoplastics, in adhesives and latexes, and as rubber and asphalt modifiers [73]. Dow Chemical and Nippon Oils & Fats are two major producers of GMA.

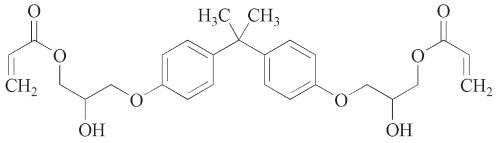


Glycidyl methacrylate (GMA)

12.3. Epoxy Acrylates

Epoxy resins are reacted with acrylic acid to form epoxy acrylate oligomers, curable via free-radical polymerization of the acrylate C=C bonds initiated by light [74]. UV lights are most commonly

used, but electron beam (EB) curing is becoming more common because of its decreasing equipment costs. This is a fast-growing market segment for epoxy resins because of the environmental benefits of the UV cure technology: low to zero VOC, low energy requirements. Major applications include coatings for overprint varnishes, wood substrates, and plastics. Radiation-cured epoxy acrylates are also growing in importance in inks, adhesives, and photoresists applications. The 2001 global market for epoxy acrylates was estimated at 40,000 MT with an annual growth rate projected to be 8–10 %.



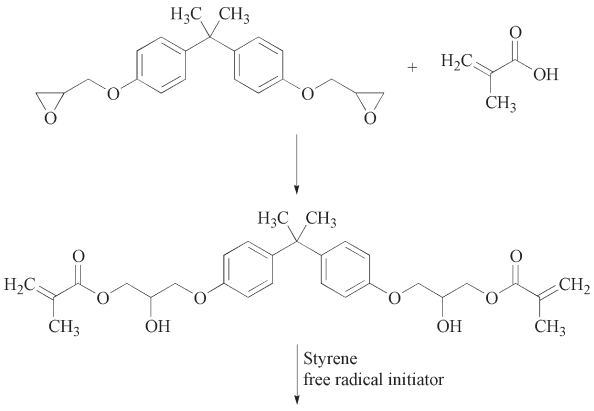
Epoxy acrylate based on DGEBA

Liquid epoxy resins such as DGEBA are most commonly used to produce epoxy acrylates. When higher thermal performance is required, multifunctional epoxies such as epoxy novolacs are used. Epoxy acrylates from epoxidized soybean oil and linseed oil are often used as blends with aromatic epoxy acrylates to reduce viscosity of the formulations. Major producers of UV-curable epoxy acrylates are UCB, Radcure, Dow Chemical, Sartomer, and Henkel.

12.4. Epoxy Vinyl Esters

A major derivative of epoxy resins is the epoxy vinyl ester resin. Originally developed by Dow Chemical [75, 76] and Shell Chemical in the 1970s, it is considered a high performance resin used in glass-reinforced structural composites, particularly for its outstanding chemical resistance and mechanical properties. The resins are made by reacting epoxy resins with methacrylic acid and diluted with styrene to 35–40 % solvent by weight. Liquid epoxy resins (DGEBA) are commonly used. Epoxy novolacs are used where higher thermal or solvent resistance is needed. Brominated epoxies are also used to impart flame retardancy for certain applications. In the final formulation, peroxide initiators are added to initiate the free-radical cure reactions of the methacrylic C=C bonds and styrene to form a random copolymer thermoset network.

The vinyl ester functionality of the epoxy vinyl esters provides outstanding hydrolysis and chemical resistance properties, in addition to the inherent thermal resistance and toughness properties of the epoxy backbone. These attributes have made epoxy vinyl esters a material of choice in demanding structural composite applications such as corrosive chemicals storage tanks, pipes, and ancillary equipment for chemical processing. Other applications include automotive valve covers and oil pans, boats, and pultruded construction parts. Significant efforts have been devoted to improve toughness and to reduce levels of styrene in epoxy vinyl ester formulations because of environmental concerns. In addition to Dow Chemical, other major suppliers of epoxy vinyl esters include Ashland, AOC, DSM, Interplastic, and Reichhold (DIC).



Vinyl ester network

12.5. Epoxy Phosphate Esters

Dow Chemical developed the epoxy phosphate ester technology in the 1980s [77]. Epoxy phosphate esters are reaction products of epoxy resins with phosphoric acid. Depending on the stoichiometric ratio and reaction conditions, a mixture of mono-, di- and triesters of phosphoric acid are obtained. Subsequent hydrolysis of the esters is used as a way to control the distribution of phosphate and glycol end groups and product viscosity. Epoxy phosphate esters can be made to disperse in water to produce waterborne coatings. They are used primarily as modifiers to improve the adhesion property of nonepoxy binders in

both solventborne and waterborne systems for container and coil coatings.

13. Characterization of Uncured Epoxies

Most industrial chemicals and polymers are not the 100 % pure, single chemicals as described in their general chemical structures. In the case of epoxy resins, they often contain isomers, oligomers, and other minor constituents. As a first requirement, one would need to know the epoxy content or EEW of the epoxy resin so the proper stoichiometric amount of cross-linker(s) can be calculated. However, a successful thermoset formulation must also have the proper reactivity, flow, and performance. Consequently, other epoxy resin properties are required by the formulators and supplied by the resin producers.

Liquid epoxy resins are mainly characterized by epoxy content, viscosity, color, density, hydrolyzable chloride, and volatile content [78]. Less often analyzed are α-glycol content, total chloride content, ionic chloride, and sodium. Solid epoxy resins are characterized by epoxy content, solution viscosity, melting point, color, and volatile content. Less often quoted are phenolic hydroxyl content, hydrolyzable chloride, ionic chloride, sodium, and esterification equivalent. Table 12 lists analytical methods adopted by ASTM [79] as standard testing methods for epoxy resins.

In addition, gel-permeation chromatography (GPC), high performance liquid chromatography (HPLC) [39, 80], and other analytical procedures such as nuclear magnetic resonance (NMR) [28] and infrared spectroscopy (IR) [81] are performed to determine MW, MW distribution, oligomer composition, functional groups, and impurities.

Resin components such as α-glycol content and chloride types and levels are known to influence formulation reactivity and rheology, depending on their interactions with the system composition such as basic catalysts (tertiary amines) and/or amine curing agents. Knowing the types and levels of chlorides guides formulators in the adjustment of their formulations for proper reactivity and flow.

Epoxide Equivalent Weight. The epoxy content of liquid resins is frequently expressed as epoxide equivalent weight (EEW) or weight per epoxide (WPE), which is defined as the weight in grams that contains 1 g equivalent of epoxide. A common chemical method of analysis for epoxy content of liquid resins and solid resins is titration of the epoxide ring by hydrogen bromide in acetic acid [82]. Direct titration to a crystal violet indicator end point gives excellent results with glycidyl ethers and cycloaliphatic epoxy resins. The epoxy content of glycidyl amines is determined by differential titration with perchloric acid. The amine content is first determined with perchloric acid. Addition of tetrabutylammonium iodide and additional perchloric acid generates hydrogen iodide, which reacts with the epoxy ring. The epoxy content is obtained by the second perchloric acid titration to a crystal violet end point.

In another procedure, a halogen acid is generated by the reaction of an ionic halide salt, e.g., tetraethylammonium bromide in acetic acid with perchloric acid with subsequent formation of a halohydrin; the epoxy group is determined by back-titration with perchloric acid using crystal violet indicator [83]. The end point can be determined visually or potentiometrically. A monograph on epoxide determinations was published in 1969 [84]. This is the method adopted by ASTM and is currently used by most resin producers.

Viscosity of epoxy resins is an important characteristic affecting handling, processing, and application of the formulations. For example, high viscosity LERs impede good mixing with curing agents, resulting in inhomogeneous

Table 12. Uncured epoxy resin test methods

Test item	Unit	Condition	ASTM method
EEW			D1652-97
Viscosity, neat	cP[a]	25 °C	D445-01
Viscosity, solution	cSt[b]	25 °C	D445-01
Viscosity, melt	cSt[b]	150 °C	D445-01
Viscosity, ICI Cone and Plate	Pa · s		D4287-00
Viscosity, Gardner–Holdt			D1545-98
Color, Co-Pt			D1209-00
Color, Gardner			D1544-98
Color, Gardner in solution			D1544-98
Moisture	ppm		E203-01
Softening point	°C		D3104-99

[a] cP = mPa · s.
[b] cSt = mm^2/s.

mixtures, incomplete network formation, and poor performance. On the other hand, too low viscosity would affect application characteristics such as coverage and appearance.

Viscosities of liquid resins are typically determined with a Cannon–Fenske capillary viscometer at 25 °C, or a Brookfield viscometer. The viscosity depends on the temperature, as illustrated in Figure 2. Viscosities of solid epoxy resins are determined in butyl carbitol (diethylene glycol monobutyl ether) solutions (40 % solids content) and by comparison with standard bubble tubes (Gardner–Holdt bubble viscosity). The Gardner color of the same resin solution is determined by comparison with a standard color disk. Recently, data have been reported for solid epoxy resins using the ICI Cone and Plate viscometers, which are much more time-efficient because they do not require sample dissolution.

Hydrolyzable Chloride (HyCl) content of liquid and solid epoxy resins is determined by dehydrochlorination with potassium hydroxide solution under reflux conditions and potentiometric titration of the chloride liberated by silver nitrate. The solvent(s) employed and reflux conditions can influence the extent of dehydrochlorination and give different results. The "easily hydrolyzable" HyCl content, which reflects the degree of completion of the dehydrochlorination step in the epoxy resin manufacturing process, is routinely determined by a method using methanol and toluene as solvents. This is the method most commonly used to characterize LER and SER.

For epoxy resins used in electronic applications, such as cresol epoxy novolacs, more powerful polar aprotic solvents such as dioxane or dimethyl formamide (DMF) have been used to hydrolyze the difficult-to-hydrolyze HyCls,

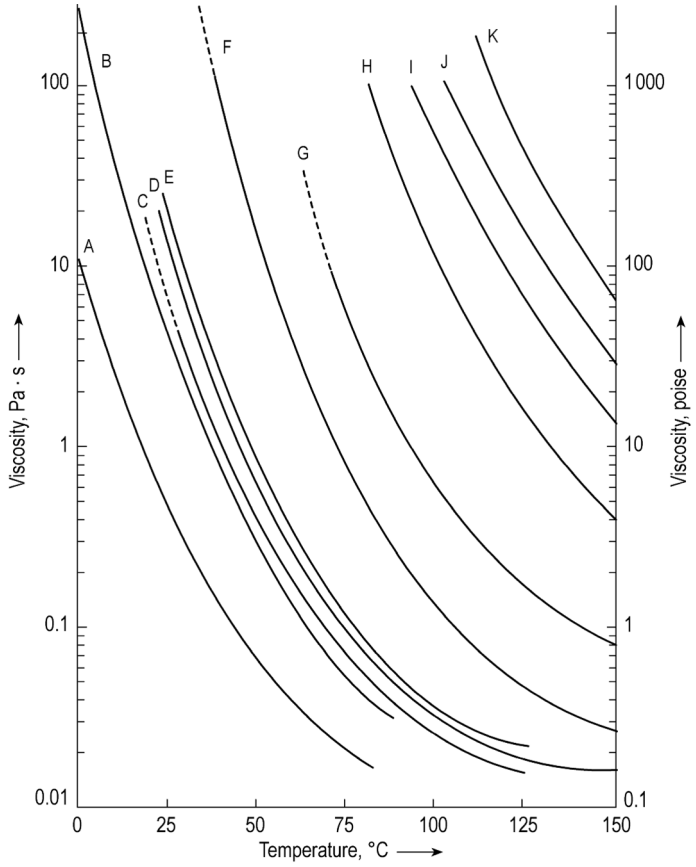


Figure 2. Viscosity–temperature profiles for bisphenol A epoxy resins with the following EEWs: A) 175–195 and 195–215 diluted resins; B) 172–178; C) 178–186; D) 185–192; E) 190–198; F) 230–280; G) 290–335; H) 450–550; I) 600–700; J) 675–760; K) 800–975.

such as the abnormal chlorohydrins and the organically "bound" chlorides. The issue here is the inconsistency in results obtained by different methods [78]. The presence of ionic hydrolyzable chlorides and total chlorides has been shown to affect electrical properties of epoxy molding compounds used in semiconductor encapsulation [85]. For these applications, producers offer high purity grade epoxy resins with low ionic, hydrolyzable and total chloride contents.

Total chloride content of epoxy resins can be determined by the classical Parr bomb method in which the sample is oxidized in a Parr bomb, followed by titration with silver nitrate [78]. The major disadvantage of this method is that it is time-consuming. Alternatively, X-ray fluorescence has been used successfully as a simple, nondestructive method to determine total chloride of epoxy resins. The method, originally developed by Dow Chemical, has been under consideration for adoption by ASTM.

The "ball and ring" and Durran's methods traditionally measure the softening point of SERs, which is important in applications such as powder coatings. The Durran's method involves heating a resin sample topped with a certain weight of mercury in a test tube until the resin reaches its softening point and flows, allowing the mercury to drop to the bottom of the test tube. The method is accurate but involves handling of highly hazardous mercury at elevated temperatures. The Mettlers' softening point method is more widely used recently because of its simplicity.

The Esterification Equivalent of solid resins is defined as the weight in grams esterified by one mole of monobasic acid. This value includes both the epoxy and hydroxyl groups of the solid resin. It is determined by esterification of the sample with acetic anhydride in the presence of pyridinium chloride, followed by titration with sodium methoxide to a thymol blue–phenolphthalein end point.

Molecular Structure of Epoxy Resins. Infrared spectroscopy (IR) is used to determine the epoxide content of resins as well as their structure. A compilation of IR spectra of uncured resins has been published [86] and their use in quality control and identification of components of resin blends has been described. Recently, near IR (NIR) has emerged as a useful tool to characterize epoxy resins [87].

NMR has been utilized to characterize epoxy resins, formulations and cured networks. It has been shown to be useful in determining the level of branching in epoxy resins and isomers distribution in epoxy novolacs [88, 89].

GPC and HPLC are utilized to characterize both liquid and solid epoxy resins [90]. MW and MW distributions are obtained from GPC measurements, but differences in chemical composition of resin samples are more apparent from HPLC chromatograms because of better resolution [91].

HPLC has proven to be a good fingerprinting tool to characterize LERs and SERs. Chromatograms of liquid epoxy resins (crude DGEBA) indicate a homologue distribution of $n = 0$, 85 %, and, in a specific case, $n = 1$, 11.5 %, although the values obtained depend on the source of the liquid resin. HPLC analysis of both liquid and solid epoxy resins has been studied in some detail using normal-phase and reversed-phase columns, respectively [39].

The difference between taffy-processed and fusion advancement solid resin can be noted in HPLC chromatograms. In the advancement process, the even-membered oligomers predominate, whereas taffy-produced resins exhibit both even- and odd-numbered oligomers. Compounds that contribute to hydrolyzable chloride and α-glycol content can be quantified by HPLC. The presence of branched chain components is detectable in studies using an improved reversed-phase gradient HPLC method [92, 93]. Excellent reviews of applications of chromatographic techniques to the analysis of epoxy resins are available [94].

14. Curing of Epoxy Resins

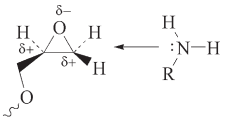
With the exception of the very high MW phenoxy resins and epoxy-based thermoplastic resins, almost all epoxy resins are converted into solid, infusible, and insoluble three-dimensional thermoset networks for their uses by curing with cross-linkers. Optimum performance properties are obtained by cross-linking (qv) the right epoxy resins with the proper cross-linkers, often called hardeners or curing agents. Selecting the proper curing agent is dependent on the requirements of the application process techniques, pot

life, cure conditions, and ultimate physical properties. Besides affecting viscosity and reactivity of the formulation, curing agents determine both the types of chemical bonds formed and the degree of cross-linking that will occur. These, in turn, affect the chemical resistance, electrical properties, mechanical properties, and heat resistance of the cured thermosets.

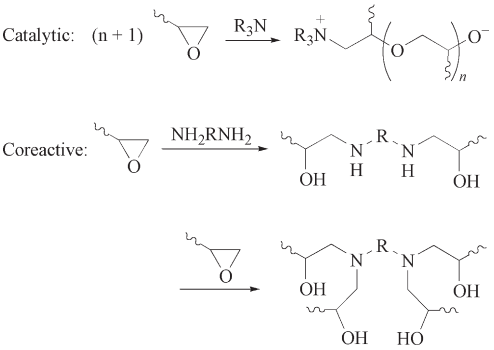
Epoxy resins contain two chemically reactive functional groups: epoxy and hydroxy. Low MW epoxy resins such as LERs are considered difunctional epoxy monomers or prepolymers and are mostly cured via the epoxy group. However, as the MW of SERs increases, the epoxy content decreases, whereas the hydroxyl content increases. High molecular weight SERs can cross-link via reactions with both the epoxy and hydroxyl functionalities, depending on the choice of curing agents and curing conditions. Reaction of the epoxy groups involves opening of the oxirane ring and formation of longer, linear C−O bonds. This feature accounts for the low shrinkage and good dimensional stability of cured epoxies. The polycondensation curing via hydroxyl groups is often accompanied by generation of volatilebyproducts, such as water or alcohol, requiring heat for proper cure and volatiles removal.

It is the unique ability of the strained epoxy ring to react with a wide variety of reactants under many diverse conditions that gives epoxies their versatility [95]. Detailed discussions on the probable electronic configurations, molecular orbitals, bond angles, and reactivity of the epoxy ring are available in the literature [96].

Compared to noncyclic and other cyclic ethers, the epoxy ring is abnormally reactive. It has been postulated that the highly strained bond angles, along with the polarization of the C−C and C−O bonds account for the high reactivity of the epoxide. The electron-deficient carbon can undergo nucleophilic reactions, whereas the electron-rich oxygen can react with electrophiles. It is customary in the epoxy industry to refer to these reactions in terms of anionic and cationic mechanisms. The terminology was attributed to the fact that an anionic intermediate or transition state is involved in a nucleophilic attack of the epoxy while a cationic intermediate or transition state is formed by an electrophilic curing agent [97]. For the sake of clarity, the nucleophilic and electrophilic mechanism terminology is used in this article.



Curing agents are either catalytic or coreactive. A catalytic curing agent functions as an initiator for epoxy resin homopolymerization or as an accelerator for other curing agents, whereas the coreactive curing agent acts as a comonomer in the polymerization process. The majority of epoxy curing occurs by nucleophilic mechanisms. The most important groups of coreactive curing agents are those with active hydrogen atoms, e.g., primary and secondary amines, phenols, thiols, and carboxylic acids (and their anhydride derivatives). Lewis acids, e.g., boron trihalides, and Lewis bases, e.g., tertiary amines, initiate catalytic cures.



The functional groups surrounding the epoxide resin also affect the curing process. Steric factors [98, 99] can influence ease of cure. Electron-withdrawing groups adjacent to the epoxide ring often enhance the reactivity of the epoxy resin to nucleophilic reagents, while retarding its reactivity toward electrophilic reagents [98, 100, 101]. In general, aromatic and brominated aromatic epoxy resins react quite readily with nucleophilic reagents, whereas aliphatic and cycloaliphatic epoxies react sluggishly toward nucleophiles [102].

Figure 3 shows the pseudo first-order kinetic response for the disappearance of the epoxy in buffered methanol solutions (lines are for clarity only).

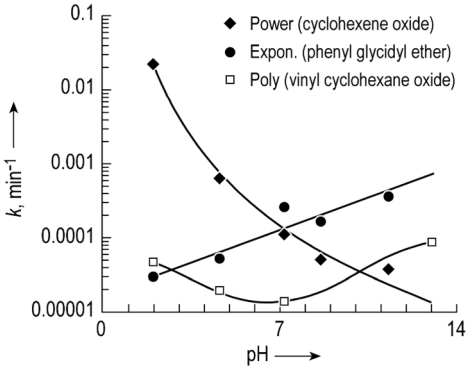


Figure 3. Effect of pH on reaction rates of epoxies

Clearly the epoxy structure dramatically influences the cure response of the epoxy as a function of pH. Cycloaliphatic epoxies are fast-reacting under low pH conditions. Aromatic glycidyl ethers are faster under high pH conditions. These results generally agree with "practical" cures: aromatic epoxies are easily cured with amines and amidoamines. Cycloaliphatics [102] are cured with acids and superacids. The behavior of the aliphatic epoxies is more complex but on balance is similar to that of cycloaliphatics.

Table 13. U.S. consumption of curing agents for epoxy resins (2001)

Curing agents	Consumption, 10^3 MT	Market percentage
Amine functional compounds	50	48
Aliphatic amines and adducts	16	
Polyamides	14	
Amidoamines	9	
Cycloaliphatic amines	6.8	
Phenalkamines	1.8	
Dicyandiamide (DICY)	1.8	
Aromatic polyamines	0.9	
Carboxylics	37	36
Polycarboxylic polyesters	22	
Anhydrides	15	
Resole resins	9	9
Amino formaldehydes	4.5	
Phenol formaldehyde	4.5	
Novolacs and other phenolics	2.7	2.6
Polysulfides and polymercaptans	14	1.3
Catalysts	3.2	3
Anionic	3.1	
Cationic	0.1	
Others	0.9	< 1

In 2001, the U.S. market for epoxy curing agents was estimated at 165×10^3 MT (see Table 13), while approximately 318×10^3 MT of epoxy resins was consumed. The most commonly used curing agents are amines, followed by carboxylic-functional polyesters and anhydrides.

A description of advantages, disadvantages and major applications of typical curing agents is given in Table 14.

15. Coreactive Curing Agents

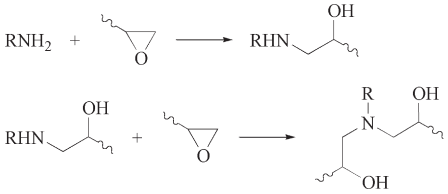
Commercially, epoxy resins are predominantly cured with coreactive curing agents. Following are important classes of epoxy coreactive curing agents.

15.1. Amine Functional Curing Agents

This section describes one of the most important classes of epoxy coreactive curing agents.

15.1.1. Primary and Secondary Amines

Primary and secondary amines and their adducts are the most widely used curing agents for epoxy resins, accounting for close to 50 % of all the epoxy curing agents used in the United States in 2001. The number of amine hydrogen atoms present on the molecule determines the functionality of an amine. A primary amine group, one which has two hydrogens bound to it, will react with two epoxy groups while a secondary amine will react with only one epoxy group. A tertiary amine group, which has no active hydrogen, will not react readily with the epoxy group, but will act as a catalyst to accelerate epoxy reactions. Reactions of a primary amine with an oxirane group or an epoxy resin are shown in the following [103].

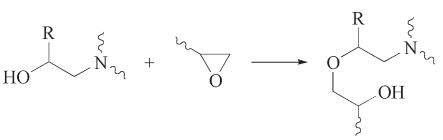


It has been reported that primary amines react much faster than secondary amines [101, 104]. Reaction of an epoxy group with a primary amine initially produces a secondary alcohol and a secondary amine. The secondary amine, in turn, reacts with an epoxy group to give a tertiary amine

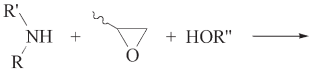
Table 14. Curing agents for epoxy resins

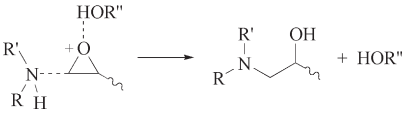
Type	Advantages	Disadvantages	Major applications
Aliphatic amines and adducts	low viscosity; ambient cure temperature; little color; low cost	short pot life; rapid heat evolution; critical mix ratio; some are moderately toxic; high moisture absorption; blush; carbonation; limited high temperature performance (< 100 °C)	flooring; civil engineering; marine and industrial coatings; adhesives; small castings
Cycloaliphatic amines	low viscosity; long pot-life; room temperature (RT) cure and heat-curable; adhesion to wet cement; good color; low toxicity; good electrical, mechanical, thermal properties (high T_g)	slower reactivity; high costs	flooring; paving; aggregate; industrial coatings; adhesives; tooling; composites; castings
Aromatic amines	excellent elevated temperature performance (150 °C); good chemical resistance; long pot life; low moisture absorption	solids; incompatibility with resins; long cure cycles at high temperature (150 °C); toxicity	high performance composites and coatings; adhesives; electrical encapsulation
Amidoamines	low viscosity; reduced volatility; good pot life; ambient cure temperature; convenient mix ratios; good toughness	poor performance at high temperature (< 65 °C); some incompatibility with epoxies	high solids, solvent-free coatings; floorings; concrete bonding; troweling compounds
Polyamides	good mix ratios; pot life; RT cure; good concrete wetting; flexibility; low volatility and toxicity	high viscosity; low temperature performance; poor color; higher cost	marine and maintenance coatings; civil engineering; castings; adhesives
Anhydrides	low exotherm; good thermal (high T_g), mechanical, electrical properties; low shrinkage and viscosity; long pot life; little color	long cure cycles at high temperature (200 °C)	composites; castings; potting; encapsulation
Catalytic	long pot life; high temperature resistance	brittle; moisture-sensitive	adhesives; prepregs; electrical encapsulation; powder coatings
Dicyandiamide	good electrical properties; high temperature resistance; latent systems	incompatibility with epoxy resins	electrical laminates; powder coatings; single-package adhesives
Carboxylic-terminated polyesters	good weatherability, corrosion resistance, and mechanical properties; low cost	poor chemical resistance	powder coatings
Isocyanates	fast cure at low temperature; good flexibility and solvent resistance	moisture-sensitive; toxic	powder coatings; maintenance coatings
Phenol–formaldehyde, novolacs	good chemical resistance, electrical properties, shelf stability, and compatibility with epoxies; high temperature resistance	high melting solids; high temperature cure; poor UV stability	molding compounds; powder coatings; electrical laminates
Polysulfides and polymercaptans	RT rapid cure times; flexible systems; moisture insensitive	poor performance at high temperature; odorous	consumer adhesives; sealants; traffic paints
Melamine–formaldehyde	good color and hardness; stable one-component systems	high temperature cure	stove paints; can coatings
Urea–formaldehyde	stable one-component systems; little color; low cost	high temperature cure; formaldehyde emission	fast-bake enamels; stove primers; can and drum coatings
Phenol–formaldehyde resoles	stable one-component systems; excellent chemical resistance	high temperature cure; brittle; gold color	baked enamels; can, drum and pail coatings; high temperature service coatings

and two secondary hydroxyl groups. Little competitive reaction is detectable between a secondary hydroxyl group in the backbone and an epoxy group to afford an ether [100], provided a stoichiometric equivalent or excess amine is maintained. However, with excess epoxy, the secondary hydroxyl groups formed gradually add to the epoxide groups [105]. This reaction can be catalyzed by tertiary amines.



Hydroxyl compounds accelerate the rate of amine curing. A mechanism has been proposed [100] in which the hydroxyl group hydrogen bonds to the oxygen atom on the epoxy group, rendering the methylene group more susceptible to attack by the nucleophilic amine. Reactivity is proportional to the hydroxyl acidity and functionality; phenolics, aryl alcohols, and polyfunctional alcohols afford the best results.

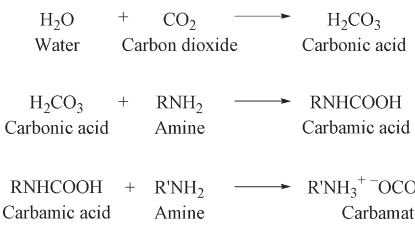




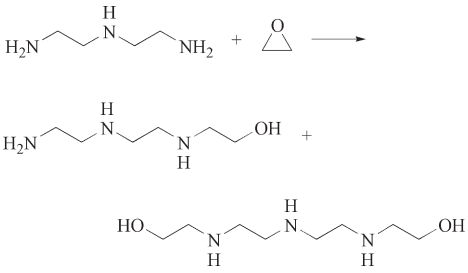
In general, reactivity of amines toward aromatic glycidyl ethers follows their nucleophilicity: aliphatic amines > cycloaliphatic amines > aromatic amines. Aliphatic amines cure aromatic glycidyl ether resins at room temperature (RT) without accelerators, whereas aromatic amines require elevated temperatures. However, with the help of accelerators, the cure rates of aromatic amines can approach those of some aliphatic amines. In general, the steric and electronic effects of substituents of the epoxy and the amine influence the reaction rate of an amine with an epoxy resin.

15.1.1.1. Aliphatic Amines

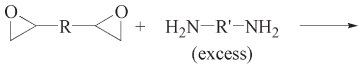
The liquid aliphatic polyamines such as polyethylene polyamines (PEPAs) were some of the first curing agents used with epoxies. They give good RT cures with DGEBA-type resins. The low equivalent weights of the ethylene amines give tightly cross-linked networks with good physical properties, including excellent chemical and solvent resistance but limited flexibility and toughness. Good long-term retention of properties is possible at temperatures up to 100 °C. Short-term exposure to higher temperatures can be tolerated. Certain aliphatic amines cured epoxies will blush (or bloom) under humid conditions. This undesirable property has been attributed to the incompatibility of some amine curing agents with epoxy resins. Incompatible amines can exude to the surface during cure and react with atmospheric carbon dioxide and moisture to form undesirable carbamates (carbonation). This, in turn, leads to gloss reduction and intercoat adhesion and recoatability problems in coating applications [106].

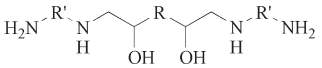


Mixing ratios with epoxy resin are very critical, and working pot lives are too short for some applications. Aliphatic polyamines are hygroscopic and volatile, have bad odor, and cause dermatitis if improperly handled. Another disadvantage is high exotherm in thick sections or large mass parts that can lead to thermal decomposition. Consequently, significant efforts have been devoted toward remedying these shortcomings by modifications of the polyethylene polyamines. Adducts with epoxy resins (resin adducts), carboxylic acids (polyamides, amidoamines), ketones (ketimines), and phenols/formaldehyde (Mannich bases) [107] are widely used commercially. Longer chain alkylenediamines such as hexamethylenediamine (HMD) and polyetheramines (polyglycol-based polyamines) have also been developed. Currently, very small amounts of unmodified polyamines are used as curing agents for epoxies. They are primarily used to produce epoxy adducts (up to 90 %). Chemical modification by reaction with epoxy groups to yield epoxy adducts affords products with better handling properties, lower vapor pressure, reduced tendency to blush, and less critical mix ratio. For example, diethylenetriamine (DETA) readily reacts with ethylene oxide in the presence of water to give a mixture of mono- and dihydroxyethyl diethylenetriamine with a longer pot life and fewer dermatitic effects than free DETA.



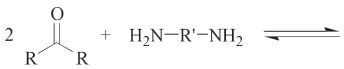
Resinous adducts are produced by reaction of excess diamine with epoxy resins.

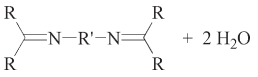




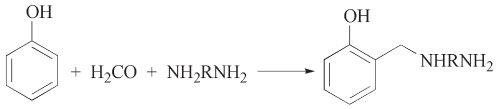
The higher molecular weight of the adduct affords a more desirable, forgiving ratio of resin to curing agent, lower water absorption, and better resin compatibility.

Ketimines. Ketimines are the reaction products of ketones and primary aliphatic amines. In the absence of reactive hydrogens, they do not react with epoxy resins. They can be considered blocked amines or latent hardeners, since they are readily hydrolyzed to regenerate the amines. They have low viscosity, cure rapidly when exposed to atmospheric humidity, and are useful in high solids coatings. Similar products have been obtained with acrylonitrile.





Mannich Base Adducts. Mannich base adduct is the reaction product of an amine with phenol and formaldehyde.



Mannich base

The resultant product has an internal phenolic accelerator. Compared to unmodified amines Mannich base adducts have lower volatility, less blushing and carbonation, and, despite their higher MW, faster reactivity.

Polyetheramines. Polyetheramines are produced by reacting polyols derived from ethylene oxide or propylene oxide with amines. The more commercially successful adducts are based on propylene oxide and are available in different MWs (JEFFAMINE* from Huntsman). The longer chain backbone provides improved flexibility but slower cure rate. Chemical and thermal resistance properties are also reduced. Polyetheramines are often used in combination with other amines in flooring, and adhesive and electrical potting applications.

15.1.1.2. Cycloaliphatic Amines

Cycloaliphatic amines were originally developed in Europe, where their use as epoxy curing agents is well established. Compared to aliphatic amines, cycloaliphatic amines produce cured resins having improved thermal resistance and toughness. Glass-transition temperatures (T_g) approach those of aromatic amines ($> 150\,^{\circ}C$), while percent elongation can be doubled. However, chemical resistance is inferior to that of aromatic amines. Because cycloaliphatic amines are less reactive than acyclic aliphatic amines, their use results in a longer pot life and in the ability to cast larger masses. Unmodified cycloaliphatic amines require elevated temperature cure, but modified systems are RT-curable. Properly formulated, they can give an excellent balance of properties: fast cure, low viscosity, low toxicity, good adhesion to damp concrete, and excellent color stability. They are, however, more expensive than other types of curing agents.

Isophorone diamine (IPDA), bis(4-aminocyclohexyl)methane (PACM), and 1,2-diaminocyclohexane (1,2-DACH) are the principal commercial cycloaliphatic polyamine curing agents. IPDA is the largest volume cycloaliphatic amine. Commercial cycloaliphatic amines are formulated products. In addition to the cycloaliphatic amines, other components such as aliphatic amines and plasticizers are also included to improve RT cure speed and end-use properties. One popular formulation consists of IPDA used in combination with trimethylhexamethylenediamines (TMDA) or *meta*-xylenediamine (MXDA), and plasticizers/accelerators such as nonyl phenol or benzyl alcohol. In some ambient cure coating applications, cycloaliphatic amines can be reacted with phenol and formaldehyde to form the Mannich base products, which have an internal phenol accelerator and cure readily at ambient temperatures.

The largest market for cycloaliphatic amines is in flooring, followed by high solids coatings, composites, adhesives, castings, and tooling. Cycloaliphatic amines experienced significant growth in the early 1990s as replacements for more toxic aromatic amines such as MDA. However, anhydrides have been more successful at replacing aromatic amines in composite applications.

15.1.1.3. Aromatic Amines

Because of conjugation, aromatic amines have lower electron density on nitrogen than do the aliphatic and cycloaliphatic amines. Consequently, they are much less reactive toward aromatic epoxies. They have longer pot-lives and usually require elevated temperature cures. Aromatic amines are usually solid at room temperature. These hardeners are routinely melted at elevated temperatures and blended with warmed resins to improve solubility. Eutectic mixtures of *meta*-phenylenediamine (MPD) and methylenedianiline (MDA or DDM) exhibit a depressed melting point resulting in an aromatic hardener that remains a liquid over a short period of time. MDA or 4,4′-diaminodiphenylmethane (DDM), 4,4′-diaminodiphenyl sulfone (DDS or DADPS), and MPD are the principal commercial aromatic amines. A new aromatic amine, diethyltoluenediamine (DETDA) has gained more significant uses in recent years.

Epoxies cured with aromatic amines typically have better chemical resistance and higher thermal resistance properties than products cured with aliphatic and cycloaliphatic amines. Their best attribute is their retention of mechanical properties at long exposures to elevated temperatures (up to 150 °C). Consequently, they are widely used in demanding structural composite applications such as aerospace, PCB laminates, and electronic encapsulation. 4,4′-DDS is the standard curing agent used with a multifunctional amine epoxy (MY 720) for high performance aerospace and military composite application. 3,3′-DDS is used in aerospace honeycomb for its excellent peel strength. MDA, which has excellent mechanical and electrical properties, is the most widely used aromatic curing agent, but recently has been classified as a potential human carcinogen and its volume has been declining. Alkyl-substituted MDAs such as tetraethyl-MDA have been developed with lower toxicity and improved performance [108, 109]. However, none of the replacement products has the performance/cost combination of MDA. Anhydrides and cycloaliphatic amines have been used to replace aromatic amines in a number of composite applications. Efforts have been made to develop ambient-curable aromatic amines by adding accelerators such as phenols to MDA.

15.1.1.4. Arylyl Amines

These amines have cycloaliphatic or aromatic backbones, but the amine functional groups are separated from the backbone by methylene groups (benzylic amines and hydrogenated derivatives). Consequently, arylyl amines are much more reactive toward epoxies than aromatic amines while having improved thermal and chemical resistance over aliphatic amines. Fast cures at ambient and sub-ambient are possible with arylyl amines. These amines are more widely used in Japan and Europe than in North America *meta*-Xylylene diamine (MXDA) and its hydrogenated product, 1,3-bis(aminomethyl cyclohexane) (1,3-BAC) are popular arylyl amines.

The commercial polyamine curing agents are given in Table 15.

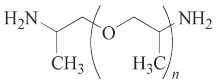
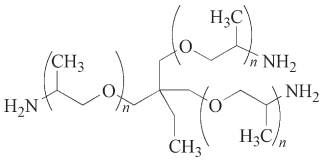
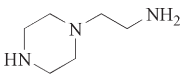
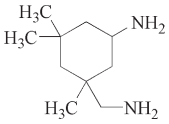
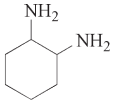
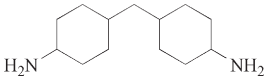
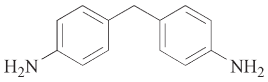
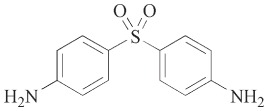
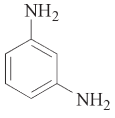
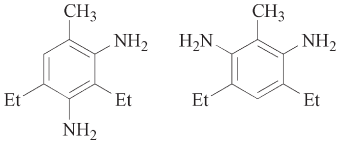
The stoichiometric quantity of polyamine used to cure an epoxy resin is a function of the molecular weight and the number of active hydrogens of the polyamine (amine equivalent weight, AEW) and the EEW or equivalent weight of epoxy resin; it is expressed as follows:

$$\left(\frac{\text{AEW}}{\text{EEW}}\right) \times 100 = \text{parts by weight polyamine per 100 parts by weight epoxy resin}$$

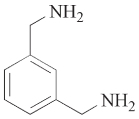
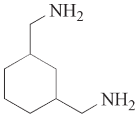
15.1.2. Polyamides

Polyamides are one of the largest volume epoxy curing agents used. They are prepared by the reaction of dimerized and trimerized vegetable-oil fatty acids with polyamines. Dimer acid is made by a Diels–Alder reaction between 9,12- and 9,11-linoleic acids. Subsequent reaction with diethylenetriamine or other suitable

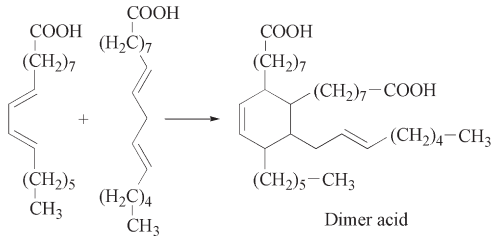
Table 15. Commercial amine curing agents

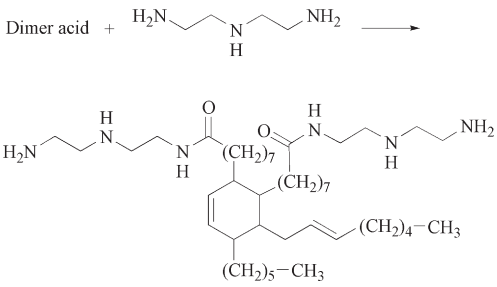
Formula	Name	Abbreviation
Aliphatic		
$NH_2CH_2CH_2NHCH_2CH_2NH_2$	diethylenetriamine	DETA
$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$	triethylenetetramine	TETA
	Poly(oxypropylene diamine)	
	poly(oxypropylene triamine)	
$NH_2(CH_2)_3O(CH_2)_2O(CH_2)_3NH_2$	poly(glycol amine)	
	*N*-aminoethylpiperazine	AEP
Cycloaliphatic		
	isophorone diamine	IPDA
	1,2-diaminocyclohexane	DACH
	bis(4-aminocyclohexyl)methane	PACM
Aromatic		
	4,4′-diamino-diphenylmethane	MDA, DDM
	4,4′-diaminodiphenyl sulfone	4,4′-DDS
	*m*-phenylenediamine	MPD
	diethyltoluenediamine	DETDA

Arylyl amines

	*meta*-xylene diamine	MXDA
	1,3-bis(aminomethyl cyclohexane)	1,3-BAC

multifunctional amines yields the amine-terminated polyamides. They are available in a range of molecular weights and compositions.





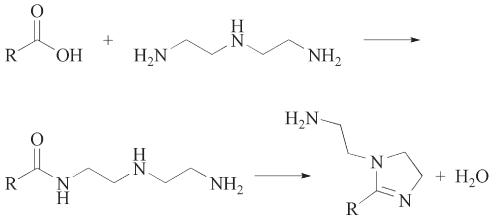
Polyamides are extremely versatile curing agents. The polyamides react with the epoxide group through the terminal amine functionality. The unreacted amide NH groups in the backbone provide good intercoat adhesion and the fatty acid structures provide good moisture resistance and mechanical properties. Wetting of cement surfaces is excellent. As a result of their relatively higher molecular weight, the ratio of polyamide to epoxy is more forgiving than with low MW polyamines. They are inexpensive, less toxic to handle; give no blushing; exhibit readily workable pot lives; and cure under mild conditions. Polyamides are mainly used in coating and adhesive formulations, mostly in industrial maintenance and civil engineering applications. The various MW polyamides exhibit different degrees of compatibility with epoxy resins. To ensure optimum properties, the polyamide/epoxy mixture must be allowed to react partly before being cured. This partial reaction assures compatibility and is known as the induction period.

Disadvantages of polyamides include slower cure speeds and darker color than polyamine-cured epoxies. Polyamide-cured epoxies lose structural strength rapidly with increasing temperature. This limits their use to applications not subjected to temperatures above 65 °C. Formulations with tertiary amines, phenolic amines, or co-curing agents help to speed up cures at low temperatures. Alternatively, polyamides derived from polyamines with phenolic-containing carboxylic acids are called phenalkamines [110]. These curing agents have low viscosity and fast ambient cure speed and are widely used in on-site marine coatings and concrete deck applications.

The high viscosity of polyamides limits their uses primarily to low solids coatings, which have been losing ground to higher solids coatings. Waterborne polyamides have been developed for use with waterborne epoxies, but their growth has been modest over the past decade because the conversion to waterborne epoxy coatings has been slower than expected. Commercial polyamides include the Versamid resins from Cognis, Ancamide resins from Air Products, and Epicure resins from Resolution.

15.1.3. Amidoamines

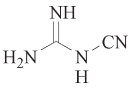
Amidoamines have all the properties of polyamides, except for a significantly lower viscosity, which make them useful in high solids and solvent-free coating formulations. They are prepared by the reaction of a monofunctional acid like tall-oil fatty acid with a multifunctional amine such as DETA, resulting in a mixture of amidoamines and imidazolines.



Imidazoline is formed by intramolecular condensation at high reaction temperatures. Commercial amidoamines are produced with different imidazoline contents to regulate reactivity and cured product performance. The pot life/reactivity of amidoamines varies with imidazoline content. High imidazoline content offers longer pot life and semi-latent curing activated by moisture. They are particularly useful in wet concrete applications. Like the polyamides, amidoamines can be used over a range of levels to enhance a specific property. However, amidoamines offer several advantages over aliphatic amines and polyamides. They offer more convenient mix ratios, increased flexibility, and better moisture resistance than aliphatic polyamines, and they offer lower color and viscosity than polyamides. Consequently, the volume of amidoamines has grown significantly in the past decade.

15.1.4. Dicyandiamide

Dicyandiamide (DICY) is a solid latent hardener (*mp* 208 °C). Its latent nature is due to its insolubility in epoxy resins at RT. DICY can be mixed with epoxy resins to provide a one-package formulation with good stability up to 6 months at ambient temperatures. Cure of epoxies with DICY occurs with heating to 150 °C. It is often used with imidazoles as catalysts. DICY offers the advantage of being latent (reacts with epoxy resin upon heating and stops reacting temporarily when the heat is removed). This partially cured or "B-staged" state is ideal for prepreg applications. Typically, DICY is used at levels of 5–7 parts per 100 parts of liquid epoxy resins and 3–4 parts per 100 parts of solid epoxy resins.



DICY is one of the first curing agents to be used with epoxy resins. It cures with epoxies to give a highly cross-linked thermoset with good mechanical strength, thermal properties, and chemical resistance, and excellent electrical properties. Because of its latency, low quantity requirements and excellent balance of properties, DICY is a widely used curing agent in powder coating and electrical laminate applications. These two applications account for 85 % of DICY consumption as epoxy curing agent.

The curing mechanism is rather complex, involving several simultaneous reactions. There are a number of conflicting proposed mechanisms in the literature. One study proposed the initial reaction of all four active hydrogens with epoxy resin catalyzed by tertiary amine catalysts followed by epoxy homopolymerization. The last step involves reactions between the hydroxyl groups of the epoxy resin with the cyano group [108, 109]. One of the more recent and plausible mechanisms of DICY cure with epoxies is that of Gilbert and co-workers [111]. The Gilbert mechanism is summarized in Figure 4. Gilbert and co-workers investigated the reaction of DICY with methyl glycidyl ether of bisphenol A (MGEBA). Products were analyzed using HPLC, NMR, and FTIR. On the basis of products that were isolated and characterized, Gilbert and co-workers proposed the mechanism shown in Figure 4.

The first step in the mechanism is the reaction of DICY with epoxy to form the alkylated DICY. This was confirmed by the imide IR peak at 1570 cm^{-1}. The second step involves further alkylation of the nitrogen that reacted in step 1, to form the *N*,*N*-dialkyldicyandiamide. No alkylation of the other amino group was

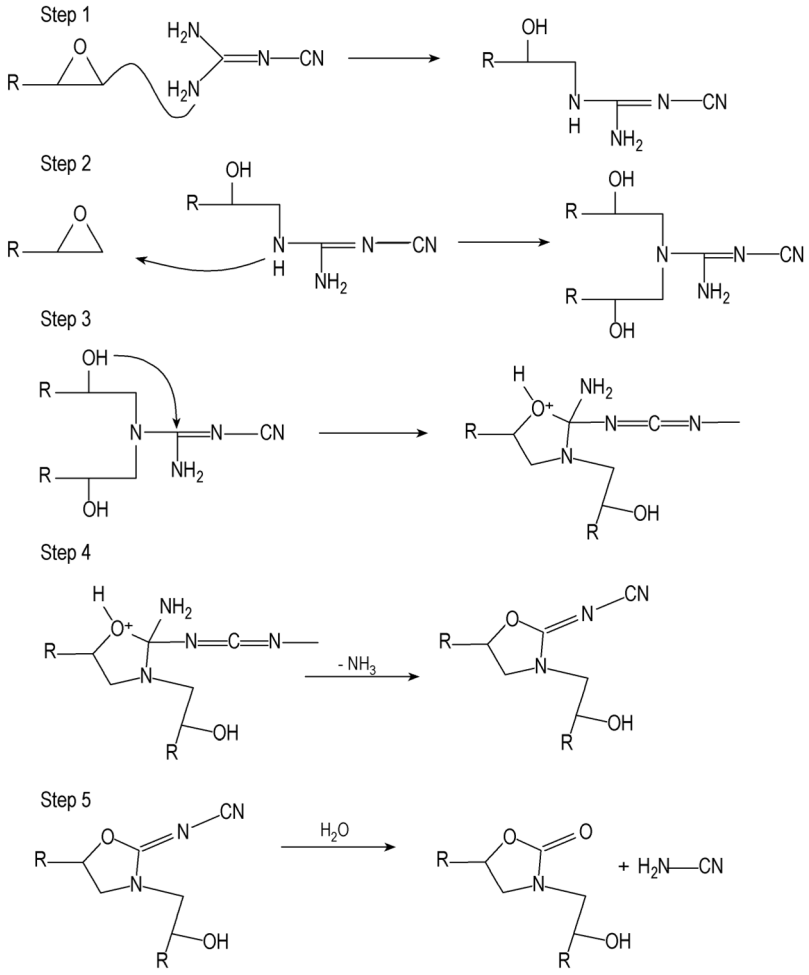


Figure 4. The Gilbert mechanism for the DICY curing of epoxy. From Ref. [111].

suggested. The third step is the intramolecular cyclization step to form a zwitterionic five-membered intermediate. This involves the intramolecular reaction of the secondary alcohol formed in step 2 with the imide functionality (−C=N−). This is in contrast with the Zahir mechanism [112] where the intramolecular cyclization involves the hydroxy and the nitrile groups. The fourth step involves the elimination of ammonia and the formation of 2-cyanoimidooxazolidine. The formation of this heterocycle is consistent with the observed bathocromic IR shift from 1570 cm^{-1} to 1650 cm^{-1}. The ammonia that is eliminated can then react with epoxy to form a trifunctional crosslink. The last step involves the hydrolysis of the oxazolidine to form the oxazolidone and cyanamide. The hydrolysis step accounts for the formation of the carbonyl group.

15.2. Carboxylic Functional Polyester and Anhydride Curing Agents

Carboxylic polyesters and anhydrides are the second most important class of epoxy curing agent. Together, they constitute 36 % of the total curing agent volume used in the U.S. market (2001 data). Polyesters have been growing rapidly in powder coatings formulations with epoxy resins, consuming the highest tonnage of epoxy curing agents. This is driven in part by

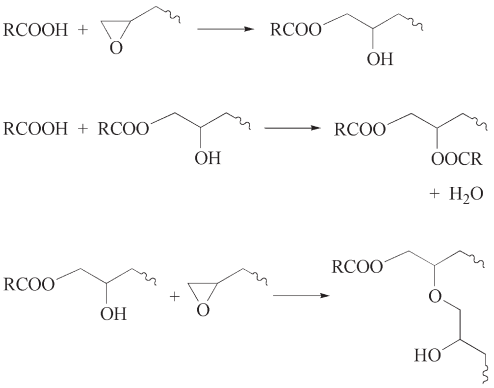
the conversion to the more environmentally friendly powder coating technologies, and in part by the versatility and cost efficiency of polyester–epoxy hybrid powder coatings. Anhydrides have been successfully replacing more toxic aromatic amines in composites. They account for 70 % of the volume of curing agents used in structural composite applications. Both polyesters and anhydrides are used in heat-cured applications only.

15.2.1. Carboxylic Functional Polyesters

The reaction of polyacids with polyalcohols produces polyesters. The terminal functionality is dictated by the ratio of the reactants. By virtue of their relatively cheap, widely available raw materials and good flexibility and weatherability, acid functional polyesters are used in hybrid epoxy powder coatings for a wide range of applications. For applications requiring good weatherability, triglycidyl isocyanurate (TGIC) is often used as curing agent for acid functional polyesters.

Terephthalic acid, trimellitic anhydride, and neopentyl glycol are commonly used raw materials to produce polyesters. Other acids, anhydrides, and glycols can also be used to modify functionality, MW, viscosity, and mechanical properties (after curing) of the polyesters. This versatility of the polyester building blocks allows many useful combinations of epoxy–polyester hybrid systems to be developed for a wide range of applications [113]. Major applications include coatings for metal furniture, general metal finishing, appliances, machinery and equipment, automotive, and wood. Automotive is a new, large, and fast growing market with many car makers converting to primer-surfacer based on epoxy–polyester powder coatings. Wood coatings are a new, emerging market.

The curing mechanism of epoxy–polyester thermosets involves reaction of the acid functionality with epoxy followed by esterification of the epoxy hydroxyl groups with the acids [114]. Compounds such as amines and phosphonium salts catalyze these reactions. Water is a condensation reactionbyproduct that must be allowed to escape during the curing process to avoid coating defects.



The first product is a β-hydroxypropyl ester, which reacts with a second mole of carboxylic acid to yield a diester. The hydroxyl ester can also undergo polymerization by reaction of its secondary hydroxyl group with an epoxy group.

15.2.2. Acid Anhydrides

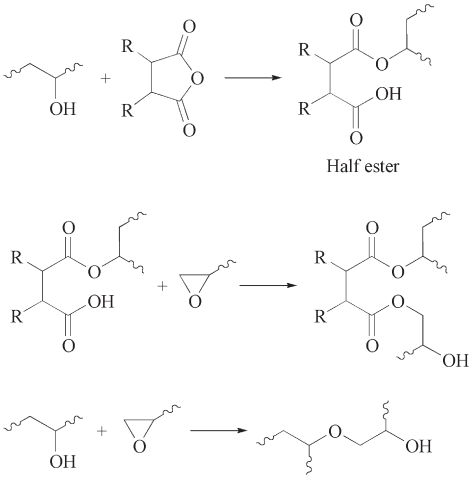
Anhydrides are some of the very first epoxy curing agents used, and they remain a major class of curing agents used in heat-cured structural composites and electrical encapsulation. Their consumption volume equals that of all aliphatic amines and adducts in 2001 in the United States. While the carboxylic-terminated polyesters find widespread uses in coatings, anhydride use in coatings is minimal.

Epoxy–anhydride systems exhibit low viscosity and long pot life, low exothermic heats of reaction, and little shrinkage when cured at elevated temperatures. The low exotherm heat generation is a unique attribute of anhydrides, making them suitable for uses in large mass epoxy cures. Curing is slow at temperatures below 200 °C and is often catalyzed by Lewis bases or acids. Postcure is often needed to develop optimum properties. Tertiary amines such as benzyldimethylamine, dimethylaminomethylphenol, tris (dimethylaminomethyl)phenol, boron trihalide amine complexes, stannic chloride, ammonium salts, phosphonium salts, and substituted imidazoles are effective catalysts. Proper catalyst concentration (0.5–2.5 % of resin weight) is critical, depending on the types of anhydrides and resins used and the cure schedules, and is known to affect high temperature performance.

Cured epoxy–anhydride systems exhibit excellent thermal, mechanical, and electrical

properties, and are used in filament-wound epoxy pipe, PCB laminates, mineral-filled composites, and electrical casting and encapsulation applications. Anhydride-cured epoxies also have better aqueous acid resistance than similar amine-cured systems. Anhydrides are the principal curing agents for cycloaliphatic and epoxidized olefin resins in electrical casting and potting. Some key physical properties of exemplary epoxy resins cured with hexahydrophthalic anhydride are shown in Table 16.

The mechanism of anhydride cure is complex and controversial because of the possibility of several competing reactions. The uncatalyzed reaction of epoxy resins with acid anhydrides proceeds slowly even at 200 °C; both esterification and etherification occur. Secondary alcohols from the epoxy backbone react with the anhydride to give a half ester, which in turn reacts with an epoxy group to give the diester. A competing reaction is etherification of an epoxy with a secondary alcohol, either on the resin backbone or that formed during the esterification, resulting in a β-hydroxy ether. It has been reported that etherification is a probable reaction since only 0.85 equivalents of anhydrides are required to obtain optimum cross-linked density and cured properties [103].



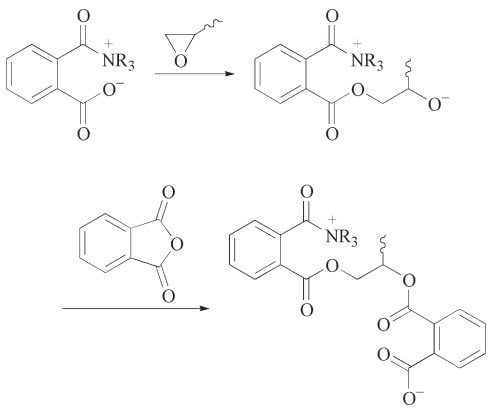
Lewis bases such as tertiary amines and imidazoles are widely used as epoxy–anhydride

Table 16. Formulation and properties of epoxy resins cured with hexahydrophthalic anhydride

	DGEBA	3′,4′-Epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate	Hexahydrophthalic acid diglycidyl ester
Formulation			
Resin, pbw[a]	100	100	100
Hexahydrophthalic anhydride, pbw[a]	85	105	100
Accelerator type	tertiary amine	metal alkoxide salt	quaternary ammonium salt
pbw[a]	3	12	4
Cure schedule, h at °C	2 at 100	4 at 120	4 at 80
	1 at 150		4 at 140
Typical cured properties at 25 °C			
Tensile strength, MPa[b]	65	68	83
Tensile modulus, MPa[b]	3400	3300	3000
Flexural strength, MPa[b]	131	89	127
Flexural modulus, MPa[b]	3400	3000	3000
Elongation, %	5.0	2.7	3.5
Compressive strength, MPa[b]	124	151	124
Heat-deflection temperature, °C	120	150	105
Water absorption, % weight gain[c]	0.5	0.4	0.4
Dielectric constant at 60 Hz	3.4	3.3	3.5
Dissipation factor at 60 Hz	0.006	0.005	0.007
Volume resistivity, $\Omega \cdot cm \times 10^{16}$	2.0	10.0	3.0

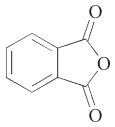
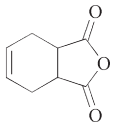
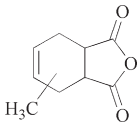
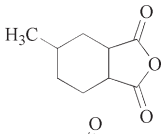
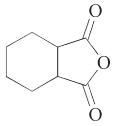
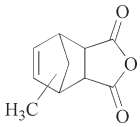
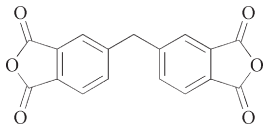
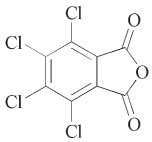
[a] Parts by weight.
[b] To convert MPa to psi, multiply by 145.
[c] After boiling for 1 h.

catalysts. Conflicting mechanisms have been reported for these catalyzed reactions [115]. The more widely accepted mechanism [103] involves the reaction of the basic catalyst with the anhydride in the initiation step to form a betain (internal salt). The propagation step involves the reaction of the carboxylate anion with the epoxy group, generating an alkoxide. The alkoxide then further reacts with another anhydride, propagating the cycle by generating another carboxylate which reacts with another epoxy group. The end result is the formation of polyester-type linkages. In practice, it has been observed that optimum properties are obtained when stoichiometric equivalents of epoxy and anhydride are used with high temperature cures, which is consistent with this mechanism and does not involve etherification reactions. At lower anhydride/epoxy ratios (0.5:1) and lower cure temperatures, some etherifications can take place by reaction of the alkoxide with an epoxy group.



Numerous structurally different anhydrides can be used as epoxy curing agents, but the most widely used are liquids for ease of handling. The most important commercial anhydrides are listed in Table 17. Methyltetrahydrophathalic anhydride (MTHPA) is the largest volume anhydride, used in filament-winding composites. Phthalic anhydride (PA) is the next largest volume and is inexpensive; so it is used widely in mineral-filled laboratory bench top manufacturing, which requires low exotherm heat generation to avoid cracking. Dodecylsuccinic anhydride (DDSA) has a long aliphatic chain in the backbone and is used as blends to improve flexibility. Benzophenonetetracarboxylic dianhydride (BTDA) is a relatively new, multifunctional anhydride developed for high temperature applications, capable of achieving a high cross-linking density with a heat distortion temperature (HDT) of 280 °C. It has been

Table 17. Commercially important anhydride curing agents

Name	Structure
Phthalic anhydride (PA)	
Tetrahydrophthalic anhydride (THPA)	
Methyltetrahydrophthalic anhydride (MTHPA)	
Methyl hexahydrophthalic anhydride (MHHPA)	
Hexahydrophthalic anhydride (HHPA)	
Nadic methyl anhydride or methyl himic anhydride (MHA)	
Benzophenonetetracarboxylic dianhydride (BTDA)	
Tetrachlorophthalic anhydride (TCPA)	

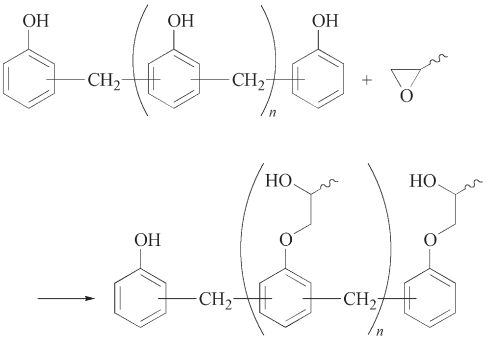
used as a replacement for more toxic aromatic amines. Tetrachlorophthalic anhydride (TCPA) is used in epoxy powder coatings for small electronic components with flame-retardancy requirements.

15.3. Phenolic-Terminated Curing Agents

Phenolics form a general class of epoxy curing agents containing phenolic hydroxyls capable of reacting with the epoxy groups. They include phenol-, cresol-, and bisphenol A terminated epoxy resin hardener. More recent additions include bisphenol A based novolacs. Cure takes place at elevated temperatures (150–200 °C) and amine catalysts are often used.

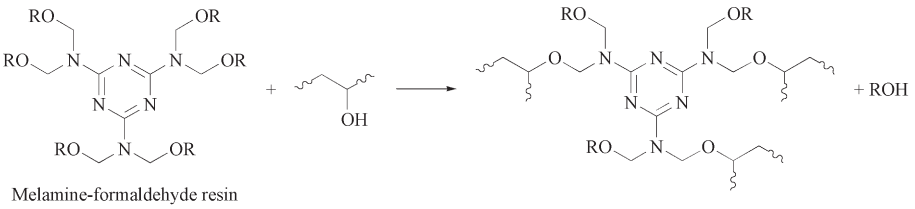
The bisphenol A terminated hardeners are produced using liquid epoxy resins and excess bisphenol A in the resin advancement process. They are essentially epoxy resins terminated with bisphenol A. They are popular in epoxy powder coating applications for rebar and pipe, providing more flexible epoxy coatings than the novolacs.

The novolacs are produced via the condensation reaction of phenolic compounds with formaldehyde using acid catalysts. They are essentially precursors to epoxy novolacs. Novolacs are multifunctional curing agents and can impart higher cross-link density, higher T_g, and better thermal and chemical resistance than other phenolics. Cresol novolacs provide higher solvent and moisture resistance, but are more brittle than their phenol novolac counterparts. Recently, bisphenol A based novolacs have been used in electrical laminate formulations to improve thermal performance (T_g and T_d) [116]. Novolacs are widely used in composites, PCB laminates, and electronic encapsulation applications. Their uses in coatings are limited to high temperature applications such as powder coatings for down-hole oil-field pipe coatings.

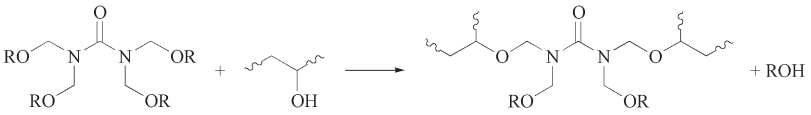


15.4. Melamine–, Urea–, and Phenol–Formaldehyde Resins

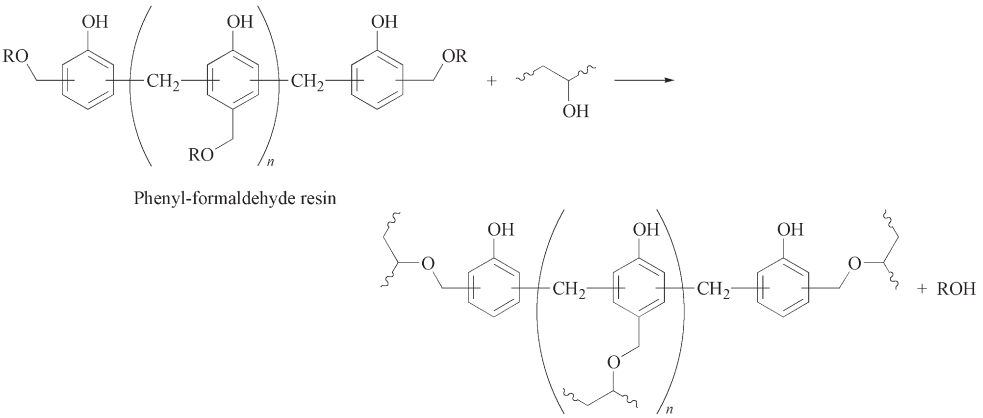
Melamine–formaldehyde, urea–formaldehyde, and phenol–formaldehyde resins react with hydroxyl groups of high MW epoxy resins to afford cross-linked networks [72].



Melamine-formaldehyde resin



Urea-formaldehyde resin



The condensation reaction occurs primarily between the methylol or alkylated methylol group of the formaldehyde resin and the secondary hydroxyl group on the epoxy resin backbone. The high bake temperatures used in these applications drive off the condensationbyproducts (alcohol or water). Acids such as phosphoric acid and sulfonic acids are often used as catalysts.

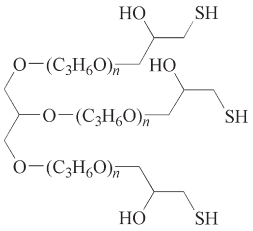
There are two types of phenol–formaldehyde condensation polymers: resoles and novolacs [117]. Phenol–formaldehyde polymers prepared from the base-catalyzed condensation of phenol and excess formaldehyde are called resoles. In most phenolic resins commonly used with epoxies, the phenolic group is converted into an ether to give improved alkali resistance. At elevated temperatures (> 150 °C), resole resins react with the hydroxyl groups of the epoxy resins to provide highly cross-linked polymers.

The melamine- and urea–formaldehyde resins are also called amino resins [118]. The phenol–formaldehyde resoles are often called phenolic resins, which is rather easily confused with phenolic-terminated cross-linkers such as novolacs and bisphenol A terminated resins.

These formaldehyde-based resins are widely used to cure high MW solid epoxy resins at elevated temperatures (up to 200 °C) for metal can, drum, and coil coatings applications. The resultant coatings have excellent chemical resistance, good mechanical properties, and no effects on taste (adding or taking away taste from packaged foods or drinks). The vast majority of the food and beverage cans produced in the world today are coated internally with epoxy–formaldehyde resin coatings. The phenol–formaldehyde resoles are also used with epoxies in coatings for high temperature service pipes and to protect against hot, corrosive liquids.

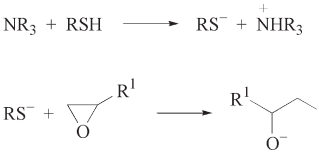
15.5. Mercaptans (Polysulfides and Polymercaptans) Curing Agents

The mercaptan group of curing agents includes polysulfide and polymercaptan compounds which contain terminal thiols.



Polymercaptans

In the language commonly used in this industry, "polysulfides" typically have a functionality of 2, while "polymercaptans" have an average functionality of 3. By itself, the thiol or mercaptan group (SH) reacts very slowly with epoxy resins at ambient temperature. However, when converted by a tertiary amine to a mercaptide ion, they are extremely reactive [119].

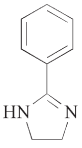


Increasing the basic strength of the amine increases the reaction rate. Polar solvents are

also known to speed up these reactions. Fast curing at ambient conditions is the primary attribute of this class of curing agent, lending themselves to applications such as the "5-minutes" consumer adhesives, concrete road repairs, and traffic marker adhesives. In practice, they are often formulated with co-curing agents such as amines or polyamides to achieve a balance of fast cure with improved mechanical properties. The tertiary amine accelerated polymercaptan/epoxy systems exhibit good flexibility and tensile strength at ambient temperature. They are used in high lap-shear adhesion applications such as concrete patch repair adhesives. One disadvantage of polymercatans is their strong odor. Aliphatic amine/polysulfide co-curing agent systems yield improved initial elevated temperature performance and are widely used as building adhesives for their excellent adhesion to both glass and concrete. However, both systems lose some flexibility on aging.

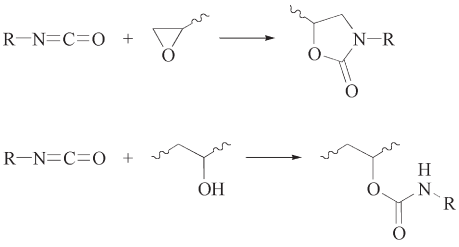
15.6. Cyclic Amidines Curing Agents

Cyclic amidine curing agents are typically used in epoxy powder coating formulations and in decorative epoxy–polyester hybrid powder coatings to produce matte surface for furniture and appliance finishes. 2-Phenyl imidazoline has been used successfully to produce low gloss epoxy powder coatings. It is highly reactive, capable of curing at relatively low temperatures (140 °C) and is suitable for curing of coatings on temperature-sensitive substrates such as wood and plastics. Other curing agents in this group include salts of polycarboxylic acids and cyclic amidines. Their volume is currently small but is expected to grow as the markets for low gloss and low temperature cure powder coatings develop. They can also be used as tertiary amine catalysts similar to imidazoles.



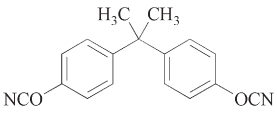
15.7. Isocyanate Curing Agents

Isocyanates react with epoxy resins via the epoxy group to produce an oxazolidone structure [120, 121] or with a hydroxyl group to yield a urethane linkage. The urethane linkage provides improved flexibility, impact, and abrasion resistance. The oxazolidone products have been successfully commercialized in high temperature resistance coating and composite applications. Blocked isocyanates are used as cross-linkers for epoxy in PPG's cathodic electrodeposition (CED) coatings. Isocyanates are also used to cure epoxies in some powder coatings, but their toxicity has limited their use.



15.8. Cyanate Ester Curing Agents

Cyanate esters can be used to cure epoxy resins to produce highly cross-linked thermosets with high modulus and excellent thermal, electrical, and chemical resistance properties. They are used in high performance electrical laminate and composite applications. Cure involves oxazoline formation catalyzed by metal carboxylates in addition to homopolymerization of both cyanate ester and epoxy [122]. The high costs of cyanate esters however limit their uses.



Bisphenol A based dicyanate ester

16. Catalytic Cure

The catalytic curing agents are a group of compounds that promote epoxy reactions without being consumed in the process. In some of the epoxy literature, catalysts are referred to as "accelerators"; the distinction of these two types of additives is discussed in later sections.

16.1. Lewis Bases

Lewis bases contain an unshared pair of electrons in an outer orbital and seek reaction with areas of low electron density. They can function as nucleophilic catalytic curing agents for epoxy homopolymerization; as co-curing agents for primary amines, polyamides, and amidoamines; and as catalysts for anhydrides. Tertiary amines and imidazoles are the most commonly used nucleophilic catalysts. Several different mechanisms are possible:

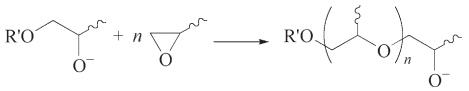
1. The catalytic curing reactions of tertiary amines with epoxy resins follow two different pathways, depending on the presence or absence of hydrogen donors, such as hydroxyl groups. In the absence of hydrogen donors [123], tertiary amines react with the electron-poor methylene carbon of the epoxy group to form an intermediate zwitterion. The zwitterion then attacks another epoxy group to continue homopolymerization via an anionic mechanism. In the presence of hydrogen donors such as alcohols, the zwitterion abstracts the proton from the alcohol to generate an alkoxide,



Zwitterion

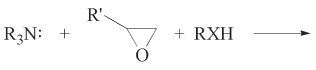


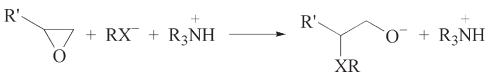




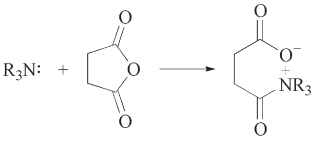
which further reacts with an epoxide group. Chain propagation continues by way of a polymeric anion mechanism.

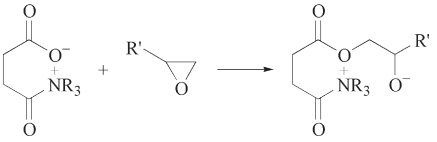
2. With more acidic hydrogen donors such as benzyl alcohol, phenols, or mercaptans, the tertiary amine acts as a co-curing agent by first abstracting the proton from the hydrogen donor:





3. With anhydrides, the catalyst facilitates the anhydride ring opening:





Commonly used tertiary amines include 2-dimethylaminomethylphenol (DMAMP) and 2,4,6-tris(dimethylaminomethyl)phenol (TDMAMP, trade name DMP-30 of Rohm and Haas), which contain built-in phenolic hydroxyl groups and can be used as a good catalysts and co-curing agents for room temperature cure of epoxies.

The rate of cure of epoxy resins with tertiary amines depends primarily upon the extent to which the nitrogen is sterically blocked. The homopolymerization reaction depends on the temperature as well as the concentration and type of tertiary amine. Benzyldimethylamine (BDMA) and TDMAMP are mainly used as accelerators for other curing agents, in the curing of anhydride- and dicyandiamide-based systems. Other tertiary amine catalysts include 1,4-diazabicyclo(2,2,2)octane (DABCO) and diazabicycloundecene (DBU).

Imidazoles such as 2-methylimidazole (2-MI) and 2-phenylimidazole (2-PI) contain both a cyclic secondary and a tertiary amine functional groups and are used as catalysts, catalytic curing agents, and accelerators [124, 125]. They are widely used as catalysts for DICY-cured epoxies in electrical laminates. For powder coatings, 2-MI adducts of LER are often used to facilitate dispersion of the components in powder coating formulations and to enhance shelf-life. Other modified imidazoles are also commercially available. The main advantage of imidazoles is the excellent balance of pot life and fast cure. 2-PI is used to increase T_g and thermal resistance.

Cyclic amidines such as 2-phenylimidazoline have also been used as a catalyst and co-curing agent in epoxy–polyester and epoxy powder coatings.

Substituted ureas are another group of epoxy nucleophilic catalytic curing agent, derived by blocking of isocyanates with dimethylamine. They are commonly used as catalysts for DICY cure of epoxies in adhesives, prepregs, and structural laminates. The ureas exhibit outstanding latency at room temperature and are widely used in one-pack adhesives. The catalytic mechanism of ureas is not well understood, but it has been postulated that DICY assists in deblocking of the urea to generate a tertiary amine, which in turns acts as epoxy curing catalyst. Commercially important substituted ureas are 3-phenyl-1,1-dimethyl urea (Amicure UR by Air Products), a reaction product of phenyl isocyanate with dimethylamine; and Amicure UR 2T, a reaction product of toluene diisocyanate (TDI) with dimethylamine.

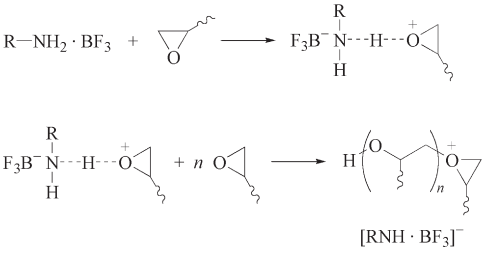
Quaternary phosphonium salts such as the tetraalkyl and alkyl-triphenylphosphonium halides have been used as fast catalysts for curing of phenolics, carboxylic acid-terminated polyesters, or anhydrides with epoxies [126]. Used in powder coatings, they showed good latency and fast cure rates at moderate temperatures.

Air Products is a major epoxy catalyst supplier. Others include Huntsman, Cognis, and SKW Chemicals.

16.2. Lewis Acids

Lewis acids, e.g., boron trihalides, contain an empty outer orbital and therefore seek reaction with areas of high electron density. Boron trifluoride, BF_3, a corrosive gas, reacts easily with epoxy resins, causing gelation within a few minutes. Complexation of boron trihalides with amines enhances the curing action. Reasonable pot lives using these complexes can be achieved because elevated temperatures are required for cure. Reactivity is controlled by the choices of the halide and the amine. The amine choice also affects other properties such as solubility in resin and moisture-sensitivity. Boron trifluoride monoethylamine ($BF_3 \cdot NH_2C_2H_5$), a crystalline material which is a commonly used catalyst, cures epoxy resins at 80–100 °C. A chloride version is also commercially available. Other Lewis acids used in epoxy curing include stannic chloride and tin octanate.

Different mechanisms have been proposed for curing epoxy resins with BF_3 complexes or salts. In general, it is assumed that complexation with the oxirane oxygen is involved, facilitating proton transfer and ether formation. Thermal dissociation of the BF_3–amine complex may form a proton that further reacts with the epoxy group to initiate the curing process [127]. Another mechanism assumes an amine adduct or salt is solvated by the epoxy groups, resulting in an oxonium ion [128]. The curing reaction is initiated and propagated by attack of other epoxy groups on the oxonium ion.

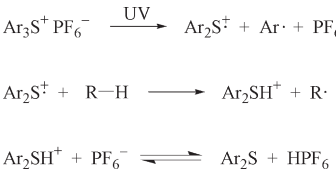


16.3. Photoinitiated Cationic Cure

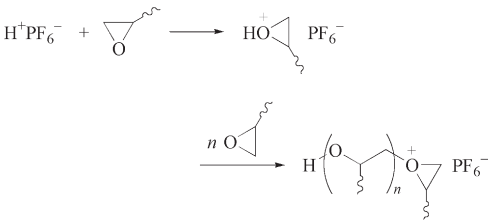
Photoinitiated cationic curing of epoxy resins is a rapidly growing method for the application of coatings from solvent-free or high solids systems. This technology allows the formulation of epoxy coatings and adhesives with essentially "infinite" shelf life, but almost "instantaneous" cure rates. Cycloaliphatic epoxies are widely cured using photoinitiated cationic initiators.

Photoinitiators used for epoxy curing include aryldiazonium salts ($ArN_2^+X^-$), diaryliodonium salts ($Ar_2I^+X^-$), and onium salts of Group VIa elements, especially salts of positively charged sulfur ($Ar_3S^+X^-$). The anions must be of low nucleophilicity, such as tetrafluoroborates or hexafluorophosphates, to promote polymer chain growth rather than chain termination. Upon UV irradiation, photoinitiators yield a "super" acid, which polymerizes the epoxy resins by a conventional electrophilic mechanism.

The photolysis of diaryliodonium and triarylsulfonium salts may proceed via formation of a radical cation, which abstracts a hydrogen atom from a suitable donor.

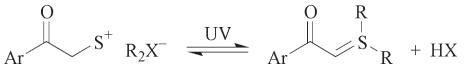


Subsequent loss of a proton yields the Brønsted acid HPF_6. Catalytic curing of the epoxy resin proceeds through an onium intermediate:



In the presence of triarylsulfonium and diaryliodonium salts, polymerization continues even if UV irradiation is terminated. This phenomenon is called "dark cure" and is due to the "living" nature of the "superacid" generated cation. The cure regime can be thought of as UV-initiated but "thermally cured." Thermally initiated cationic catalysts are also available [129].

In contrast, dialkylphenacyl sulfonium salts undergo reversible dissociation upon photolysis with formation of an ylid and a Brønsted acid. Cessation of UV activation results in termination of epoxy homopolymerization, since the acid is consumed in a reverse reaction with the ylid.



This type of behavior provides a means of controlling the degree of cure. Dialkylphenacyl sulfonium salts are thermally stable in epoxy resins at room temperature and up to 150 °C for 1–2 h. Significant interest in thermal cationic cure of epoxies, especially cycloaliphatic epoxies, has developed [130].

17. Formulation Development With Epoxy Resins

The most important step in using epoxy resins is to develop the appropriate epoxy formulation since most are used as precursors to a three-dimensional cross-linked network. With the exception of the very high MW phenoxy resins and the epoxy-based thermoplastics, epoxy resin is rarely used by itself. It is usually formulated with modifiers such as fillers and used in composite structures with glass fiber or metal substrates (coatings). To design a successful epoxy formulation that will give optimum *processability* and *performance*, the following factors must be carefully considered:

1. Selection of the proper combination of epoxy resin(s) and curing agent(s) structures
2. Epoxy/Curing agent stoichiometric ratio
3. Selection of catalyst/accelerator
4. Curing/postcuring processes and conditions
5. Formulation modifiers such as fillers, diluents, toughening agents, etc
6. Interactions among the formulation ingredients and with the composite materials (fibers, metals, etc) on the system chemistry, adhesion, rheology, morphology, and performance

The development of an epoxy formulation containing a high number of components can be very resource and time-consuming. Techniques such as design of experiments (DOE) are useful tools to facilitate the formulation development process and to obtain optimum performance [131, 132]. Future developments should include application of high throughput techniques to epoxy formulation development and optimization.

17.1. Relationship Between Cured Epoxy Resin Structure and Properties

The following diagram illustrates the formation of cured epoxy networks using different ratios of a difunctional epoxy and a tetrafunctional hardener. The structures formed are significantly different, depending on the ratio used. Consequently, it is expected that performance of these networks will be quite different despite the fact that they are derived from identical building blocks (Fig. 5).

The structure between the cross-linking position and the distance between any two of these points are important characteristics. Molecular weight between cross-links (M_c) and cross-link density are terms developed to describe "distance" between cross-link points. The concept originated with the rubber elasticity theory developed for the lightly cross-linked elastomers and has been adopted for use with epoxy thermosets with mixed success [133, 134]. The cured epoxy system derives its properties mostly from a combination of cross-link density, monomer structure and the curing process.

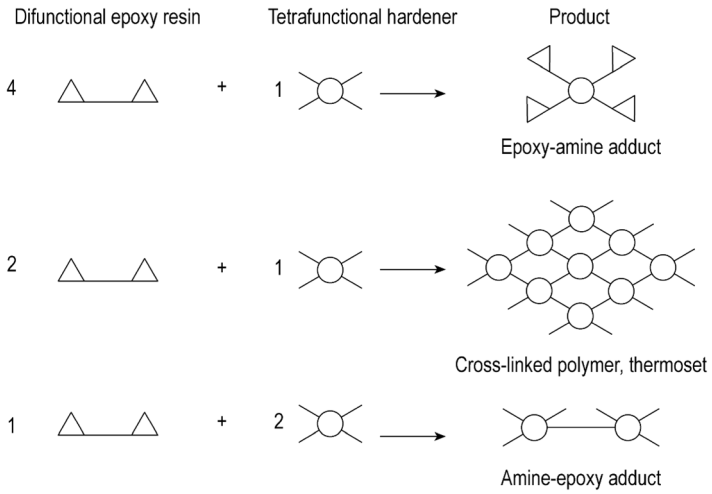


Figure 5. Formation of resin–hardener networks

The two-dimensional schematic network structures do not represent spatial reality but have been devised to help understand the nature of the various structures [135]. A good understanding of the structure/property relationship is critical in designing the appropriate epoxy/curing agent combination. For example, cross-linking with dicarboxylic anhydrides yields polyesters that are resistant to oxidation, but less so to moisture, especially in the presence of basic components. Amine cross-linked systems are resistant to saponification but not to oxidation. There is a large body of specific structure/property relationship knowledge in the epoxy industry and literature, but only a few systematic treatments are available [136–138].

Cross-link density increases with degree of cure up to its limit at full conversion of the (limiting) functional groups. The curing temperature and process strongly influence cross-link density, molecular architecture, network morphology, residual stress, and the ultimate performance. The effects of degree of cure and subsequent cross-link density on the chemical resistance of a cured DGEBA–aromatic polyamine adduct system are depicted in Figure 6.

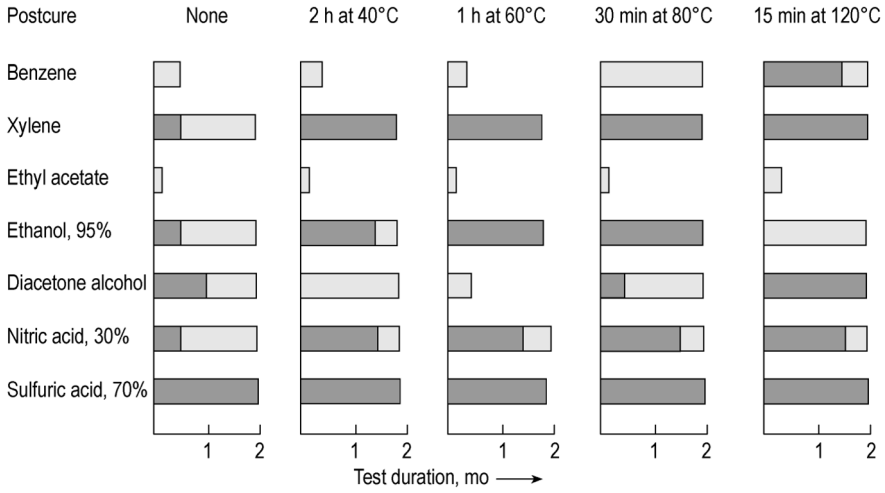


Figure 6. Chemical resistance of a DGEBA–aromatic polyamine adduct. Postcured substrate: sandblasted mild steel; film thickness: 300–350 μm; cure: 7 d at 20 °C. ▭ degraded; ■ resistant.

The increase in chemical resistance properties after postcure also demonstrates the effects of increased cross-link density. The cross-link density of a cured epoxy system can be estimated by a number of different techniques as described in the characterization of cured epoxy section.

17.2. Selection of Epoxy Resins

Successful performance of epoxy-based systems depends on proper selection and formulation of components. The components that have the most significant influences are the epoxy resins and the curing agents. As discussed in earlier sections, there are numerous choices of epoxy resins and curing agents presenting a wide variety of structure and functionality. Figure 7 shows the general attributes of common types of epoxy resins.

Epoxy resins can be used separately or in combination, such that formulations can be designed to take advantage of the desirable characteristics of several components. Because combining resins from different families can result in certain trade-offs, a careful balance of components should be investigated to produce optimal performance for specific applications. Table 16 shows effects of different resin backbones on cured properties with formulations based on hexahydrophthalic anhydride as curing agent.

The difunctional DGEBA resins are offered commercially in a wide range of molecular weights. As the molecular weight increases, so does the chain length between the epoxy end groups. Table 5 shows the effects of increasing EEW and MW of bisphenol A based epoxy resins on resin properties. The cross-link density of a difunctional resin cured by way of the epoxy group decreases as the resin molecular weight increases. High molecular weight resins are frequently cured via the secondary hydroxyl group, chemistry that results in a different set of structure–property relationships.

Multifunctional epoxy resins are available with functionalities ranging from above 2 to about 5. When cured to the same degree using a given curing agent at stoichiometric ratios, they produce a higher cross-link density, higher glass-transition temperature, and better thermal and chemical resistance compared with difunctional epoxy resins.

17.3. Selection of Curing Agents

The selection of curing agents is just as critical as the selection of resins. As discussed in the Curing Agents section, there are numerous types of chemical reagents that can react with epoxy resins. Since coreactive curing agents become part of the network structure, careful consideration must be paid to their contributions. Besides affecting viscosity and reactivity of the formulation, curing agents determine both the types of chemical bonds formed and the functionality of the cross-link junctions that are formed. Table 18 show performance examples of a liquid epoxy resin cured with different curing agents. Several authors have attempted to rationalize the curing agent selection process for different applications [106, 139].

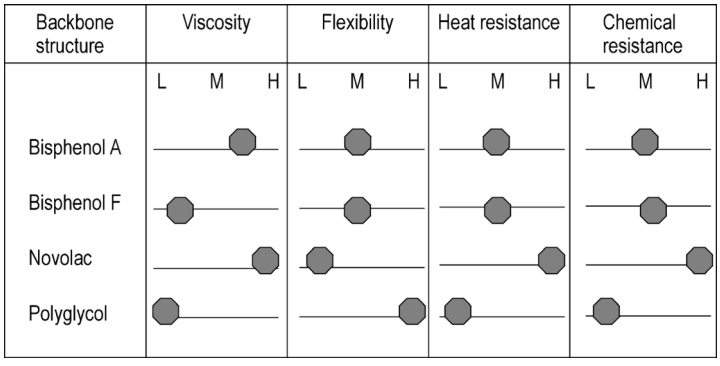


Figure 7. Comparison of relative properties of common epoxy resins
L, low; M, medium; H, high.

Table 18. Typical properties, chemical resistance, and thermal degradation of liquid DGEBA resin (185 EEW) cured with common hardeners (Dow Chemical data)

	Curing agent				
	TETA[a]	**MDA**[b]	**Polyamide**[c]	**Anhydride**[d]	**BF_3–MEA**[e]
Property					
phr[f]	13	26	43	87.5	3
Formulation viscosity, Pa · s[g] (°C)	2.25 (25)	0.110 (70)	1.25 (50)	0.038 (80)	0.040 (100)
Cure schedule, h (°C)	16 (25) 3 (100)	16 (55) 2 (125) 2 (175)	16 (25) 3 (100)	4 (100) 4 (165) 16 (200)	4 (100) 16 (150)
Heat distortion temperature, °C	111	160	101	156	168
Strength, MPa[h]					
Compression	112	116	85.6	126	114
Flexural	96	93	67	97	100
Tensile	79	70.4	57.3	69	39.4
Modulus, GPa[i]					
Compression	3.05	2.6	2.6	3.04	2.3
Flexural	3.05	2.7	2.14	3.05	3.1
Textile elongation,%	4.4	4.4	3.9	2.5	1.6
Dielectric constant at 10^3 Hz	3.90	4.06	3.19	3.14	3.45
Dissipation factor at 10^3 Hz	0.020	0.015	0.0070	0.0054	0.0053
Resistivity at 25 °C, 10^{-17} Ω · m					
Volume	6.1	12.2	12.2	6.1	8.6
Surface	7.8	> 7.9	5.5	> 7.3	> 7.9
Chemical resistance					
% Weight gain after 28 d					
50 % NaOH	0.04	−0.05	0.07	−0.12	−0.02
30 % H_2SO_4	1.8	1.6	1.9	0.83	1.1
Acetone	2.1	4.6	7.3	15.0	1.2
Toluene	0.07	0.13	3.7	0.09	0.17
Water	0.86	1.1	1.3	0.82	1.2
Thermal degradation					
% Weight loss after 300 h at 210 °C	6.8	5.5	5.0	1.5	4.9

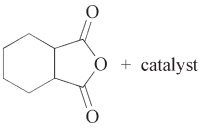
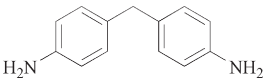
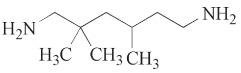
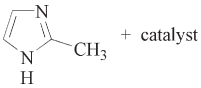
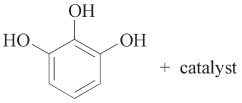
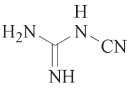
[a] Triethylenetetramine.
[b] 4,4′-Methylenedianiline.
[c] Versamide 140 (Henkel Corp.).
[d] Methylbicyclo[2.2.1]heptene-2,3-dicarboxylic anhydride catalyzed with 1.5 phr benzyldimethylamine.
[e] Methylethylamine.
[f] Parts per hundred epoxy resin.
[g] To convert Pa · s to P, multiply by 10.
[h] To convert MPa to psi multiply by 145.
[i] To convert GPa to psi, multiply by 145,000.

The effect of hardener structure on the heat resistance of a cross-linked DGEBA resin is shown in Table 19 [140]. Thermal stability is affected by the structure of the hardener. The heat resistance of aliphatic amine cured epoxy is low as measured by TGA. The nitrogen atoms are oxidized by atmospheric oxygen to amine oxides, which attack the polymer backbone. Anhydride systems tend to split off the anhydride at temperatures well below their decomposition point at about 390 °C. The ether segments formed by 2-MI and phenolic cured epoxies have the highest thermal stability.

17.4. Epoxy/Curing Agent Stoichiometric Ratios

In addition to the choices of epoxy resins and curing agents, the stoichiometric ratio of epoxy/curing agent is another factor that has significant effects on the network structure and performance. A variety of products are obtained from different ratios. Network formations for a difunctional epoxy resin and a tetrafunctional amine are illustrated in Figure 5. The products range from an epoxy–amine adduct with excess epoxy to an amine–epoxy adduct with excess amine.

Table 19. Effect of hardener structure on reactivity and heat resistance of a cross-linked bisphenol a diglycidyl ether

Curing agent	T_{rmax}, °C	E_a, J/mol[a]	TGA, 4 °C/min	
			Weight loss before decomposition	T_{dec}, °C
	125	92	12	392
	154	50	0	390
	90	58		320
	126	67	3.2	420
	185	54	2.9	400
	207	125	0	373

[a]To convert J to cal, divide by 4.184.

Theoretically, a cross-linked thermoset polymer structure is obtained when equimolar quantities of resin and hardener are combined. However, in practical applications, epoxy formulations are optimized for *performance* rather than to complete stoichiometric cures. This is especially true when curing of high MW epoxy resins through the hydroxyl groups.

In primary and secondary amines cured systems, normally the hardener is used in near stoichiometric ratio. Because the tertiary amine formed in the reaction has a catalytic effect on reactions of epoxy with co-produced secondary alcohols, slightly less than the theoretical amounts should be used. However, if substantially less than the theoretical amount of amine is used, the epoxy resin will not cure completely unless heat is applied (postcure). The use of excess amine will result in unreacted amine terminated dangling chain ends and reduced cross-linking, yielding a polymer that can be somewhat tougher but which is considerably more susceptible to attack by moisture and chemicals. In formulations containing anhydrides, less than stoichiometric ratios of curing agents normally are used (0.50 to 0.85 of anhydride to 1 epoxy stoichiometric ratio) because of significant epoxy homopolymerization.

Ladder studies are often conducted varying the stoichiometric ratios and other factors to determine the optimum formulations. Statistical design of experiment (DOE) methodology has been used to efficiently carry out ladder studies [141]. Information concerning network structures can be obtained using dynamic mechanical analysis (DMA) [142, 143] and chemorheology to guide formulation development [144, 145].

17.5. Catalysts

The choice of a catalyst and of its amount is important. As discussed in previous sections, some tertiary amine catalysts can play multiple roles in the curing reaction. Anhydride cure in particular is highly sensitive to catalyst amount. Nucleophilic catalysts, used with acidic curing agents such as anhydrides and novolacs, can greatly reduce the gel time. In the case of anhydrides, a nucleophilic catalyst attacks the

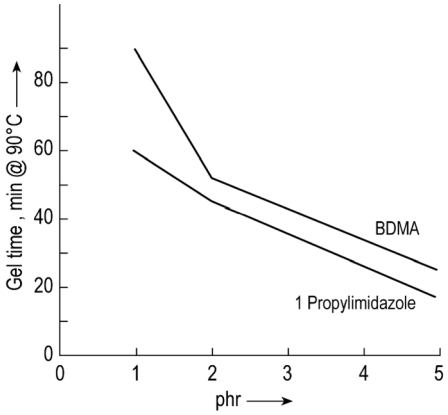


Figure 8. Effects of catalyst on epoxy/nadic methyl anhydride cure

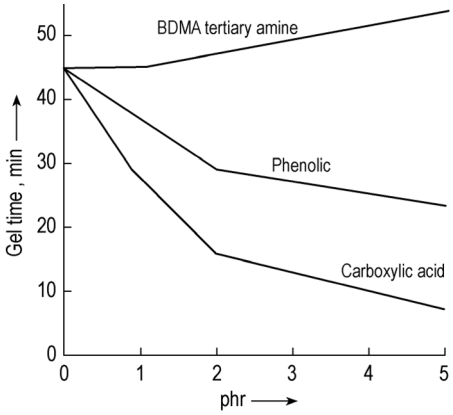


Figure 9. Effects of accelerator on epoxy/triethylene triamine cure

anhydride ring, causing the ring to open and promote bonding to the epoxy ring. Figure 8 shows the effect of BDMA and 1-propylimidazole levels on the pot life of a system combining D.E.R. 331 resin and nadic methyl anhydride at 90 °C (194 °F) [146]. Imidazoles are more efficient catalysts than tertiary amines; only half the concentration is required to produce the same catalytic effect.

17.6. Accelerators

Accelerators are commonly added to epoxy systems to speed up curing. This term should be used to describe compounds which increase the rate of catalyzed reactions but which by themselves are not catalysts. However, the term accelerator is often used synonymously with catalyst in some of the literature. Hydrogen donors such as hydroxyl groups facilitate epoxy reactions via hydrogen bonding or reaction with the oxygen on the epoxide ring. More acidic donors such as phenols and benzyl alcohols increase the rate of acceleration. However, very strong acids can interfere with amine curing agents by protonation of the amine to form an amine salt, resulting in increased pot life. Figure 9 shows the effects of different accelerators on the rate of a DGEBA/triethylenetriamine formulation.

18. Epoxy Curing Process

The epoxy curing process is an important factor affecting the cured epoxy performance. Consequently, it is imperative to understand the curing process and its kinetics to design the proper cure schedule to obtain optimum network structure and performance. Excellent reviews on this topic are available in the literature [147, 148].

The curing of a thermoset epoxy resin can be expressed in terms of a time–temperature-transformation (TTT) diagram (Fig. 10) [149, 150]. Later, a CTP (cure-temperature–property) diagram was proposed as a modification of the TTT diagram [151]. For nonisothermal cure, the conversion-temperature-transformation (CTT) diagram has been shown to be quite useful [152]. In the TTT diagram, the time to gellation and vitrification is plotted as a function of

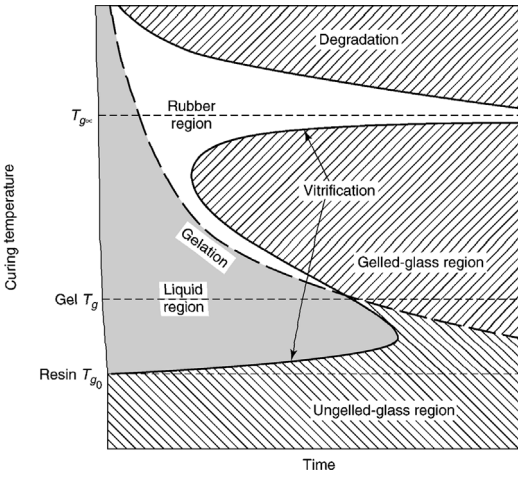


Figure 10. Time–temperature-transformation diagram

isothermal cure temperature. Important features are the gel point and the onset of vitrification. The gel point is defined as the onset of the formation of insoluble, cross-linked polymer (gel fraction) in the reaction mixture. However, a portion of the sample may still be soluble (sol fraction). The onset of vitrification is when the glass-transition temperature (T_g) of the curing sample approaches the curing temperature T_c. Ideally, a useful structural thermoset would cure until all monomers are built into the network, resulting in no soluble fraction.

The S-shaped vitrification curve and the gelation curve divide the time–temperature plot into four distinct states of the thermosetting-cure process: liquid, gelled rubber, ungelled glass, and gelled glass. T_{g0} is the glass-transition temperature of the unreacted resin mixture; $T_{g\infty}$ the glass-transition temperature of the fully cured resin; and gel T_g the point where the vitrification and gellation curves intersect.

In the early stages of cure prior to gelation or vitrification, the epoxy curing reactions are kinetically controlled. When vitrification occurs the reaction is diffusion controlled, and the reaction rate is orders of magnitude below that in the liquid region. With further cross-linking of the glass, the reaction rate continues to decrease and is eventually quenched. In the region between gelation and vitrification (rubber region) the reaction can range from kinetic to diffusion control. This competition causes the minimum in vitrification temperature seen in the TTT diagram between gel T_g and $T_{g\infty}$. As the cure temperature is raised the reaction rate increases and the time to vitrification decreases until the decrease in diffusion begins to overcome the increased kinetic reaction rate. Eventually, slower diffusion in the rubbery region decreases the overall reaction rate and thus the increase in time to vitrify is seen. Below $T_{g\infty}$, the reaction does not go to completion. As curing proceeds, the viscosity of the system increases as a result of increasing molecular weight, and the reaction becomes diffusion-controlled and eventually is quenched as the material vitrifies [153]. After quenching, the cure conversion can be increased by raising the temperature. This is often practiced as postcure for certain epoxy systems to achieve maximum cure and performance. Postcure is only effective at temperatures higher than $T_{g\infty}$. However, it must be noted that at temperatures sufficiently above $T_{g\infty}$, onset of network degradation can also be seen if sufficient time is involved. Thus one must be careful about potential "over-curing."

The TTT diagram is useful in understanding the cure kinetics, conversion, gelation, and vitrification of the curing thermoset. Gelation and vitrification times can be determined from the intersections of the storage and loss moduli and the maxima in the loss modulus of an isothermal dynamic mechanical spectrum, respectively. Recently, techniques have been developed using rheological and dynamic mechanical analysis instruments to determine the gel point and vitrification [154]. Understanding the gelation and vitrification characteristics of an epoxy/curing agent system is critical in developing the proper cure schedule/process to achieve optimum performance.

One important application is the management of cure temperatures (T_c) and heating rate: if T_c is too low, vitrification may occur before gelation and further reactions may not be completed, resulting in an incomplete network structure and poor performance. This is of particular relevance in ambient cures and radiation cures [155]. Furthermore, attention must be paid to the relationship between mixing of reactants and gel point. Epoxy resins and curing agents must be thoroughly mixed prior to the gel point since the rapid viscosity buildup at gel point inhibits homogeneous mixing of reactants, resulting in potential network and morphological inhomogeneities and defects [156].

Curing and quenching processes of epoxies have been reported to affect performance of certain epoxy coatings and composites. These effects have been attributed to phenomena known as internal or residual stress and physical aging of cured epoxies [147].

Internal stresses arise mainly because of the diminishing capacity of the cross-linked polymer to expand or contract to the same extent (volume) with the solid substrate to which it is adhered. This phenomenon is caused by mismatches of coefficients of thermal expansion (CTE) of the substrates (metal, glass, etc) and the cross-linked epoxies during nonisothermal cures; and cure shrinkage (solvent loss, cross-linking). The effect often contributes to adhesion failures and is more prominent in metal coatings and large composite parts manufacturing, especially when the T_g of the cross-linking polymer approaches T_c. As discussed previously, while curing of epoxy

functional groups via polycondensation reaction results in relatively low shrinkage, failures attributable to internal stresses such as delamination have been observed in certain epoxy coatings of metal substrates, epoxy encapsulants for electronic devices and glass-fiber-reinforced composites [157]. The effect can be very severe in the case of photoinitiated curing of epoxy acrylates as well as free-radical curing of epoxy vinyl esters. Shorter bonds are formed during these free-radical curing processes, which result in significant shrinkage. Postcure with heat is often required to release some of the internal stresses and to improve adhesion. Efforts have been focused on understanding the mechanism of stress development, and stress minimization by modifications of the cure and postcure cycles [158].

Physical aging is a well-known phenomenon in glassy polymers and has been studied quite extensively in amorphous thermoplastics [159]. The term physical aging refers to the gradual changes in polymer physical properties with time after a glassy polymer is heated above its T_g and rapidly cooled (quenching) to temperatures below T_g. The physical aging process differs from chemical aging processes, in which breakage or formation of chemical bonds are involved such as continuing cure, hydrolytic aging, and photochemical and thermal degradation. The phenomenon has been attributed to the non-equilibrium state of the glassy polymer at temperatures below its T_g, in which the polymer contains excessive free volume as it is quenched. As the polymer recovers gradually over time to approach equilibrium, a reduction in free volume and an increase in density results. Consequently, the term densification is sometimes used to describe physical aging. For certain epoxy systems, physical aging has been reported to cause increases in stiffness and decreases of toughness [160, 161]. Hardening of certain baked epoxy coatings with time and failures of the coatings due to loss of ductility have been observed. However, physical aging has been reported to be reversible (erasable) by postheating above polymer T_g. Proper selection of the cure and postcure schedules including quenching cycle is important to minimize the potential detrimental effects of physical aging [162]. In some epoxy systems, it is difficult to distinguish physical aging from the effects of residual solvent loss and/or continuing cross-linking. They all can contribute to increases in stiffness of the system.

To develop a proper curing process, it is important to understand the reactivity of different curing agents toward the epoxy structure of interest. The effect of hardener structure on reactivity of a cross-linked DGEBA resin (determined by DSC) is shown in Table 19. Aliphatic amines show a maximum reaction rate, called T_{rmax}, at 90 °C (heating rate 10 °C/min). The same epoxy resin is somewhat less reactive (T_{rmax} = 126 °C) when homopolymerized via initiators. Aromatic amines and phenols cure considerably more slowly, requiring higher curing temperatures. The highest temperatures are required for dicyandiamide curing, which can, however, be accelerated by basic components.

Relative reaction rates are often expressed in terms of the activation energy E_a (Arrhenius type relationship). E_a allows comparisons of reaction rates at different temperatures and is influenced by the type of chemical reactions involved in the cure. Curing of epoxy resins with phenols or aromatic and aliphatic amines proceeds with a fairly low activation energy of 50–58.5 kJ/mol (12–14 kcal/mol). Activation energies are higher when epoxy compounds having low hydroxyl content are cured alone in the presence of catalysts (92 kJ/mol = 22 kcal/mol) or with dicyandiamide (125.5 kJ/mol = 30 kcal/mol).

18.1. Characterization of Epoxy Curing and Cured Networks

Cured thermoset polymers are more difficult to analyze than thermoplastics since they are insoluble and generally intractable. Their properties are influenced by factors at the molecular level, such as backbone structures of epoxy resin and curing agent; nature of the covalent bond developed between the epoxy resin and the curing agent during cross-linking; and density and extent of cross-linking, i.e., degree of cure.

Epoxy resin formulators are concerned with formulation reactivity and flow during application. Reactivity tests or gel time tests are used to determine the proper reactivity of the formulations. Formulators also developed flow tests to check for the formulation rheology profile. The coatings industry widely uses MEK (methyl ethyl ketone) double rubs as an indication of cure. While the test does give a relative indication of

cure for a certain system, caution must be exercised when comparing different systems, which may have very different inherent resistance against MEK. In general, these end-use tests do not provide insights on the structure–property relationship of the system.

Epoxy curing process can be monitored by a number of different techniques:

1. Analysis of the disappearance and/or formation of functional groups
2. Indirect estimation of cure conversion
3. Measurements of changes in thermal, physical, and mechanical properties of the system

Comprehensive reviews of different techniques for epoxy cure monitoring are available [86, 94]. Wet chemical or physical analysis methods, such as solvent swell [163], titration of functional groups, IR, near IR [164], or NMR spectroscopy, are commonly used to monitor epoxy cure.

The thermal properties of the system reflect the degree of cure, andthermal analysis of polymers (DSC, DMA, TGA) has been used extensively in studies of epoxy resins [156]. Correlation between T_g and degree of cure has been well established for many systems.

Viscosity build is observed with increased reaction conversion in epoxy curing. More recently, chemorheology, which utilizes rheological measurement (qv) and thermal analysis such as DSC, has been applied to study epoxy cure [166, 167].

Since epoxy curing involves epoxy ring opening and the generation of polar groups, which have a high dipole moment, dielectric measurements have been applied to monitor cures. Dielectric methods [168, 169] encompass both macroscopic and microscopic features: the dipoles being oriented during dielectric measurements are on a microscopic scale, whereas the degree and rate of orientation may depend on macroscopic properties such as viscosity and density.

The mechanical properties of a resin system can also be used to estimate the degree of cure [170]. The methods range from hardness evaluation to complex static measurements or sensitive dynamic mechanical analysis (DMA). Table 20 gives ASTM standard procedures for measuring the properties of cured or partially cured epoxy resin systems.

Direct measurement of the cross-link density of thermoset polymers including those from epoxy resins remains one of the most difficult analytical challenges in the field. A far too common approach simply relates the rubbery modulus (G_r), the thermoset modulus above T_g, to the molecular weight between cross-links (M_c) using the theory of rubbery elasticity [133, 134]. Unfortunately thermoset networks have much more complex features than do true elastomers, including non-Gaussian chain behavior, interchain interactions, and entanglements [172]. These factors render rubbery elasticity theory inadequate as an absolute measure of M_c from G_r, and doing so can lead to totally erroneous conclusions on the network structure [173]. In a given family of thermosets, changes

Table 20. ASTM[a] procedures for cured or partially cured epoxy resin systems

Test	ASTM standard
Chemical	
Density by displacement	D792
Water absorption in plastics	D570
Moisture absorption properties in composites	D5229
Void content in composites	D2734
Electrical	
Volume resistivity	D257
Surface resistivity	D257
Dielectric strength	D149
Dielectric constant and dissipation factor	D150
Insulation resistance	D257
Thermal	
Heat-deflection temperature	D648
Glass-transition temperature	D696
Dynamic mechanical properties of plastics	D4065
Coefficient of thermal linear expansion	D296
Coefficient of linear thermal expansion by thermomechanical analysis	E831
Coefficient of thermal conductivity	C177
Mechanical	
Tensile strength	D638
Compressive strength (plastic)	D695
Compressive testing (composite)	D3410
Flexural strength	D790
Impact strength	D256
Fracture strength in cleavage of adhesives in bonded metal joints	D3433
Fracture strength in “T” peel of adhesives in bonded joints	D903
Fracture testing in 180 ° peel of adhesives	D5528
Mode I interlaminar fracture toughness of composites	D2344
Apparent interlaminar shear strength of composites	D5045
Plane strain fracture toughness of plastics	D4255
On-plane shear response of composites	
Hardness, Barcol	D2583
Hardness, Rockwell M	D785

[a] From Ref. [171].

in G_r can be considered to reflect *relative* changes in M_c. Estimates of the expected M_c can be calculated from monomer MW and functionality for stochiometric systems [174]. More extensive network structure calculations including M_c are done using statistical relations developed by MILLER and MAKOSCO [175].

In many applications, epoxy systems derive their high thermal and mechanical performance characteristics from highly cross-linked network structures. However, this often results in brittleness of the epoxy thermosets and loss of end-use properties such as impact resistance. Elongation at break (% elongation) has been a popular test used in the industry for many years to measure toughness, ability to resist failure under tensile stress. While useful in certain applications, good correlations between elongation at break and end-use properties of cured epoxies are not always possible. The failure envelope concept has been useful in looking at the entire time–temperature failure spectrum of epoxies [176]. More recently, progress in the field of fracture mechanics [177, 178] has led to advanced fracture toughness tests that are more useful in characterizing cured epoxy performance. Examples of such tests are critical elastic strain release rate (G_{IC}) and critical stress intensity factor (K_{IC}) [179].

Dynamic mechanical analysis (DMA) of cross-linked epoxy resins typically shows, in order of decreasing temperature, an α transition corresponding to T_g, a β transition associated with relaxation of the glyceryl groups, and a γ transition due to methylene group motions [180]. Both the β and the γ transitions, which are typically observed at −30 to −70 °C and at about −140 °C, respectively, are attributed to crankshaft motions of the polymer chain segments. The appearance of transitions between the α and β transitions is highly variable and has been attributed to segmental motions due to particular curing agents [181]. No definitive correlations between the appearance of sub-T_g relaxations and mechanical properties have been observed [182]. Like many other plastics, cross-linked epoxy resins undergo a change in fracture mechanism from brittle to ductile (T_b) with increasing temperature. The window between T_g and T_b has been shown to correlate well with the formability of epoxy can coatings in the draw-redraw (DRD) process [183, 184].

Adhesion is an important issue in epoxy applications since epoxy is almost always used as part of a composite system. Examples are epoxy coatings on metal substrates, epoxy adhesives for metal surfaces, and matrix resin in fiber-reinforced composites such as PCB laminates and aerospace composites. Consequently, optimum epoxy adhesion to the substrate is a prerequisite for good system performance in terms of static and dynamic mechanical properties and environmental durability. In rubber-toughened composite systems, it has been reported that a threshold of interfacial adhesion between both phases (rubber and resin matrix) is needed for maximum toughening by promoting the cavitation mechanism and by activating the crack-bridging mechanism [185]. Excellent review papers are available on the issue of adhesion of epoxy in composites [186], coatings, and adhesives [187]. Effects of internal stresses on coating adhesion failures including the role of coating defects and pigments as potential stress concentrators have been reported [188].

Surface properties such as dynamic contact angle and surface tension are used to ensure proper wetting of epoxy and the substrate. Microscopic techniques, such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM), are widely used to study morphology, fracture, and adhesion issues of cured epoxy systems. Chemical analysis techniques, such as micro-IR, X-ray photoelectron spectrometry (XPS), and secondary ion mass spectrometry (SIMS), are useful in providing functional group analysis at the interfaces.

Consumers of products which use epoxy resins have developed increasing expectations for longer and more reliable performance. In automobiles, for example, the coating is expected to maintain its initial "Class A" finish for 10 years and the composite leaf spring is designed to last for the life of the vehicle. To meet these expectations, the long-term durability of epoxy thermosets is a key material-specific and application-specific consideration. The durability of polymeric materials in general depends on phenomena such as physical aging, environmental exposure (such as weathering), and mechanical experience (such as impact and load). A detailed discussion of this topic is beyond the scope of this review; interested readers are referred to a leading reference [189].

In addition, the processing of epoxy formulations into their final thermoset structure and form

has a major effect on ultimate performance. Material properties such as rheology and reaction kinetics interplay with processing variables such as temperature and shear rate to affect key properties of extent of cure, orientation, and residual stress. Design of the final form of the material also should incorporate fundamental thermoset properties using finite element analysis methods. Optimization of any given epoxy thermoset application is therefore very specific to formulation, processing conditions, and final form and use of the material, and involves the contributions from chemistry, engineering, and material science disciplines to be fully successful.

19. Formulation Modifiers

The processing behavior (mainly viscosity and substrate wetting) and other properties of an epoxy system can be modified by diluents, fillers, toughening agents, thixotropic agents, etc. Most commercial epoxy resin systems contain modifying agents.

19.1. Diluents

Diluents affect the properties of the cured resin system and, in particular, lower the viscosity in order to improve handling and wetting characteristics. They are often used in the range of 2–20 wt. % based on the epoxy resin. Diluents can be classified into *reactive* and *nonreactive* types.

The *reactive* diluents are products with low viscosity (1–500 cP at 25 °C) used to lower the viscosity of standard epoxy formulations. The effect of reactive diluents on DGEBA viscosity is illustrated in Figure 11. Lower viscosity allows higher filler loading, lower costs, and/or improved processability. Because of the epoxy functionality, the diluents become part of the cured network. However, the reactive diluents can negatively impact properties, and so balancing of viscosity reduction and property loss is an important consideration. Decreases in tensile strength, glass-transition temperature, chemical resistance, and electrical properties are usually observed. Toxicity is another concern, particularly the aromatic mono glycidyl ethers such as phenyl glycidyl ether (PGE) and *o*-cresol glycidyl ether (CGE). *n*-Butyl glycidyl ether (BGE) is one of the most efficient viscosity reducers, but it has been losing favor because of its volatility

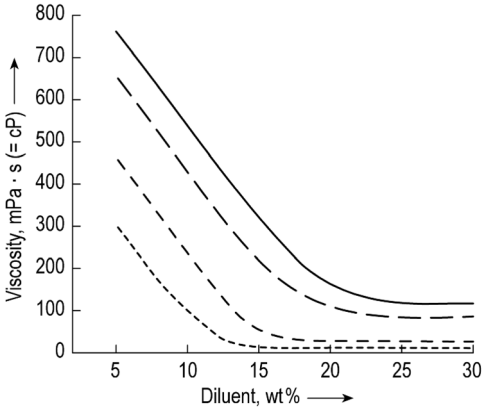


Figure 11. Reduction of DGEBA viscosity by reactive diluents: ——, *o*-cresol glycidyl ether; – – –, butanediol diglycidyl ether; ----------, C_{12}–C_{14} aliphatic glycidyl ether (Epoxide 8); ·····, *n*-butyl glycidyl ether.

and noxiousness. Longer chain alkyls, polyfunctional or aromatic glycidyl ethers such as bisphenol F epoxy, neopentylglycol diglycidyl ether, and triglycidyl ether of propoxylated glycerine are gaining popularity as epoxy reactive diluents. Cycloaliphatic epoxies and glycidyl esters of acids such as neodecanoic acid are also used as reactive diluents.

Acrylics such as 1,6-hexanediol diacrylate and trimethylolpropane triacrylate are nonepoxy multifunctional diluents, which react readily with primary and secondary amines by means of Michael addition of the the amine to the acrylic double bond [190]. They have been used to increase cure speed or to lower cure temperature of epoxy–amine systems. Caprolactone acrylates have also been used for this application [191].

Solvents and plasticizers are *nonreactive* diluents. The most common nonreactive diluents are nonyl phenol, furfuryl alcohol, benzyl alcohol, and dibutyl phthalate. These materials have the advantage of being able to add to the amine side of the system to better balance mix ratios. Nonyl phenol and furfuryl alcohol also improve wet-out and accelerate cure slightly. They are also capable of reacting with the epoxy group under high temperature cure conditions. Benzyl alcohol is a popular diluent used with amine-cured systems. In addition to viscosity reduction, it is also known to increase cure speed. Benzyl alcohol can be used up to 10 wt. % level without significant effects on cured properties. Dibutyl phthalate is widely used as a nonreactive diluent

for liquid resins. However, performance properties will drop off more quickly with increasing levels of nonreactive diluents than with increasing levels of reactive diluents.

Aromatic hydrocarbons, such as toluene or xylene, significantly reduce the viscosity of liquid DGEBA resins, but their use can be accompanied by a 15–25 % decrease in compressive yield strength and a 10–20 % reduction in compressive modulus. If the solvent is trapped in the cured system, solvent resistance is reduced and cracks develop if the resin is used in heat-cured castings. The use of solvents and reactive diluents in epoxy systems is reviewed in References [192] and [193].

19.2. Thixotropic Agents

Thixotropy is the tendency of certain colloidal gels to flow when subjected to shear, and then to return to a gel when at rest. A thixotropic gel can be produced through the addition of either high surface area fillers such as colloidal silicas and bentonite clays or of chemical additives. Thixotropy is desirable in applications such as encapsulation where the coating is applied by dipping. The resin will wet out and coat the object being dipped, but will not run off when the object is removed from the dipping bath.

19.3. Fillers

Fillers are incorporated in epoxy formulations to enhance or obtain specific desired properties in a system. The type and amount of filler used are determined by the specific properties desired. Fillers can also reduce the cost of epoxy formulations. Inert commercial fillers (qv) can be organic or inorganic, and spheroidal, granular, fibrous, or lamellar in shape. The properties of commercial fillers are given in Table 21, and some effects on epoxy resins are shown in Tables 22 and 23. Some formulations contain up to 90 wt. % fillers. For certain applications, fillers can have significant effects on thermoset morphology, adhesion, and the resulting performance.

Table 21. Typical properties of fillers

Name	Composition	Particle shape	Surface area volume	Bulk density, kg/m^3	Characteristics and main use
Marble flour, dolomitic	magnesium–calcium carbonate	granular	medium	1120–1300	general-purpose fillers, particularly recommended for castings requiring machining
Chalk powder	precipitated calcium carbonate	crystalline	high	800–880	
Sand	quartz, feldspar, and subsidiary minerals	spheroidal	low	1500–1700	bulk filler giving high compressive strength and abrasion resistance; difficult to machine
Silica flour	ground quartz	granular	medium	1100–1150	standard filler for large electrical castings; high abrasion resistance; difficult to machine
Mica flour	muscovite[a]	lamellar	high	300–400	filler giving high crack resistance to castings exposed to mechanical and thermal shock
Slate powder	slatea	mainly lamellar	medium	700–900	general-purpose filler giving high abrasion resistance; difficult to machine
Vermiculite[b]	vermiculite[a]	exfolidated laminae	high	100–150	fillers giving lightweight bulk in cores or thick backing to increase the rigidity of thin sections
Phenolic microballoons	phenolic resins	hollow spheres	medium	100–150	
Zircon flour	zircon[a]	granular	medium	1700–1900	filler giving high abrasion resistance; difficult to machine
Aluminum powder	metallic aluminum	granular	medium	1000–1100	filler imparting thermal conductivity, e.g., to prevent excessive temperature buildup in electrical components or in tools for hot-forming plastics
Chopped glass strand[c]	low alkali glass	fibrous	medium	100–250	fillers improving the mechanical strength of prominent edges and thin sections
Hydrated aluminum oxide	alumina trihydrate	granular	medium	700–1300	filler improving wet and dry arc-track resistance and flame retardance

[a] Silicate.
[b] Grain size = 0.15–0.32 cm.
[c] Length = 0.60 cm.

Table 22. Effect of fillers

Advantages	Disadvantages
Lower cost of product	increased weight[a]
Reduced shrinkage upon curing	loss of transparency
Decreased exothermic temperature rise on curing[a]	tendency to entrap air
Increased thermal conductivity[a]	difficulty of machining hard fillers
Reduced expansion and contraction with temperature change	decreased impact and tensile strengths
Higher deflection temperature	increased dielectric constanta and power factor[a]
Improved heat-aging properties[a]	
reduced water absorption[a]	
Improved abrasion resistance[a]	
Increased surface hardness[a]	
Increased compressive strength[a] and Young's modulus[a]	
Increased electric strength[a]	

[a]Certain fillers, such as vermiculite and phenolic microballoons, have the reverse effect.

Filler loading is often limited for a given application by the maximum viscosity allowable and/or the reduction in some mechanical properties such as tensile and flexural strength in the cured material. Viscosity can be modified by heat or by addition of a reactive diluent; heating is preferred since diluents affect overall system properties. Some of the major property enhancements affected by fillers are described below.

Pot life and exotherm. Fillers can increase pot life and lower exotherm of epoxy systems. Fillers reduce the reactant concentration in the formulation and act as a heat sink. Generally, they have higher heat capacities than the epoxy resins. They are also better heat conductors than the resins, and thus help to dissipate exotherm heat more readily. Commonly used fillers are silica, calcium carbonate, alumina, lithium aluminum silicate, and powdered metals.

Thermal shock resistance. Fillers help to increase thermal shock resistance and to decrease the thermal expansion coefficient of an epoxy system by replacing part of the resin with a material that does not change its volume as significantly with temperature variations. Such fillers are clay, alumina, wood flour, sawdust, silica, and mica. Epoxy molding compounds (EMC) can contain up to 90 % of fused silica to manage the thermal stress experienced by encapsulated semiconductors. Powdered metals are used when bonding metals together to better match the coefficient of thermal expansion of the bond with that of the metal, thus minimizing thermal stress.

Shrinkage. Using fillers as a partial replacement for a reactive resin that shrinks on curing can reduce shrinkage of the system. Any inert filler will decrease shrinkage, but the most commonly used are silica, calcium carbonate, alumina talc, powdered metals, and lithium aluminum silicate.

Machinability and abrasion resistance. The addition of fillers can increase the machinability and abrasion resistance of an epoxy resin system by increasing the hardness of the thermoset. Greater hardness leads to a higher energy required to scratch but cleaner cuts upon machining. Fillers used for this purpose are powdered metals, wood flour, calcium carbonate, sawdust, clay, and talc.

Electrical conductivity. In certain applications, conducting fillers are added to epoxy formulations to reduce the good insulating properties of the epoxy systems. The most commonly used fillers are graphite and powdered metals.

Other properties that can be affected with the proper choice of fillers for a specific application include compressive strength, adhesion, arc and tracking resistance, density, and self-lubricating properties.

19.4. Epoxy Nanocomposites

Significant recent developments in polymer property enhancement involve polymer nanocomposites. This is a special class of fillers (mostly clay derivatives) in which the nanoscale, highly oriented particles are formed in the polymer matrix through monomer intercalation and particle aggregate exfoliation [194, 195]. The objective is to combine the performance attributes of both hard inorganic and plastic materials. Significant efforts have been dedicated to develop epoxy nanocomposites in the past decade. Improvements in electrical and

Table 23. Influence of fillers on epoxy resin properties[a]

Filler	Ease of dispersion	Antisettling properties	Cost	Shrinkage	Exotherm	Thermal conductivity	Coefficient of expansion	Deflection temperature	Weight	Machinability	Abrasion resistance	Impact strength	Tensile strength	Flexural strength	Compressive strength	Thixotropy	Dielectric constant	Power factor	Protectionagainst		
																			Electric strength	Mineral acids	Caustic alkalies
Marble flour, dolomitic	P	N	–	–	–	+	–	+	+	O	O	–	–	–	+	O	+	O	O	– –	–
Chalk powder	N		–	–	–	+	–	O	+	O	O	– –	–	–	O	O	+	O	O	– –	–
Sand	P	N	– –	–	–	+	– –	+	+	–	+ +	–	O	O	+	O	+	+	+	O	O
Silica flour		N	–	–	–	+	– –	+	+	–	+ +	–	O	O	+ +	O	+	+	+	O	O
Mica flour	N		–	–	–	+	–	+	+	–	+	+	O	–	O	O	+	+	+	O	O
Slate powder	P	N	–	–	–	+	–	+	+	–	+ +	–	O	O	+	O	+	+	+	O	O
Vermiculite	N	P	– –	O	+	–	O	O	– –	+	– –	– –	– –	– –	– –	O	–	–	– –	[b]	[b]
Phenolic microballoons	P	P	– –	O	+	–	O	O	– –	+ +	– –	– –	– –	– –	– –	O	–	–	– –	[b]	[b]
Zircon flour	P	N	–	–	–	+	– –	+	+ +	– –	+ +	–	O	O	+	O	+	+	O	O	O
Aluminum powder	P	N	O	–	–	+ +	–	+	+	+	–	–	O	O	+	O	+ +	O	– –	–	–
Chopped glass strand	N	P	O	–	–	+	–	+	+	–	+	+	+	+	+	O	+	+	O	O	O
Asbestos fiber	N	P	O	–	–	+	–	O	+	–	+	+	+	O	+	O	+	+	O	O	O
Hydrated aluminum oxide	N	P	–	–	–	+	–	+	+	O	O	– –	–	–	+	O	+	+	O	O	O

[a]Key: P = positive effect; N = negative effect; O = no significant effect; – = significant decrease; – – = large decrease; + = significant increase; + + = large increase; · = fillers taken for arbitrary standard for comparison of dispersibility and setting.
[b]Porosity of filler reduces protection provided by resin.

Table 24. Effect of flexiblizers

Flexiblizers	Concentration, %	Advantages	Disadvantages
Poly(propylene glycol) diglycidyl ether	10–60	low viscosity, good flexibility	poor water resistance fair impact resistance
Polyaminoamides	30–70	good abrasion resistance, good flexibility	fair chemical resistance
Liquid polysulfides	10–50	good corrosion resistance, excellent flexibility	odor Poor heat resistance tendency to cold flow
Aliphatic polyester adducts	10–30	good water resistance fair flexibility over a range of temperatures	high viscosity

mechanical properties, chemical resistance, high temperature performance, and flame retardancy have been reported. Other silica-based organic hybrids have been developed [196] for military and aerospace applications.

The emerging field of nanotechnology has produced new materials such as the carbon nanotubes, which are filaments of carbon with atomic dimensions. Recent publications claimed exceptional property enhancement from nanotube-laced epoxy (hardness, electrical and heat-conducting properties) [197]. However, cost remains a barrier for commercialization.

19.5. Toughening Agents and Flexiblizers

Some cross-linked, unmodified epoxy systems exhibit brittleness, poor flexibility, and low impact strength and fracture resistance. Modifiers can be used to remedy these shortcomings. However, there usually will be some sacrifices of properties. In general, there are two approaches used to modify epoxies to improve these features.

1. *Flexiblization.* Aliphatic diepoxide reactive diluents enhance the flexibility or elongation by providing chain segments with greater free rotation between cross-links. Polyaminoamide hardeners, based on aliphatic polyamines and dimerized fatty acids, perform similarly. Liquid polysulfide polymers possessing terminal mercaptan functionality improve impact properties in conjunction with polyamine hardeners.

   Flexible chain segments are incorporated in an epoxy resin by many means [189]. One approach is the incorporation of oligomeric aliphatic polyesters containing carboxylic acid end groups, forming an epoxy resin adduct. This is one of the reasons that epoxy–polyester hybrid powder coatings have become very popular. The effects of flexiblizers are shown in Table 24. Flexiblization can enhance elongation of the system but is often accompanied by a reduction of glass-transition temperature, yield stress, and elastic modulus. Other properties (e.g. water absorption and thermal and chemical resistance) may also be affected.
2. *Toughening* refers to the ability to increase resistance to failure under mechanical stress. Epoxies derive their modulus, chemical, and thermal resistance properties from cross-link density and chain rigidity. Increasing cross-link density to meet higher thermal requirements (T_g) often comes at the expense of toughness. Toughening approaches for epoxies [199–202] include the dispersion of preformed elastomer particles into the epoxy matrix and reaction-induced phase separation of elastomers or thermoplastic particles during cure.

   Elastomers such as carboxyl-terminated poly(butadiene-*co*-acrylonitrile)s (CTBN) have been popular tougheners for epoxies. Toughening by elastomers can be attributed to the incorporation of a small amount of elastic material as a discrete phase of microscopic particles embedded in the continuous rigid resin matrix. The rubbery particles promote absorption of strain energy by interactions involving craze formation and shear deformation. Craze formation is promoted by particles of 1–5 μm size, and shear deformation by particles > 0.5 μm. Systems possessing both small and large particles, i.e., bimodal distribution, provide maximum toughness [203]. The rubber is incorporated in the epoxy resin in a ratio of 1 : 8 in the presence of an esterification catalyst. The product is an epoxy ester capped with epoxy

groups. The adduct is then formulated with unmodified resin and cured with standard hardeners and accelerators. Phase separation, of the adduct occurs during the curing process, resulting in the formation of segregated domains of elastomer-like particles covalently bound to the epoxy resin matrix. Optimum particle size and particle-size distribution, phase separation, and phase morphology are crucial for the development of desirable properties of the system. If the elastomer remains soluble in the epoxy matrix, it serves as a flexiblizer and reduces the glass-transition temperature significantly. Some reductions in T_g and modulus are typical of CTBN-modified epoxies. Amine-terminated poly(butadiene-*co*-acrylonitrile)s (ATBN) are also available [68].

Elastomer-modified epoxy resins are used in composites and structural adhesives, coatings, and electronic applications. A similar approach to toughen epoxy vinyl esters using other elastomeric materials has been reported [204]. Other elastomer-modified epoxies include epoxy-terminated urethane prepolymers, epoxy-terminated polysulfide, epoxy–acrylated urethane, and epoxidized polybutadiene. Preformed dispersions of epoxy-insoluble elastomers have been developed and reported to achieve toughening without T_g reduction [205, 206].

Other epoxy toughening approaches include chemical modifications of the system either through the epoxy backbone and/or crosss-linker. Dow Chemical developed a cross-linkable epoxy thermoplastic system (CET) [207]. The concept involves introducing stiffer polymer segments into the network structure to maintain the glass-transition temperature while allowing cross-link density reduction to improve toughness. Thermoplastics, core-shell rubbers (CSR), and liquid crystal polymers (LCP) have also been used. Semi-interpenetrating network (IPN) approaches involve formation of a dispersed, cross-linked epoxy second phase in a thermoplastic matrix. The systems were reported to have good combinations of toughness, high T_g, high modulus, and processability.

Incorporation of block copolymers has been shown to improve toughness of certain epoxy systems [208]. More recently, nanocomposites and self-healing epoxy systems [209] represent new approaches to develop more damage-tolerant epoxies.

Through the proper selection of resin, curing agent, and modifiers, the cured epoxy resin system can be tailored to specific performance characteristics. The choice depends on cost, processing and performance requirements. Cure is possible at ambient and elevated temperatures. Cured epoxies exhibit good combinations of outstanding properties and versatility at moderate cost: excellent adhesion to a variety of substrates; outstanding chemical and corrosion resistance; excellent electrical insulation; high tensile, flexural, and compressive strengths; good thermal stability; relatively low moisture absorption; and low shrinkage upon cure. Consequently, epoxies are used in diverse applications.

20. Coatings Applications

Commercial uses of epoxy resins can be generally divided into two major categories: protective coatings and structural applications. U.S. consumption of epoxy resins is given in Figure 12. The largest single use is in coatings (> 50 %), followed by structural composites. Among the structural composite applications, electrical laminates contribute the largest epoxy consumption. A similar trend is observed for the European market, but the Asian consumption is heavily tilted toward electrical laminate and electronic encapsulant applications [210]. Electrical and electronic applications account for the largest consumption of epoxy resins in Japan (> 40 %). In 2000, it is estimated that the Asia-Pacific region consumed up to 70 % of all epoxies used in electrical laminate production worldwide. While the overall epoxy markets continue to grow at a steady pace over the past two decades, more rapid growth has occurred in powder coatings, electrical laminates, electronic encapsulants, adhesives, and radiation-curable epoxies.

The majority of epoxy coatings are based on DGEBA or modifications of DGEBA. Chemical and corrosion-resistant films are obtained by curing at ambient and/or elevated temperatures. Ambient temperature cured coatings primarily involve cross-linking of the epoxy groups in mostly two-package systems, while elevated

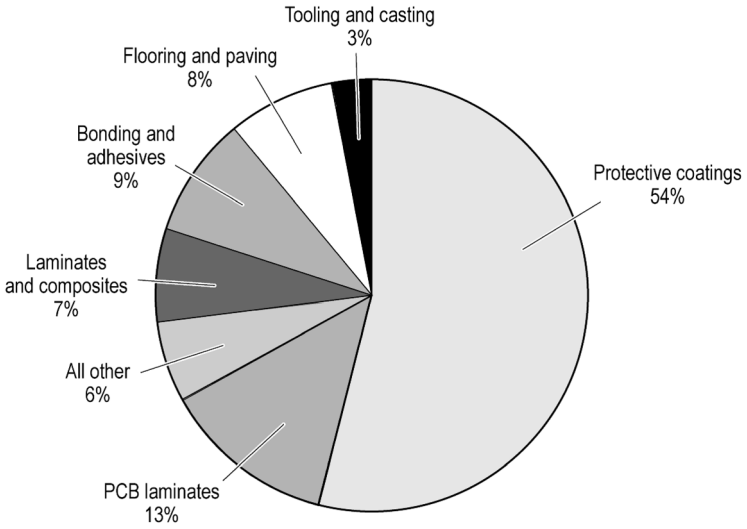


Figure 12. End-use markets of epoxy resins (U.S. data, 2000)

temperature cured coatings in one-package systems take advantage of the reactivity of both the epoxy and the secondary hydroxyl groups. As a class, epoxy coatings exhibit superior adhesion (both to substrates and to other coatings), chemical and corrosion resistance, and toughness. However, epoxy coatings have been employed mainly as primers or undercoats because of their tendency to yellow and chalk on exposure to sunlight.

Epoxy-based coatings are the preferred and dominant choices for cathodic electrodeposition of automotive primers, marine and industrial maintenance coatings, and metal container interior coatings. Use of epoxy flooring for institutions and industrial buildings has been growing at a steady rate as the industry becomes more aware of its benefits.

Solvents are commonly used to facilitate dissolution of resins, cross-linkers, and other components, and for ease of handling and application. Although most of the epoxy coatings sold in the 1970s were solventborne types, they made up only 40 % of epoxy coating consumption in 2001 [211]. Economic and ecological pressures to lower the volatile organic content (VOC) of solventborne coatings have stimulated the development of high solids, solvent-free systems (powder and liquid), and waterborne and radiation-curable epoxy coatings technologies [212]. These environmentally friendly coating technologies have experienced rapid growth in the past decade. For example, epoxy powder coatings have been growing at rates exceeding those of other coating technologies as new applications such as automotive primer-surfacer and low temperature cure coatings for heat-sensitive substrates are developed. Radiation-curable liquid coatings based on epoxy acrylates and cycloaliphatic epoxies have also been growing significantly over the last decade. The current distribution of coating technologies is summarized in Figure 13.

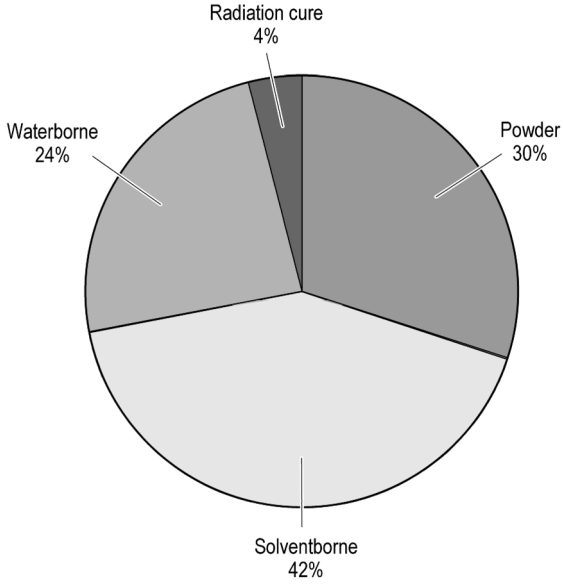


Figure 13. Global epoxy coating application technologies [211]

20.1. Coatings Application Technologies

20.1.1. Low Solids Solventborne Coatings

These traditional low solids coatings contain less than 60 % solids by volume (typically 40 %). Their advantages include established application equipment and experience, fast drying and cure at ambient temperatures and excellent film formation at extremely fast cure conditions like those used in coil coatings (< 30 s, > 200 °C). However, because of stricter VOC regulations, solvent-based coatings have been losing market share steadily to more environmentally friendly technologies.

20.1.2. High Solids Solventborne Coatings

High solids coatings contain 60–85 % by volume of solids. They are mostly based on standard LERs or low molecular weight SERs modified by reactive diluents, low viscosity multifunctional aliphatic epoxies, or bisphenol F epoxy resins. High film build is one key advantage of high solids coatings. Examples include the coal-tar epoxy coatings that contain up to 85 % solids used in industrial protective coatings.

20.1.3. Solvent-Free Coatings (100 % Solids)

Ecological concerns have led to increasing uses of these materials. Low viscosity LERs based on bisphenol A and bisphenol F epoxies are often used in combination with reactive diluents. The advantages include high buildup in a single application, minimization of surface defects owing to the absence of solvents, excellent heat and chemical resistance, and lower overall application costs. Disadvantages include high viscosity, difficulties to apply and produce thin films, poor impact resistance and flexiblity, short pot life, and increased sensitivity to humidity. Weatherable cycloaliphatic epoxies can be used to formulate solvent-free thermally curable coatings because of their low viscosities [213].

20.1.4. Waterborne Coatings

In the switch from solventborne to waterborne systems, epoxies are successfully bridging the gap largely by adaptation of conventional resins. Waterborne coatings accounted for almost 25 % of epoxy coating consumption in 2001.

In addition to the waterborne epoxy dispersions which are typically supplied by epoxy resin producers, significant advances in waterborne coatings have been made by coatings producers such as PPG Industries, ICI Paint, and others utilizing modified epoxies. PPG coatings are used in cathodic electrodeposition systems that are widely accepted for automobile primers. Many patents have been issued for this important technology [214]. The Glidden Co. (now ICI Paint) developed a waterborne system for container coatings based on a graft copolymerization of an advanced epoxy resin and acrylic monomers [215]. These two waterborne epoxy coatings were significant breakthroughs in the coatings industry in the 1970s and are still widely used today.

For ambient temperature cure applications such as industrial maintenance and marine coatings, LERs or low molecular weight SERs (type 1 resin) are dispersed in water with a surfactant package and small amounts of co-solvents [216]. Some producers offer waterborne curing agents that, typically, are salts of polyamines or polyamides. Key disadvantages include higher costs, slow cure at ambient and humid conditions, and tendency to cause flash rush. In addition, expensive stainless steel equipment are required for application. Recent developments include the elimination of co-solvents in some epoxy dispersions [217]. Custom synthesized acrylic latexes have shown promise when thermally cured with cycloaliphatic epoxies [218]. While the overall volume is still relatively modest (estimated at < 20,000 MT in 2000 for the global market), it is expected that future growth rate for this segment will be much higher than standard epoxy resins, particularly in Europe where environmental pressures are stronger.

20.1.5. Powder Coatings

Epoxy-based powder coatings exhibit useful properties such as excellent adhesion, abrasion resistance, hardness, and corrosion and chemical resistance. The application possibilities are diverse, including metal finishing, appliances, structural rebars, pipes, machinery and

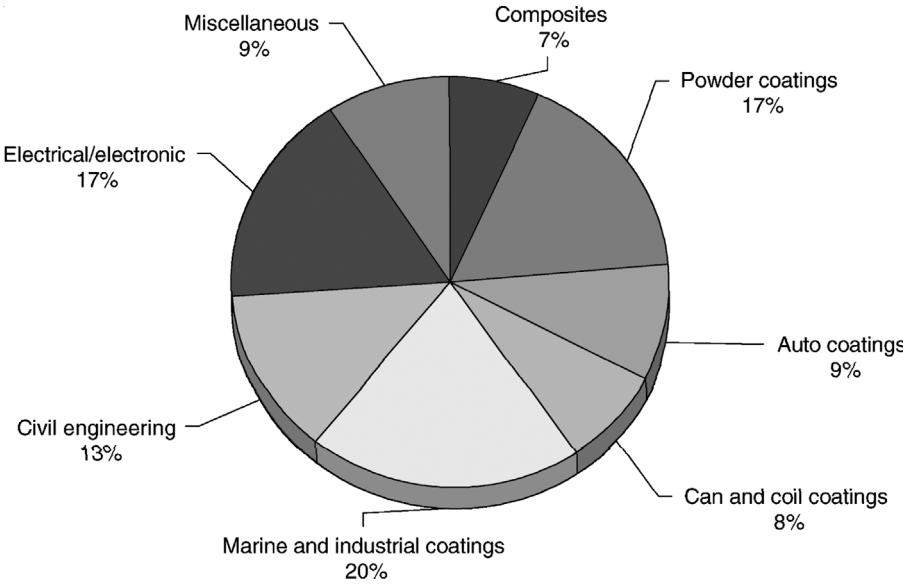


Figure 14. Major global epoxy resin markets (Dow Chemical data, 2001)

equipment, furnitures, and automotive coatings. Together, these applications accounted for 30 % of epoxy coatings (Fig. 13) and 17 % of epoxy resin consumption globally in 2001 (Fig. 14). This is a high growth segment of epoxy coatings (see → Paints and Coatings, 1. Introduction).

The development of highly reactive powder systems which cure using low energy (150 °C) and the possibility of economical thin films (30–40 μm) have made powder coatings competitive with waterborne and high solids systems. Powder coatings can be applied by fluidized-bed (thick films, 50–150 μm) or electrostatic spray (thin films, 30–40 μm).

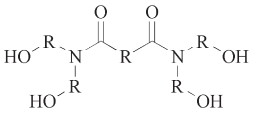
In powder coatings, epoxies are continuing to grow at rates exceeding other technology segments mainly because of the 100 % solids feature, improved coverage, and recyclability of overspray materials. Pipeline projects, important because of worldwide energy problems, are significant consumers of epoxy powder coatings. The value of improved service life is being increasingly accepted even at the somewhat higher material cost of epoxy systems. Four types of epoxy resin systems are commonly used as powder coatings.

1. *Epoxy powder coatings* are based on SERs of intermediate molecular weight (800–2000 EEW). They provide good flow and reactive terminal epoxy functionality. The properties of these thermoset coatings depend on the curing agents, which are friable solids such as dicyandiamide (DICY), phenol-terminated epoxy hardener, and anhydrides. Epoxy powder coatings are generally employed for interior or undercoat uses. Functional epoxy powder coatings are thick films (0.1–0.5 mm, 5–20 mil) used to protect automotive and truck parts, pipe, and concrete reinforcing bars. Fusion-bonded-epoxies (FBE), first developed by 3M Co., are epoxy powder coatings used to protect oil and gas pipelines where long-term corrosion protection under adverse conditions (for example, the Alaska oil and North Sea underwater pipelines) is critical. The performance requirements for FBEs are challenging as the hard, cross-linked coatings are expected to survive the pipe bending/unwinding processes and handling abuses in the field. FBEs are also used to protect rebars embedded in critical concrete structures such as bridges, tunnels, and highways. Their primary function is to extend the lifetime of the concrete structures (5–10 years when built with uncoated rebars) to 20–30 years, reducing maintenance and repair costs. Epoxy powder coatings also serve as electrical insulation for bus bars, motor

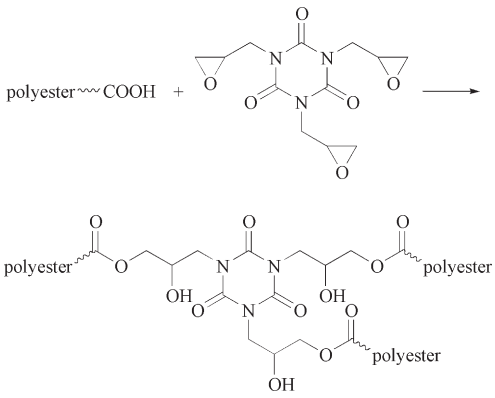
armatures, and similar articles. Decorative epoxy coatings are applied as a thin film (0.02–0.1 mm, 1–5 mil) and used mainly in appliance and general metal product applications. Coating for heat-sensitive substrates is an emerging market for epoxy powders.

2. *Epoxy–polyester hybrids* are mixtures of solid epoxy resins based on bisphenol A and acid-terminated polyester solid resin (25–85 acid equivalent weight). These hybrids are typically less expensive than the epoxy-based powder coatings and offer improved weatherability, and better resistance to overbake yellowing while retaining many of the properties of the standard epoxies. Corrosion resistance is equivalent to epoxy powders in most cases, although solvent and alkali resistance is inferior. One significant new application of the epoxy–polyester hybrids is the primer-surfacer coating for automobiles. Primer-surfacer coatings based on epoxy–polyester hybrid is applied in between the epoxy primer and the topcoats. Its functions are to provide intercoat adhesion and to improve the chip resistance properties of the coatings. Automakers have also found that the epoxy–polyester hybrid primer-surfacer give a smoother surface under the top coats, resulting in a better quality appearance [219]. Epoxy–polyester hybrids have experienced exceptional growth in the global market in the past decade.
3. *Polyester–TGIC,* a third type of epoxy powder coating, is based on a mixture of polyester polycarboxylic acids (18–37 acid equivalent mass) and triglycidyl isocyanurate (TGIC). The TGIC-cured powder coatings have excellent UV resistance, good gloss and color retention, as well as good adhesion and mechanical properties. They were originally developed in Europe for coating metal window frames and buildings, exterior siding, outdoor hardware, high quality outdoor furniture, and other articles requiring superior outdoor durability. These polyester–TGIC powder coatings have gained popularity worldwide.

   In recent years, there have been concerns over toxicity of TGIC, and a number of potential replacement compounds have been developed. Among these, β- hydroxyalkylamide (HAA), trade named Primid by EMS-Chemie is gaining in popularity, particularly in Northern Europe.



Hydroxy alkylamide (HAA)



4. *Glycidyl methacrylate–acrylic.* These powder coatings are based on copolymers of glycidyl methacrylate (GMA) and acrylic monomers. They are often thermally cured with dodecanedioic acid (DDDA) and are used in automotive primer-surfacer and clear coats of luxury automobiles such as BMW [220, 221].

Recent developments in powder coatings based on epoxy include UV-curable GMA–acrylic coating for automotive parts; lower temperature cure coatings for heat-sensitive substrates such as wood [222, 223] and plastics; and dual cure (thermal/UV) systems.

20.1.6. Radiation-Curable Coatings

UV and electron beam (EB) radiation curable coatings [74] is a fast-growing segment of epoxy coatings, increasing at 8–10 % annual growth rate. The technology is environmental-friendly. No solvent is used, and volatile emission is essentially eliminated. Cure is highly effective and energy-efficient at ambient temperatures, lending the technology highly

applicable to heat-sensitive substrates such as wood, plastics, and paper. Capital cost requirements are low especially when compared to new thermal ovens for solventborne and waterborne coatings. EB cure is a relatively new technology which initiates cure via highly energetic electron beams, and unlike UV cure, no photoinitiator is needed. However, EB capital cost is higher.

Epoxy acrylates are widely used as the base resin in many UV-initiated free-radical cure varnish formulations. Epoxy acrylates provide varnishes with excellent scuff resistance, high gloss, and good adhesion. Major markets are overprint varnishes for papers (books, magazines, cards, labels, etc) and exterior can coatings. Wood furniture and particle board are new but growing markets for this technology. Alternatively, cycloaliphatic epoxies can be UV-cured via a photo-initiated cationic mechanism. They are used in metal container exterior overprint varnish and inks, and high performance electronic applications. While cycloaliphatic epoxies are more expensive than epoxy acrylates, they offer several advantages: better adhesion to metals, fewer hazards in handling, and continued curing in the dark (which is important in certain applications). A related and high value market is inks and resists, where radiation and heat-curable epoxies and epoxy acrylates are used. As discussed in the powder coatings section, radiation-curable epoxy powder coatings are being developed for a number of applications.

20.2. Epoxy Coatings Markets

The major global market segments of epoxies are represented in Figure 14. The marine and industrial protective coating is the largest market for epoxy coatings, followed by powder coatings, automotive, and container coatings.

20.2.1. Marine and Industrial Maintenance Coatings

The combined marine and industrial maintenance coatings application constitutes the largest epoxy coating market segment globally. While the end-use markets and application requirements are different, the basic epoxy systems utilized in these two markets are quite similar. The basic function of these coatings is to protect metal and concrete structures from degradation in aggressive environments for extended periods of time. The long service life of the coating and/or extended intervals between repairs are critical requirements, especially for marine applications because of the high costs of dry-docking of ships for re-painting. The excellent corrosion, abrasion, and chemical resistance properties of epoxy coatings allow their dominant position in these markets. They are used in new construction as well as in maintenance and repair works. Examples are corrosion-resistant coatings for ships, shipping containers, offshore oil rigs and platforms, transportation infrastructures such as bridges, rail car coatings, coatings for industrial storage tanks, and primers for light industrial and agricultural equipment.

Most coatings used in these markets are two-component systems applied and cured at ambient conditions. LERs and low molecular weight SERs based on bisphenol A and bisphenol F epoxies are commonly used [224]. Aliphatic polyamines, adducts of epoxy resins with aliphatic and aromatic amines, ketimines, phenalkamines, amidoamide, and polyamide resins are employed as curing agents. The working pot life of the amine–epoxy resin systems depends on the curing agent, solvents, catalysts, and temperature. High solids solventborne coatings are most popular. Tighter VOC regulations have facilitated the development of lower VOC, 100 % solids, and waterborne epoxy coating systems. Important types of epoxy coatings in this segment include the following.

1. *Two-component epoxy–amine coatings* are used primarily as a primer or mid-coat over the inorganic zinc-rich primer coating. High solids epoxy mastics can be applied over contaminated substrates and form thick, good barrier coatings. These coatings account for the majority of epoxies used in marine and industrial protective coatings markets.
2. *Organic (epoxy) zinc-rich primers* are used in place or to repair imperfections of the inorganic zinc-rich primer. Their advantages over inorganic zincs include improved adhesion to the epoxy primer coating and better tolerance to poor surface cleaning.

3. *Coal-tar epoxies* are historically some of the most popular high solids epoxy coatings, having excellent water barrier, chemical resistance properties, and low costs. They are typically cured with polyamides and are used as ship bottom or primer coatings for tanks, pipes, and steel pilings. However, their use has been declining or banned in certain countries because of concerns and regulations over the toxicity of coal-tar as a suspected carcinogen.
4. *Epoxy esters* are used as primers in less demanding applications. Their performance is inferior to epoxy–amine systems but their costs are lower.
5. *Waterborne coatings.* These are based on two-component epoxy–polyamine/polyamidoamine or epoxy–acrylic latex hybrids. One limitation of the waterborne systems is their poor cure in high humidity conditions. They have made some penetration in industrial maintenance coatings and are expected to grow more significantly in the future.

Epoxy coatings are known to have poor weatherability and often chalk when exposed to sunlight for long periods of time. Over the years, significant efforts have been dedicated to develop weatherable epoxy resin systems such as hydrogenated bisphenol A epoxy cured with siloxane-modified epoxy curing agent [225], but higher costs and compromises in curing characteristics and performance limited their commercialization. Today, most industrial structures are only coated with epoxy coatings which can last up to 10–15 years. When appearance is critical, epoxy primers are often topcoated with aliphatic isocyanate based polyurethane coatings. Marine coatings have very diverse requirements depending on the specific functions of the parts of the ship being coated. For example, ship decks are coated with antislip, abrasion- and corrosion-resistant epoxy coatings; the cargo tanks require highly chemical-resistant coatings; ship exteriors above the water line are coated with epoxy primers followed by urethane top coats for appearance; underwater ship bottoms are coated with multilayer coatings including a zinc-rich or epoxy primer, epoxy intermediate coats and antifouling top coats based on vinyls or acrylates.

Concerns over the safety of large tankers have led to regulations and construction of double-hull ships, increasing epoxy coatings consumption. While Japan was the center of the ship-building industry since the 1980s, Korea and China have emerged as major players in this market because of their low cost advantages. According to data from the Japanese Ship Building Industry Association, Korea has overtaken Japan as the global leader in ship building in the year 2000. The combined market shares of these three Asian countries now account for more than 80 % of the global ship-building business. In addition, China already owns 80 % of the world shipping container construction business.

The migration of ship building yards to Korea and China has led to significant increases in marine epoxy coatings consumption in that region, and has resulted in increased demands for lower temperature cure (LTC) epoxy systems. Traditional ambient-cure epoxy coatings do not cure well at temperatures below 10 °C (50 ° F). They often require excessive cure time, affecting productivity and performance, and shorten the painting season in colder climates such as in Korea. A number of LTC epoxy coating technologies have been developed. Uses of accelerators such as tertiary amines, organic acids or alkyl-substituted phenols have allowed cures at 4.45 °C (40 ° F) temperature range. However, shorter pot-life is a limitation of these systems. Newer epoxy coatings utilizing cycloaliphatic amines, phenalkamines as curing agents can cure at temperatures of about 0 °C (30 °F). For industrial protective coatings, systems developed by Ameron International (Amerlock 400) and ICI-Devoe (Bar-Rust 235) are claimed to achieve LTC down to −18 °C (0 °F).

Other new technology developments in this market segment include surface-tolerant epoxy coatings for aged or marginally-prepared surfaces, interval-free epoxy coatings to extend coating service life, mineral spirit-soluble epoxy coatings for shipping containers repairs, and styrene-free coatings to replace foul-smelling and regulated organic solvents such as toluene and xylene in coatings for new shipping containers.

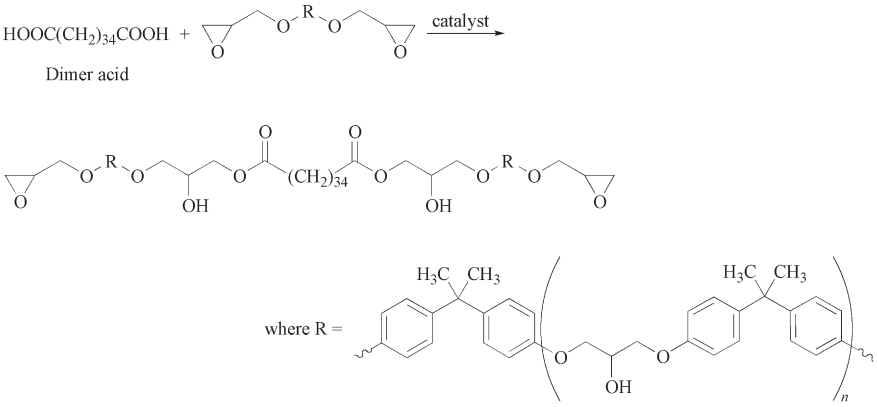
20.2.2. Metal Container and Coil Coatings

Metal container and coil coatings represent a major outlet for epoxy resins considering there are more than 100 billion beverage cans and 30 billion food cans produced annually in the United States. Globally, the metal can market is estimated at over 300 billion cans. While the majority of metal containers coated with epoxy coatings are aluminum and steel food and beverage cans, coatings for drums, pails, and aerosol spray cans are included in this market segment. Coil coating is a highly efficient, automated coating process used to produce precoated metal coils, which are subsequently stamped and fabricated to parts. The majority of epoxy coil coatings are used to produce metal can ends and can bodies with smaller amounts going to building products, appliance panels, transportation, and metal furniture applications.

Higher molecular weight SERs (EEW = 2000–4000), which contain predominantly secondary hydroxyl groups, are used in these coatings where maximum resistance to chemicals, good flexibility, freedom from off-taste, good thermal stability, blush (hydrolysis) resistance, and the ability to hold corrosive foods and beverages are needed. In addition, compliance with food regulations such as the Food and Drugs Administration (FDA) rules is required for food and beverage interior can coatings. This application is where the unique combination of properties of epoxy resins stand out.

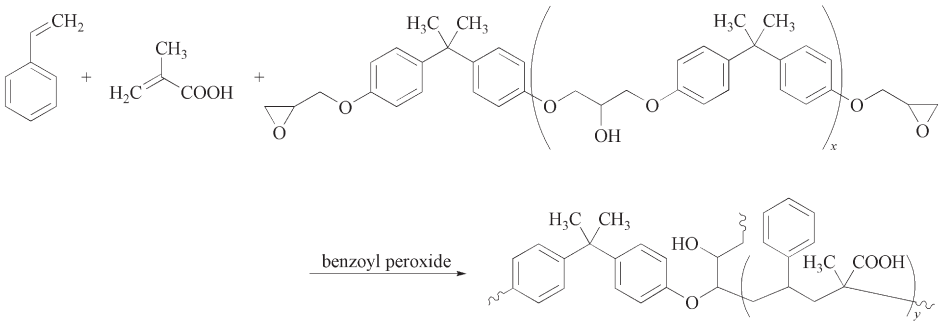
The can and coil coatings, generally, are crosslinked with phenol, melamine, or urea–formaldehyde condensation products at elevated temperatures (150–200 °C) with acid catalysts. Normal epoxy–amino resin weight ratios are epoxy–urea, 70 : 30; epoxy–benzoguanamine, 70 : 30; epoxy–melamine, 80 : 20 and 90 : 10. Increasing crosslinker levels give improved thermal and chemical resistance at the sacrifice of coating flexibility and adhesion.

Phenol–formaldehyde resole cured epoxies have excellent chemical resistance and hardness and are the popular choices for drum coatings. Their golden color is affecting their uses in food can coatings because of the increasing popularity of the water-white coatings based on melamine–formaldehyde resins, which are perceived to be “cleaner” by the consumers and the food industry. Melamine–formaldehyde resins are the primary crosslinker for beer and beverage interior can coatings. Urea–formaldehyde resins can be cured at lower temperatures and faster speed than phenol and melamine–formaldehyde resins and are widely used in the coil coatings industry where cure schedules are extremely short. However, their use has been declining because of concerns over the release of formaldehyde fumes. Recently, there have been regulatory issues in the can industry concerning worker exposure to volatile formaldehyde emissions from the formaldehyde resins. A number of new, formaldehyde-free coating formulations have been introduced by coating suppliers [226].



High solids binders for metal can coatings have been developed on the basis of dimer acid modification of epoxy resins, whereby a flexible C_{34} difunctional acid is used to esterify a conventional diepoxide resin [227]. The resultant epoxy ester possesses a sufficiently lower viscosity to provide binders with solids contents > 70 vol. %. Curing is accomplished by a melamine–formaldehyde resin (Cymel 303, from Cytec) in conjunction with phosphoric acid catalyst.

In the 1970s, a waterborne coating system for aluminum beverage can coatings was developed by the Glidden Company (ICI Packaging Coatings) on the basis of a graft copolymerization of an advanced epoxy resin and acrylic monomers [228, 229]. The acrylic–vinyl monomers are grafted onto preformed epoxy resins in the presence of a free-radical initiator; grafting occurs mainly at the methylene group of the aliphatic backbone on the epoxy resin:



The polymeric product is a mixture of methacrylic acid–styrene copolymer, SER, and graft copolymer of the unsaturated monomers onto the epoxy resin backbone. It is dispersible in water upon neutralization with an amine, and cured with an amino–formaldehyde resin. The technology revolutionized the can coatings industry in the 1970s which was primarily based on low solids, solventborne coatings. This waterborne epoxy coating system and its variations continue to be the dominant choices for interior beer and beverage can coatings globally today. They are also formulated with phenol–formaldehyde resole and used as interior coatings in the new two-piece food can plants in the United States.

UV-curable coatings based on cycloaliphatic epoxies are used on the exterior of some beer, beverage, and food cans, as well as food and composite can ends. The technology is environmentally friendly and energy-efficient.

Coil coatings have been gaining in the appliance market. More OEMs have turned to precoated metal coils as an efficient manufacturing alternative to produce appliance panels, eliminating the needs for postformed coating processes. PVC organosol (copolymers of vinyl chloride and vinyl acetate) coatings for coil-coated can ends and bodies have been under environmental pressures and epoxy has been gaining as PVC coatings are replaced [230].

The growth of can coatings has been steady globally because of the expansion of new can plants in Asia-Pacific and South America in the 1980s and early 1990s, which made up for the stagnant growth of the U.S. market. However, growth of plastic bottles based on PET [poly (ethylene terphthalate)] has recently eroded the metal can position in beverage packaging, affecting epoxy can coatings growth. In addition, new can fabrication technologies utilizing other polymers are being developed which may challenge the dominant position of epoxy coatings in metal cans.

In the 1980s, Toyo Seikan Co. of Japan successfully developed and commercialized TULC (Toyo Ultimate Laminate Cans), a revolutionary technology in which cans are fabricated using a deep draw process from metal coils laminated with thermoplastic polyester films [231, 232]. No epoxy coating is used in this technology. Special polyester film combinations were used (in a much higher thickness than typical epoxy coatings) to facilitate the demanding deep draw process while maintaining all of the other requirements of can coatings. This technology is a significant breakthrough with claimed benefits such as no solvent emission, lower energy and water usage, and

excellent quality cans. The costs however are significantly higher than those of conventional cans, and the technology has found widespread application only in Japan where higher packaging costs are acceptable. Other companies such as British Steel have been actively promoting laminated cans as a way to produce differentiable packaging like shaped cans with very limited success. Higher cost is the biggest barrier to their broad commercialization. Recent developments include attempts to fabricate can ends and bodies from extrusion-coated metals by companies such as Alcoa. Thermoplastics like modified polyesters are providing challenges to epoxies in these new technologies due to their excellent formability. However, their resistance against aggressive drinks, foods, and retort are inferior to those of epoxies.

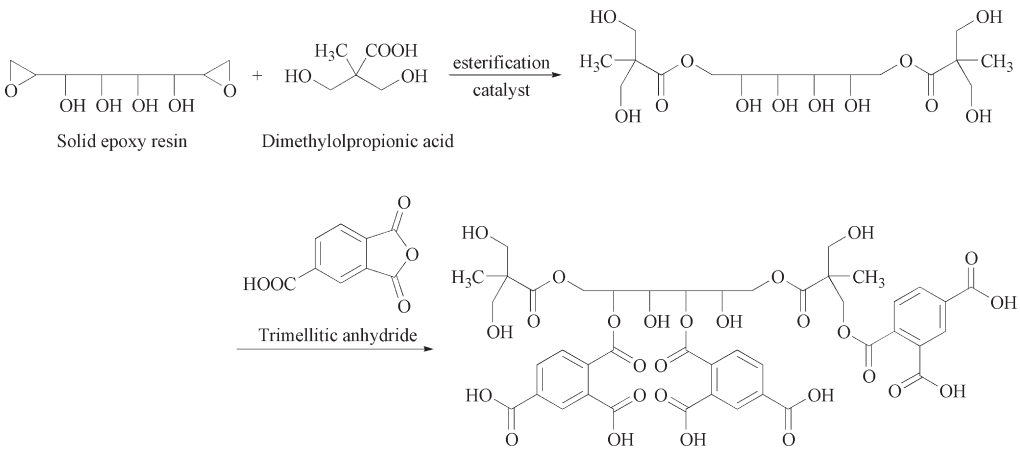
More recently in the United States, Campbell Soup Co. has successfully launched a new line of microwaveable, ready-to-eat plastic cans. These cans are constructed from a molded thermoplastic can body (polypropylene, high density polyethylene) and an easy-open-end (EOE) of coated metal. In addition, flexible pouches have made inroad as an alternative for metal cans in certain markets such as packaged tuna fish.

Recently, there have been debates in the can coatings industry concerning the potential health effects of residual bisphenol A and DGEBA in epoxy can coatings. The resin suppliers, can coatings producers, and can makers have jointly formed an industry group to coordinate a number of studies on this issue. Results indicated that epoxy can coatings, when properly formulated and cured, are safe and in compliance with global food contact regulations. Current regulatory guidelines such as the Specific Migration Levels for Europe set extractable limits of 1 mg/kg for DGEBA and 3 mg/kg for bisphenol A. Additional information is available in the references [233, 234]. Some polyester coatings have been developed as epoxy coating alternatives, but high costs and inferior pasteurization-resistance limit their uses [235].

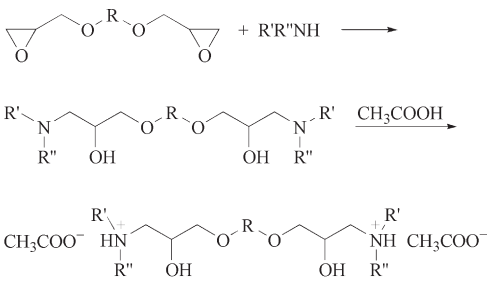
20.2.3. Automotive Coatings

Automotive coatings are another major application for epoxy resins. The excellent adhesion and corrosion resistance properties of epoxies make them the overwhelming choice for automotive primers. One new, growing application is the use of epoxy–polyester or acrylic–GMA powders in primer-surfacer coatings. In addition, glycidyl methacrylate (GMA) is used as a comonomer in etch-resistant liquid top coats containing acrylic acid/anhydride [236] and in GMA-acrylic powder coatings for clear coats and automotive parts [220]. Epoxy powder coatings for automobiles are expected to grow significantly in the near future.

Electrodeposition processes using epoxy-based automotive primers were developed for anodic and cathodic systems. Anodic systems (AED) employ carboxylated epoxy resins neutralized with an amine. A typical binder is prepared by the esterification of the terminal epoxy groups of a solid resin (EEW = 500) with stoichiometric quantities of dimethylolpropionic acid to form a hydroxyl-rich resin. This intermediate is subsequently treated with a cyclic anhydride to form an acid functionalised polymer, which is then neutralized with the amine.

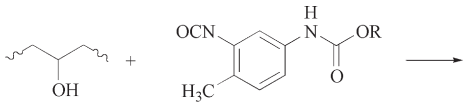


Significant advances in waterborne automotive coatings have been made by PPG Industries and others utilizing epoxies as co-resins in the 1970s. These coatings are used in cathodic electrodeposited (CED) systems, which are widely accepted for automobile primers. Many patents have been issued for this important technology [214]. Cathodic systems, which have superior corrosion resistance, have replaced anodic systems. A typical epoxy binder for cathodic electrodeposition is prepared by first forming a tertiary amine adduct from an epoxy resin and a secondary amine, followed by neutralization with an acid to form a water-soluble salt:

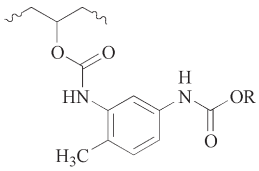


water soluble

Cross-linking is achieved by reaction of the hydroxyl groups with a blocked isocyanate, which is stable at ambient temperature.



Partially blocked cross-linking agent



Blocked isocyanate cross-linking agent

where R = 2-Ethylhexyl

The ability of the CED coating system to thoroughly coat all metal surfaces of the car and the resultant superior corrosion resistance was a significant breakthrough, enabling its dominant position in the global automotive industry.

PPG has continued to develop new generations of improved CED epoxy coatings [237]. Dupont, BASF, and a number of Japanese coating companies such as Nippon Paint and Kansai Paint have contributed to the epoxy primer coating technology by developing advanced coating systems to meet higher performance and regulatory requirements of the automotive industry [238–240]. The popular pigment systems based on heavy metals such as lead and chromium in primer coatings have been recently banned in certain countries, leading to efforts to develop new formulations with improved corrosion resistance. Nippon Paint has proposed pigment-free CED systems [241].

Epoxy–polyester and acrylic–GMA powder coatings have made significant advances recently in the area of primer-surfacer coatings. They offer better adhesion to topcoats and significantly improve chip resistance compared to the traditional liquid polyester and epoxy ester coatings. This translates to warranty cost reductions, leading many car manufacturers to convert to the powder coating technologies.

While epoxy coatings based on DGEBA and other aromatic epoxies are limited to undercoats and under-the-hood applications because of their poor UV resistance, GMA-based coatings have been developed for improved acid-etch performance automotive top coats. They compete with traditional acrylic polyol–melamine topcoats that are highly susceptible to acid rain-induced hydrolysis, and offer better mar resistance and less worker exposures than isocyanate-based topcoats [242, 243]. BMW has coverted to a GMA–acrylic powder clear coat developed by PPG.

20.3. Inks and Resists

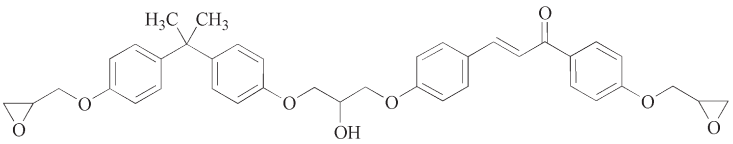
Inks and resists comprise a relatively small but high value and growing market for epoxies and epoxy derivatives. In 2001, there were an estimated of 6800 MT of epoxies and epoxy derivatives used in this market to produce ink and resist formulations worth almost $400 million in the U.S. market. Epoxies are often used with other resins such as polyester acrylates and urethane acrylates in these formulations. The largest applications are lithographic

and flexographic inks followed by electronic inks and resists.

Resist technology is widely used in the electronics industry to manufacture printed circuits. The resist (a coating or ink) is applied over a conducting substrate such as copper in a pattern to protect its surface during etching, plating, or soldering. Cure is either by radiation or heat. The uncured coating (or ink) is removed later by solvents. Solder masks perform similar functions in the manufacturing of printed circuit boards. The growth of the computer and electronics industries has fueled growth of epoxy-based inks and resists. The market is projected to grow at 10 % annually.

The primary resins used in this market are the radiation-curable epoxy acrylates, accounting for 60 % of the resins used. A small amount of cycloaliphatic epoxies are also used in UV-curable inks and resists. Phenol and cresol epoxy novolacs, and bisphenol A based epoxies are used in thermally cured formulations. The epoxy novolacs are used where higher heat resistance is needed such as in solder masks. Both free-radical and cationic-curable UV inks and colored base coats have grown rapidly because of the needs for higher line speeds, faster cleanup or line turnaround, less energy consumption, less capital for a new line, and fewer emissions.

A unique epoxy (epoxy chalcone) produced by Huntsman can be used for dual cure [244]:



Radiation-initiated free-radical cure is possible via the double bonds, while the epoxy groups are available for thermal cure. Epoxy chalcone is used as a photopolymerizable solder mask and in photoresists.

21. Structural Applications

Next to coatings, structural applications account for the second largest share of epoxy resin consumption (~ 40 %). Epoxy resins in structural applications can be divided into three major areas: fiber-reinforced composites and electrical laminates; casting, encapsulation, and tooling; and adhesives. Within this segment, the largest applications are electrical laminates for PCB and composites made of epoxy and epoxy vinyl ester for structural applications.

21.1. Structural Composites

Epoxy resins and epoxy vinyl ester resins are well suited as fiber-reinforcing materials because they exhibit excellent adhesion to reinforcement, cure with low shrinkage, provide good dimensional stability, and possess good mechanical, electrical, thermal, chemical, fatigue, and moisture-resistance properties. Epoxy composites are formed by aligning strong, continuous fibers in an epoxy resin-curing agent matrix. Processes currently used to fabricate epoxy composites include hand lay-up, spray-up, compression molding, vacuum bag compression molding, filament winding, resin transfer molding reaction, injection molding, and pultrusion (see → Composite Materials, Section 4.2.).

Important fiber materials are surface-treated glass, boron, graphite (carbon), and aromatic polyaramides (e.g. DuPont's Kevlar). In most composites the reinforcement constitutes ca. 65 % of the final mass. Orientation of the fibers is important in establishing the properties of the laminate. Unidirectional, bidirectional, and random orientations are possible. The characteristics of the cured resin system are extremely important since it must transmit the applied stresses to each fiber. A critical region in a composite is the resin–fiber interface. The adhesive properties of epoxy resins make them especially suited for composite applications.

The most important market for epoxy composites is for corrosion-resistant equipment where epoxy vinyl esters is the dominant material of choice. Other smaller markets are automotive, aerospace, sports/recreation, construction, and

marine. Because of their higher costs, epoxy and epoxy vinyl esters composites found applications where their higher mechanical strength and chemical and corrosion resistance properties are advantageous.

21.1.1. Epoxy Composites

Composites made with glass fibers usually have a bisphenol A based epoxy resin–diamine matrix and are used in a variety of applications including automotive leaf springs and drive shafts, where mechanical strength is a key requirement. A large and important application is for filament-wound glass-reinforced pipes used in oil fields, chemical plants, water distribution, and as electrical conduits. Low viscosity liquid systems having good mechanical properties when cured are preferred. These are usually cured with liquid anhydride or aromatic–amine hardeners. Similar systems are used for filament-winding pressure bottles and rocket motor casings. Other applications that use fiber-reinforced epoxy composites include sporting equipment, such as tennis racquet frames, fishing rods, and golf clubs, as well as industrial equipment. The wind energy field is emerging as a potential high growth area for epoxy composites, particularly in Europe where a number of new wind energy farms are planned. With windmill blades increasing in lengths (up to 50 m), the strength and fatigue properties of epoxy composites provide benefits over competitive chemistries.

In the aerospace industry, particularly in military aircraft construction, the use of graphite fiber-reinforced composites has been growing because of high strength-to-weight ratios. Some newer commercial airliners now contain up to 10 % by weight of composite materials. High performance polyfunctional resins, such as the tetraglycidyl derivative of methylenedianiline in combination with diaminodiphenylsulfone or nadic methyl anhydride, are used to provide good elevated temperature properties and humidity resistance. Handling characteristics are well suited to the autoclave molding technique primarily used in the manufacture of such components. The low viscosity and high T_g of cycloaliphatic epoxies has led to their use in certain aerospace applications. Newer resins such as diglycidyl ether of 9,9′-bis(4-hydroxyphenylfluorene) have been developed.

While the overall growth of composites in the aerospace industry is continuing, epoxy has been facing stiff competition from other materials and the growth rate has been relatively small (2 % annually). While epoxies are still used in many exterior aircraft parts, carbon fiber composites based on bismaleimide and cyanate esters have shown better temperature and moisture resistance than epoxies in military aircaft applications. In the commercial aircraft arena, phenolic composites are now preferred for interior applications because of their lower heat release and smoke generation properties during fires. High performance thermoplastics, such as polysulfone, polyimides, and polyetherether ketone (PEEK), have also found some uses in aerospace composites.

21.1.2. Epoxy Vinyl Ester Composites

Epoxy vinyl ester composites are widely used to produce chemically resistant glass-reinforced pipes, stacks, and tanks by contact molding and filament-winding processes. Epoxy vinyl ester resins provide outstanding chemical resistance against aggressive chemicals such as aqueous acids and bases and are materials of choice for demanding applications in petrochemical plants, oil refineries, and paper mills. Epoxy vinyl ester composites are also used in demanding automotive applications such as engine and oil pan covers where high temperature performance is required. Exterior panels and truck boxes are also growth automotive applications for vinyl esters. However, in less demanding automotive applications, cheaper thermoplastics and thermosets such as unsaturated polyesters or furan resins are often used. In general, epoxy vinyl ester is considered to be a premium polyester resin with higher temperature and corrosion resistance properties at higher costs. It is used where the cheaper unsaturated polyesters cannot meet performance requirements. For the same reason, epoxy vinyl ester has not grown significantly in less demanding civil engineering applications. Other uses of epoxy vinyl ester composites include boat hulls, swimming pools, saunas, and hot tubs.

Improved versions of the high performance resin systems continue to be developed [245, 246]. Toughening of epoxies and epoxy vinyl esters has emerged as an area for investigation

[247]. Lower styrene content vinyl esters have been developed to reduce worker exposure. Performance enhancements with epoxy and vinyl ester nanocomposites have been reported in the literature, but commercialization has not been yet realized.

21.1.3. Mineral-Filled Composites

Epoxy mineral-filled composites are widely used to manufacture laboratory equipment such as lab bench tops, sinks, hoods, and other laboratory accessories. The excellent chemical and thermal resistance properties of epoxy thermosets make them ideal choices for this application. Typically, liquid epoxy resins of bisphenol A are cured with anhydrides such as phthalic anhydride, which provide good exotherm management and excellent thermal performance. The systems are highly filled with fillers such as silica or sand (up to 70 wt. %). Multifunctional epoxy novolacs can be added when higher chemical and thermal performance is needed.

21.2. Civil Engineering, Flooring, and Construction

Civil engineering is another large application for epoxies, accounting for up to 13 % of total global epoxy consumption. This application includes flooring, decorative aggregate, paving, and construction [248]. Key attributes of epoxies such as ease of installation, fast ambient cure, good adhesion to many substrates, excellent chemical resistance, low shrinkage, good mechanical strength, and durability make them suitable for this market. In the United States an estimated 20,000 MT of resins were used for flooring applications in 2000. The building boom in China has provided significant growth for this market during the past decade. Epoxy flooring compounds are expected to grow well as the construction industry becomes more aware of their benefits.

Epoxy resins are used for both functional and decorative purposes in monolithic flooring and in factory-produced building panel applications. Products include floor paints, self-leveling floors, trowelable floors, and pebble-finished floors. Epoxy floorings provide wear-resistant and chemical-resistant surfaces for dairies and food processing and chemical plants where acids normally attack concrete. Epoxies are also used in flooring for walk-in freezers, coolers, kitchens, and restaurants because of good thermal properties, slip resistance, and ease of cleanup. In commercial building applications, such as offices and lobbies, terrazzo-like surfaces can be applied in thin layers. Continuous seamless epoxy floors are competitive with ceramic tiles. They are usually applied by trowel over a prepared subfloor. Semiconductive epoxy/carbon black floorings are used in electronics manufacturing plants because of their ability to dissipate electrical charges. Decorative slip-resistant coatings are available for outdoor stair treads, balconies, patios, walkways, and swimming-pool decks. Epoxy aggregates are highly filled systems, containing up to 90 % of stones or minerals. They are used for decorative walls, floors, and decks.

Usually, two-component systems consisting of liquid epoxy resin, diluents, fillers (e.g. sands, stones, aggregates), pigments, thickening agents, and polyamine or polyamide curing agents are employed. Cycloaliphatic amines and their adducts are used when either better low temperature cure or adhesion to wet concrete is desired. The other components of the flooring formulation are as critical as the resin and hardener. Typical filler and pigment levels are 10 % for paving, 30 % for flooring, and 40 % or higher for decorative aggregates. Self-leveling floors consist of resin-hardener mixtures with low filler content or unfilled compositions with high gloss. In epoxy terrazzo floors, an epoxy binder replaces the cement matrix in a marble aggregate flooring, providing impact resistance, mechanical strength, and adhesion.

Epoxy systems for roads, tunnels and bridges are effective barriers to moisture, chemicals, oils, and grease. They are used in new construction as well as in repair and maintenance applications. Typical formulations consist of liquid epoxy resins extended with coal tar and diethylenetriamine curing agent. Epoxy resins are widely used in bridge expansion joints and to repair concrete cracks in adhesive and grouting (injectable mortar) systems. Epoxy pavings are used to cover concrete bridge decks and parking structures. Formulations of epoxy resins and polysulfide polymers in conjunction with

polyamine curing agents are used for bonding concrete to concrete. After cleaning the old surface, the epoxy adhesive is applied and good adhesion between the old and the new concrete is obtained.

Recent developments in the construction and civil engineering industry include the development of "intelligent concrete" with self-healing capability in Japan [249]. Some of the systems are based on epoxy resins encapsulated in concrete which when triggered by cracks open and cure to repair the concrete.

21.3. Electrical Laminates

Printed wiring boards (PWB) or printed circuit boards (PCB) are used in all types of electronic equipment. In noncritical applications such as inexpensive consumer electronics, these components are made from paper-reinforced phenolic, melamine, or polyester resins. For more critical applications such as high end consumer electronics, computers, complex telecommunication equipment, etc., higher performance materials are required and epoxy resin-based glass fiber laminates fulfill the requirements at reasonable costs. This application constitutes the single largest volume of epoxies used in structural composites. In 2000, an estimated 200,000 MT of epoxy resins were used globally to manufacture PCB laminates.

Systems are available that meet the National Electrical Manufacturers Association (NEMA) G10, G11, FR3, FR4, FR5, CEM-1, and CEM-3 specifications. Both low viscosity liquid (EEW = 180–200) and high melting solid (EEW = 450–500) epoxy resins are used in printed circuit prepreg manufacture. Currently, the most widely used boards (> 85 %) are manufactured to the flame-retardant FR4 specification using epoxy thermosets. Flame retardance is achieved by advancing the liquid DGEBA epoxy resin with tetrabromobisphenol A (TBBA). This relatively low cost resin which contains about 20 wt. % bromine is the workhorse of the PCB industry. Epoxy resins based on diglycidyl ether of TBBA are also available, which allow the preparation of resins with even higher bromine content, up to 50 wt. %. Multifunctional epoxy resins such as epoxy novolacs based on phenol, bisphenol A, and cresol novolacs or the tetraglycidyl ether of tetrakis (4-hydroxyphenyl)ethane are used as modifiers to increase the glass-transition temperature (T_g > 150 °C), thermal decomposition temperature (T_d), and chemical resistance.

The most commonly used curing agent for PWBs is dicyandiamide (DICY) catalyzed with imidazoles such as 2-methylimidazole (2-MI), followed by phenolic novolacs and anhydrides.

The epoxy–DICY systems offer the following advantages:

1. Cost effectiveness (DICY is a low equivalent weight, multifunctional curing agent)
2. Stable formulations
3. Excellent adhesion to copper and glass
4. Good moisture and solder resistance
5. Good processability

The primary disadvantage of the standard epoxy–DICY systems is their relatively low thermal performance (T_g < 140 °C, T_d = 300 °C), which limits their uses in more demanding applications such as the FR-5 boards and other high density circuit boards. Specialty epoxy–DICY systems are available with T_g approaching 190 °C but at higher costs. Alternatively, high temperature epoxy systems are obtained using diaminodiphenyl sulfone (DDS) as curing agent and boron trifluoride monoethylamine (BF_3/MEA) complex, benzyldimethylamine (BDMA), or various imidazoles as catalysts. However, concerns over the toxicity of DDS have led to significant decrease of its use. More recently, higher thermally resistant laminates using novolac curing agents, including bisphenol A based novolacs, have become popular in the industry. However, brittleness is a significant disadvantage of these systems.

Prepreg is commonly prepared by passing the glass cloth through a formulated resin bath followed by heat treatment in a tower to evaporate the solvent and partially cure the resin to an intermediate or B stage. Prepreg sheets are stacked with outer layers of copper foil followed by exposure to heat and high pressure in a laminating press. This structure is cured (C-staged) at high temperature (150–180 °C) and pressure for 30–90 min. Attempts to develop continuous prepreg and laminating processes have only achieved limited

commercialization. Laminate boards may be single-sided (circuitry printed on only one side), double-sided, or multilayered (3 to 50 layers) for high density circuitry boards. Electrical connections for mounted components are obtained via drilled holes which are plated with copper.

The 1990s witnessed the explosive growth of the personal computer, consumer electronics, and wireless telecommunication industries, resulting in significant demands for PWB based on epoxy resins. The PWB industry trends toward device miniaturization, multilayer laminates, high density circuitries, lead-free solder, and faster signal transmission speeds have resulted in increased performance requirements. For example, lead-free legislation which bans electronics containing lead in the European Union became law in 2003 with an implementation date of 2006. This legislation is expected to speed up the phase-out of lead-based solders globally, forcing the industry to use alternatives such as tin alloys which have much higher soldering temperatures, and thereby drives the need for epoxy systems with higher thermal performance.

The end-use industries' demands for PCB boards with better heat resistance [250, 251], higher glass-transition temperature (T_g), higher thermal decomposition temperatures (T_d), lower water absorption, lower coefficient of thermal expansion (CTE), and better electrical properties (dielectric constant D_k and dissipation factor D_f) have led to the development of new, high performance epoxies and cross-linker systems [252]. Toughness is also becoming an issue as electrical connection holes are drilled in the highly cross-linked, high T_g laminates.

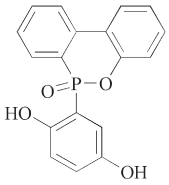
Since reinforcing materials make up from 40 to 60 wt. % of the PCB laminates, their contributions to the laminate dielectric properties are significant. The standard reinforcing glass–cloth compositions in electrical laminates are designated E (electrical) glass. Woven E glass is most commonly used, but other reinforcing materials such as nonwoven glass mat, aramid fiber, S-2 glass, and quartz are available. In recent years, the PCB industry has been evaluating materials with better dielectric properties, but they are much more expensive than standard E glass (Table 25).

In recent years, environmental concerns over toxic smoke generation during fire and end-of-life incineration of electronic equipment containing brominated products, particularly in Europe and Japan, have driven development efforts on halogen-free resins. This has resulted in a number of alternative products such as phosphorous additives and phosphor-containing epoxies [254–256]. Some examples of these phosphorous compounds are as follows:

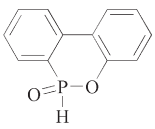
Table 25. Reinforcing material comparison[a]

Reinforcing material	D_k (at 1MHz)	D_f (at 1MHz)	Relative cost
E glass	6.5	0.003	1
S-2 glass	5.3	0.002	4
D glass	3.8	0.0005	10
Quartz	3.8	0.0002	30
Aramid	3.8	0.012	10

[a]From Ref. [253].



9,10-Dihydro-9-oxa-10-phosphathenanthrene-10-oxide



6*H*-Dibenz(*C*,*H*)(1,2)oxaphosphorin-6-oxide

However, commercialization of phosphor-containing epoxies has been limited because of higher costs and other disadvantages such as poorer moisture resistance and lower thermal performance. In addition, concerns over phosphine gas emission during fires and potential leakage of phosphorous compounds in landfills have raised questions about their long-term viability. Alternatively, the industry has been researching new epoxy resins based on nitrogen, silicon, sulfur-containing compounds, and new phenolic resins as potential halogen-free, phosphor-free replacements. Inorganic fillers such as alumina trihydrate, magnesium hydroxide, and zinc borate have also been evaluated as flame-retardant alternatives in epoxy systems.

While brominated epoxy resin remains the workhorse of the PCB industry (FR-4 boards)

because of its good combination of properties and cost, it is facing competition from other thermoset and thermoplastic materials as industry performance requirements increase. Thermosets with higher temperature performance (> 180 °C T_g) and lower dielectric properties include polyimides, cyanate esters, and bismaleimide–triazine (BT) resins. They are used alone or as blends with epoxies in high performance chip-packaging boards and military applications. GE's GETEK system is an interpenetrating network of polyphenylene oxide (PPO) in epoxy and has lower dielectric constant than standard epoxies. Polytetrafluoroethylene (PTFE) has a very low dielectric constant (Table 26) and is used primarily in high performance PCBs for military and high frequency (e.g. radars) applications. While these alternative materials offer certain performance advantages over standard epoxies, they are generally more expensive and more difficult to process. Thermosets such as polyimides, cyanate ester, and BT resins are very brittle and have higher water absorption than epoxies. PTFE has very poor adhesion to substrates, requiring special treatments. Consequently, they are limited to niche, high performance applications [250].

In flexible printed circuits, polyimide and polyester films are the preferred choices over epoxies. Molded interconnects based on heat-resistant thermoplastics such as polyether sulfone, polyether imide, and polyarylate have been developed to replace epoxy-based PCBs in certain applications. However, their uses are limited to special applications.

There has been a significant migration of the PCB laminate manufacturing capacity to Asia (mainly Taiwan and China) in the late 1990s. In 2001, 70 % of epoxy resins used in PCB laminates was consumed in the region and the trend is expected to continue in the near future.

21.4. Other Electrical and Electronic Applications

21.4.1. Casting, Potting, and Encapsulation

Since the mid-1950s, electrical-equipment manufacturers have taken advantage of the good electrical properties of epoxy and the design freedom afforded by casting techniques to produce switchgear components, transformers, insulators, high voltage cable accessories, and similar devices.

In casting, a resin-curing agent system is charged into a specially designed mold containing the electrical component to be insulated. After cure, the insulated part retains the shape of the mold. In encapsulation, a mounted electronic component such as a transistor or semiconductor in a mold is encased in an epoxy resin based system. Coil windings, laminates, lead wires, etc, are impregnated with the epoxy system. Potting is the same procedure as encapsulation except that the mold is a part of the finished unit. When a component is simply dropped into a resin-curing agent system and cured without a mold, the process is referred to as dipping. It provides little or no impregnation and is used mainly for protective coatings.

The choice of epoxy resin, curing agent, fillers, and other ancillary materials depends on factors such as cost, processing conditions, and the environment to which the insulated electrical or electronic component will be exposed.

Table 26. Base resin systems used in PCB laminates

Resin system	T_g, °C	D_k (at 1MHz)	D_f (at 1MHz)	Estimated relative resin cost	Laminate cost
Standard Epoxies	135–140	4.6–4.8	0.015–0.020	1	1
High performance Epoxy	170–180	4.6–4.8	0.015–0.020	1.5–2	1.5
PPO/Epoxy	175–185	3.6–4.2	0.009–0.015	4–6	2–3
BT/Epoxy	170–220	3.9–4.2	0.008–0.013	8–15	2–5
Polyimide	260	3.9–4.4	0.012–0.014	5–16	3–6
Cyanate ester	230–260	3.5–3.7[a]	0.005–0.011[a]	5–16	4–8
Polyester	135–140	3.1–3.2[b]	0.004–0.014[b]	—	7–10
PTFE	NA	2.1–2.5[b]	0.0006–0.0022[b]	40	15–50

[a] Measured at 1GHz.
[b] Measured at 10 GHz.

The type and amount of filler that can be incorporated into the system are very important and depend on the viscosity of the resin at the processing temperature. Filler loading reduces costs, increases pot life, improves heat dissipation, lowers exotherms, increases thermal shock resistance, reduces shrinkage, and improves dimensional stability.

The exotherm generated during the resin cure must be controlled to prevent damage to the electrical or electronic component. The exotherm is easily controlled during the production of small castings, pottings, and encapsulations. In the production of large castings, the excess heat of reaction must be dissipated in order to prevent locked-in thermal stresses. During the 1970s, the pressure gelation casting process was developed [257]; this method provides better temperature control and reduces cycle times. The heat generated by polymerization is used to heat the resin mass and is not dissipated in the mold.

Both DGEBA and cycloaliphatic epoxy resins are used in casting systems. Most systems are based on DGEBA resins cured with anhydride hardeners and contain 60–65 wt. % inert fillers. The cycloaliphatic resin systems exhibit good tracking properties and better UV resistance than DGEBA resins, the latter of which causes crazing and surface breakdown. An electrical current is more likely to form a carbonized track in aromatic-based resins than in nonaromatic ones. Their lower viscosity also facilitates device impregnation. The cycloaliphatic epoxies are often used as modifiers for DGEBA resin systems. This application represents a significant outlet for cycloaliphatic epoxies.

Amine curing agents are used in small castings, and anhydrides are used in large castings. Anhydrides are less reactive and have lower exotherms than amines. In addition, their viscosity and shrinkage are low and pot lives are longer.

21.4.2. Transfer Molding

Epoxy molding compounds (EMC) are solid mixtures of epoxy resin, curing agent(s) and catalyst, mold-release compounds, fillers, and other additives. These systems can be formulated by dry mixing or by melt mixing and are relatively stable when stored below room temperature. Molding compounds become fluid at relatively low temperatures (150–200 °C) and can be molded at relatively low pressures (3.5–7.0 MPa) by compression, transfer, or injection molding. Advantages of molding over casting are elimination of the mixing step immediately before use, improved handling and measuring procedures, and suitability for high production quantities. A typical standard EMC formulation contains approximately 30 % epoxies, 60 % filler, and 10 % of curing agents and other additives such as release agent.

An important application of epoxy molding compounds is the encapsulation of electronic components such as semiconductor chips, passive devices, and integrated circuits by transfer molding. Transfer molding is a highly automated, efficient method of encapsulation. High purity phenol and cresol epoxy novolacs and phenol and cresol novolacs and/or anhydride curing agents are used most often in semiconductor applications. For passive device encapsulation, standard epoxy novolacs can be used as blends with bisphenol A based solid resins. The ECN or EPN molding powders can be processed at relatively low pressures and provide insulation for the electronic components. Ionic impurities, i.e., NaCl or KCl, must be kept to a minimum, since trace quantities can cause corrosion and device failure. In addition, residual stress and thermal and mechanical shock resistances are issues that must be managed properly [258].

Efforts have been made to improve the high temperature performance of these systems by replacing the epoxy novolacs with other multifunctional epoxy resins. Hydrocarbon based epoxy novolacs (HEN) were developed to improve the moisture resistance of molding compounds. Crystalline epoxy resins derived from biphenol and dihydroxy naphthalenes were developed for high end semiconductor encapsulants using Surface Mount Technology (SMT). The emergence of SMT as a key semiconductor manufacturing technology requires epoxy molding compounds with a high filler loading capacity (up to 90 wt. %) to enhance solder crack resistance. SMT uses new solder alloys to attach components to the PCB board at high temperatures (215–260 °C). Solder reflow, delamination, and package cracks are problems

often encountered with conventional molding compounds based on cresol epoxy novolacs. The high filler content helps lower costs, reduces moisture absorption, and decreases the thermal expansion coefficient of the system. Crystalline products with very low melt viscosity such as biphenyl epoxies facilitate the processing of the high silica filler formulations while maintaining other critical requirements: moisture resistance and electrical, thermal, and mechanical properties [61]. The majority of high purity epoxies used in epoxy molding compounds (EMC) for semiconductor encapsulations are supplied by Japanese producers and a few Asian companies.

21.5. Adhesives

Epoxy-based adhesives provide powerful bonds between similar and dissimilar materials such as metals, glass, ceramics, wood, cloth, and many types of plastics. In addition, epoxies offer low shrinkage, low creep, high performance over a wide range of usage temperatures, and noby-products (such as water) release during cure. The epoxy adhesives were originally developed for use in metal bonding in the aircraft industry [259, 260]. In aircraft wing assemblies, high strength epoxy adhesives are used in place of metal fasteners to avoid corrosion problems inherent with metal fasteners, to reduce weight, and to eliminate "point" distribution by spreading the load over a large area. Today, epoxy is the most versatile engineering/structural adhesive, widely used in many industries including aerospace, electrical/electronic, automotive, construction, transportation, dental, and consumer. The market is of high value, consuming 25,000 MT of epoxies in North America in 2001 worth almost $500 million.

The broad range of epoxy resins and curing agents on the market allows a wide selection of system components to satisfy a particular application. Although the majority of epoxy adhesives are two-pack systems, heat activated one-pack adhesives are also available. Low molecular weight DGEBA liquid resins are the most commonly used. Higher molecular weight (EEW = 250–500) DGEBA epoxy resins improve adhesive strength because of the increased number of hydroxyl groups in the resin backbone. For applications requiring high temperature or improved chemical performance, the multifunctional epoxy phenol novolac and triglycidyl-*p*-aminophenol resins are employed. More recent products include vinyl epoxies. Adhesive systems modified with reactive diluents facilitate wetting of the substrate, allowing more filler to be added and modifying handling characteristics; however, adhesive strength is reduced. Toughened epoxy adhesives are available.

Table 27. Epoxy adhesive lap-shear strengths

Hardener	Lap-shear strength,[a] MPa[b]
Aliphatic polyamine	19
Polythiol cohardener	18
Aromatic diamine	24

[a] Adhesive strength.
[b] To convert MPa to psi, multiply by 145.

Polyamines or polyamides are the curing agents for ambient or slightly elevated temperature cures, and aromatic polyamines or anhydride hardeners are used for hot cures. These systems provide exceptional bonding strength but slower cure time. Boron trifluoride amine complexes and dicyandiamide are used in one-component adhesives. Polythiols (polysulfides, polymercaptans) are the fast-curing hardeners in "5-min." consumer epoxy formulations. The lap-shear strengths of a DGEBA epoxy cured with different hardeners are given in Table 27.

Cationically cured UV laminating adhesives based on cycloaliphatic epoxies are emerging as an alternative to solvent-based adhesives. The "dark cure" of cationics allows UV exposure and post lamination in line. This process does not require UV exposure "through" the plastic barrier material.

Epoxy adhesives are expected to grow at GDP (3–4 %) over the next decade. Increased usage in the automotive and recreational markets, and replacement of mechanical fasteners help offset the slowdown in the aerospace industry (see also Adhesive Compositions).

21.6. Tooling

Tools made with epoxy are used for producing prototypes, master models, molds and other parts for aerospace, automotive, foundry, boat

building, and various industrial molded items [261]. Epoxy tools are less expensive than metal ones and can be modified quickly and cheaply. Epoxy resins are preferred over unsaturated polyesters and other free-radical cured resins because of lower shrinkage, greater interlaminar bond strength and superior dimensional stability.

Most epoxy-based tooling formulations are based on liquid DGEBA resins. Aliphatic polyamines, amidoamines, or modified cycloaliphatic amines are used for ambient temperature cure, and modified aromatic diamines and anhydrides are used for high temperature cure. When high heat resistance is required ($> 350\,^{\circ}F$) epoxy novolac resins can be employed. Reactive diluents such as aliphatic glycidyl ethers are often employed to permit higher filler load or to reduce the system viscosity for proper application. Fillers, reinforcing fibers, toughening agents, thixotropic agents, and other additives are often used depending on the desired application and final properties.

Tooling production uses four major processing methods: lamination, surface cast, splining, and casting. Lamination is made by alternating layers of glass cloth or fabric and formulated resin, usually on a framework of metal or plastic. Surface cast utilizes a filled resin compound that is applied onto the surface of a mold, which is later filled with a core material that adheres to the casting compound. Splining employs heavily filled formulations that are directly applied to a surface and manually molded or leveled to the desired shape, before or after curing, with the help of proper tools. Lastly, casting compounds are filled formulations that are directly poured or compressed into a mold coated with a release agent.

22. Health and Safety Factors

There have been many investigations of the toxicity of various classes of epoxy-containing materials (glycidyloxy compounds). The use and interpretation of the vast amount of data available has been obscured by two factors: (*1*) proper identification of the epoxy systems in question and (*2*) lack of meaningful classification of the epoxy materials. In general, the toxicity of many of the glycidyloxy derivatives is low, but the diversity of compounds found within this group does not permit broad generalizations for the class. Information on toxicity and safe handling of epoxy compounds are summarized in References [262, 263] and [264].

Diglycidyl ether of bisphenol A. Bisphenol A based epoxies are the most commonly used resins. Although unmodified bisphenol A epoxy resins have a very low order of acute toxicity, they should be handled carefully and personal contact should be avoided. Prolonged or repeated skin contact with liquid epoxy resins may lead to skin irritation or sensitization. Susceptibility to skin irritation and sensitization varies from person to person. Skin sensitization decreases with an increase in MW, but the presence of low MW fractions in the advanced resins may present a hazard to skin sensitization. Inhalation toxicity does not present a hazard because of low vapor pressure. DGEBA-based resins have been reported to cause minimal eye irritation. Toxicological studies support the conclusion that bisphenol A based epoxy resins do not present a carcinogenic or mutagenic hazard.

Because of the solvents used, solution of epoxy resins are more hazardous to handle than solid resins alone. Depending on the solvents used, such solutions may cause irritation to the skin and eyes, are more likely to cause sensitization responses, and are hazardous if inhaled.

Epoxy phenol novolac resins. Acute oral studies indicate low toxicity for these resins. Eye studies indicate only minor irritation in animals. The EPN resins have shown weak skin sensitizing potential in humans.

Low MW epoxy diluents, particularly the aromatic monoepoxides such as phenyl glycidyl ether (PGE) are known to have high toxicity and should be handled with care. They are capable of causing skin and eye irritation and sensitization responses in people. They may also present a significant hazard from inhalation.

Curing agents. In general, amine curing agents are much more hazardous to handle than the epoxy resins, particularly at elevated temperatures. Aliphatic amines and anhydrides are capable of serious skin or eye irritation, sensitization, and even burns. Other curing agents possess consideration variation in the degree of health hazards because of the variety of their chemical structures and it is impossible to generalize.

All suppliers provide material safety data sheets (MSDS), which contain the most recent toxicity data. These are the best sources of information and should be consulted before handling the materials.

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Phenolic Resins

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1. Introduction

History. The first synthetic resins and plastics were produced by polycondensation of phenol with aldehydes. In 1872 von Bayer first reported the reaction between phenol and aldehydes. The resins formed were, however, not of industrial, and certainly not of scientific interest.

The first plastic used on and industrial scale was phenolic resin, which is a polycondensation product of phenol and formaldehyde normally cured under heat and pressure The birth of phenolic resins and the start of a century of plastics usage are inseparable and are linked to a Belgian-born chemist, who worked in the United States, Leo Hendrik Baekeland. From his work in electrochemistry and electrical engineering he recognized the lack of suitable insulating materials, so in 1904 he started to develop a hard moldable plastic that would be suitable for this type of application. In 1907 he was finally successful and his "Pressure and Heat" patent provided the basics for the utilization of phenolic resins on an industrial scale. The first production of phenolic resins started in 1909, mainly to provide molding compounds to be used as electrically insulating materials for plugs, switches, etc. The rapid development of the electrical industry at that time was one of the success factors of this new thermoset material. In 1910 subsidiary of the Rütgers company was established in Erkner to produce the new material, which became world famous under the trade name "Bakelite".

In addition to being used in the production of plastics, phenolic resins were also sought as replacements for natural resins, which were then used on a large scale for oil varnishes. In 1910 oil-soluble modified phenolic resins were produced by Behrends by polycondensation of a suitable phenol, formaldehyde and rosin.

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Between 1928 and 1931 phenolic resins gained increased importance through the treatment of resols with fatty oils to give air-drying varnishes. The main problem, an inadequate compatibility of phenolic resins with other varnish raw materials, was solved by using either alkylphenols or by the etherification of the hydroxymethyl groups of resols with monohydric alcohols.

These varnish applications and the use of phenolic resins as thermosets and electrical insulating materials were originally the main areas of interest. However, the availability of other polycondensates and above all polymers increasingly limited the market for phenolic resins from the mid 1930s onwards. Theoretical work on the composition and mechanism of the formation of phenolic resins was being carried out at that time by VON EULER, HULTZSCH, MEGSON, ZIEGLER, and others, which led to the development of new application areas for phenolic resins (i.e., as adhesives, printing-ink binders, waterborne paints, temperature-resistant binders, and laminated plastics).

The industrial development of phenolic resins is still continuing despite its long history, and such resins are likely to remain of considerable importance because the raw materials required to manufacture them can be obtained at reasonable cost from both petroleum and coal. In turn phenolic resins can be used as raw materials for synthetic fibers and in photoresists for the production of microchips which characterizes the continuing relevance of this group of resins [7]. Phenolic resins themselves are still used today and even find new application areas due to combining superior properties like heat resistance, chemical resistance, insulating properties and nontoxic combustion gases with reasonable cost. New developments have also been made regarding high performance materials in the aerospace and aircraft industry, and for light weight construction materials.

Classification. Phenolic resins are polycondensation products of phenols and aldehydes, in particular phenol and formaldehyde. (DIN EN ISO 10082 attempts to define the relevant terms and properties.)

The hydrogen atoms in the *para*- and both *ortho*-positions of the ring, relative to the hydroxyl group, may react with formaldehyde and thus cross-link to form a three-dimensional network. If at least one of these three positions bears a substituent other than hydrogen, cross-linking is no longer possible and comparatively low molecular mass compounds are formed as the end products of the polycondensation.

Phenolic resins are classified as novolacs and resols. In *resols* the polycondensation is base-catalyzed and the condensation degree is adjusted to the intended application. The molar ratio phenol/formaldehyde is normally < 1. Characteristic functional groups of this class of resins are the hydroxymethyl group and the dimethylene ether bridge. Both are reactive groups. During processing the polycondensation can be restarted by heating and/or addition of catalysts (i.e., resols are self-cross-linking). In the case of *novolacs* the polycondensation is brought to completion during the production process. Novolacs are phenols that are linked by alkylidene (usually methylene) bridges, without functional groups (apart from the phenolic hydroxyl groups), and cannot cure on their own. However, novolacs can be cross-linked by the addition of curing agents, such as formaldehyde, hexamethylenetetramine or resols, and give end products similar to resols.

The classification of phenolic resins as novolacs and resols is only strictly valid if phenols that are trifunctional towards formaldehyde are used as starting materials; this is because resols from bifunctional phenols cannot cross-link by themselves. Nevertheless, the polycondensates from substituted phenols are differentiated according to their characteristic groups as *alkylphenol novolacs* (alkylidene bridge) or *alkylphenol resols* (hydroxymethyl group, dimethylene ether bridge).

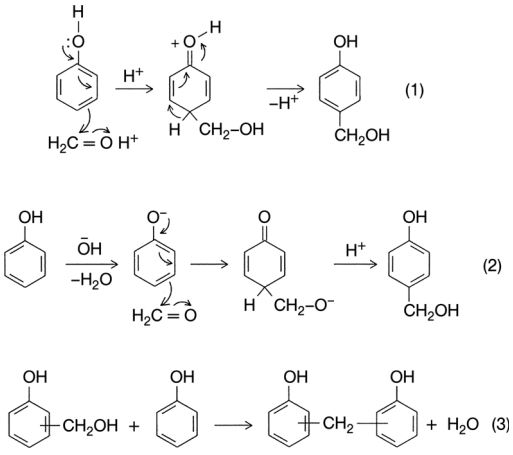
The third large group comprises *phenolic resins modified by natural resins*. Besides phenolic hydroxyl groups, they contain double bonds, ester links, and carboxyl groups.

Novolacs. Novolacs are obtained by a polycondensation reaction with an acidic catalyst (most common is oxalic acid) and a $1:< 1$ molar ratio of phenol/formaldehyde. Normally novolacs are solids with melting points between 50°C and 130°C, which can be used in the form of flakes, pills, powder resins or solutions in organic solvents. Novolacs themselves are thermoplastic materials, but their main use is as thermosets using curing agents.

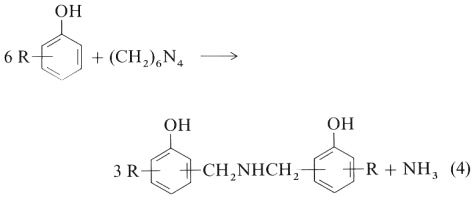
The first step in phenolic resin polycondensation is always the electrophilic attack of a carbonyl compound (generally formaldehyde) on the *para*- and/or *ortho*-positions of

a phenol molecule (acid catalysis, Eq. 1) or a phenolate anion (base catalysis, Eq. 2).

Since hydroxymethyl-substituted phenols are more reactive than phenol itself, the hydroxymethylation continues. The hydroxymethyl compounds formed are unstable in acidic medium and are rapidly converted into compounds linked by methylene bridges (Eq. 3). This reaction also occurs in both the *ortho*- and *para*-positions. In basic media hydroxymethyl groups can be stable, but at elevated temperatures they react with the formation of methylene bridges according to Equation (3). To hinder polyalkylation by cross-linking, which would make further processing more difficult or impossible, less than one molecular equivalent of formaldehyde must be added per mol of phenol.

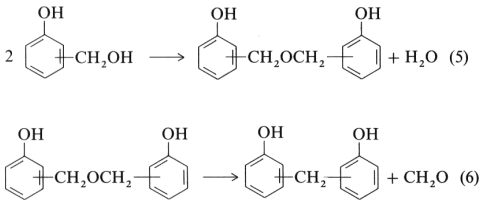


Novolacs are sometimes used as chemically unmodified synthetic resins. Their main application is based, however, on their capability to undergo cross-linking with hexamethylenetetramine. The reaction occurs at ca. 150°C according to Equation (4) [8].



Resols. Resols are obtained by polycondensations with basic catalysts and a molar ratio phenol/formaldehyde 1:> 1. Normally, they are used in the liquid form either dissolved in water or in organic solutions (alcohols and ketones). For special applications solid resols are in use.

In a strongly acidic medium, hydroxymethyl groups are rapidly converted into methylene bridges, therefore, the synthesis of resols can only be catalyzed by bases or the salts of weak acids or bases. By analogy with the novolacs the hydroxymethyl groups are formed in the *ortho*- or *para*-positions (Eq. 2). At temperatures above ca. 40°C the hydroxymethyl groups can react to form dimethylene ether bridges with the elimination of water, according to Equation (5). No catalyst is needed for this type of reaction. The dimethylene ether bridges formed are more stable in the *ortho*- than in the *para*-position. They can be converted into methylene bridges with the elimination of formaldehyde (Eq. 6); the formaldehyde liberated is then available for the formation of new hydroxymethyl groups if a suitable catalyst is present.

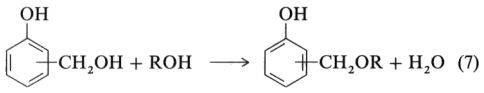


The hydroxymethyl groups of resols can also condense directly with other phenol molecules according to Equation (3). In resols therefore, three different types of formaldehyde-derived units occur: (1) relatively stable methylene bridges (the only type of linkage in novolacs), (2) hydroxymethyl groups, which are both capable of condensation reactions, and (3) dimethylene ether bridges.

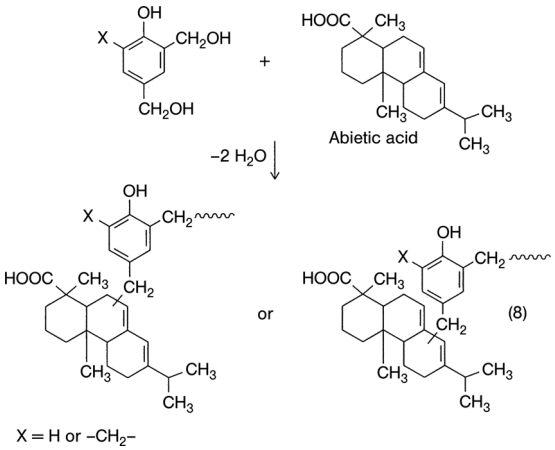
The structures of resols depend not only on the choice of raw materials and their molar ratios, but also on the temperature of formation, concentration of raw materials, presence or absence of solvents, type of catalyst, and catalyst concentration. These parameters determine the structure to a much greater extent than in the case of novolacs.

The catalyst-containing synthetic resins formed are ready to be used industrially. However, the catalyst can also be removed, either before application or during production, as no catalyst is required for the conversion of hydroxymethyl groups into dimethylene ether bridges, a rise in temperature is sufficient.

To affect compatibility (i.e., miscibility) properties the hydrophilic character of resols can be lowered by etherification of the hydroxymethyl group with alcohols according to Equation (7).



Modified Phenolic Resins. Rosin, a natural resin (→ Resins, Natural), contains abietic acid and its double bond isomers as main components. Resols react with the unsaturated centers of these resin acids to form polycarboxylic acids with methylene bridges (Eq. 8) [9].



These condensation products from rosin and phenol–formaldehyde resin are known as albertol acids. They can be converted by esterification with polyols, or by salt formation, into higher molecular mass products which are readily soluble in nonpolar solvents but can release the solvent rapidly.

Albertol acids are also obtained by direct condensation of rosin, phenols, and formaldehyde.

Resols also undergo analogous reactions with other natural or synthetic unsaturated compounds such as fatty oils, rubbers, and polymer oils. A limited increase in the molecular mass or crosslinking can thus be achieved. Whether a particular reaction can be carried out successfully depends upon the ratio of the rates of autocondensation of the starting materials to cocondensation with the other reaction partners, but particularly on their mutual compatibility. Phenolic resins are therefore often classified as "water-soluble", "alcohol-soluble", "oil-soluble" etc.

Compatibility of resols with other components can be influenced in many ways, e.g., (1) by using ring-alkylated phenols as the raw materials; (2) by etherification of the hydroxymethyl groups with alcohols; (3) by cocondensations of the resol with natural resins; or by a combination of these measures.

2. Physical Properties

Phenolic resins are yellow to brown in color and the coloration can be very intense. Pale phenolic resins become colored immediately after production, during storage or processing. The coloration is enhanced in the presence of oxygen and alkali. The coloration is less intense only in the case of phenolic resins from *para*-alkylated phenols. Characteristic UV absorption maxima lie at 254 nm and 280 nm. The IR spectra of phenolic resins are described in [10].

Phenolic resins which are not cross-linked are commercially available as solids or solutions. Due to the self-curing properties of resols they have a limited shelf life. For particular applications, e.g., in thermosets, the polycondensation can be driven so far that the resins are no longer soluble but can only be swelled by organic solvents. The *softening point* of solid resins can be determined by the capillary melting point according to DIN 53 244, by the ring and ball method, or similar procedures. These temperatures are not melting points in the thermodynamic sense. They characterize a lowering of viscosity caused by a rise in temperature, as a result of which previously crushed resin particles can be observed to coalesce or undergo another change in form.

The *miscibility* of resins with solvents, usually described as "solubility," depends upon the structure of the resin, and ranges from solubility in water to that in naphtha. Resins often have limited miscibility with certain solvents. Typical solvents are alcohols and ketones.

The *viscosity* of phenolic resins or their solutions is measured at high concentrations, e.g., in 30–80% solution. Estimation of the degree of condensation from the viscosity is only possible

for the same type of resin, because the molecular structure, in particular the presence of hydroxymethyl groups and dimethylene ether bridges, has a great effect on the viscosity. Usually, the results obtained do not depend on the type of viscometer used. Soluble phenolic resins have a broad *molecular mass distribution*; determination of which (usually by gel permeation chromatography) gives values of more than 50 000, depending upon the type of phenol monomer.

Cross-linked phenolic resins are hard substances which only have a small fracture strain and cannot be melted. Decomposition reactions begin at 120–250°C, depending on the molecular structure. There are, however, also types of phenolic resin (phenolic ether resins) which are stable for some time up to 300°C.

Phenolic resins can be plasticized. Their compatibility with plasticizers can be adjusted by introduction of hydrophilic or hydrophobic groups. Plasticizers increase the flexibility of the phenolic resin network by introducing compact spherical molecules such as tricresyl phosphate or molecules with aliphatic chains like polyglycols.

3. Raw Materials

3.1. Phenols

Phenol (→ Phenol). Unsubstituted phenol is by far the most important of this group.

Cresols (→ Cresols and Xylenols). Resins produced from cresols are more compatible with hydrophobic substances than those produced from phenol. Cresols are therefore important principally for the production of varnish resins. The cresol fractions obtained in tar distillation are mixtures of isomers comprising all three cresol isomers and usually also 2,6-dimethylphenol. For the application of these fractions their *meta*-cresol content (which is the most reactive component) is particularly important; thus, as only the *meta*-position is substituted, *meta*-cresol is trifunctional towards formaldehyde. Of the pure isomers *ortho*- and *para*-cresols are the usual raw materials for special applications.

para-Alkylphenols (→ Phenol Derivatives). *para*-Alkylphenols are bifunctional towards formaldehyde, i.e., resols produced from *para*-alkylphenols cannot cross-link directly on heating. If a mixed condensation of different phenols with formaldehyde is carried out, their different reaction rates towards formaldehyde must be taken into account. 4-*tert*-Butylphenol (*mp* 99°C), 4-isooctylphenol (*mp* 72–74°C), 4-hydroxybiphenyl (*mp* 167°C), and 4-nonylphenol (a liquid at room temperature) are mainly used. Other alkylphenols such as isopentylphenol, cyclohexylphenol, dodecylphenol, and cashew oil are also sometimes used. The latter mainly contains phenols with C_{14}-alkenyl substituents bonded to the *meta*-position.

2,2-bis(4-Hydroxyphenyl)propane, (diphenylolpropane, bisphenol A, Dian, *mp* 155–156°C) is tetrafunctional towards formaldehyde. Polycondensation of bisphenol A and formaldehyde gives relatively pale resins.

Resorcinol (1,3-dihydroxybenzene, *mp* 117°C) reacts particularly rapidly with formaldehyde and gives resins, which can be cross-linked even in an alkaline medium at room temperature.

Other phenol derivatives that can be used as starting materials are, for example, phenol ethers, phenols containing carboxyl groups, and phenoxyacetic acid.

3.2. Aldehydes

Formaldehyde. The most important aldehyde for the production of phenolic resins is formaldehyde (→ Formaldehyde), which is used as an aqueous solution at concentrations between 30 and 60%. Besides formaldehyde, the aqueous solutions contain formic acid (oxidation product of formaldehyde) and methanol. Methanol is added to inhibit formation of higher molecular mass polyoxymethylenes, which would precipitate from the aqueous solution. Methanol can intervene in the polycondensation reaction between phenol and formaldehyde by the formation of ethers, acetals, and hemiacetals, and the promotion of side reactions. Thus, knowledge of the methanol concentration (which should be as low as possible) is important for carrying out polycondensation reactions. Formaldehyde solutions can also be stabilized by certain amines. The methanol concentration can then be kept low.

Paraformaldehyde is a polyoxymethylene with a relatively low molecular mass. Paraformaldehyde depolymerizes in the reaction mixture. The quantity of formaldehyde liberated per unit time increases with decreasing molecular mass of the paraformaldehyde used as starting material. Since phenolic resin condensations can often take place very vigorously, it is important to assess the reactivity of the paraformaldehyde correctly.

Higher aldehydes are less important. In the presence of basic catalysts they frequently undergo side reactions and can therefore generally only be reacted with phenol in an acidic medium. Besides butyraldehyde, benzaldehyde, salicylaldehyde, acrolein, and crotonaldehyde, acetaldehyde, and glyoxal are also important. Glyoxal is tetrafunctional towards phenol and gives novolacs with a low content of low molecular mass condensation products.

Hexamethylenetetramine forms adducts with phenols and novolacs very easily, which cross-link on heating. Hexamethylenetetramine is particularly important in the production of thermosetting materials.

3.3. Catalysts

The catalytic action of *acids* on the condensation to produce novolacs is essentially a function of the hydrogen ion concentration. The nature of the anion is less important but must be taken into account because of possible side reactions (sulfonation, ester formation). Besides mineral acids, oxalic acid is often used. It decomposes on heating above 180°C and thus allows the production of catalyst-free novolacs.

Bases or *salts of weak acids and bases* are suitable as catalysts for resols and novolacs. The cations of catalysts are particularly important; whereas alkali hydroxides catalyze the reaction of phenol with formaldehyde in both the *ortho*- and *para*-positions, alkaline-earth metal hydroxides particularly favor the formation of *ortho*-products.

Ammonia, amines and hexamethylenetetramine have a catalytic effect. They can be incorporated into the resin by the Mannich reaction.

4. Production

The production of phenolic resins can involve several separate stages. The substitution and condensation reactions between phenols and aldehydes can be carried out separately in terms of both time and location if required, and also with various catalysts. In addition, hydroxymethyl groups or phenolic hydroxyl groups can be etherified and reactions with unsaturated compounds can be carried out. Resins are frequently distilled to give concentrated solutions or solid resins. Examples relating to production can be found in [11] and [12].

Resols are normally produced in a batch process. Continuous processes mainly using a kind of cascade are described in the literature but are not very common.

Principle steps of the batch process:

- Dosing of raw materials
- Heating to reach condensation temperature
- Condensation until desired parameters are reached
- Distillation of excess water (only if needed)
- Cooling
- Adjustment of final parameters
- Unloading and filtration of the resin

Resin production is normally done in vessels which can be heated and cooled by jackets or coils. They vessels are equipped with condensers for reflux or distillation and often vacuum can be applied.

In case of solvent based resins explosion proof devices are necessary. The vessel size also depends on the application, so for mineral wool resins or binders for wood materials vessels of 50 m^3 are in use. Due to the corrosive raw materials the vessel and the auxiliary facilities like tubes and storage tanks are made from stainless steel. Modern plants utilize higher concentrated formalin (about 50%) and molten (100%) phenol to save energy cost for heating and distillation and to minimize the amount of wastewater. In this case the storage facilities and all the tubes and dosing systems have to be heated. The phenolic resin plant shown in Figure 1 can be used for all steps in batchwise

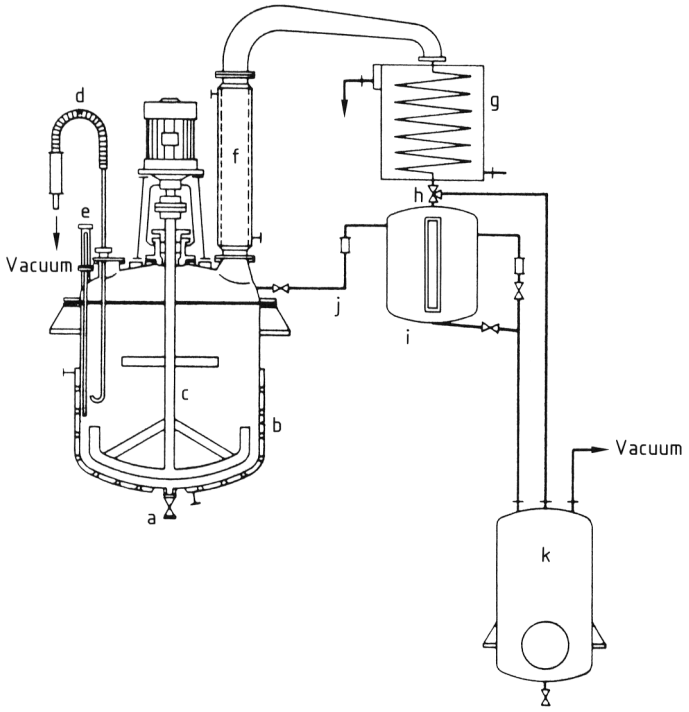


Figure 1. Phenolic resin plant
a) Outlet tap; b) Heater; c) Stirrer; d) Evacuation system; e) Thermometer; f) Reflux condenser; g) Main condenser; h) Three-way tap; i) Reflux and separation vessel; j) reflux return with siphon; k) Receiver

production. Substitution and condensation reactions between phenol and formaldehyde are strongly exothermic (the heat of reaction for the formation of methylene bridges in novolacs is −98.7 kJ/mol [11]) and can proceed very fast and vigorously. Therefore, the access to the condensers and overhead and outlet pipes must be kept very wide and the cooling capacity must be designed for rapid condensation and removal of the condensate. To achieve safe industrial production, phenol is always charged to the reactor first and formaldehyde is then added continuously to avoid a run-away reaction. Due to the low MAK and TLV values of the monomers (phenol MAK and TWA = 5 ppm, formaldehyde MAK = 0.5 ppm, TWA = 1 ppm, STEL = 2 ppm) working areas must be well ventilated.

Emptying the reactor vessel is not problematic for dissolved, low viscosity resins, but for solid phenolic resins—particularly resols with a high melt viscosity—rapid discharging and cooling of the resin is very important to avoid further condensation. Besides discharging into pans, removal by cooling conveyors or pelletizing machines has come into use. Phenolic resins which cannot cross-link, such as novolacs or alkylphenol resols, are processed in thin-layer evaporators or other continuous evaporation plants.

In general, phenolic resins are produced in small quantities of a very great variety of types, so that batchwise processes are more economic. Some types (e.g., novolacs for thermosets or resols for the production of wood glues) are, however, produced in large quantities, so that a continuous process is more favorable from the point of view of both obtainable throughput and properties of the substance. Processes described in the literature suggest the use of tubular reactors and series of tank reactors [13, 14].

4.1. Novolacs

In the formation of novolacs, substitution and condensation reactions occur simultaneously. In large reaction vessels formaldehyde is continuously metered to a phenol–catalyst mixture and

the rate of addition is controlled depending on the heat evolved for safety reasons.

Under industrial conditions, analytical control of the course of the reaction is not necessary, because the degree of polycondensation and molecular structure of the resin are determined by the reaction conditions and the concentration of the starting materials. A temperature/time program is usually used.

Example [11]: phenol (1880 parts) is melted in a reaction vessel to which oxalic acid (50 parts) is added and heated to 100°C; an 30% aqueous formaldehyde solution (1560 parts) is then gradually metered in over ca. 2 h. The reaction mixture is held at 98°C for 5 h, and the volatile components are then distilled off under reduced pressure until a temperature of 160°C is attained at a pressure of 2.0 kPa, A novolac (1968 parts), with a softening point of 124°C, remains in the vessel.

4.2. Resols

Resols from Trifunctional Phenols. The production of resols(see Fig. 2) differs from that of novolacs in that the reactions between phenol and formaldehyde are not allowed to go to completion, but are stopped at the stage where the self-curing resols are still liquid or soluble. The continuation of the condensation reaction beyond the resol stage (*A-stage*) leads to resins, which are no longer soluble, but can only be swelled and which are known as *resitols* (*B-stage*). The final cross-linking to form *resites* (*C-stage*) gives completely cross-linked plastics.

In resol production the degree of condensation must be controlled during the reaction. The degree of condensation is controlled by measurement of the viscosity, if necessary after dilution with solvents. Other possibilities include the determination of solubility, melting point, and B-time (see Chap. 6). The reaction temperatures for the production of resols are between room temperature and ca. 100°C. The molar ratio of phenol to formaldehyde can vary widely. The upper limit is determined by the functionality of the phenol towards formaldehyde (i.e., a molar formaldehyde/phenol ratio of 3:0). Resols are also formed, however, if an excess of phenol is used. In this case a major portion of the phenol does not react.

The reaction is controlled by the type and quantity of catalyst used and the temperature. High alkali concentrations (up to 1 mol per phenolic hydroxyl group) in combination with low temperatures promote the formation of hydroxymethyl groups and stabilize them. Low catalyst concentrations and particularly high temperatures promote the condensation reactions.

The catalyst can remain in the resin and, in the case of alkali hydroxides, render it water-soluble. These catalyst-containing resols can be used industrially. The catalysts can also be neutralized and, if necessary, removed by washing out or by filtration. The resols thus lose their water solubility partially or completely and must then be employed in polar organic solvents.

The heat of formation of hydroxymethyl groups is only −20.3 kJ/mol, as compared with −98.7 kJ/mol for the formation of

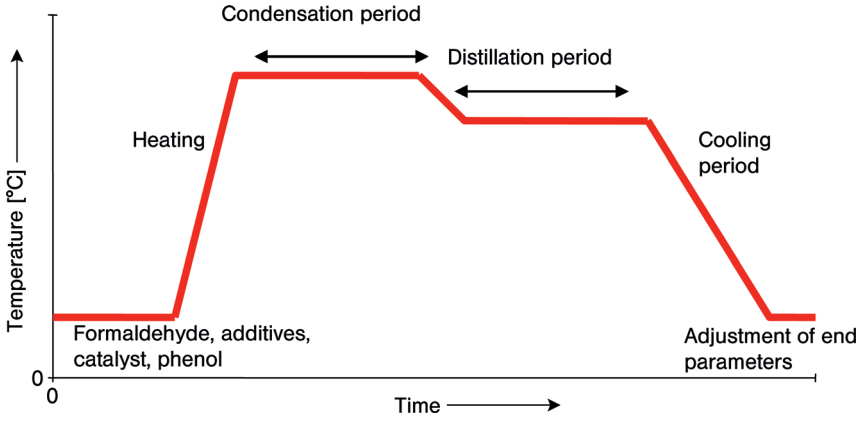


Figure 2. Production scheme of a resol

methylene bridges [11]. Thus, the heat of formation of resols is theoretically lower than that of novolacs. However, hydroxymethyl groups are only stable at low temperatures and can be converted into methylene bridges at higher temperatures. Therefore, in the production of resols a great quantity of heat is evolved if the reaction gets out of control. As a result of the high formaldehyde/phenol ratio resol production demands high safety requirements.

To *etherify* the hydroxymethyl groups, a solution of the resol is heated in, for example, butanol. The water formed is distilled off azeotropically with the organic solvent as entrainer, which is recycled to the reactor. Condensation reactions between the hydroxymethyl groups to form ether bridges occur simultaneously. The reaction is controlled by measurement of the viscosity and the solubility. Etherification of alkyd- and oil-modified phenolic resins should be carried out in the presence of a plasticizer, because the compatibility between the reaction components is thus established more quickly. The removal of solvents or water by distillation may be necessary during the various reaction stages or as a final step. During the distillation the condensation reactions continue. Distillation must therefore be carried out under mild conditions.

Example [11]. *Condensation*: phenol (846 g, 9 mol) and 30% formaldehyde solution (1600 g, 16 mol) are mixed at 20°C and the pH is adjusted to 9.5–10 by the addition of 38% aqueous sodium hydroxide solution (ca. 110 mL) with stirring. The mixture is heated to 60°C and kept for 4 h at this temperature. The decrease in formaldehyde concentration is monitored by titration with hydroxylamine hydrochloride. At the end of the reaction only ca. 1% formaldehyde is present. The mixture is cooled, and carefully neutralized almost completely with ca. 5% hydrochloric acid with stirring. The reaction solution must not become acidic and should have a pH of ca. 7.2–7.5. Water and excess phenol are subsequently distilled off under vacuum, such that the temperature may reach a maximum of 60°C (at 1.5 kPa). A viscous resin (1360 g) is obtained as residue.

Etherification: butanol (1360 g) and toluene (125 g) are added to the residue and the mixture is stirred at 40°C until the components have completely dissolved. After cooling, precipitated sodium chloride is filtered off. Butanol (900 g) is then added to the filtrate and the pH is adjusted to 6 with a concentrated solution of phosphoric acid in ethanol with vigorous stirring. The reaction mixture is then heated to boiling with stirring in a three-necked flask fitted with a Dean–Stark head which is filled with a 1:1 butanol/toluene mixture. In the Dean–Stark head, the water which has been distilled off is separated and the solvent is recycled into the reaction vessel. After ca. water (72 mL) has been distilled off, a sample of the reaction solution can be diluted at 20°C with xylene (4 parts) or petroleum ether (1.4 parts) without the resulting solution becoming cloudy (before the etherification a sample could only be diluted by 0.7 or 0.4 parts, respectively). The solution is concentrated (to 2620 g) under reduced pressure and traces of salt are filtered off at 20°C, after 48 h.

Alkylphenol Resols. *para*-Alkylphenols can only react with formaldehyde in the *ortho*-positions. Hydroxymethyl groups or dimethylene ether bridges in the *ortho*-position differ from those in the *para*-position by their greater stability. In the production of alkylphenol resols the hydroxymethyl groups therefore remain relatively stable in alkaline medium even at elevated temperatures of between 60°C and 70°C. To prevent the conversion of dimethylene ether bridges to methylene bridges according to Equation (6), the production of alkylphenol resols is often performed in two steps. In the first step a resin, rich in hydroxymethyl groups, is produced in the presence of alkali. The catalyst is subsequently removed by neutralization and washing out. The substance is then heated to >100°C to carry out the actual polycondensation, the etherification of hydroxymethyl groups to form dimethylene ether bridges. Catalysts are not required in this step.

4.3. Phenolic Resins Modified by Natural Resins

The reactions of resols with rosin to give albertol acids are carried out in the melt at 100–200°C. The albertol acids are subsequently reacted with polyols to give polyesters or with metal oxides to give resinates (both procedures can also be combined). These reactions must be

carried out at temperatures of up to 280°C because the tertiary carboxyl groups of the abietic acids are only esterified slowly and the melt viscosities and softening points of the rosin-modified phenolic resins can be very high. Suitable resol components are the reaction products of formaldehyde with phenol, cresols, alkylphenols, or bisphenol A, or mixtures of these. The properties of the resins are determined by the composition and structure of the resol, the resol/rosin ratio, and the nature and quantity of the polyols or metal oxides used for the subsequent reaction. The modified phenolic resins vary greatly with respect to viscosity, softening point, miscibility with solvents, and compatibility with varnish or printing ink raw materials.

The reaction sequence between rosin, resol, and esterification components can also be reversed. In this case the natural resin acids are first esterified and the esters are then reacted with resols.

4.4. Phenolic Resins with Special Properties

Resols for Water-Soluble Varnishes. Water-soluble resols exist as phenolates that are unsuitable for varnishes because they do not form adhesive varnish films. For the production of self-curing binders for water-soluble varnishes, carboxyl groups are introduced into the resols. These carboxyl groups impart water solubility when they are converted into salts with amines or ammonia. The phenolic hydroxyl groups are reacted with chloroacetic acid according to the Williamson ether synthesis usually at the temperature of formation of the resol. Alkali is used as the condensation agent. To achieve water solubility it is not necessary to introduce carboxyl groups into all resol molecules. The reactions are generally carried out in the presence of auxiliary solvents, mostly glycol ethers, which then also remain in the varnish formulation [15].

Water-soluble phenolic resins for varnishes are mostly applied in combination with plasticizers; for example, epoxy resins or fatty oils. It is thus often sufficient to incorporate the groups that impart water solubility into one of the components. The second component is then carried into the aqueous phase by the first.

Ether Resins from Resols and Novolacs. The phenolic hydroxyl groups can be etherified with, e.g., benzyl chloride or allyl chloride. The etherification always lowers the rate of curing. On the other hand, it reduces disadvantages which are due to the presence of phenolic hydroxyl groups, e.g., oxidizability, tendency towards coloration, and sensitivity towards alkalis. A strong decrease in viscosity is often associated with etherification. This is particularly the case with allyl ethers. The phenolic hydroxyl groups of resols and novolacs can also be etherified with epoxy compounds such as ethylene oxide, propylene oxide, or styrene oxide in the presence of catalytic quantities of alkali. The nucleophilic opening of the oxacyclopropane ring by the phenolic hydroxyl groups is very fast. It is thus possible to work in aqueous solution without significant nucleophilic attack of water at the epoxy group. Reaction of the epoxy compounds with hydroxymethyl groups only occurs if the epoxy compound is added in a nearly stoichiometric ratio to the phenolic hydroxyl group.

Condensation Reactions between Phenol Ethers or Hydrocarbons with Formaldehyde and Phenol. Phenol ethers can form polycondensates with formaldehyde. Known examples are diphenyl ether, phenoxyacetic acid, diphenylglycerol ethers, and phenoxyisopropanol. The condensation reactions can only be carried out with acid catalysts. Depending on the polarity of the ether, strong acids must be used, sometimes in very large quantities. Aromatic hydrocarbons, e.g., xylene, are even less reactive than phenol ethers. The hydroxymethyl groups and dimethylene ether bridges are fairly stable in the phenol ether resins in spite of the high acid concentration and remain as reactive groups in the resin.

Because of the low tendency towards self-curing, these resins are usually reacted with (excess) phenol to form methylene bridges between the phenol ether (or hydrocarbon) and the phenol.

4.5. Wastewater

In the production of phenolic resins phenol-containing wastewater is produced, which can also be contaminated by formaldehyde, salts, acids and alkali, and organic solvents. This must

be rendered harmless in a way that will not pollute the environment, for example by incineration polluted wastewater. In addition, phenol can be degraded very readily by bacteria. The purification in biological sewage plants—after dilution with other waste water, if necessary—is therefore very effective. It can be economic to extract the phenol before the incineration of the waste water.

5. Storage and Transportation

Solid phenolic resins which are sold in broken pieces, flakes, pastilles, or granules, can be packed in sacks, drums, or large containers. If the resins (e.g., rosin-modified types), have a tendency towards autoxidation, they should be stored in the absence of oxygen. *Phenolic resin solutions* are not corrosive and can therefore be stored in iron containers, if a possible coloration of the resin is acceptable. Otherwise the containers must be coated on the inside. *Liquid phenolic resins* are transported in tank cars, containers, or drums. When stored at room temperature, aqueous alkaline resol solutions often lose their viability after a few days or weeks. These solutions must be kept cool during transportation and stored in refrigerated areas. The storage life of solid resols at room temperature is generally longer; it is nevertheless advisable to keep all resols cool during storage. Certain phenolic resins have relatively low softening temperatures and compact during storage which impairs their storage stability.

6. Testing and Analysis

A summary of the testing methods is contained in DIN EN ISO 10 082

General Tests. Color index, viscosity, flash point, density, melting point (softening point) are measured according to DIN 53 244.

Determination of *water* is carried out by the Karl Fischer method.

Hydroxyl Groups. The total quantity of hydroxyl groups is determined by acetylation according to DIN 53 240. The presence of unsaturated groups, for example in modified natural resins, can give rise to values which are too high.

Reactivity Determination for Resols: B-Time. The cross-linking rate of resols, the transition from the A- into the B-stage is determined on a hot plate at a predetermined temperature, usually 120°C or 150°C.

Differentiation between the Various Types of Phenolic Resin. Neutral resol solutions in polar solvents give a blue or purple coloration with iron(III) chloride. With novolacs this coloration only appears after the addition of a small amount of hexamethylenetetramine. Alkylphenol novolacs often give a black-violet coloration. Modified natural resins do not show the color reaction, but can be identified by the Storch–Morawski color reaction (→ Resins, Natural) [16, 17].

Chromatographic Methods. Thin layer chromatography is very suitable for the determination of phenolic resins (e.g., monomer content) and can also be used for the quantitative determination of components by comparison of the spot size. The sodium salt of diazotized sulfanilic acid in aqueous solution, or iodine vapor can be used to develop the spots.

Gel permeation chromatography on polystyrene columns is applied to determine the molecular mass distribution of phenolic resins. In the low molecular mass range it also gives information on the concentrations of phenols, hydroxymethylated phenols etc. The columns must be calibrated with phenolic compounds [18].

Gas chromatography is suitable for the determination of free phenols. Phenols up to and including butylphenol can be detected by direct injection. Higher phenols are determined after esterification (acetylation, silylation).

Spectroscopic Methods. IR spectroscopy of phenolic resins is described in detail in [10]. The groups typical of phenolic resins can be determined and analyzed semiquantitatively.

Phenolic resins show UV absorption bands at 254 and 280 nm. UV spectroscopy is sometimes used for product monitoring; however, the shift of the bands due to other resin components or because of substitution must be taken into account.

NMR spectroscopy enables detailed examination of the molecular structure of phenolic resins and at the same time kinetic studies of the

formation reactions under different conditions [19].

The most common analytical methods are described in the following standards:

- **DIN EN ISO 3251.** Paints, varnishes and plastics - Determination of nonvolatile-matter content (ISO 3251:2008); German version EN ISO 3251:2008
- **DIN EN ISO 8974.** Plastics - Phenolic resins - Determination of residual phenol content by gas chromatography (ISO 8974:2002); German version EN ISO 8974:2002

  Plastics - Phenolic resins - Determination of reactivity on a B-transformation test plate (ISO 8987:2005); German version EN ISO 8987:2005
- **DIN EN ISO 8989.** Plastics - Phenolic resins - Determination of water miscibility (ISO 8989:1995); German version EN ISO 8989:1998
- **DIN EN ISO 11402.** Phenolic, amino and condensation resins - Determination of free-formaldehyde content (ISO 11402:2004); German version of EN ISO 11402:2005
- **DIN ISO 8975.** Plastics; phenolic resins; determination of pH; identical with ISO 8975:1989
- **DIN EN ISO 9396.** Plastics - Phenolic resins - Determination of the gel time of resols under specific conditions using automatic apparatus (ISO 9396:1997); German version EN ISO 9396:2000
- **DIN EN ISO 8619.** Plastics - Phenolic resin powder - Determination of flow distance on a heated glass plate (ISO 8619:2003); German version EN ISO 8619:2004
- **DIN EN ISO 8988.** Plastics - Phenolic resins - Determination of hexamethylenetetramine content - Kjeldahl method, perchloric acid method and hydrochloric acid method (ISO 8988:2006); German version EN ISO 8988:2006
- **DIN EN ISO 11401.** Plastics - Phenolic resins - Separation by liquid chromatography (ISO 11401:1993); German version EN ISO 11401:1998

7. Uses

The use of phenolic resins is determined by their superior properties, which include:

- FST (fire–smoke–toxicity) properties
- Heat resistance
- Chemical resistance
- Moisture resistance
- High carbon yield, after decomposition
- Electrical insulating properties

Thus, from an economic point of view, phenolic resins are quite cost efficient.

7.1. Novolacs

7.1.1. Cross-Linked Novolacs

For industrial use novolacs can be delivered in flakes, prills, powder resin, dispersions, solutions in organic solvents, or even in the molten state.

For cross-linking, novolacs are processed together with *curing agents*, mainly hexamethylenetetramine. Cross-linking occurs at a sufficient rate at 140–160°C and can be carried out within a few minutes, particularly if a part of the polycondensation reaction has already taken place.

Novolacs are sometimes cross-linked with *resols*. This reaction gives resins with high hardness, high stability, but a lower fracture strain.

Cross-linked phenolic resins are much less flammable than thermoplastics. Phenolic resins can be rendered virtually nonflammable by the addition of usual plastics additives such as phosphates, borates, red phosphorus, phosphoric acid esters, and other flame retardant agents, mainly based on phosphorus/nitrogen synergies.

Thermosets/Molding Materials. Phenolic resin molding materials are produced with heated rollers or extruders. Treatment of a mixture of novolac, hexamethylenetetramine, fillers, and additives leads to an intermediate, which is the actual molding material. The polycondensation is driven so far that the molding material in the final molding step can still flow,

but so that the final cross-linking occurs very quickly. Phenolic resin thermosets are standardized according to DIN EN 14598 part 1-3. The application properties of the final products depend very much on the choice of filler material. The processing properties, in contrast, are affected primarily by the novolacs used. Especially important processing properties are good flow characteristics and rapid curing. Molding technology which predominated until the end of the 1960s has in the meantime been substituted by transfer molding and injection molding, particularly in the mass production of less complicated preforms. Thus the expression "thermosetting molding materials" has come into common use.

Grinding Wheels. In the production of phenolic resin-bound grinding wheels, the grinding material (usually corundum of various granularities) is impregnated with a liquid phenol resol and mixed with a ground, pulverized mixture of phenol novolac and hexamethylenetetramine. The binder cures to a three-dimensional cross-linked resite under a carefully controlled temperature and pressure program. No defects may occur in this process because grinding wheels are exposed to high thermal and mechanical stresses.

Friction Linings. Brake linings and clutch facings are made of reinforced phenolic resins. Novolac–hexamethylenetetramine mixtures can also be used here as binders. For better heat conduction, copper wire or copper gauze is often incorporated. Novolacs modified with alkylphenols or cashew oil are used to adjust hardness and lubricating properties, particularly in brake linings.

Reinforcing Resin for Rubber (→ Rubber, 9. Chemicals and Additives). The hardness of rubber is increased by the incorporation of novolac–hexamethylenetetramine mixtures. This hardness can be so great as to enable fabrication of solid, tough molded articles, for example for bodywork parts. Often, however, as in car tire mixtures, only slight improvement of the rubber hardness is desired. The reinforcing effect is thought to be caused by strong intermolecular interactions between the cured, thermoplastic phenolic resin and the rubber-elastic vulcanized product. Both types of macromolecule are not bonded by covalent bonds.

Novolac Powder Resins for Felt Bonding. Felts → Felts are used as acoustic and thermal insulation material for the automotive industry and household appliances.

Felt is a combination of reclaimed fabric, mainly cotton, and powder resin, which is used as a binder. Phenolic resins offer the best compromise regarding performance and economy in use.

The final properties of the phenolic resin bonded textile felt, including mechanical strength, damping behavior, thermal resistance and environmental behavior are determined by the composition of the felt and the processing parameters. Normally novolac–hexamethylenetetramine mixtures are in use.

Novolac Solutions for Car Filter Media. Novolacs dissolved in alcohols are widely used for the impregnation of filter papers for car filter media. They are cured by hexamethylenetetramine and/or resols. Novolac solutions in combination with resols are mainly used for oil and fuel filters and airfilters are produced with solvent based resols.

7.1.2. Novolacs without Cross-Linking

The use of novolacs which are not cross-linked is less important and is based particularly on their solubility and compatibility properties. As polyalkylidenephenols they have strong inter- and intramolecular interactions and can be adapted to the most varying requirements by alkyl substitution.

Varnishes (→ Paints and Coatings, 2. Types, Section 13.2). The use of uncured novolacs in varnishes is the oldest application of phenolic resins. Because of their high susceptibility towards oxidation and coloration, particularly in the case of unsubstituted phenol novolacs, this application area has hardly developed further. Noncross-linked novolacs are now only important in specialist areas such as model lacquers and bituminous paints.

Printing Technology. Novolacs are often added to aniline printing inks because of their high affinity for these dyes. Because aniline printing inks are often used for printing on

food packaging materials, the novolacs must be phenol-free. Novolacs are also used in the formulation of ballpoint pastes.

Novolacs are applied, together with diazo compounds, to zinc or aluminum plates in a thin layer for the production of positive offset printing plates (→ Imaging Technology). Similar systems are used as photoresists for the photolithographic production of integrated circuits.

Raw Materials for Epoxy Resins. The reaction of epichlorohydrin with novolacs (instead of bisphenol A) leads to polyfunctional epoxy resins (→ Epoxy Resins, Chap. 5). Their curing products are characterized by their particularly high usage temperatures.

Alkylphenol Novolacs, particularly those based on 4-hydroxybiphenyl, 4-isooctylphenol, and formaldehyde are used for the production of copying paper.

Tackifiers for Rubber (→ Rubber, 9. Chemicals and Additives). Nonvulcanized rubber mixtures are often not tacky enough to adhere to each other. This is a considerable disadvantage in the production of laminated rubber articles, e.g., car tires. Tackifiers are used in rubber technology to improve this. Besides mineral oils and natural and synthetic resins, alkylphenol novolacs are particularly effective and when used with other tackifiers have a synergistic effect. In addition to alkylphenol–formaldehyde novolacs, *para*-alkylphenols–acetaldehyde resins, and *para*-alkylphenol–acetylene resins are often used as tackifiers.

Crude Oil Separators. Ethoxylation (i.e., reaction with ethylene oxide) of alkylphenol novolacs gives water-soluble, surface-active substances. If the degree of ethoxylation is suitably adjusted, they have de-emulsifiying properties. Addition of small quantities to the crude oil that is extracted as an oil–saltwater emulsion effects a faster separation into an oil and an aqueous phase.

7.2. Resols

7.2.1. Water-Soluble Resols

Water-soluble condensation products of phenol and formaldehyde are used mainly as adhesives for wood or wood chips, as binders for organic and inorganic fibers and for granular material such as corundum or sand. Curing is performed thermally at 100–180°C and, if possible, under pressure. If curing is carried out under atmospheric pressure the cross-linking process must be carefully controlled and performed slowly to avoid the formation of bubbles or cavities.

The waste-gas from the thermal curing process contains phenol, formaldehyde, and sometimes solvent vapors. When legally stipulated limiting values are exceeded, the waste-gases must be incinerated.

Cross-linked phenolic resins have a low flammability. They can be rendered virtually nonflammable by additives. In the event of fire the flue gases are relatively nontoxic and, compared to the flue gases from other burning plastics, are relatively transparent. For example, this makes them particularly suitable in the interiors of vehicles.

Binder Systems for Wood Fibers. Aqueous, alkaline resol solutions are used in the production of fiber boards (HDF, MDF), particle board, oriented strand boards (OSB) and plywood. Wooden substrates bound by phenolic resin are moisture-resistant in contrast to those bound by urea resins, and are therefore suitable for the production of exterior walls in buildings and related uses.

Construction Adhesives. Resorcinol–formaldehyde resins are used as wood glues. Resorcinol is treated with a substoichiometric amount of formaldehyde in an alkaline medium and the stable solution is treated with more formaldehyde (usually in the form of paraformaldehyde) immediately before use. The polycondensation with resorcinol, which is very fast at, and even below, room temperature, is thus restarted. The resorcinol–formaldehyde resin cross-links three-dimensionally. Glues containing resorcinol resins have high mechanical stability and are highly water-resistant.

Binding Agents for Molding Sand (→ Foundry Technology, Section 2.3.4). Phenol resols or novolac–hexamethylenetetramine mixtures that can be sufficiently diluted with water, are used as binders for casting molds, which consist mainly of sand. Mixtures of both resins are sometimes used for full molds. For

hollow and thin-walled molds (Croning process), alcoholic solutions of novolac–hexamethylenetetramine adducts are used. To achieve special properties or to make the process cheaper, phenolic resins are sometimes modified with furan or urea resins.

Laminates. High quality laminates for mechanical and electrical equipment are obtained by impregnation of paper, cotton, glass fiber, carbon fiber or aramide fiber with phenolic resins and subsequent thermal cross-linking. They are used as insulation and construction materials. For the production of laminates with high electrical performance, e.g., for printed circuit boards, unmodified resols and tungoil-plasticized resols are used together for impregnation. Both resins have different functions. The unmodified resins — with as low a molecular mass as possible — penetrate into the fiber and the tungoil-plasticized resins remain on the fiber surfaces and bind them together.

In *decorative laminates*, water-soluble, alkaline resol solutions can only be used for the production of core resins because of their dark coloration. Melamine resins are used as decorative facings. By modifying the phenolic resins different properties can be achieved such as postforming laminates, flame-retardant laminates, compact boards or laminate flooring, produced by HPL (high pressure)-, CPL (continuous press)- or short-cycle press technologies.

Fiber Bonding. Organic or inorganic fibers or rock wool can be bonded to plates or nonwoven fabrics by impregnation with an aqueous resol solution or this can be sprayed on them. Curing is carried out continuously with heated rollers or in presses. Matting or insulating plates bound with phenolic resin have moderate heat-insulation properties in comparison to thermoplastic foams but have the advantage of being virtually nonflammable, and at the same time soundproof.

Nowadays the greatest amount of phenolic resins is used to produce glass-wool and stone –wool insulating materials.

Phenolic Foam. Phenolic foam is used in three applications:

- Flower foam with open cells to store the necessary water for the flowers
- Insulation foam with closed cells with high insulation effects
- Mining foam to stabilize the stone in mines (operating mines or old mines)

Water-soluble resols can be used for the production of foamed plastic. For foaming, the addition of surfactants and the use of blowing agents are necessary. Phenolic resin foams have the advantage of low flammability. However, the corrosive effect of the strong acids used as hardeners limits their general use.

Coated Abrasives. To produce abrasives such as sandpaper, abrasive cloth, or flexible sanding disks on vulcanized fiber, abrasive grains are applied to a moving backing cloth on one side. These grains are fixed together and to the surface of the backing cloth with a binder. For heat-resistant abrasives, phenol resols are preferably used as binders.

Since the carrier material (usually cellulose) is sensitive to high temperatures, a prolonged application of temperatures >130°C must be avoided. Therefore, cross-linking of the phenol resol to resite takes a long time. Phenolic resins that are suitable for the production of abrasives must therefore be very reactive, to limit the curing time to a few hours. This naturally limits their storage life. The cross-linking reactions are carried out under atmospheric pressure in festoon dryers and the carrier materials, coated with phenolic resin and abrasive grains are introduced into a dryer where the temperature and humidity must be carefully controlled.

7.2.2. Resols in Organic Solvents

The resols produced as aqueous alkaline solutions can be dissolved in polar solvents after neutralization of the catalyst. Basically such solutions do not differ from aqueous solutions. Catalysts can be added to accelerate cross-linking. Since, however, phenolic resins are often used in combination with other components, these resins must be compatible with the other substances, and for this purpose their solution properties must be altered. This can be done using alkylated phenols as raw materials or in the etherification of the methylol groups with alcohols.

Epoxy Resin–Phenolic Resin Coatings. Resols based on cresols are used in cross-linking together with epoxy resin. The enamels baked at temperatures around 200°C stand out by virtue of their very good ductility and very high chemical stability. They are principally used for the inner coating of food and drink cans, and other containers.

Oil-Plasticized Resols. Resols—mainly based on cresol or bisphenol A—are modified by fatty oils or alkyds and are used as baking enamels. These varnishes have good chemical stability and very high ductility and are used, in particular, as inner coatings for containers. Other uses of oil-plasticized resols lie in the area of cylinder-head gaskets and electric insulation materials.

7.2.3. Alkylphenol Resols

Resols from *para*-alkylphenols are also soluble in nonpolar solvents. The solubility increases with increasing size of the alkyl group. *para*-Alkylphenol resols differ from other resols in their bifunctionality towards formaldehyde. Thus, *para*-alkylphenol resols cannot cross-link by themselves, but are used as cross-linking agents for other, polyfunctional substances. Examples are fatty oils, rubbers, long-chain epoxy resins, alkyd resins, and phenol novolacs.

Vulcanization. Rubbers can be vulcanized by alkylphenol resols. As phenolic resins are considerably more expensive than sulfur, this possibility is only exploited for special cases, e.g., butyl rubber.

Adhesive Resins. The properties of polychloroprene adhesives can be improved by natural and synthetic resins. Alkylphenol resols not only increase the stickiness of the adhesive but also its binding and heat stability. Since the amount of resin needed to be added is about half the quantity of polychloroprene, adhesive resins have considerable economic importance.

The alkylphenol resols do not act as such in polychloroprene adhesives but in the form of their magnesium and zinc complexes. These are formed with the magnesium and zinc oxides present in the polychloroprene adhesive. The complexes described as chelate polymers have a very high molecular mass, but are nevertheless readily soluble in aromatic hydrocarbons and even in naphtha [20].

7.3. Phenolic Resins Modified by Natural Resins

Printing Inks. Rosin-modified phenolic resins are used as binders for book or offset printing inks for the following reasons: (1) they are soluble in mineral oil and aromatics, (2) compatible with other printing-ink raw materials, and (3) have a high melting point, which allows a rapid transition from the liquid to the solid state on printing. Phenol resins, modified by natural resins, are very varied so that they can be adapted to the continually increasing rate of working in the production of printed articles.

7.4. Waterborne Paints, Phenol Ether Resins

Waterborne Paints. The amine and ammonium salts of resols containing carboxyl groups are water-soluble. They are used as baking enamels and give coatings which are resistant to chemicals but are brittle. To plasticize them they are mixed with fatty oils, alkyds, or unsaturated hydrocarbons (which have been rendered water-soluble by the addition of maleic anhydride, and subsequent salt formation). Their main use lies in the electrodeposition coating of car bodies and vehicle parts. See also, → Paints and Coatings, 2. Types, Chap. 13.

Allyl Ether Resols. Resols etherified with allyl groups at the phenolic hydroxyl group have a very low viscosity and can be used as solvent-free or low-solvent binders in varnishes. Higher baking temperatures must be used for cross-linking than in the case of simple phenolic resins.

Phenol Ether and Hydrocarbon–Formaldehyde Polycondensates. Mixed condensates from (1) phenol ethers–formaldehyde–phenol, or (2) hydrocarbons–formaldehyde–phenol are used in thermosets which have an increased stability towards chemicals and oxygen.

7.5. High-Temperature Coking

Phenolic resins, whether resols or novolacs, coke upon heating in the absence of oxygen. They can therefore be used as binders for refractories based, for example, on magnesite or dolomite, which are used for the lining of blast furnaces and similar constructions. Phenolic resins can also be used as high-temperature materials after coking and in some cases graphitization. These materials can be reinforced with temperature-resistant fibers.

7.6. Phenolic Resins in Composite Materials

Although phenolic resins are quite old materials there are new applications in the field of advanced composite materials, used, e.g. in the aerospace or aircraft industry. In particular, the superior FST properties of phenolic resin bonded composite materials are valued in these sophisticated industries. Here limiting aspects for the use of phenolic resins are associated with their mechanical properties such as low impact strength and toughness due to the rigid polymer network. To overcome such problems highly modified and plasticized resins are in use.

Some examples for the usage of phenolic resins in high performance applications are:

- Light weight honeycomb composites used for interior parts of airplanes
- Carbon–carbon composites (using the carbon network) for aircraft brakes, heat pipes, reentry vehicles, rocket motor nozzles, biomedical implants.
- Prepregs for ballistics like helmets, bullet proof jackets, armoured cars.

7.7. Development Trends

- Broader usage of modified phenolic resins in composite materials due to their superior FST properties and cost efficiency
- Combinations with other polymers
  - □ Modification of thermoplastics
  - □ Phenolic–melamine–urea resin combinations
  - □ Phenolic–epoxy resin combinations
  - □ Phenolic resins–acrylates combinations
- Usage of nano structures
- Usage of renewable materials in combination with synthetic raw materials for new binder systems

8. Economic Aspects

In 1978, 728 000 t phenolic resin were produced in the United States [21] and in 1994, 730 000 t [22].

In Europe in the years 2003–2009 about 650000–850000 t/a of phenolic resins were produced.

No conclusions about the turnover value can be drawn from the quantity data, for although phenolic resins for mass applications are cheap, very high prices are often demanded for specialist applications.

9. Toxicology and Occupational Health

Cured phenol–aldehyde resins are classified as nontoxic. The toxicity of phenolic resins is therefore assessed according to their content of unreacted monomers [23]. In Germany phenolic resin formulations with a content of more than 5% free phenol must be labeled with a skull and crossbones and those with more than 1% with a cross. Substances liberated in the thermal cross-linking of phenolic resins, particularly formaldehyde, are toxic and lead at least to irritation. Contact with phenolic resins can lead to allergies in sensitized people.

Occupational Health. No TLV or MAK values have been established for phenolic resins. The corresponding values of the most important monomers are as follows: formaldehyde TLV-TWA 1 ppm (1.2 mg/m^3), TLV-STEL 2 ppm (2.5 mg/m^3), MAK 0.5 ppm; phenol TLV-TWA 5 ppm (19 mg/m^3), MAK 5 ppm.

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Resins, Synthetic

ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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1. Definition

The term "resin" is a versatile expression that is not sharply defined. Originally, the term was applied to low molecular mass natural products, which were usually defined as yellowish to brown-colored, transparent to opaque, soft to brittle, easily fusible, tacky and noncrystallizable materials that are soluble in most common organic solvents and virtually insoluble in water. With the development of the chemical industry, the term resin has also been applied to synthetic

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materials that are used as substitutes for natural resins, or to materials with similar physical properties. In the international standards ISO 472 (Plastics — Vocabulary) and ISO 4618/3 (Paints and Varnishes — Vocabulary — Part 3: Terminology of Resins), resins are defined similarly, i. e., as solid, semisolid, or pseudosolid organic materials that have an indefinite and often high relative molecular mass, and generally soften or melt over a range of temperatures on heating. Very often, the term resin is also used to designate any polymer that is a basic material for plastics (e. g., polyethylene resin, → Plastics, General Survey). In the German standard DIN 55 958, resin ("Harz") is defined as a collective term for solid to liquid organic products. Their molecular mass distribution can vary within wide limits. Resins include a large variety of organic substances of different chemical composition, but with many similar physical properties.

Generally, resins are products with medium molecular mass. Their average molecular mass does not exceed 10 000 and, in most cases, is even lower, Resins have an amorphous and often complex structure. They do not exhibit a sharp melting point, but like every amorphous polymeric system, resins have a glass transition temperature and are characterized by their softening point, which denotes the transition temperature from a pseudosolid to a plastic state on heating.

Resins can be subdivided into natural and synthetic resins.

Natural Resins. In ISO 4618/3, natural resins are defined as resins of vegetable or animal origin. The term includes rosins (gum, wood, or tall-oil rosins from tree and plant exudates; wood extracts; or byproducts from paper manufacturing), fossil resins such as amber; mined resins such as asphaltite; shellac as secretion product from an insect; and their main derivatives.

Synthetic Resins. In ISO 4618/3, synthetic resins are defined as resins resulting from controlled chemical reactions such as polyaddition or polycondensation between well-defined reactants that do not themselves have the characteristics of resins. Synthetic resins are also obtained by polymerization (ISO 472) of unsaturated monomers. This term includes two subgroups:

1. Hydrocarbon resins, i.e., synthetic resins from coal tar, petroleum, and turpentine streams, produced by polymerization. These resins are used like natural ones, e.g., in combination with other polymers to impart special properties such as tack, flow, and hardness to a material.
2. Synthetic resins obtained mainly by addition polymerization and polycondensation, which are intermediates in the synthesis of higher molecular mass plastics.

2. Hydrocarbon Resins

2.1. Classification

The term hydrocarbon resin is generally applied to low molecular mass thermoplastic polymers that are composed mainly of carbon and hydrogen. With respect to their origin, hydrocarbon resins can be classified in four main groups:

1. Petroleum hydrocarbon resins, derived from cracked petroleum distillates
2. Indene – coumarone resins, based on coal-tar oils
3. Terpene resins from turpentine fractions
4. Resins from pure monomers

The oldest family of hydrocarbon resins is the indene – coumarone resins, discovered by KRÄMER and SPILKER in 1890 and produced on an industrial scale since about 1910. In the mid-1930s the terpene resins were developed, which are based on byproducts of rosin extraction. Only in the 1940s did the petroleum resins become known, initiated by the rapid development of the petrochemical industry. These resins established their position as the most important group of these products, Resins from pure monomers came onto the market in the mid-1970s.

2.2. Raw Materials

The main sources of raw materials for the chemical industry are pyrolysis processes [e. g., of coal in coke ovens and, to a larger extent, of petroleum fractions in steam crackers (→ Ethylene, Section 5.1.)].

Pyrolysis of coal gives high-temperature coal tar as byproduct of coke production. The most important products are:

Coke	ca. 75 wt %
Coke-oven gas	13 wt %
Crude tar	3 wt %
Crude benzole	1 wt %

The first stage of coal-tar distillation gives water and the coal-tar light oil. The latter and the following carbolic oil fraction contain the aromatic unsaturated compounds that are useful in indene – coumarone resin production [4].

The pyrolysis of naphtha fractions can generate the following products and quantities, depending on the origin of the naphtha and the cracking conditions:

Hydrogen	1.0 wt %
Methane-rich gas	15.0 wt %
Ethylene	28.0 wt %
Ethane	3.5 wt %
Propene	14.0 wt %
C_4 fraction	9.0 wt %
C_5 fraction	3.0 wt %
Benzene	7.5 wt %
C_6 fraction	1.0 wt %
Toluene	5.0 wt %
C_8 aromatics	3.0 wt %
C_9 aromatics	3.5 wt %
Residual oil	5.5 wt %

The following crude feeds are used as starting materials in the production of hydrocarbon resins:

1. C_5 streams that contain linear and cyclic olefins and diolefins as resin formers are used for the production of aliphatic hydrocarbon resins
2. C_8 – C_{10} streams containing styrenes, indenes, and dicyclopentadiene (DCPD) are used for the production of aromatic hydrocarbon resins

The composition of the feedstock is very important for the properties of the final resin. It affects color, degree of unsaturation, softening point, molecular mass distribution, solubility, and compatibility of the product, The crude cuts can be processed in various ways to give suitable raw materials for the manufacture of different resin types.

2.2.1. Indene – Coumarone Feedstocks

Coal-tar light oil and carbolic oil, containing aromatic resin formers such as styrene, α-methylstyrene, vinyltoluenes, indene, methylindenes, and coumarone, are treated to remove phenols and pyridine bases by extraction. Further treatment steps to improve resin color and properties are generally applied [5]. A typical composition of an indene – coumarone resin feedstock is as follows:

Styrene	2.0 wt %
α-Methylstyrene	1.0 wt %
Alkylbenzenes	30.0 wt %
Vinyltoluenes	4.0 wt %
Dicyclopentadiene	5.0 wt %
Coumarone	7.0 wt %
Indene	48.0 wt %
Methylcoumarones and methylindenes	3.0 wt %

2.2.2. Petroleum Resin Feedstocks

C_5 Streams. C_5 streams from dependanizer effluents consist of olefins and diolefins such as isoamylene, isoprene, piperylene, and cyclopentadiene, together with C_5 paraffins. A straight dependanizer C_5 stream gives only poor resin quality. The resulting resin is highly susceptible to oxidation. Lowering the cyclopentadiene content by heat soaking and subsequent distillation improves product quality. Modern C_5 resins are made from distilled concentrated piperylene streams that are obtained in isoprene recovery. Special qualities are produced from extractively distilled piperylene concentrates. Some typical compositions are given in Table 1.

The diolefin/monoolefin ratio and the nature of monoolefins present in the feedstock affect the overall course of the polymerization process and the molecular mass distribution of the final resin and are therefore carefully controlled.

C_8/C_9 Streams are obtained from a special separate downstream column. The BTX (ben-

Table 1. Typical composition (weight percent) of C_5 resin feeds from steam cracking

Raw materials	Straight	Distilled concentrate	Extractive distillation concentrate
Cyclo- and dicyclopentadiene	19.0	7.5	2.0
Isoprene	30.0	8.0	0.5
Piperylene	14.0	38.0	69.0
Pentenes	15.0	12.5	0.5
Pentanes	11.0	15.0	2.0
Cyclopentene	2.0	8.5	18.0
Other hydrocarbons	9.0	10.5	8.0

zene, toluene, xylenes) fraction is drawn off as the top product, and a C_8/C_9 material is obtained as a sidestream or residue, depending on the process. This material contains high-boiling unsaturated benzene homologues, such as styrene, α-methylstyrene, vinyltoluenes, indene, and methylindenes, together with some dicyclopentadiene that arises from the depentanizer bottoms by dimerization of cyclopentadiene. Suitable C_8/C_9 streams can be pretreated to improve resin color and properties. A typical composition is given below:

Styrene	2.0 wt %
α-Methylstyrene	4.0 wt %
Vinyltoluenes	20.0 wt %
DCPD and codimers	6.0 wt %
Indene	20.0 wt %
Methylindenes	5.0 wt %
Naphthalene	5.0 wt %
Other nonreactive aromatics	38.0 wt %

Dicyclopentadiene concentrates are generated in the heat-soaking of depentanizer effluents and subsequent distillation of C_5 fractions. Besides dicyclopentadiene, such streams may contain codimers of cyclopentadiene with other dienes, such as butadiene or isoprene, and methyl derivatives of dicyclopentadiene. Dicyclopentadiene concentration may vary from high (90 – 95 %) through medium (70 – 80 %) to relatively low. A typical composition is given below:

Dicyclopentadiene	65 – 98 wt %
Codimers	2 – 35 wt %
Benzene	1 wt %
Sulfur	150 ppm

C_4 streams contain mainly isobutenes. After removal of butadiene, a suitable feedstock for resin production may have the following composition:

1-Butene	ca. 10 wt %
cis- and *trans*-2-butene	10 – 15 wt %
Isobutene	15 – 30 wt % or more
n-butane	ca. 30 wt %
Isobutane	ca. 30 wt %
C_{5+} components	balance

Pure Commercial Monomers. The pure commercial monomers styrene, α-methylstyrene, and vinyltoluenes are used individually, as blends, or together with terpenes or other selected unsaturated aliphatic compounds in resin manufacture. Styrene is produced in large quantities by alkylation of benzene and subsequent dehydrogenation. Its main use is in the manufacture of polystyrene. α-Methylstyrene is a byproduct of the large-scale production of phenol. Vinyltoluenes are produced in smaller quantities by alkylation of toluene, followed by dehydrogenation, Commercial vinyltoluene is a mixture of 64.5 % *m*- and 35.5 % *p*-vinyltoluene.

Terpene Monomers. The raw material for the production of terpene resins is based on natural terpene monomers that are obtained from various sources such as naval stores (gum and wood turpentine) and kraft paper production (tall-oil turpentine). Citrus terpenes, obtained by extraction from orange peel in the production of orange juice, are also used as raw materials. The most important terpenes for resin manufacture are α-pinene, β-pinene, and dipentene (*dl*-limonene). Typical compositions of terpene oils are listed in Table 2.

2.3. Production

Hydrocarbon resins are produced by polymerization of the unsaturated compounds contained in the fractions described in Section 2.2 by using mainly Friedel – Crafts catalysts such as aluminum chloride and its complexes, as well as boron trifluoride and its complexes. Brønsted acids (e.g., sulfuric acid) may be also used. The term "catalyst" is scientifically incorrect with respect to cationic polymerization and should be replaced by the term initiatior – coinitiatior (initiating system) [6]. The reaction can be performed batchwise or continuously and includes the following steps:

1. Feed preparation (distillation, pretreatment, blending)
2. Polymerization

Table 2. Typical compositions of terpene oils (in wt %)

	Gum turpentine	Wood turpentine	Tall-oil turpentine
α-Pinene	58 – 65	ca. 80	60 – 70
β-Pinene	23 – 35	0 – 2	20 – 25
Camphene	4 – 8		
Other terpenes	5 – 8	15 – 20	6 – 12

3. Deactivation of iniating system
4. Resin separation

The most important reaction parameters are feed composition, total and relative concentration of resin formers in the feed, type of catalyst and cocatalyst, catalyst concentration, and temperature. These parameters must be carefully controlled. They affect the reaction widely, in terms of yield, type (polymerization, alkylation), molecular mass, and molecular mass distribution, The particular resin feed is contacted with the initiating system by vigorous stirring. The reaction is exothermic and must be strictly temperature controlled, After reaction, the initiating system is inactivated (e.g., by addition of water, alkali, lime, or ammonia). Then the unreacted feed and the low molecular mass oligomers are removed by distillation, usually in combination with a steam-stripping process. The residual resin is conditioned in flakes, bulk, or other forms.

The proportion of catalyst in the reactant medium influences molecular mass and composition of the resin. High concentrations give resins with lower molecular mass, and lower concentrations give resins with higher molecular mass. A low concentration of catalyst may influence resin composition by selectivity (i.e., only the most reactive components are transformed). Reaction temperature affects product molecular mass, yield, and color. Molecular mass decreases and yield increases with increasing temperature.

Dicyclopentadiene resins are usually manufactured by thermal polymerization of various dicyclopentadiene feedstreams that may also contain styrene or indene.

2.4. General Properties

Depending on raw material and polymerization conditions hydrocarbon resins may range from viscous liquids to very hard solids with light to amber coloration. Special water-white types also exist. Solubility and compatibility characteristics are a function of the special resin type. All unmodified types have in common an apolar structure that gives them good water repellency and high resistance to acid, alkali, and salt solutions. They are soluble in aromatic and most common aliphatic solvents, ethers, esters, ketones, and chlorinated hydrocarbons. Unmodified resins are compatible with a wide range of other resins and polymers. The absence or presence of double bonds in the resin structure determines whether the resin is stable and/or reactive. Thus, both resins with excellent heat and weather stability and highly reactive grades are commercially available. The structure of hydrocarbon resins is very complex, The major principles involved are the following:

1. Mixtures of mono- and diolefin monomers result in paraffinic and naphthenic structures; diolefins (DCPD type) give unsaturated resins
2. Vinyl aromatic monomers (styrenes, indenes) generate chain structures with high aromatic substitution and a low degree of unsaturation
3. Bicyclic terpenes react mainly to produce cyclic structures by rearrangement

2.5. Characterization and Analysis

Hydrocarbon resins are usually characterized by their softening point, color, degree of unsaturation, saponification number, density, and ash content, These properties are determined by standardized methods (see Table 3).

Because of their complex structure, hydrocarbon resins do not exhibit a definite melting point but soften on heating within a temperature interval, The *softening point* is defined as the temperature at which a resin, poured in a ring of defined diameter and thickness, flows under the pressure of a given weight. The most widely applied method is the ring-and-ball (RB) method; the older Krämer – Sarnow (KS) method is used more rarely. A more recent method is the Mettler method.

Color is determined optically in solution by comparison with a color standard on the Gardner scale or less commonly on the Barrett scale. For light colors the Saybolt, Hazen, or APHA method is used. A comparison of Barrett and Gardner color numbers is given in what follows:

Barrett	Gardner
B 1/2	1 – 6
B 1	7 – 10
B 1 1/2	11 – 12
B 2	12 – 13
B 2 1/2	14
B 3	15
B 4	16 – 17
B 5	18

Table 3. Characterization of hydrocarbon resins

Property	Method (unit)	Standard
Softening point	ring and ball RB (°C)	ASTM D 3461–76, ISO 4625
	Krämer – SarnowKS (°C)	DIN 53 180,NFT 67 001
	Mettler	ASTM D 3461–76
Color	Gardner (50 % solution in toluene)	ASTM D 1544–80(0–18), ISO 4630
	Barrett (8 % solution in toluene)	
	Saybolt, Hazen, APHA (for very light colors)	
Unsaturation	bromine number (g Br_2/100 g)	ASTM D 1159–84, DIN 51 774, part 1
	Wijs iodine number (g I_2/100 g)	ASTM D 1959–69
Acid number	mg KOH/g	DIN 51 558, DIN 53 402,ASTM D 974–80
Saponification number	mg KOH/g	DIN 51 559, DIN 53 401
Density	at 20 °C (g/cm^3)	DIN 51 757
Flash point	Cleveland open cup (°C)	ISO 2592

Unsaturation is indicated by the iodine or bromine number. Neither number gives reliable information on the true degree of unsaturation, because along with addition reactions to the double bonds, substitution reactions may occur.

Other properties determining the end use of resins are solubility, compatibility, melt and solution viscosity, molecular mass, and molecular mass distribution. *Solubility and compatibility* are measured by determining the cloud point. Although generally accepted, this method is not standardized for resins. *Molecular mass and its distribution* are important resin characteristics and are determined by size exclusion (gel permeation) chromatography. Some information on resin structure is obtained by spectroscopic methods such as IR, UV, and NMR. The relation of aromatic to aliphatic protons evaluated by NMR is a useful tool for determining the aromaticity of a resin.

2.6. Resin Types

2.6.1. Aliphatic Hydrocarbon Resins

Aliphatic hydrocarbon resins are based on C_5 feedstreams and can be divided into general-purpose or basic resins, high-quality special piperylene resins, and dicyclopentadiene resins. Typical data for aliphatic petroleum resins are listed in Table 4.

C_5 Olefin – Diolefin Resins. Basic resins are produced from more or less narrow C_5 cuts and are available in large quantities as multipurpose resins. They have satisfactory color and color stability and a moderate degree of unsaturation. They are highly soluble in aliphatic solvents and compatible with a wide range of other resins, polymers, and waxes. Their softening point is usually between 70 and 100 °C (RB).

Piperylene resins exhibit an improved quality and are produced from highly concentrated streams that contain up to 70 % piperylene. They have properties similar to those of terpene resins because of their cycloaliphatic structure. Thus they are often called "synthetic terpene resins." They have excellent light stability and light color. A wide range of piperylene resins is produced — from viscous, liquid resins to hard resins.

Dicyclopentadiene Resins. Dicyclopentadiene resins can be divided in two main groups:

1. Those that contain predominantly dicyclopentadiene (DCPD), with high degrees of unsaturation (bromine number ca. 65 – 100 or higher) and which are distinctly heat- and oleoreactive
2. Those containing substantial amounts of aromatic structures (formed by co-reaction with unsaturated aromatics), with moderate unsaturation (bromine number ca. 55 – 57)

Table 4. Typical data for aliphatic petroleum resins

Property	C_5 Olefin – diolefin resins	Piperylene resins
Softening point RB, °C	70 – 100	liquid – 115
Gardner color	5 – 7	3 – 7
Bromine number, g Br_2/100 g	15	25
Density at 20 °C, g/cm^3	0.93 – 0.97	0.88 – 0.97

Table 5. Typical data for dicyclopentadiene resins

Property	Straight DCDP resins	Aromatic-modified DCPD resins
Softening point (RB), °C	liquid – 160	10 – 150
Gardner color	6 – 11	5 – 15
Bromine number, g Br_2/100 g	95 – 100	ca. 55
Density at 20 °C, g/cm^3	ca. 1.1	1.05 – 1.12

Because of the presence of reactive unsaturation these DCPD resins may be modified with other unsaturated components such as maleic anhydride, drying oils, or rosin (see Table 5).

Polybutenes, manufactured from butadiene-free C_4 fractions, are low molecular mass copolymers of the butene isomers. These polybutenes are normally low-colored, viscous liquids that are chemically stable, oxidation resistant, nondrying, and tacky (→ Polybutenes, Chap. 2.)

2.6.2. Aromatic Hydrocarbon Resins

Aromatic hydrocarbon resins are based on coal-tar-derived indene – coumarone streams or petroleum-derived C_8/C_9 streams. Typical properties of aromatic hydrocarbon resins are listed in Table 6.

Indene – Coumarone Resins [4], [5]. The oldest family of hydrocarbon resins is now available with an acceptably light color. Indene – coumarone (IC) resins are on the market as viscous liquids and as solids with high softening points, up to 170 °C (RB). The resins are soluble in most common solvents (except low molecular mass alcohols) and compatible with a wide range of polymeric materials. They exhibit high water repellency and resistance to acid and alkali. When not stabilized, they are subject to yellowing by autoxidation under the influence of UV light.

Table 6. Typical properties of aromatic resins

Property	Coal/tar based	Petroleum based
Softening point RB, °C	liquid – 170	liquid – 150
Gardner color	6 – 18	5 – 12
Iodine number, g I_2/100 g	35 – 105	25 – 90
Density at 20 °C, g/cm^3	1.08 – 1015	1.06 – 1.11

Petroleum Resins. The C_9 aromatic hydrocarbon resins are obtained from streams of cracked petroleum fractions that are purified to a greater or lesser extent, Depending on its origin and pretreatment, the raw material contains a varying percentage of dicyclopentadiene. The degree of unsaturation of the resin can thus be controlled by the choice of raw material. The properties of petroleum resins are generally similar to those of indene – coumarone resins, but petroleum resins are often characterized by a lower degree of unsaturation, higher light and heat stability, and a wider range of solubility and compatibility. They are produced in many different grades from viscous liquids to solids of high softening point.

2.6.3. Terpene Resins

Terpene resins are based on naturally occurring monomers. The presence of tertiary carbon in their structure makes them very susceptible to oxidation; thus they must be protected by antioxidants.

Terpene resins are usually light colored and soluble in most common solvents. They are widely compatible with other resins and polymers, and have excellent tackifying properties. They are available as viscous liquids and in solid form. Typical properties are presented in Table 7.

2.6.4. Resins from Pure Monomers

Pure monomers such as styrenes or isobutene are excellent resin formers for the manufacture

Table 7. Typical data for terpene resins

Property	Derived from		
	α-Pinene	β-Pinene	*d*-Limonene
Softening point RB, °C	25 – 135	10 – 135	100 – 135
Gardner color	3 – 5	1 – 4	1 – 4
Bromine number, g Br_2/100 g	25 – 30	15 – 30	27 – 28
Density at 20 °C, g/cm^3	0.90 – 0.98	0.93 – 0.99	0.99

Table 8. Typical properties of resins from pure aromatic monomers

Property	Styrene	α-Methylstyrene	α-Methylstyrene – vinyltoluenes
Softening point RB, °C	liquid – 160	70 – 145	75 – 120
Gardner color	1 – 3	< 1	< 1
Bromine number, g Br_2/100 g	0	2 – 8	2
Density at 20 °C, g/cm^3	0.98 – 1.08	1.06 – 1.07	1.05

of very stable, light- colored to colorless (water-white) resins. Industrially, resins based on styrene or α-methylstyrene, or blends of mainly α-methylstyrene and vinyltoluenes, are produced. Resins from the copolymerization of terpenes and styrene are also available. Typical data of resins from pure aromatic monomers are given in Table 8.

2.6.5. Modified Resins

In the previous sections, resins are described that are obtained from steam cracker fractions or monomer mixtures. They contain predominantly carbon and hydrogen, but no polar or functional groups. With the exception of dicyclopentadiene resins, they are chemically nonreactive. This section deals with resins that are either obtained from special, modified feedstreams or are modified after polymerization. Thus, properties of aliphatic- or aromatic-type resins may be adapted by blending initial feedstreams or by addition of selected monomers, Mixed resins of $C_5 - C_9$ types, as well as terpene – aromatic resins, are available. Typical properties are given in Table 9.

Addition of dicyclopentadiene to the initial feedstream increases the degree of unsaturation and thus the reactivity of the final resin. Also coreaction of dienes (e.g., dicyclopentadiene with maleic anhydride) may be applied, Resins made by coreaction of aromatic or terpene resin formers with phenol are well known. Their properties are listed in Table 10.

Table 9. Typical properties of mixed resins

Property	$C_5 - C_9$ Resins	Terpene – aromatic resins
Softening point RB, °C	liquid – 105	105 – 115
Gardner color	2 – 10	2 – 5
Iodine number, g I_2/100 g	< 25	not available
Density, g/cm^3	0.86 – 1.07	1.02

The high reactivity of terpenes makes them suitable for copolymerization reactions with other monomers, e.g., styrenes or maleic anhydride.

Resins may also be modified by further reaction of the final resin; for example, dicyclopentadiene resins can react with maleic anhydride, unsaturated fatty acids, or rosin upon heat treatment. A very important modification is the catalytic hydrogenation of resins, which gives high-quality water-white resins with a different solubility and compatibility profile than the original resin. Dicyclopentadiene resins are hydrogenated in large quantities. Hydrogenated aromatic resins derived from steam cracker streams or pure monomers and hydrogenated terpene resins are also available. Typical properties are listed in Table 11.

2.7. Uses

Hydrocarbon resins are used in numerous fields of application because of their versatile properties. They are seldom used alone but mainly in conjunction with other materials to adapt their properties to special requirements. Hydrocarbon resins are mostly used as tackifiers, binders, processing aids, film formers, reinforcing agents, and extenders.

With regard to their specific properties, the following classification is often used:

- Hard resins (binders, film-formers) in the paint, varnish, printing and coatings industries

Table 10. Phenol-modified resins

Property	Based on	
	C_9 and indene – coumarone	Terpene
Softening point RB, °C	liquid – 120	95 – 155
Gardner color	5 – 8	4 – 11
Hydroxyl number, mg OH/g	56 – 112	80 – 260
Density at 20 °C, g/cm^3	1.08 – 1.1	1.03 – 1.09

Table 11. Typical properties of hydrogenated resins

Property	Based on			
	DCPD	C_9 Fraction	Aromatic monomer	Terpene
Softening point (RB), °C	85 – 140	70 – 140	liquid – 125	85 – 115
Gardner color	< 1	> 1	crystal clear	< 1
Bromine number, g Br_2/100 g	2 – 3	not available	not available	10 – 20
Density at 20 °C, g/cm^3	1.10	0.98 – 0.99	0.92 – 1.04	0.94 – 1.01

- Tackifiers in the adhesives, sealants, and rubber industry
- Processing aids (plasticizers) in the plastics industry (rubber goods, tires, PVC)
- Fixing agents, e.g., in wood protection
- Water repellents in various applications (e. g., wood protection, coatings)

The most important applications are in adhesives (construction, solvent-or water-based, hot-melt and pressure-sensitive adhesives), coatings (paints, varnishes, roadmaking), the rubber and plastics industry (mainly mechanical rubber goods and tires, also PVC), printing inks, and, to a lesser extent, in various other industrial fields. A generalized view of the main application areas by resin type is given in Table 12. The large group of modified resins is used in applications where special properties are required.

Aliphatic resins are used extensively in hot-melt adhesives; in pressure-sensitive adhesives based on natural or thermoplastic rubber; in coatings, road-marking formulations, mastics, caulks, and sealants; and in rubber formulations for mechanical goods and tires. *Aromatic C_9* and *indene – coumarone* resins are widely applied in hot-melt formulations based on ethylene – vinyl acetate or thermoplastic rubber; in solvent-based and waterborne adhesive formulations; in the rubber industry (tires and mechanical goods); and in paints, varnishes, coatings, printing inks, sealants, wood protection, and concrete curing. *Terpene resins* are used almost exclusively in the adhesive industry as excellent tackifiers for pressure-sensitive adhesives and hot-melt formulations. *Dicyclopentadiene resins* are generally applied in paints, varnishes, and coatings where they are introduced in the binder system, and in the printing ink industry. *Water-white resins* are used in adhesives and coating formulations where light color and color stability are important. The liquid polybutylenes are used in sealants, caulks, mastics, and pressure-sensitive formulations. The large group of modified resins is used in applications where special properties are required.

Table 12. Main application areas by resin type

Resin type	Adhesives	Coatings	Paints	Printing inks	Rubber
Aliphatic C_5 *	x	x	x		x
Aromatic C_9 **	x	x	x	x	x
Mixed aliphatic/ aromatic	x	x	x	x	
Dicyclopentadiene		x	x	x	x
Modified DCPD			x		
Butene	x	x			
Pure monomer	x	x	x		
Hydrogenated	x	x			
Terpene	x				

* Petroleum resins;
** Petroleum and indene – coumarone resins.

Adhesives [7]. Most synthetic adhesives are based on a "backbone" polymer, tackifying resins, and a carrier (solvent, water, or heat) that gives the formulation the necessary consistency for application. Tackifying resins regulate the final rheological properties of the system (tack, specific adhesion, and wetting).

Solvent-borne adhesives, mainly based on SBR and polychloroprene rubber, are frequently combined with hydrocarbon resins (aromatic C_9 and indene – coumarone , aliphatic and mixed C_5/C_9), as well as rosin, rosin esters, terpene – phenolic, and *p-tert*-butylphenolic resins.

Waterborne adhesives are increasingly being used for environmental reasons. Polymer dispersions based on poly(vinyl acetates), latexes, or acrylates may be modified by addition of tackifying resins such as petroleum and indene – coumarone resins, terpene resins, as well as rosin esters, terpene – phenolic resins, and ketone resins.

Hot-melt adhesives are thermoplastic solids which are liquified by heating for application. Backbone polymers for these adhesives are ethylene – vinyl acetate (EVA), thermoplastic rubbers, such as styrene – isoprene – styrene block copolymers, polyethylene, and polypropylene, formulated together with tackifying resins. Polyesters and polyamides, which are also used in hot-melt adhesives, do not need additional tackification. Hot-melt adhesives formulated with the above-mentioned polymers contain paraffins or waxes, tackifying resins, and fillers. Tackifying resins of various types may be used, mainly hydrocarbon resins (aliphatic C_5, aromatic C_9, indene – coumarone, mixed aliphatic – aromatic, terpene and hydrogenated resins), rosin and rosin esters, and terpene – phenolic resins.

Pressure-sensitive adhesives are defined as adhesives which in solvent-free form remain permanently tacky and adhere instantaneously with application of a minimum of pressure. Their main use is in tape and label manufacturing. Formulations are based on backbone polymers such as rubbers (natural rubber, SBR), and block copolymers, together with tackifying resins, or on acrylic resins. Tackifying resins for this use are aliphatic C_5, aromatic C_9, mixed C_5/C_9, pure monomer, terpene, and hydrogenated resins, as well as rosin and rosin esters.

Sealants. Sealants are based on polymers such as butyl rubber, polyisobutene, thermoplastic elastomers, SBR, neoprene, and polysulfides. Addition of tackifying resins is necessary to improve instantaneous adhesion. Practically all hydrocarbon resin types as well as rosin and modified rosin are usable. Other basic raw materials for sealants, such as silicones or urethanes, do not need additional tackification.

Coatings. Coatings [5, 8] range from protective to decorative and can be intended for temporary or permanent use. Hydrocarbon resins are extensively used, as illustrated by the following examples:

- Hot-melt coatings are mainly used in the packaging industry. Formulations and tackifiers used are very similar to those for hot-melt adhesives.
- Paints and varnishes, based on a variety of binder systems, may use rosin derivatives as well as hydrocarbon resins of the aromatic, aliphatic, and DCPD type as hard resins. Aromatic hydrocarbon resins are especially important in the formulation of aluminum paints.
- Road-marking material of the paint or hot-melt type uses mainly aliphatic C_5 resins but also C_9 types, modified by straight or cyclic aliphatics, as well as hydrogenated and special C_9 resins.
- Anticorrosion paints may be based on C_5, C_9 and DCPD resins, mixed C_5/C_9 resins, and phenol-modified aromatic resins.
- Concrete curing membranes, applied to concrete to avoid too rapid drying, contain hydrocarbon resins (DCPD, C_5 and C_9) in solution or dispersion.
- Wood protection by impregnation or surface treatment is carried out with, e.g., solutions containing aromatic C_9 resins because of their excellent water-repellent and fixing properties.

Printing Inks. Use of hydrocarbon resins in ink formulation takes advantage of their good compatibility with many ink components, e.g., alkyds, oils, and ink solvents, and gives the ink gloss and good resistance to water and alkali. Hydrocarbon resins are usually formulated together with the classical ink binders such as alkyd resins and modified rosins. High-softening-point hydrocarbon resins of the aromatic C_9 and indene – coumarone type, unmodified and modified, as well as DCPD and functional modified DCPD resins are used. The main use is in offset and gravure inks.

Tires and Mechanical Rubber Goods. Rubber stocks are compounded with a multitude of different additives: processing aids, plasticizers, reinforcing agents, tackifiers, pigments, antioxidants, and curing agents. Resins widely used in this application are generally referred to as processing aids, but in fact they have multiple functions. They promote processing by lowering viscosity, improve the building tack of unvulcanized mixtures, and may improve elongation, tensile strength and flex resistance of the vulcanized materials. Besides alkyl-phenolic resins, the largest volume resins for this

application, considerable quantities of hydrocarbon resins, aromatic C_9 and indene – coumarone resins, C_5 aliphatic, mixed aromatic/aliphatic, and DCPD resins, as well as some unmodified rosin are used. The main criteria for choice are availability, consistency, and price.

Other Uses. Hydrocarbon resins are used in many other applications, such as in compounding floor tiles, in the foundry industry as binder and lustrous carbon former, as oil additives, in investment casting, the ceramic industry, in textile treatment and waterproofing, as well as in gypsum waterproofing.

2.8. Economic Aspects [9]

The total capacity for synthetic hydrocarbon resin production is estimated to be about 1×10^6 t/a worldwide in 1991. Main capacities are located in the United States, Canada, and Brazil (ca. 0.45×10^6 t/a); Europe (roughly 0.25×10^6 t/a); and the Asia/Pacific region (about 0.3×10^6 t/a).

Aromatic resins represent a volume of ca. 44 %, C_5 and DCPD resins ca. 37 %, and hydrogenated resins ca. 19 %. Producers and trade names of hydrocarbon resins are listed in Table 13.

Table 13. Resin manufacturers and trade names

	Trade names	Resin types[a]
Europe		
Hexion (Netherlands)	Setalin	hydrocarbon-modified phenolic resins
Cray Valley (France)	Norsolene	C_9 and $C_5 - C_9$ resins
DRT (France)	Dercolyte, Dertophene	terpene and modified terpene resins
Exxon (France)	Escorez	C_5 and $C_5 - C_9$ resins, DCPD and hydrogenated DCPD resins
Eastman (Netherlands)	Hercures, Regalite Kristalex, Hercoflex	C_5 and C_9 resins $C_5 - C_9$ resins, resins from pure monomers, hydrogenated resins
Neville Chemical Europe (Netherlands)	Necires, Nevchem, Nevex, Nevbrite, Nevroz, Nevillac	C_9 and $C_5 - C_9$ resins, DCPD and modified DCPD resins, phenol-modified resins
Rütgers–VFT (Germany)	Novares	C_9 and modified C_9 resins, IC and phenol-modified IC resins
United States		
Arizona	Zonatac, Sylvagum, Sylvares	terpene and modified terpene resins, C_5 and
Eastman	Eastotac, Tacolyn, Piccotac, Regalrez, Piccolastic, Kristalex, Piccotex, Endex	$C_5 - C_9$ resins, hydrogenated resins, DCPD resins, terpene and modified terpene resins, resins from pure monomers
Exxon	Escorez	C_5, $C_5 - C_9$, and C_9 resins, hydrogenated resins
Cray Valley	Wingtack, Norsolene	C_5 and $C_5 - C_9$ resins
Hexion	Setalin, Petro-Rez, Alpha-Rez	C_9 and modified C_9 resins, DCPD and modified DCPD resins
Neville	Nevillac, Nevchem, Nevoxy, Cumar, Nevex, Nevpene, Nevroz, Nebony, Nevtac	IC resins, C_5, C_9, $C_5 - C_9$, and DCPD resins and modified resins
Resinall	Resinall	C_9, modified C_9, and modified DCPD resins
SI Group	SP	terpene phenolic resins
Japan		
Arakawa	Arkon	hydrogenated resin
Maruzen	Marukarez	C_5 and DCPD resins, hydrogenated C_5 and DCPD resins
Mitsui	Hi-rez, FTR	C_5 and C_9 resins, resins from pure monomers
Nippon Petrochemical	Nisseki Neopolymer	C_9 resins, liquid resins
Nippon Zeon	Quintone	C_5 and modified C_5 resins, DCPD and modified DCPD resins
Exxon	Escorez	C_5, C_9, $C_5 - C_9$, and DCPD resins, hydrogenated DCPD resins
Tosoh	Petcoal	C_9 and $C_5 - C_9$ resins
Yasuhara	YS, Polyster, Clearon	terpene, modified and hydrogenated terpene resins
Other countries		
Korea	Kolon	C_5, C_9, and IC resins
Kolon Korea		
P.R. China		
Sunresin	Sunresin	C_5, C_9, and modified C_9 resins, modified DCPD resins
Taiwan		
Yung Tung	Sunrez	C_9 resins
India		
Indian Petrochemical Corp.	Petrez	C_9 resins

[a] IC = indene – coumarone

3. Resins by Condensation

3.1. Furan Resins

The term "furan resins" describes generic polymers or resins that are derived from the condensation of furfural and/or furfuryl alcohol alone, and with a variety of coreactants. These include formaldehyde or a formaldehyde precursor such as paraformaldehyde, urea – formaldehyde concentrates or syrups, phenol, phenol – formaldehyde resins, aldehydes, ketones, and polyhydroxyl-substituted aromatics. Polymers or resins derived from 2,5-bis(hydroxymethyl) furan (BHMF) have been reported, With 2,5-BHMF, both condensation and addition polymers can be synthesized.

3.1.1. Monomers

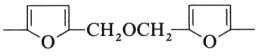
Although many chemicals possess a furan nucleus in their molecular structure, furfural and furfuryl alcohol are the only monomers of major industrial significance. *Furfural* [98-01-1] is produced commercially from agricultural byproducts such as corncobs, sugarcane bagasse, oat hulls, and wood residues [10] (→ Furfural and Derivatives, Chap. 2.). *Furfuryl alcohol* [98-00-0] is produced by hydrogenating furfural in a vapor- or liquid-phase process with a variety of catalysts based primarily on copper [11]. *2,5-Bis(hydroxymethyl)furan* [1883-75-6] is synthesized by selective hydroxymethylation of furfuryl alcohol [12] or by hydrogenation of the less readily available 5-hydroxymethylfurfural [13].

3.1.2. Production – Characteristics

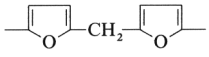
Furfural and furfuryl alcohol are converted to resins by *condensation polymerization*.

Furfural-Based Resins. Homopolymerization of furfural, although studied extensively [14], has no industrial importance. Copolymers of furfural with phenol, phenol – formaldehyde resins, and other hydroxyl-substituted aromatics have been available commercially for many years. Since the acid-catalyzed reaction of furfural and phenol is difficult to control, most industrial processes involve the use of alkaline catalysts such as alkali hydroxides or carbonates. Furfural and ketones (usually acetone) condense with alkaline catalysts to form furfurylidene acetone monomer, which polymerizes to a thermoset resin in the presence of strong acid.

Furfuryl Alcohol-Based Resins. The mechanism proposed up to the early 1950s for the polymerization of furfuryl alcohol was reported by DUNLOP and PETERS in their treatise on furans [10]. As a result of the growing importance of furfuryl alcohol resins since the 1950s, the chemistry of furfuryl alcohol polymerization initiated by heat, acid, and alumina has been studied extensively and has proved to be complex, Studies dealing with the identification of intermediates and byproducts by spectroscopic and chromatographic techniques [15–18], the reaction kinetics involved in polymerization [19–21], the structure of the resulting polymers [22], and the nature of the oxygen- or acid-catalyzed cross-linking of the initial resin have all led to a better understanding of this complex chemistry [23]. A comprehensive review examines the literature up to 1977 and interprets the resinification mechanisms [14]. A more recent review further clarifies the two-stage polymerization of furfuryl alcohol [12]. Based on accumulated data, furfuryl alcohol must be considered a bifunctional monomer in the initial stages of weak acid catalysis, and its "normal" reactions give linear chains or oligomers containing essentially two repeating units (1, 2), with 2 predominating:



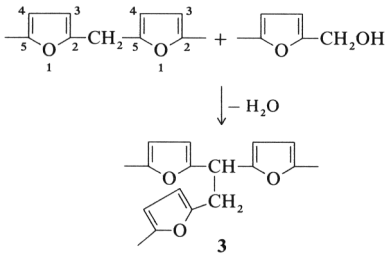
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The polymerization or resinification of furfuryl alcohol is highly exothermic and, depending on the activity and concentration of the catalyst used, requires careful control of reaction temperature. Generally, weak acids such as carboxylic acids or metallic salts are used to produce oligomeric prepolymers with repeating moieties 1 or 2. Further conversion of these prepolymers to cross-linked thermoset

resins is accomplished by the addition of strong inorganic or organic acids. Aromatic sulfonic acids are the preferred catalyst. Earlier investigators postulated cross-linking through the C-3 and C-4 positions of the furan ring. However, more recent studies [24], suggested, on the basis of analytical data, that the main cause of branching and cross-linking is a condensation reaction between methylene groups within a chain and a hydroxymethyl group at the end of another chain to yield structures such as 3.



2,5-Bis(hydroxymethyl)furan. The 2,5-BHMF monomer behaves as a diol and undergoes esterification (base- catalyzed transesterification), alkoxylation, glycidyl ether formation, cyanoethylation, and urethane formation. In the presence of an acid catalyst, resinification of 2,5-BHMF occurs, similar to that of furfuryl alcohol, although the end groups of the resulting resin are hydroxymethyl, These resins are characterized by enhanced reactivity compared to acid- catalyzed furfuryl alcohol resins [25]. 2,5-Bis(hydromethyl)furan resins convert to highly cross-linked thermosetting polymers that demonstrate unique characteristics in composites, including a desirable high char yield on carbonization, low flame propagation, corrosion resistance, and superior high-temperature stability.

3.1.3. Uses

Furan resins are used in a variety of applications including sand cores and molds for metal casting; corrosion-resistant fiberglass-reinforced plastics; low flammability and low smoke generating composites and foams; carbonaceous products; polymer concretes; wood adhesives; and proppants in oil-well sand consolidation.

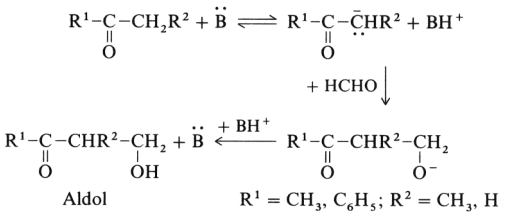
The use of *furfuryl alcohol resins* in the worldwide foundry industry remains the only important application. Total world production of furan resins for use as binders to produce sand cores and molds for metal castings exceeds 75 000 t/a.

3.2. Ketone and Aldehyde Resins

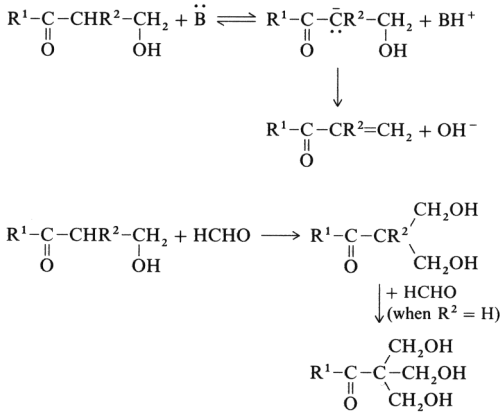
Ketone and aldehyde resins are obtained from aliphatic aldehydes and aliphatic or aliphatic – aromatic ketones by self- condensation, or more frequently by cocondensation with formaldehyde [26, 27]. Other monomers such as phenols or urea are also sometimes incorporated. Although these resins have been known for a long time, new types of resin and new areas of application are always being found. In paints and coatings, as in many other areas, these resins are used in combination with other binding agents, plasticizers, pigments, and process materials [28–40].

They are also used in printer and copier technology [41–43], the production of printed circuit boards [44], adhesives [45–48], binding agents for corrugated cardboard [49–51], molding sands [52, 53], and laminates [54–56]. The production of aqueous dispersions has also been described [57].

Reaction Mechanism. The condensation of aliphatic or aliphatic – aromatic ketones with formaldehyde is base catalyzed [58]. Formaldehyde adds first to the ketone, with formation of the aldol:



The aldol is then either dehydrated to give vinyl ketones, which can polymerize or reacted with excess formaldehyde to form highly reactive methylol compounds. The reaction pathway followed depends on the molar ratio of ketone to formaldehyde and on reaction conditions (pH, temperature, concentration).



The resins are formed by polymerization of the vinyl ketones to give polymers with an alternating structure (see Fig. 1) or by complex condensation of the methylol compounds with one another or with other ketone molecules to give partially branched products, In industrial processes, both mechanisms often operate in parallel. An excess of formaldehyde can lead to reduction of carbonyl groups to hydroxyl groups [59]. The tendency of the vinyl ketone intermediate to polymerize is rather independent of the nature of the ketone used [60, 61], provided the vinyl group is not substituted.

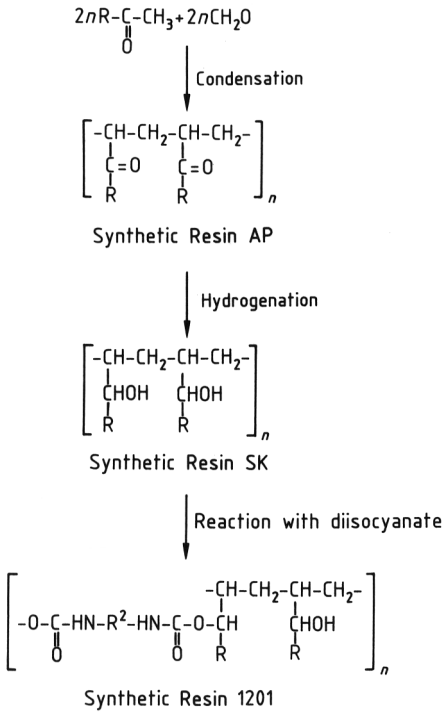


Figure 1. Resins from acetophenone and formaldehyde R = Phenyl, R^2 = Aliphatic hydrocarbon.

3.2.1. Resins from Aliphatic – Aromatic Ketones

Industrially mainly acetophenone is reacted with formaldehyde. Derivatives of acetophenone with alkylated benzene rings, such as methyl-, ethyl-, *tert*-butyl-, or cyclohexylacetophenone can also be employed [62]. Besides the unmodified resins, their hydrogenation products and the resins derived from them are available commercially (see Fig. 1).

3.2.1.1. Acetophenone – Formaldehyde Resins

Acetophenone – formaldehyde resins are light-colored nonhydrolyzable products, with sufficient lightfastness and softening points of 75 – 85 °C. They are readily soluble in aromatic hydrocarbons, esters, ketones, and glycol ethers, but insoluble in alcohols, aliphatic hydrocarbons, and mineral oils. Other physical and technical properties are listed in Table 14. The resins are compatible with nitrocellulose; copolymers of vinyl chloride; chlorinated rubber; maleic, urea, melamine, and ketone resins; plasticizers; and a few alkyd resins. They are incompatible with the majority of alkyd resins, drying oils, polyesters, and polyacrylates. Their relatively low price, gloss-improving properties, and capacity to increase the solid material content of coatings (i.e., the coating can be laden with a higher solids content and the viscosity remains constant when ketone resins are added) should be mentioned in particular.

Production. *Light, soluble, hard resins* are obtained by heating an aqueous mixture of acetophenone, formaldehyde, and potassium or sodium hydroxide to the boiling point. Solvents such as alcohols can also be used, Strong acids, such as sulfuric acid, or dehydrating salts, such as zinc chloride, are also suitable condensing agents but are less common. Quaternary nitrogen or phosphorus bases [63] are used as condensing agent to obtain particularly high-melting resins. Under suitable conditions, sodium sulfite leads to low molecular mass,

Table 14. Physical and technical properties of ketone and aldehyde resins

	Synthetic Resin (Hüls)				Laropal (BASF)				
	AP	**SK**	**1201**	**CA**	**K 80**	**A 81**	**A 101**	**A LR 8768**	**A LR 8825**
Resin type	ketone hydrogenated aliphatic ketone	aromatic modified aliphatic	ketone aldehyde	aldehyde	aldehyde	aldehyde			
Softening point, °C, DIN 53 180	76 – 82				75 – 85	80 – 90	95 – 110	ca. 80	90 – 100
Softening point, °C, DIN 53 181		110 – 120	155 – 170	92 – 108					
Iodine color index (50 % solution) DIN 6162	1 – 2.5	0 – 1	0 – 1	max. 2	max. 2	max. 3	max. 5	max. 5	max. 4
Acid value, mg KOH/g, DIN 53 402	max. 0.1	max. 0.1	max. 0.1	max. 0.3	max. 1	max. 3	max. 3	max. 3	max. 3
OHvalue, DIN 53 240		ca. 325	ca. 210	ca. 325		40 – 60			
Solubility in									
Alcohols	±	+	+	+	±	+	+	+	+
Esters	+	+	+	+	±	+	+	+	+
Ketones	+	+	+	+	±	+	+	+	+
Aromatics	+	−	±	+	+	+	+	+	+
Aliphatics	−	−	−	−	+	±	−	+	±
Compatibility with nitrocellulose	+	+	+	+	+	+	+	+	+
Chlorinated rubber	+	−	−	+	+	+	+	+	+
Vinyl chloride polymers	+	−	−	+	±	+	+	+	+
Polyacrylates	−	±	±	±	±	±	±	±	±
Urea resins	+	+	+	+	±	+	+	+	+
Melamine resins	+	+	+	+	±	+	+	+	+
Alkyd resins	±	±	±	±	+	+	+	+	+

[a] + = compatible or soluble; ± = some products compatible or only miscible in certain ratios; − = incompatible or insoluble.

water-soluble condensates [64]. Formaldehyde is added mostly as a 30 % aqueous solution or as paraformaldehyde.

Larger quantities of alkali hydroxide and higher temperature result in resins that are infusible and not readily soluble, because the methylol intermediates cross-link with one another. Readily soluble, fusible condensates are obtained with ca. 0.2 mol of hydroxide per mole ketone and a sufficiently short reaction time, so that the molecular mass cannot rise above 400 – 800. Generally, increasing the reaction temperature and time results in a higher softening point, while the solubility and compatibility deteriorate. This is probably due to competing reaction mechanisms during condensation. If conditions are such that vinyl phenyl ketone is produced mainly as the intermediate, resins with low softening point and solubility in a broad range of solvents are formed. For example, reaction of 1 mol of acetophenone with 0.05 – 0.5 mol of formaldehyde gives an oil-compatible resin. If methylol intermediates are predominantly formed, the resins have higher melting points and are limited in their solubility and compatibility. Resins with these properties are obtained from acetophenone and formaldehyde in the ratio 1: 1.

Uses. Acetophenone – formaldehyde resins are used as favorably priced binding agents in coatings and printing inks, in combination with other coating raw materials such as nitrocellulose. They improve gloss, intensity, covering capacity, solid material content, adhesion, and drying. In nitrocellulose lacquers the ease of pigmenting and polishing on wood is increased. Acetophenone – formaldehyde resins are also used in vinyl chloride copolymer coatings for metal coating and road-marking paints. Adhesives and hot melts are also formulated with these resins.

Trade Name. Synthetic Resin AP (Evonik, Germany).

3.2.1.2. Modified Acetophenone Resins

Hydrogenation of acetophenone – formaldehyde resins, in particular, gives products that differ markedly from the usual ketone and aldehyde resins and therefore open up new areas of application. The reaction of hydroxyl groups, which are formed from the keto groups on hydrogenation, with aliphatic diisocyanates gives high-quality special binding agents (see Fig. 1 and Table 14).

Properties. The hydrogenated resins are very light-colored and particularly stable. They are completely free of formaldehyde, which can no longer be formed by retroaldol-type reactions. Depending on hydrogenation conditions, resins are obtained in which only the keto groups are converted into hydroxyl groups or in which the aromatic ring is also hydrogenated [65]. Only the former are available on the market. Their softening points lie in the range 110 – 120 °C and they are readily soluble in alcohols. The resins can be diluted with aromatics but are insoluble in aliphatics and mineral oil. Their compatibility with alkyd resins is better than that of nonhydrogenated products.

The hydroxyl values of these resins are > 300 mg KOH/g, The OH groups can be reacted with diisocyanates to give extremely high-melting resins (*mp* ca. 160 °C), which are also alcohol soluble. Diisocyanate-modified resins are even more stable and exhibit rapid solvent release.

Production. Under mild hydrogenation conditions only the keto groups are hydrogenated (Fig. 1). The reaction is controlled by determination of the oxygen content and the melting point [66]. Hydrogenation can be carried out catalytically in solution or in the melt [67, 68]. Reactions with diisocyanate take place at slightly elevated temperature with the usual catalysts.

Uses. Modified acetophenone – formaldehyde resins are high melting and stable. They are therefore used as hard resin components together with other binding agents in paints and coatings, printing inks, and adhesives, if high-quality coatings are required. The *hydrogenated resins* are used for lightfast nitrocellulose-based overprinting inks for paper. They are also used in ballpoint pen pastes, inks, and toners; as flow-control agents for powder coatings; as hard resin components in isocyanate reactive systems; and for modification of alkyd resins.

The *isocyanate-modified resins* are used in high-quality printing inks, in paper and wood varnishes, and in the formulation of coatings with good adhesion to plastic surfaces. They are particularly suitable for wetting and stabilizing aluminum pigments in paints and printing inks.

Trade Names. Synthetic Resin SK (hydrogenated resin) and Synthetic Resin 1201 (diisocyanate-modified, Evonik, Germany).

3.2.2. Resins from Aliphatic Ketones

Resins are produced from linear aliphatic ketones — principally methyl ethyl ketone and acetone — and formaldehyde. Methyl isobutyl ketone is also used, mainly for the production of adhesives [69, 70]. Cyclohexanone and methylcyclohexanone are most important in the synthesis of alicyclic resins, although reactions of cyclopentanone, cycloheptanone, and cyclic ketones with longer side chains have also been described [71].

3.2.2.1. Methyl Ethyl Ketone – Formaldehyde Resins

Methyl ethyl ketone is still important for the production of binding agents for paints, coatings, and adhesives. These resins differ from alicyclic and aromatic ketone-based products in certain application-relevant properties, such as solubility in various solvents and compatibility with other lacquer raw materials. These properties may be explained by the high polarity of the ketone and its special behavior in the alkali-catalyzed condensation with formaldehyde [59].

Physical Properties. Methyl ethyl ketone – formaldehyde resins are lightly colored and are soluble in polar organic solvents such as alcohols, esters, ketones, and glycol ethers. The hydroxyl values are in the range 80 – 190 mg KOH/g. The strongly polar resins have a total oxygen content of 21 – 29 wt % and are hygroscopic. Depending on production conditions, the molecular mass lies between 3000 and 5000, and the melting range between 80 and

120 °C. Other physical data and compatibilities are described in [27].

Chemical Properties. Methyl ethyl ketone – formaldehyde resins are unhydrolyzable, The keto and hydroxyl groups and the carbon double bonds give the compounds a certain degree of chemical reactivity. Hydrogenation leads to clear, colorless resins [72]. The hydroxyl groups can be esterified with carboxylic acids or acid anhydrides [73] and can react with isocyanates [74].

Production. Industrially, ketone resins are obtained by alkali-catalyzed condensation of methyl ethyl ketone and formaldehyde (molar ratio 1: 2 – 1: 2.5). Condensation is performed mainly batchwise [59, 75, 76]. Continuous production has also been described [77]. The unpurified ketone is treated with formaldehyde in the presence of water and sodium or potassium hydroxide as catalyst. By increasing the formaldehyde content, the melting range can be raised to 80 – 120 °C.

Special purification processes give light, high-melting products [78]. High softening points are also achieved by using phase-transfer catalysts [72]. The reaction mechanism is not completely understood and involves many concurrent reactions [27].

Uses. Methyl ethyl ketone – formaldehyde resins are used in combination with film-forming agents such as nitrocellulose, acetylcellulose, cellulose ethers, and natural resins. They impart hardness, drying, polishing ability, and good lightfastness. The capability to gelatinize nitrocellulose is exploited in the production of high-gloss nitro lacquers. The free hydroxyl groups are used for cross-linking in isocyanate-reactive coatings, adhesives [79], and molding sands [74].

3.2.2.2. Acetone – Formaldehyde Resins

The alkali-catalyzed condensation of acetone and formaldehyde does not lead to useful, solid synthetic resins. The considerably greater hardening tendency of the unstable methylol intermediates from acetone in comparison to those of other carbonyl compounds [80, 81] leads to a cross-linked, insoluble final product. *Self-hardening precondensates* can, however, be produced, which are used alone or in combination with other hardenable precondensates, such as phenol resols.

Uses. Hard foams [82] are obtained by foaming the methylol compounds in the presence of alkali hydroxide alone or of alkali hydroxide and an elastomer latex [83]. Sands can be hardened with acetone – formaldehyde precondensates for the production of moldings [84–86]. Rapidly hardening moldings made from cement have also been described [87, 88]. Acetone – formaldehyde condensates are used widely in paper [89] and wood adhesives [90]. Phenol resols are often cocondensed to obtain particularly weather-resistant wood materials and chipboard [91–93] or for the waterresistant adhesion of corrugated paperboard [94]. Other uses of acetone precondensates are in photoreceptors in electrophotography [95, 96] and in production of thickeners and emulsifiers [97, 98].

3.2.2.3. Cyclohexanone Resins

Cyclohexanone and methylcyclohexanone readily undergo self-condensation, in addition to mixed condensation with formaldehyde [99]. The former involves aldol condensation between the carbonyl group of one molecule and the activated methylene group of another. The carbonyl group of the intermediate then reacts with another cyclohexanone molecule, etc. The reaction occurs at elevated temperature and can be catalyzed by basic, acidic, or neutral agents.

Properties. The softening points of the light, neutral resins are between 80 and 120 °C. Under normal conditions the resins are resistant to acids and bases. However, they eliminate water in the presence of acids at elevated temperature (> 80 °C), thus altering their properties significantly, Cyclohexanone resins are lightfast, soluble in many solvents, and compatible with most coating raw materials (see Table 14). They are more expensive than cyclohexanone – formaldehyde resins [99]. An example of the production process (according to [100, 101]) is given in [27].

Uses. Cyclohexanone resins are used in coatings, mainly to improve intensity, gloss, and hardness. They can also improve light and weather resistance, as well as adhesion. In quantities of 5 – 50 % (based on the film-forming agent) these resins are added to coatings based on alkyd resins, vinyl chloride copolymers, chlorinated rubber, nitrocellulose, or oils.

Their use as carrier resins for pigment preparations has also been described [102].

Trade Name. Laropal K 80 (BASF).

3.2.2.4. Cyclohexanone – Formaldehyde Resins

Cyclohexanone can react with aldehydes, in particular formaldehyde, to give defined methylol compounds or resinous products. The molar ratio and the reaction conditions determine the final products. A large formaldehyde excess promotes the formation of methylol compounds, whereas basic catalysis leads to resin formation [103, 104]. Higher aldehydes can also be used instead of formaldehyde, but they have not gained any industrial importance. In addition to cyclohexanone, methylcyclohexanone or mixtures of cyclohexanone with aliphatic ketones are also used as the component with the activated methylene group [105]. The resins can be modified with phenols [100, 106], epoxides [107], polyesters [108], and sulfonamides [109]. Gritty products are obtained by the addition of dispersion agents [110]. Continuous production has been described in [111] and [112]. The lightfastness can be increased by hydrogenation [113] and treatment with reducing agents [114].

Properties. Cyclohexanone – formaldehyde resins do not exhibit the broad compatibility and solubility of cyclohexanone resins. However, they are cheaper and nevertheless sufficiently lightfast. They can be combined with a range of binders for coatings, but not with oils (see Table 14). The use of methylcyclohexanone as a raw material generally leads to better solubility and compatibility.

Production. Industrially, cyclohexanone is condensed with formaldehyde in the presence of alkali. An example of the production procedure is given in [27], where the modification with phenol is also described.

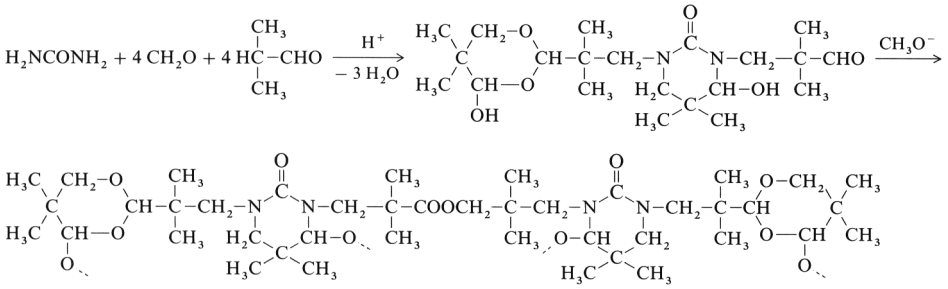
Uses. In many cases, cyclohexanone – formaldehyde resins are used to improve drying, hardness, intensity, gloss, and solid material content, In paints and coatings they are always used as additives in addition to other binding agents, for example, in alkyd – acrylate varnishes [115], cement paints [116], epoxy resin systems [117], and marine paints [118]. In addition to their use in conventional printing inks [119, 120], they are increasingly being used in UV-hardening printing inks [121–123]. Another important area of application is in adhesives [124–126] and sealants [127]. The use of these resins in optical recording media has also been described [128, 129].

Trade Names. Synthetic Resin AFS (Bayer), Synthetic Resin CA (Hüls), L2 Resin (Leuna), Krumbhaar type resins (Lawter).

3.2.3. Aldehyde Resins

In the 1970s, aldehyde resins synthesized from isobutyraldehyde, formaldehyde, and urea were developed to an industrial level. α-Ureidoalkylation formed the basis of the synthesis and is described in detail in [130]. Aldehyde resins from isobutyraldehyde and phenol are used in melt adhesives [131, 132].

Isobutyraldehyde – Formaldehyde – Urea Resins. Both the reaction of urea with enolizable aldehydes [133] and the reaction of urea, formaldehyde, and enolizable aldehydes [134] in an acidic medium lead, on subsequent treatment with alkali alkoxides, to resinous products. The process can be described as follows:



Properties. The isobutyraldehyde – formaldehyde – urea resins are slightly colored and fairly lightfast. Their melting points lie in the range 80 – 110 °C. The solubility and compatibility with other coating binders can be varied, depending on the production process, Thus products soluble in aliphatics and all other common solvents are on the market. Their compatibility is, however, limited to acrylate resins and some cellulose derivatives (see Table 14). The available functional groups can be seen in the above formula scheme.

Production [134]. Formaldehyde, isobutyraldehyde, and urea are reacted in the presence of sulfuric acid. The condensation is carried out for 3 h at 80 °C. After the addition of xylene the mixture is stirred for another 20 min at 75 °C, and the aqueous phase is separated. The organic phase is treated first with sodium methoxide and then neutralized with 75 % sulfuric acid. The resin resulting after work-up has a pale-yellow color and a softening point of 80 – 82 °C.

Uses. Like ketone resins, aldehyde resins can be added to other coating binders, Improvements in hardness, gloss, intensity, flow, resistance to yellowing, and solid material content are achieved in coatings based on alkyd resins, nitrocellulose, or chlorinated polymers. By the addition of aldehyde resins, the overall formulation can often be made more economical (e.g., in powder coatings, where the flow is improved at the same time). Another area of use is in hot meltings and spray plastics for road markings. Some aldehyde resins are suitable as mixing resins for pigment pastes with broad solubility and compatibility. A high pigment-binding capacity and low solution viscosity have thus far not been achieved with ketone resins. For aqueous dispersions see [135].

Trade Names. Laropal A types (BASF).

3.3. Polyamide Resins

Polyamides are thermoplastic polymers with repeating amide units (−CO−NH−) in the main chain (→ Polyamides).

Polyamide resins (PA resins) also belong to the polyamide group. However, PA resins are based on dimerized fatty acids, and their molecular mass is generally less than 15 000; thus they differ considerably from high molecular mass polyamides in their chemical structure and properties [136]. Whereas high molecular mass polyamides are important synthetic fibers and engineering plastics, polyamide resins are used as hotmelt adhesives, casting compounds, and binders for printing inks.

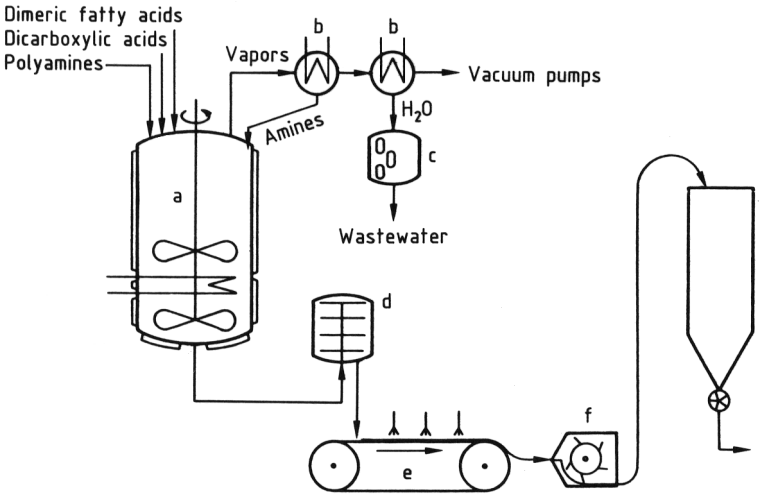


Figure 2. Polyamide resin production
a) Reaction vessel; b) Condenser; c) Separator; d) Filter; e) Cooling band; f) Granulator

3.3.1. Physical and Chemical Properties

The physical and chemical properties of PA resins can be varied within wide limits through the choice and ratio of raw materials used. Brittle, tough-hard, or flexible PA resins can be produced, which have very different tensile strengths and elongation values [137].

The density of PA resins is ca. 0.95 g/cm^3. The *softening point* is in the range of 80 – 250 °C, preferably between 90 and 190 °C. Melt viscosities are between 0.1 and 100 Pa · s at 220 °C. The water absorption of PA resins is between 0.5 and 3 % after 28-d storage in water and is thus much lower than the water absorption of industrially relevant polyamides, All PA resins show good resistance to chemicals. They are generally resistant to water, dilute alkali, weak acid, oils, and fats. Most PA resins are moderately stable to unstable toward esters, ketones, alcohols, and aliphatic hydrocarbons, Some are resistant to chlorinated hydrocarbons.

3.3.2. Raw Materials

The dimerized fatty acids required for the production of PA resins are obtained by heating mono- or polyunsaturated fatty acids, such as oleic, linoleic, or linolenic acids or their esters with or without a catalyst. The dimerized fatty acids formed have an open-chained, cyclic-unsaturated, or aromatic structure [138].

In addition to dimerized fatty acids, dicarboxylic acids are frequently used as comonomer. Examples are adipic acid, azelaic acid, sebacic acid, decamethylenedicarboxylic acid, terephthalic acid or its ester, or isophthalic acid. Ethylenediamine, hexamethylenediamine, 1,12-diamino-4,9-dioxadodecane, piperazine, dipiperidylpropane, and polyoxypropylenediamine are used as the polyamine component [139]. 6-Aminocaproic acid in the form of its lactam and 11-aminoundecanoic acid are the preferred aminocarboxylic acids.

3.3.3. Production

Polycondensation of the aforementioned monomers is carried out in a reactor equipped with a stirrer and condenser at 150 to 250 °C with exclusion of air (Fig. 2). The reaction is performed initially under normal pressure and then under reduced pressure, The water formed in the reaction is distilled off. When the condensation reaction has gone to completion the product is removed as a melt, cooled, and ground or poured into special molds.

3.3.4. Quality and Analysis

For quality testing and characterization of the products the following procedures are used:

The *softening range* is measured by the ring-and-ball method (DIN 52 011 or ASTM E-28). Melting points determined by differential scanning calorimetry or thermomechanical analysis, or microscopic melting points are sometimes given.

Melt viscosities are measured with rotation viscometers, The values obtained can vary considerably, depending on the type of viscometer used. For highly viscous products the *melt index*according to DIN 53 735 or ASTM D-1238 is sometimes determined. The *tensile strength* and *elongation* are determined according to DIN 53 455 or ASTM D-1708. The *water absorption* is determined according to DIN 53 495 or ASTM D-570. The *acid value* is determined according to DIN 53 402 and the *amine value* according to DIN 16 945.

3.3.5. Storage

Polyamide resins are usually supplied as pellets. Because many machines for further processing can only handle rods, cylinders, or rectangular blocks, PA resins are also supplied in these forms.

Since problems can arise in processing if the product is damp, moisture-proof packaging is recommended. With proper storage, the shelf-life of PA resins is virtually unlimited.

3.3.6. Uses

Thermoplastic PA resins are used as high-performance hotmelt adhesives [140], casting compounds [141], binders for printing inks, overprinting lacquers [142], and thixotropic agents for alkyd resin coatings [143].

In the shoe industry, PA hotmelt adhesives have been used for many years as an aid in

assembly for bonding the upper leather to the insole (lasting). The furniture industry utilizes PA hotmelt adhesives for heat-resistant edge banding of chip or particle board.

In the automobile industry, PA hotmelt adhesives are used for interior trim. The bonding of air and oil filters by using PA hotmelt adhesives is particularly important. A relatively new area of application is the sealing of wires and cables into car-connectors by potting with PA resins, Connectors are being incorporated more frequently in the car because of the increased use of electronic control systems. In the electrical and electronics industries, PA resins are used because of their relatively high heat resistance and good insulating properties. In addition to bonding radio and television housings and loudspeakers, in particular coil winding, coil ends, and other electronic components are fixed and bonded with PA hotmelt adhesives.

In the telecommunications sector, PA hotmelt adhesives are used to bond and seal cables and heat-shrink components, and to protect telephone cables from moisture and corrosion at the ends or connection points. In the textile industry, PA resins are used for "cleaning-resistant" bonding of interlining to textiles [144].

PA resins are also used as binders for printing inks. Printing inks based on PA resins are particularly suitable for printing on nonporous materials, such as plastic films, because of their good adhesion, flexibility, and gloss, Since the printed films show good resistance to chemicals and abrasion, they are also used as overprint lacquers.

In the area of transparent lacquers, which are applied by gravure or flexographic printing, PA resins are used as cold-seal release lacquers, antislip varnishes, or heat-seal varnishes.

3.3.7. Producers, Trade Names

The PA resins are sold under the following trade names: Euremelt, Eurelon (Huntsman Advanced Materials, Switzerland); Versamid, Macromelt (Cognis, Germany); Reamide (Chemplast, Italy); Unirez (Arizona, United States); Flex-Ref (United States); Casamid (Swan, United Kingdom); Polymide (Sanyo, Japan).

4. Natural and Synthetic Resins — Toxicology and Legislation

4.1. Toxicology

4.1.1. Rosins and Their Derivatives

For review, see [145].

Crude Rosins (→ Resins, Natural, → Resins, Natural, Section 5.3., → Resins, Natural, Section 5.4., → Tall Oil). In contrast to refined rosins, crude rosins contain volatile, neutral components (→ Terpenes), which may impose properties on them that resemble those of organic solvents.

Resin Acids. *Abietic acid*, the major component of *refined rosins*, has an acute oral LD_{50} in mice of about 2500 mg/kg. The acute oral LD_{50} of its *methyl ester* is > 5000 mg/kg in rats and rabbits. Resin acids were not mutagenic in the Ames test.

Refined rosins, original or chemically modified, have a negligible acute oral toxicity in rodents and guinea pigs, the LD_{50} values ranging from 4000 to 12 000 mg/kg; no acute dermal toxicity was found in rabbits for pale rosins.

On oral administration, *dark rosins* with a high phenolic fraction and *rosin esters* showed no acute toxic symptoms.

In longterm feeding studies with pale and esterified rosins on rats and dogs (90 days or two years), no toxic symptoms were observed at the 0.2 % to 1 % dietary level. Therefore rosins and their derivatives may be regarded as safe.

Generally, rosin acids, rosins, and their derivatives are not considered skin irritants. However, a small portion of the population shows an allergic response on patch tests. A high sensitization level was reported among printers exposed to gum arabic, a constituent of printing ink [146].

Fumes from rosins may cause ocular and bronchial irritation: ca. 80 % of humans exposed to products of wood rosin at a level > 0.12 mg/m^3 experienced severe irritation of the eye, nose, or throat. The TLV for rosin core solder pyrolysis products is 0.1 mg/m^3 aliphatic aldehydes measured as formaldehyde.

4.1.2. Hydrocarbon Resins

The acute oral toxicity (LD_{50}) of hydrocarbon resins in rats is generally greater than 5 g/kg body weight, and they were found to be nonirritating to the skin and eye under experimental conditions [147]. In the EEC directives, most hydrocarbon resins are not classified as harmful, toxic, or irritant to the skin and eyes. Handling of resins requires the usual precautions for working with chemicals. Inhalation of dust or fumes (the latter generated on heating or combustion) must be avoided, More specific information is given in the manufacturers safety data sheets.

Food legislation concerning hydrocarbon resins is regulated by many national authorities but will likely be harmonized with the requirements of the FDA and the EU. The main attention is directed to migration of residual monomers, oligomers, and additives that might contaminate contiguous media by diffusion, and to the stability of resin formulations under application conditions.

In the United States, numerous resins are CFR approved substances for the following:

175.105: Adhesives
175.300: Resinous and polymeric coatings
176.170: Components of paper and paperboard in contact with aqueous and fatty food
176.180: Components of paper and paperboard in contact with dry food
177.1210: Closures with sealing gaskets for food containers
177.2600: Rubber articles intended for repeated use
178.3800: Preservatives for wood.

In the EU, the use of materials intended — in their final state — to come in contact with products for human consumption is regulated by the framework directive 89/109/EEC, followed by several subordinate directives, one of which concerns the use of plastics materials, e.g., in food packaging (90/128/EEC). Implementation by the EU member states was required by January 1, 1993.

Monomers and additives are not allowed to be used for food packaging unless listed in the annexes of the latter directive (positive-list principle). Not all hydrocarbon resins have yet been covered there. Therefore, an industrial motion to enclose those resins in the additive list, among others of the IC type, was directed to the European Scientific Committee for Food, but has not yet been settled.

4.1.3. Polyamide Resins

Polyamide resins do not need to be labeled [EC guideline 79/831/EEC (classification, packaging, and labeling of hazardous substances), GefStoffV]. Some PA resins are licensed by the FDA for contact with foods.

If PA resins are used in the molten state, vapors can sometimes be formed, which do not impair general health or have any toxic effects, according to the current state of knowledge. Nevertheless, extraction of the vapors above processing equipment and adequate ventilation of the workplace are recommended.

4.2. Legal Aspects

Food legislation concerning resins is regulated by many national authorities, but will likely be harmonized with the requirements of the FDA (United States) and the European Community. The main questions are directed to the migration of residual monomers, oligomers, and additives that might contaminate contiguous media by diffusion, and to the stability of resinous formulations under the conditions applied (→ Foods, 4. Food Packaging, Section 8.1., → Foods, 4. Food Packaging, Section 8.2.).

In the *European Community,* the application of resins in the food sector will be regulated in connection with materials intended to come in contact with foods [148, 149] and with use of food additives other than colors and sweeteners [150]. Several directives that are especially relevant [151–153] have already been adopted.

In the United States, the use of resinous materials in contact with food is regulated in the Code of Federal Regulations (CFR) under Title 21 (Food and Drugs): Besides the use of resins, other additives such as stabilizers, fillers, and linker reagents are also addressed (e.g., Parts 172, 175, 176).

Natural gums, synthetic as well as natural terpene resins,indene coumarone,and petroleum

hydrocarbon resins may be used as chewing gum bases with limitations (121.1059, 121.90). Terpene resins are permitted for coatings in direct use (e.g., coating of fruits) when the precursors originate from wood (172.280). In indirect applications, most resins (synthetically or naturally derived) may be used.

Petroleum hydrocarbons are authorized for indirect use as components of paper and paperboard (Part 176).

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Part 5

Inorganic Polymers

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Inorganic Polymers

ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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1. Introduction

Inorganic polymers are macromolecules linked by covalent bonds, whereby there is an absence or near-absence of organic units within the backbone. Inorganic polymers include many of the most important "natural" materials as well as many synthetic materials. Natural inorganic polymers include many of the rocks about us, diamond, graphite, sulfur, boric oxide, silica, polyphosphates, quartz, and glass. Sulfur, selenium, and tellurium form macromolecules. Chalcogenide glasses are three-dimensional polymers, as are the asbestoses and a number of silicates. Most of these are industrially important, and some exhibit properties that are utilized in high-technology applications. Thus, arsenic sulfide, a chalcogenide glass, is used as an infrared-transparent window, and modified zeolites as selective chelating agents and catalysts.

Many scientific societies, including the National Research Council [1], have emphasized that the major hindrance to progress in most technological areas is the lack of suitable materials. The search for new materials in the 1970s and 1980s generally focused on rearranging, mixing, blending, and copolymerizing well-known organic polymers. Although great success has been achieved, many new applications require materials whose performance greatly exceeds that of currently available materials. Such performance requirements can be achieved only by materials containing other elements in addition to those found in the usual carbon-based polymers. For example, although the first polysiloxane, polydimethylsiloxane, was prepared in 1924 by Kipping [2], the initial products were infusible and insoluble. In fact, these properties were so unfavorable that polysiloxanes were not developed until more than five decades later. Today, polysiloxanes offer combinations of chemical, mechanical, and electrical properties not common to any other commercially available class of materials.

Major applications of inorganic polymers include their use as bulk and specialty building materials, biologically inert and biologically active materials, high-strength materials, catalysts, and speciality coatings. The breadth of the field in relation to more traditional polymer chemistry is exemplified by comparing the number and variety of elements typically found in commercial organic polymers (C, H, N, Cl, F, O)

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with the number and variety of readily available inorganic materials. The relative abundance of elements in the earth's crust also attests to the importance of noncarbon-based materials. In fact, the most abundant natural building materials are based on silicon – oxygen polymers, including the majority of rocks, soil, and sand.

The alternative of utilizing heteroatom backbones or noncarbon-based polymers is attractive because of the great variety of available reactants. Thus, a wide range of compounds can be exploited to obtain materials with specific properties. Furthermore, these materials are of interest because the resulting bonds may have bond energies greater than that of the C−C single bond in alkanes (ca. 343 kJ/mol). Approximate bond energies for other elements, in kilojoules per mole, are B−N 389, Si−N 439, Si−O 795, P−N 615, and Be−O 448. Bonding in these materials is a combination of ionic (nondirectional) and covalent (directional) components; the ionic character increases as the electronegativity difference between adjacent atoms increases. Furthermore, the tendency to form multiple bonds is high for many of the elements involved. The thermal stability of many inorganic and organometallic materials has been described [3].

As in inorganic chemistry there is a shift from purely inorganic compounds such as sodium chloride to metal- and nonmetal-containing compounds that contain organic moieties. This shift continues. Another trend is the movement to more diversified areas including ceramics, optical and thermal applications, composites, communications, and high-strength materials. This movement is fuelled by the unique properties offered by the presence of metal and inorganic atoms. This shift will continue. Probably the most rapidly growing area in materials is the emergence of carbon nanotubes.

Inorganic and organometallic polymers represent a rapidly growing field of chemical research and already have many applications [4–27]. Any division between inorganic and organometallic polymers is necessarily somewhat arbitrary. The classification used here is convenient but far from perfect. The reader is therefore referred to several other articles which review the scope of organometallic polymers and discuss many other systems which could also be regarded as inorganic polymers [8, 10–14, 42].

The variety of structures continues to increase and includes, along with hybrids, geometrically differing structures including ladders, cages, dendrimers, and hyperbranched and network structures.

2. Polysilanes, Polygermanes, and Polystannanes

Carbon has an unique ability to form strong single, double, and triple bonds to itself. Because of the relatively high bond energies (C−C single bonds are of the order of 340 kJ/mol) compounds containing carbon in their backbone do not readily cleave. By comparison, fellow members of group 14 have only recently been synthesized because of the low bond energies (generally on the order of 85 – 125 kJ/mol). Polysilanes may have been prepared by KIPPING in 1924 [2]. Only more recently have soluble, well-characterized polysilanes been synthesized [30–32]. (Topics related to polysilanes have been reviewed [33–41].)

Production. Polysilanes have been synthesized by four methods:

1. Reductive coupling
2. Dehydrogenative coupling
3. "Masked" dienes
4. Anionic ring opening

Attempts to prepare polysilanes in the late 1940s and 1950s gave insoluble, intractable materials; the major route employed was the reaction of dichlorosilanes with sodium (Fig. 1). For example, polydimethylsilane [28883-63-8] was investigated at Union Carbide but found to be insoluble [43]. The key developments leading to soluble polysilanes were the introduction of large substituent groups to decrease order, the use of two different substituents, and the copolymerization of different monomers (Fig. 1) [44, 45]. This resulted in high molecular mass (>400 000), tractable, soluble polymers, which could be purified easily, cast into films, and molded.

Improved methods for preparing high molecular mass polysilanes are being sought,

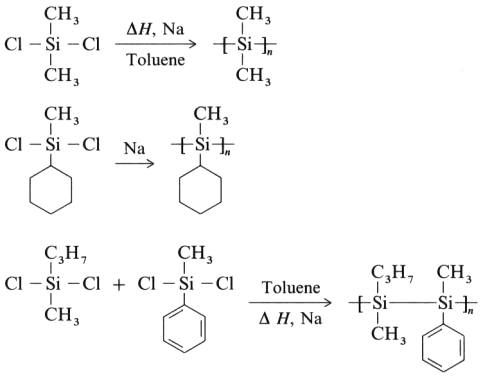


Figure 1. Synthesis of polysilanes

because the reaction of dichlorosilanes with sodium frequently gives low yields of high molecular mass polymers and because bimodal molecular mass distributions are obtained [43, 44, 46–50]. Carrying out the coupling reaction at low temperature by using ultrasonication gives monomodal polymers with low polydispersity [50].

Alternating copolymers are formed from the coupling of dichlorodisilanes with dilithium salts of 1,2-diethynyldisilanes [51] or dilithio polythiophenes [51, 52]. These products exhibit $\sigma - \pi$ conjugation. Some of these materials also undergo solid-state transitions to liquid-crystalline mesophases [51].

Water-soluble products are formed by coupling silanes with oligomeric poly(ethylene glycol) side chains [53].

Dehydrogenative coupling of dialkyl and monoalkyl silanes in the presence of transition metal catalysts such as titanocene and zirconocene dialkyls has given polysilylenes [51–63]. Functionalized polysilanes have also been produced. When the side chains contain amine functional groups, the products can be made water-soluble by formation of an amine salt network [64–66]. Dendrimeric [67–69] products can also be formed by dehydrogenative coupling. These products exhibit σ conjugation in many directions and show good conductivity. They have been used as negative-type photoresists because exposure to the air or light gives insoluble products.

Polygermanes and polystannanes have also been prepared by similar routes [70–73]. Many of these materials show better σ conductivity than the corresponding polysilanes and have been used as light-emitting diodes [74]. Reviews are available on polysilane synthesis by Wurtz-type reductive coupling [75], dehydrocoupling of hydrosilanes to form polysilanes [76], and formation of silicon-containing dendrimers [77] and ladders [78].

Properties and Uses. Much of the interest in the polysilanes, polygermanes, and polystannanes involves their σ delocalization and their $\sigma - \pi$ delocalization when coupled with arenes or acetylenes. This is not unexpected since silicon exists as a covalent network similar to diamond. In exhibiting electrical conductivity, germanium and tin show more typical "metallic" bonding. Some polystannanes have been referred to as "molecular metals" [79]. Conductivity is increased by doping [80], illumination [81], and application of an electric field. (reviews: [82–85]). The use of polysilane–metal complexes for organic semiconductors has been reviewed [86], as have organogermanium polymers [87] and organotin polymers [88].

Because of a number of interesting electronic and physical properties exhibited by polysilanes, a number of potential uses have been suggested and/or shown to exist, including precursors of β-SiC fibers [89–97], impregnation of ceramics [97, 98], polymerization initiators [99, 100], photoconductors for electrophotography [101–104], nonlinear optical materials [105–113], mid-UV photolithography bilayer materials [114–117], contrast enhancement layers in photolithography [118], deep UV-sensitive photoresists [116, 119–126], and self-developing by excimer laser or deep UV exposure [125–127]. The unusual absorption spectra of polysilanes have indicated potential uses in a number of conducting areas. The copolymer of polysilastyrene, when doped with arsenic pentafluoride, becomes a semiconductor. Conducting films have been reported [128].

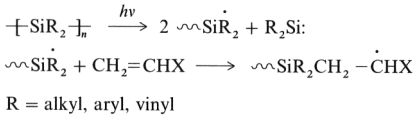
Polysilanes display UV absorption due to silicon – silicon bonds of the backbone. For example, poly(cyclohexylmethylsilane) exhibits an absorption band at 326 nm [45]. This absorption is not found in saturated carbon chains. Polysilanes with phenyl side chains show strong absorption near 330 nm, resulting from interaction between the phenyl groups and the silicon backbone, which acts as a $\sigma \rightarrow \sigma^*$ or $\sigma \rightarrow \pi^*$ chromophore.

Polysilanes have a high sensitivity to degradation by UV light. After light is absorbed, chain cleavage occurs with measured quantum yields of 0.20 – 0.97. This has led IBM to examine polysilanes as resists for bilayer UV lithography [129–131]. They serve as excellent reactive-ion etching barriers for bilevel resist applications because a protective layer of silicon dioxide is formed during exposure of the polymers to oxygen plasmas [130, 131].

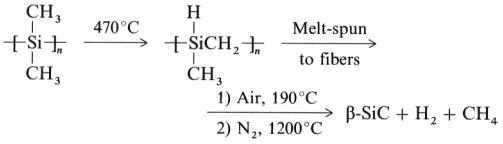
The wavelength at which maximum absorption occurs (λ_{max}) depends on the polysilane chain length. During irradiation nonlinear bleaching (decrease in UV absorption) occurs, because the polymer undergoes chain cleavage to give shorter fragments of lower absorptivity. As the irradiation continues, the polysilanes become increasingly transparent. This unique bleaching latency is useful in contrast-enhanced lithography [130, 131].

The λ_{max} for UV absorption also depends on the conformation of the polysilane backbone [132, 133]. Polysilanes having a planar zigzag backbone conformation absorb at much longer wavelengths than those in which the backbone is disordered or helical. The solid materials are strongly thermochromic [132]. For example, the λ_{max} of poly(di-*n*-hexylsilane) in solution or immediately after baking at 100 °C is 317 nm, but after 3 h at 21 °C films exhibit λ_{max} = 371 nm.

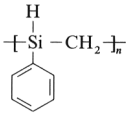
Polysilanes are excellent photocatalysts for making high molecular mass vinyl polymers. On irradiation, chain cleavage occurs to give free radicals [134], which initiate vinyl polymerization and curing. The 3M Company has commercialized this process. Polysilane initiators are relatively insensitive to termination of polymerization by oxygen.



Pioneering work by YAJIMA, [135] showed that poly(dimethylsilane) can be converted into β-SiC fibers with very high tensile strength (350 kg/mm^2) by a series of pyrolysis steps. Thermolysis of poly(dimethylsilane) at 470 °C gives a poly(carbosilane) which is fractionated and then melt-spun into fibers at 350 °C. The resulting fibers are oxidized at the surface in air at 190 °C (cross-linking occurs) to provide rigidity, then pyrolyzed at 1200 °C under nitrogen to give crystalline β-SiC (see also → Fibers, 13. Refractory Fibers).



Objects have been manufactured from silicon carbide by Shin Nisso Kako using poly(silastyrene):



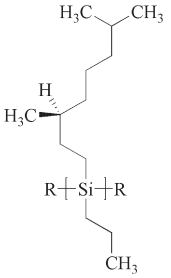
These materials contain 20 – 30 vol% of microvoids, which lower the ultimate strength slightly but also inhibit crack growth, so that they can be machined to exact dimensions.

Delocalization in the Si–Si σ-bond framework makes polysilanes potential electrical conductors. Although neutral polysilanes are insulators, they become semiconductors when doped with AsF_6 or SbF_5 [46]. Conductivities up to 0.5 Ω^{-1} cm^{-1} have been measured. Polysilanes are excellent photoconductors operating through hole migration with high hole mobilities (10^{14} cm^2 V^{-1} s^{-1} at ambient temperature) [136]. This has possible applications in electrophotography and communications technology. The discovery that poly(methylphenylsilane) has nonlinear optical properties suggests eventual applications in laser technology [137].

A variety of linear, two- and three-dimensional polysilanes are under investigation for use as specialty caulks, adhesives, oils, sealants, viscosity regulators [46, 138, 139], biologically active materials [139, 140], as well as in electrophotography [141] and reprography [142]. Although these applications are largely in the research stage, the unique all-silicon backbone provides an alternative to carbon and siloxane polymers.

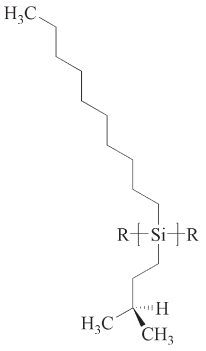
There is continued interest in the electronic properties and applications of polysilanes. Another aim is the synthesis of and studies

on optically active polysilanes [143–145]. Thus, a series of enantiopure polysilanes were synthesized. It is believed that each of the polymers adopts helical conformations in solution with the same helical screwlike geometry. Thin films of **1** showed a second-order transition at about −47 °C (T_g) and a first-order transition at about −8 °C attributed to a helical-coil-associated transition. This helical-coil solid-state transition is reversible and may allow their use as chiroptical switches.



1

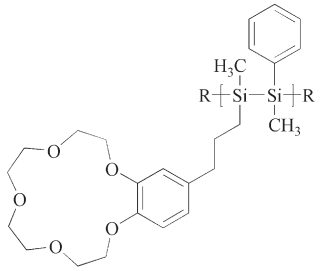
Similar behaviors were found for other optically pure polysilanes. This may allow their use as switches and memory devices with rewritable and write-once read-many (WORM) CDs. The temperature at which the helical structure switches is sensitive to molecular weight and may allow the introduction of mixtures of polysilanes with multiple structural "switches" available to them. Spin-coated and chemically grafted films of optically active polysilanes, such as **2**, on quartz showed helical coil shifting from optically active coils to optically inactive rigid-rod structures.



2

Similar results were found for optically active polygermanes [147]. The topic of photoprogrammable molecular hybrid materials for write-as-needed optical materials has been recently reviewed [148].

A polysilane copolymer containing a benzo-15-crown-5 ether, **3**, was synthesized. It showed high sensitivity and selectivity for the fluoride ion in nanomolar concentrations [149–152].

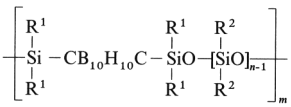


3

3. Poly(Carborane – Siloxanes), Polycarbosilanes and Polysilazanes

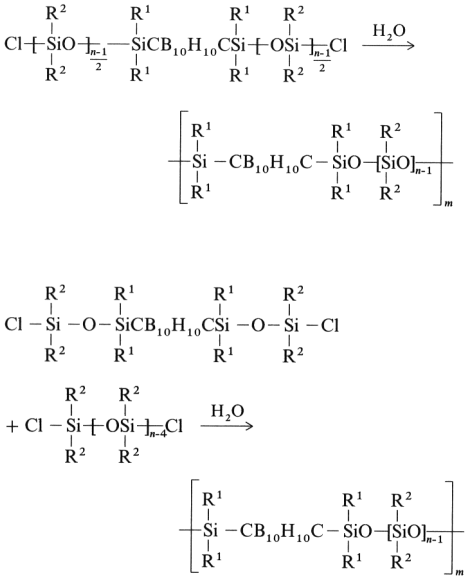
Silicon forms bonds with itself to give polysilanes, but it can also bond to other elements. Here several of these families are considered. (For polysiloxanes, see → Silicones).

Poly(Carborane – Siloxanes). The poly(carborane – siloxanes) have a linear structure **4** in which R^1 and R^2 can be alkyl, fluoroalkyl, or aryl groups. The main chain contains carborane polyhedra. Although the polyhedral carborane $C_2B_{10}H_{10}$ is most commonly employed in the preparation of poly(carborane –siloxanes), the *closo*-carboranes $C_2B_5H_7$ and $C_2B_{10}H_{12}$ have also been used as precursors [153, 154]. Major interest in this class of polymers results from the need for enhanced flame resistance and their high thermal and oxidative stability.



4

Production. The hydrolysis – condensation of carborane – siloxane monomers containing terminal Si−Cl bonds is one synthetic route to the poly (carborane – siloxanes) [155]. Cohydrolysis – condensation leads to other compositions of **4**



Another route involves reacting a dihalosilane with a carborane-containing dihydroxydisilane [156]. Synthetic routes to the required monomers have been reported [157, 158]. More recently, poly(carborane–siloxane) alternating and block copolymers have been synthesized by employing a two-step polycondensation process. Initially, a trisiloxane is condensed with a dilithiocarborane [159, 160]. The product is then treated with dilithiodiacetylene to produce low molecular weight (up to 9000 Da) products. Hydrosilylation of the Si-H end group allowed the synthesis of carbohydrate-functionalized silicones [161].

Properties and Uses. For polymers of series **4**, where $R' = R = CH_3$ and $n = 1 - 5$, the glass transition temperature (T_g) decreases with increasing siloxane content from −42 to −88 °C as n increases from 1 to 5 [162]. Replacing R^2 by phenyl groups gives a completely amorphous polymer, but T_g increases to −12 °C. When R^2 is a mixture of methyl and phenyl groups, T_g is lower. Trifluoropropyl-modified polymers are amorphous and exhibit T_g values that decrease with increasing n.

The thermal stability of poly(carborane – siloxanes) is excellent. In an inert atmosphere, rapid weight loss occurs only upon heating above 400 °C [162]. Phenyl-substituted polymers are more stable than their methyl analogues [163]. The amorphous polymers are elastomers and are formulated with fillers and vulcanized by using standard silicon technology. The high-temperature capabilities have resulted in the application of poly(carborane – siloxanes) as stationary phases in gas chromatography and the fabrication of these polymers into O-rings, gaskets, and wire coatings for operating temperatures >300 °C [153, 156].

Polycarbosilanes have generally been made as precursors for silicon carbide. Recently, polysilaethylene and related functionalized products have been prepared [164–166]. Polysilaethylene has a low T_g (about − 140 °C) and melts at about room temperature (ca. 25 °C). Ease of substitution of the chloro derivative by alkoxide, amine, and other functional groups may lead to a number of interesting products with derivative chemistry like that of polyphosphazenes. Fluorinated polysilaethylenes have also been made [167, 168]. It is suggested that these materials might exhibit piezo and pyroelectric properties similar to those of poly (vinyl fluoride).

Polysilazenes and Poly(N-methylsilazenes). Most research focuses on the use of polysilazenes as precursors to ceramics [169–172]. These products have not proved to be very useful since the ceramic yield is low (about 50 % at 1000 °C) and the free carbon content is high (about 30 % at 1000 °C).

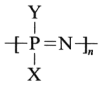
They are mainly synthesized by aminolysis and ammonolysis of dichlorosilanes [173, 174], deamination or redistribution reactions of aminosilazanes [175, 176], and more recently by the anionic and cationic ring-opening polymerization of cyclosilazanes. The latter products are soluble in typical organic liquids. The Si−N bond energy is greater than the Si−O bond energy. The temperature of initial weight loss for the products formed from the ring-opening reaction is about 50 °C higher than that of polydimethylsiloxane. Future applications will focus on areas similar to those of polysiloxanes themselves.

4. Polyphosphazenes

Polyphosphazenes are a well developed versatile class of inorganic polymers pioneered by Allcock and co-workers with over 2000

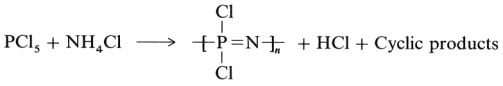
different polymers formed in the past four decades [177–186].

Polyphosphazenes (**5**) are polymers containing alternating nitrogen and phosphorus atoms in the backbone and alternating single and double bonds [187]. Phosphorus is pentavalent and has two pendant substituents (X and Y) which can be alkyl, aryl, alkoxy, aryloxy, arylamino, alkylamino, halogen, or pseudohalogen. Variation of X and Y leads to a wide variety of materials with highly diverse properties and applications [187–191].



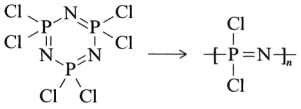
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Production. Polyphosphazenes can be prepared in several ways [187–191]. Reaction of ammonium chloride with phosphorus pentachloride yields a mixture of cyclic and linear oligomeric phosphazenes with a degree of polymerization (DP) of up to 20:



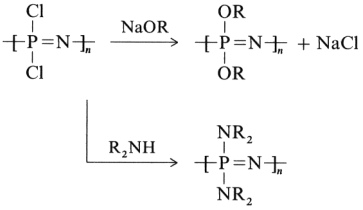
The ring opening polymerization (ROP) of hexachlorocyclotriphosphazene[*940-71-6*], [*16422-79-0*] (**6**) leads to a rubbery material, but when a carefully purified starting material is polymerized under controlled conditions, a degree of polymerization of up to 15 000 can be obtained and the polymer can be purified readily. The formation of cross-linked materials is a problem in this synthetic approach. A mechanistic study of the ROP of hexachlorocyclotriphosphazene in a titanium reactor using diglyme as solvent allowed the synthesis of linear polymer with little or no cross-linking [192].

The substitution of the chloro groups continues to serve as a much-used approach to obtaining other polyphosphazenes.

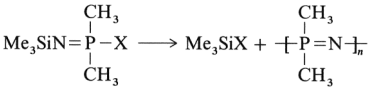


6

Poly(dichlorophosphazene) [*26085-02-9*] degrades slowly in a moist environment. However, the chlorine atoms are readily (and completely) displaced by many different nucleophiles. This reaction leads to a variety of highly stable polymers [187, 190, 191, 193–195].



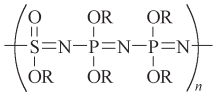
The condensation polymerization of appropriate *N*-silylphosphoramines has resulted in the successful preparation of the first polyphosphazene to have only alkyl substituents on phosphorus [196]:



4

Recently, polyphosphazenes have been prepared by room-temperature cationic (living) polymerization of phosphoranimines [197–199]. Certain initiators allow the formation of multiple initiating sites and the formation of star-branched polyphosphazenes with a narrow polydispersity. Block structures with polymers such as poly(ethylene oxide) have been made that contain reactive amine end groups [200]. Copolymers with polyurethanes have also been produced [201].

A number of polythionylphosphazenes have been produced with a variety of aryloxy, alkoxy, and amino appendages [202].



Polyphosphazenes have also been coupled with organosilicon compounds [203].

Properties. The poly(organophosphazenes), unlike their precursors the poly(dichlorophosphazenes), are resistant to hydrolysis and can be

Table 1. Glass transition temperatures (T_g) and crystalline melting points (T_m) for some polyphosphazenes, $[P(Y)_2 = N]_n$

Substituent (Y)	T_g, °C	T_m, °C
Cl	−63	30
OCH_3	−76	
OCH_2CF_3	−66	242
OC_6H_5	6	390
$N(H)C_6H_5$	105	

vulcanized to form elastomers. Copolymers with trifluoroethoxy and heptafluorobutoxy (1 : 1) groups are elastomeric with $T_g = -77$ °C [193], whereas T_g values for poly(arylaminophosphazenes) are much higher (see Table 1). Poly-(aryloxyphosphazenes) tend to be intermediate between these two classes.

Polyphosphazenes exhibit some of the lowest known rotational barriers for skeletal backbone bonds in polymers (as low as 420 J/mol of repeating units), which is consistent with their low T_g values. Two first-order transitions are usually found, with a temperature interval of ca. 150 – 200 °C [187, 190, 191]. The nature of the lower temperature transition resembles the change into a mesomorphic state similar to that observed in nematic liquid crystals. In practice, polyphosphazenes are usually soft just above this lower transition temperature, which allows compression molding of films to be carried out. Table 1lists representative data.

The thermal stability of some polyphosphazenes is outstanding. Several classes exhibit onset of weight loss above 300 °C, as shown by thermogravimetric analysis (TGA), but these studies overestimate the stability. Poly(diphenoxyphosphazene) [28212-48-8], for example, undergoes rapid depolymerization above 150 °C.Fluoroalkoxyphosphazene vulcanizates have excellent resistance to solvents (e.g., lubricants and fuels) and display low volume swells after long immersion in lubricants [204]. Polyphosphazenes also display good flame-retardant properties, with oxygen index values in the range 20 – 70, and they give off only moderate amounts of smoke [205, 206].

Uses. The favorable properties of polyphosphazenes, as well as the high elastomer elongations, which are greater than those of polysiloxanes from −60 to 200 °C, have resulted in the use of various polyphosphazenes as gaskets, specialty damping materials, and petroleum piping for arctic applications. They have also been used as specialty membrane materials [195]. Polyphosphazene – salt complexes, which have the highest ionic conductivities at ambient temperature of all polymer – salt electrolytes, are reported to be semiconducting materials [195]. Other uses include catalytic templates [195], biomedical materials [205], and their most prominent use as specialty elastomers in O-rings, gaskets, and fuel hoses [187, 206–210].

The first commercial polyphosphazene elastomers were synthesized and subsequently developed by the Firestone Tire and Rubber Co. [211] and represent the first new class of semi-inorganic elastomers to be developed commercially since silicone rubber. Ethyl Corporation holds the rights to many commercial uses and produces both commercial polymers and finished products from this interesting class of materials [212].

Thin films of amino-substituted polythionyl phosphazenes exhibit an unusual permeability to molecular oxygen [213]. When a phosphorescent dye that is quenched by oxygen is dispersed in the polymer film, the product can be used as a visually interpretable oxygen sensor. One potential use is to follow differences in pressure across a surface area such as a wing of a plane.

Polyphosphazene materials containing a sulfonyl-based chromophore have been synthesized that show second-order nonlinear optical properties [214]. Polymer electrolytes based on polymethoxyethoxyethoxyphosphazenes (MEEP) show high room-temperature ionic conductivities with charge transport occurring in the presence of certain salts [215].

There have been several recent reports related to biological uses of polyphosphazenes [184]. Nanofibers of polyphosphazenes have been produced by electrospinning. These nanofibers promote the adhesion of bovine coronary artery endothelical cells and osteoblast-like MC3T3-E1 cells [216]. Polyphosphazenes containing carboxyl substituents have been investigated for their biological activity with possible use as microencapsulating materials [217]. Hydroxyapatite–polyphosphazene composites have been investigated as bone substitutes [218].

Polyphosphazenes have also been used as drugs themselves. Allcock and co-workers synthesized a variety of polyphosphazenes that acted as carriers for a cisplatin-like moiety. These products showed good inhibition in the ascites test and 5/7 survival after the eighth day for the P388 mouse test. Thus, these materials exhibited good inhibition of some cancer cell lines and lower toxicity. This and related work has been reviewed [218, 219].

Water-soluble polyphosphazenes are emerging as an important class of synthetic polymers with much of the effort aimed at biomedical applications [221]. Another area of continued emphasis is the construction of fuel cells. New photon-conductive fuel-cell membranes have been produced through the linkage of acidic functional groups to aryloxy side units attached to the polyphosphazene backbone [222].

A wide range of hybrid metallocene–phosphazene polymers have been synthesized, including ferrocene and ruthenocene [223].

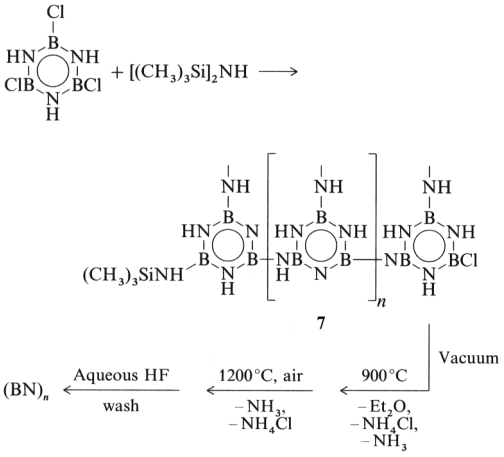
Polyphosphazenes are considered as additive and inherently flame-retardant materials and have the potential to be more widely employed as fire-resistant materials and fireproofing agents [224].

5. Poly(Boron Nitride)

Boron nitride [10043-11-5] occurs in three crystalline forms — α, β, and γ (→ Boron Carbide, Boron Nitride, and Metal Borides, Chap. 2.). The α-form is a layered, hexagonal polymer much like graphite. A crystalline, tetrahedral network polymer similar to diamond also exists [225–228]. Although boron nitride is isoelectronic with the diamond and graphite forms of carbon, it exhibits different properties. For example, layered boron nitride is white and an electrical insulator. Thus its electrons appear to be highly localized in contrast to those of graphite. Like graphite, layered boron nitride is soft and easily machined. Articles are fabricated by sintering or machining. These articles can be used in air up to 800 °C or in an inert atmosphere up to 1600 °C. Boron nitride has a Young's modulus : density ratio of 20 (versus 4 for iron) and a tensile strength : density ratio of 8 (versus 1.7 for glass and 0.3 for iron). The tetrahedral form of boron nitride is almost as hard as diamond and is therefore employed as a substitute for diamond in both cutting and grinding and in jewelry. Industrial applications include its use as an abrasive, insulator, and refractory material.

The hexagonal modification of boron nitride has been prepared from combinations of cheap boron and nitrogen compounds, such as $B(OH)_3$, $(NH_2)_2CO$, and N_2, or KBH_4 and NH_4Cl [207–212, 225–231]. More recently, chemical vapor deposition (CVD) methods have used mixtures of BCl_3 and NH_3, BF_3 and NH_3, or B_2H_6 and NH_3 to produce hexagonal boron nitride [231–234].

Polymeric precursors to boron nitride are beginning to attract attention. The reaction of difunctionalized borazines with bis(trimethylsilyl)-amines gives soluble oils that form films which can be pyrolyzed at 1200 °C to yield a boron carbide – boron nitride ceramic, but removal of all of the carbon has not yet been achieved [229]. The use of trifunctional borazines (shown below) leads to hexagonal boron nitride in good yields, with good crystallinity via intermediates such as **7**:



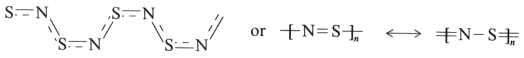
The formation of boron nitride nanocomposites has been reviewed [235].

6. Poly(Sulfur Nitride)

The topic of poly(sulfur nitride) has been reviewed [236].

Poly(sulfur nitride) [*56422-03-8*] was first prepared in 1910 by Burt, who passed vapors of cyclic tetrasulfur tetranitride [*28950-34-7*], S_4N_4, over heated silver gauze or silica wool

[237]. However, it was not studied extensively until the 1970s, when purer products were obtained [238]. Poly(sulfur nitride) films have a lustrous golden color and are very striking in appearance. Polymeric sulfur nitride is a crystalline, fibrous material that is malleable under mild pressure. Electron micrographs reveal that the crystals are composed of fiber layers which are stacked parallel to one another along the crystal axis; X-ray studies show that the polymer consists of almost planar chains of alternating sulfur and nitrogen atoms. All the S–N bond lengths are similar and correspond to a sulfur – nitrogen bond order intermediate between a single and a double bond. The polymer decomposes on heating at ca. 140 °C.



The polymer exhibits highly anisotropic electrical conductivity. Room-temperature conductivities as high as 3700 Ω^{-1} cm^{-1} along the crystal axis have been measured [240, 241]. Conductivity increases markedly upon cooling to 4.2 K, and the polymer becomes superconducting at 0.26 K [242]. Poly(sulfur nitride) was the first example of a polymeric superconductor. The conductivity increases on doping with bromine, and $(SNBr_{0.4})_n$ at room temperature has a conductivity of 3.8×10^4 Ω^{-1} cm^{-1} parallel to the fibers, but only 8 Ω^{-1} cm^{-1} perpendicular to the fiber axis. This strong directionality is related to efficient conductivity along the molecular chain axis, whereas a lower degree of order in chain packing along the perpendicular axis results in lower conductivity.

The large-scale production of poly(sulfur nitride) does not appear to have attracted much attention because of its rather low thermal stability and because S_4N_4 is explosive.

Further, polymerization is slow (6 – 8 weeks). Efforts have aimed at developing alternate synthetic routes.

Poly(sulfur nitride) has been prepared from solution by addition of trimethylsilyl azide to $(NSCl)_3$ and other similar routes [243–245]. In these processes, a powdered product is obtained rather than the larger crystalline grains. Microcrystalline layers of poly(sulfur nitride) have been prepared on platinum electrodes by electrolysis of $[S_5N_5]^+$ [246, 247]. Additional synthetic routes have also been found [236]. Even so, the classical route appears to be the method of choice for the synthesis of pure poly(sulfur nitride).

The fine structure of poly(sulfur nitride) continues to be elucidated [236]. Currently, it is believed the polymer chains are planar and lie along the (crystallographic) *b* axis that develops along the *a* axis of S_2N_2. There are two chains in each unit cell with two SN units per chain. Disordered chains are present between the "ordered" chains. Secondary interaction between the chains is significant.

Polymer crystals are stable in air and water for several days. Stress and strain properties are like those of an anisotropic metal. The Young's modulus parallel to the axis of the chain is on the order of 10^{10} N/m^{-2}.

Poly(sulfur nitride) becomes superconductive at 0.26 K [248]. This property has been extensively studied [236]. The onset of superconductivity T_c increases with increasing pressure up to about 9000 bar, whereupon it decreases, but at higher pressures T_c again increases to about 3 K. It is possible that at higher pressures small amounts are converted to a –SNNS– polymer [249]. Poly(sulfur nitride) exhibits the Meissner – Ochsenfeld effect (→ Superconductors, Section 2.2.) below about 20 K. Below 4.2 K negative transverse magnetoresistance occurs in the presence of weak magnetic fields (<3 T), though a normal positive magnetoresistance is found above 77 K or in stronger fields [236].

Thin films have been produced with properties that at times are similar to and under certain conditions appears to differ from those of the crystals themselves. The reason(s) for these differences are not currently fully understood. The ability to make large crystals has been reported [250, 251].

Recent interest has focused on electrical applications because of its unusual magnetic and electrical properties. Suggested uses include light-emitting diodes, solar cells, and transistors [252, 253]. A poly(sulfur nitride) – Ga – As solar cell with an efficiency of 6.2 % has been described [254]. Blue light-emitting diodes have been made on ZnS with either gold or poly (sulfur nitride) barrier electrodes [255]. The polymer gives barriers about 0.75 eV higher with a hundredfold increase in quantum efficiency in comparison to the gold-based

electrode. A power output of 440 W h/kg at 200 mA was found for a lithium cell with a poly (sulfur nitride) electrode [248]. Patents for the use of poly(sulfur nitride) have been issued for a variety of uses including the cathode in batteries [256, 257], coatings on an image recording sheet [258], etching mask [259–261], explosive initiator [262], electroconductive resins [263], multilayered wiring patterns [264], sublimable polishing grains for semiconductor devices [265], and in light-emitting diodes [266].

Extensive work has been done on poly(sulfur nitride) electrodes [236]. A ruthenium(II)-modified poly(sulfur nitride) electrode generated hydrogen continuously in aqueous sulfuric acid solution at − 0.1 V under visible light [267]. Molybdenum(VI) electrodes using film and crystalline poly(sulfur nitride) can convert ethyne to ethene at rate 10^6 times that achieved by chemical systems [268]. Paste electrodes of poly(sulfur nitride) exhibit metallic electrochemical behavior in nonaqueous liquids [269].

7. Polysulfur

The topic of sulfur-based polymers had been reviewed [270–272].

Because of its removal from industrial waste to meet environmental standards, sulfur has been stockpiled and is available in large quantities at a modest price. Although the stable form at room temperature is cyclooctasulfur, S_8, linear polysulfur is formed on heating. Unfortunately, the thermodynamically stable form of sulfur is the S_8 monomer and the polymer undergoes depolymerization after some time. Various methods have been used to retard depolymerization to the S_8 monomer. Removal of minute amounts of the monomer through judicious extraction with carbon disulfide retards depolymerization to some extent. Probably the most effective method involves the addition of olefins, such as limonene, cyclopentadiene, and myrcene [273]. Some of these result in polysulfur that is stable for more than five years. Such stabilized polysulfur has been incorporated into concrete and asphalt mixes to strengthen them. Concrete blocks, posts, highway pavement, and parking tire restrainers that contain stabilized polysulfur are produced.

8. Organometallic Polymers

The topic of organometallic polymers has been reviewed [15–28].

A variety of organometallic polymers have been synthesized for a number of applications. Examples are shown in Figure 2. The metals may be an integral part of the polymer chain (**8**) or side chain (**9**); they can be connected through carbon (**10**) or other atoms (**11**); they may be bonded by coordination (**11**), covalent (**8–10**), or p – metallocene-like bonding (**12**); or they can be part of a linear (**10–12**) or cross-linked (**9**) product. A classical coordination polymer is described by **13**, and stacked metal-chain complexes are depicted by **14**, where the circles represent organic macrocycles such as phthalocyanine.

Polymeric metal phosphinates may have single-, double-, or triple-bridged structures, such

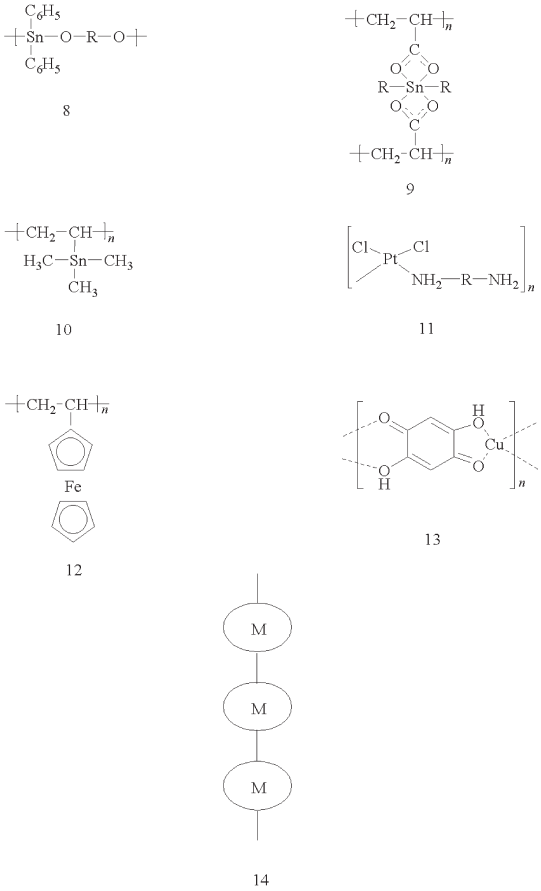
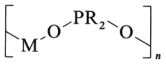
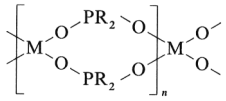


Figure 2. Some organometallic polymers

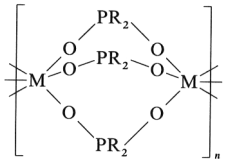
as **15**, **16**, and **17**, respectively. Such structures are known for aluminum, beryllium, cobalt, chromium, nickel, titanium, and tin [274]. They form films, with thermal stability up to 450 °C claimed in some instances. The chromium(III) polyphosphinates have been used as thickening agents for silicone grease to improve its high-pressure physical properties.



15



16



17

The metal moiety of an organometallic polymer imparts particular properties. First, the metal atom is typically a site for reaction with Lewis bases and redox reactants. These sites have been exploited for catalysis and may be responsible for internal rearrangement and degradation. Second, the metal generally contributes to polymer stiffness through added volume occupation and π-bond formation. Thus, flexibility must be derived from the organic moiety. Third, the metal-containing portion typically contributes to the dipolar, ionic character of the products. The high chemical reactivity of the metal site results in polymers with poor thermal stability. For example, products derived from bis(cyclopentadienyl)titanium dichloride [*1271-19-8*] typically begin to undergo small weight losses between 60 and 150 °C due to the evolution of cyclopentadiene and formation of a more thermally stable material. Because of the tendency of the metal site to undergo reaction, care is needed in selecting solvents so that "permanent" bonding does not occur between the metal-containing moiety and the solvent.

The variety of structures and properties offered by organometallic polymers is enormous and cannot be summarized in a representative fashion in this short chapter. The reader is referred to reviews on organometallic polymers [11–14, 42, 275–288]. Important uses of organometallic polymers are as follows:

1. Catalysis [286, 273, 289]
2. Biological uses, general [285, 290–301]
3. Additives: coatings, textiles, plastics, and paper [285, 302, 289, 303–306]
4. Electrical conductors, semiconductors, and piezoelectric devices [307–315]
5. Electrocatalysis, photoelectrocatalysis, photovoltaic cells, specialized electrodes, sensor devices, electrochromism, electroluminescence, and multicolor displays [285, 286, 310, 316–322]
6. Analytical reagents [323–327]
7. Photoprotective agents [302, 289, 303–306]
8. Thickening agents [274]
9. Energy-transfer agents [329–331, 311, 312]
10. Permanent coloring agents [302–306]
11. Composites [332, 333]
12. Metal deposition [334–338]
13. Solar energy conversion [339, 340]
14. Ceramic precursors [341–346]
15. Superconductivity [347]
16. Functionalized electrodes (electrocatalysis, photoelectrocatalysis, photovoltaic cells) [348–351]
17. Ferromagnetic materials [352]
18. Photoconductive materials [326, 327, 351]
19. Poly(vinyl alcohol) heat stabilizers [285]
20. Electrochemical sensors [282]
21. Nonlinear optics [282]
22. One-dimensional conductivity [282]
23. Nanostructures and nanotechnology [286].

While organometallic and metal-containing polymers can be synthesized in a number of ways, the three most common routes are condensation, coordination, and addition.

Condensation Polymers. Carraher and coworkers have produced a wide variety of organometallic condensation polymers based on the Lewis acid–base concept. These have been reviewed [15, 17–21, 29]. Polymers have been produced from Lewis bases containing

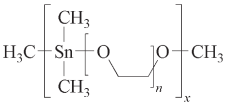
amine, alcohol, acid, thiol, and related units including a number of drugs such as ciprofloxacin and acyclovir. Lewis acids containing such metals and metalloids as Ti, Zr, Hf, V, Nb, Si, Ge, Sn, Pb, As, Sb, Bi, Mn, Ru, P, Co, and Fe have been employed. These compounds have potential uses in the biomedical arena as antifungal, antibacterial, anticancer, anti-Parkinson's, and antiviral drugs. These polymers show promise in a wide variety of other areas including electrical, catalytic, and solar-energy conversion [17, 18]. Polymers referred to as polydyes, because of the presence of dye moieties in the polymer backbones, have been used to impregnate paper products, plastics, rubber, fibers, coatings, and caulks, giving the impregnated material color, (often) added biological resistance, and special photo properties [21]. Some of the polymers, including the metallocene-containing products, show the ability to control laser radiation [21]. Depending on the range of radiation, laser energy can be focused, allowing the material to be cut readily, or it can be dispersed, imparting to the material containing the polymer added stability towards the radiation.

A number of these polymers exhibit a phenomenon called "anomalous fiber formation," reminiscent of metallic whiskers [353].

There are more organometallic compounds containing tin than any other metal. These materials are employed to improve the heat stability of PVC when it is formed into pipe. Today, because polymers leach much slower than small molecules, organotin polymers are being used as heat stabilizers in PVC pipe [18].

The industrial emphasis on tin-containing polymers is the result of Federal laws that prohibit the use of leachable, monomeric organotin compounds in a variety of coatings and protective applications. This resulted in a move to polymeric materials that did not suffer the same leachability and which were allowed by law.

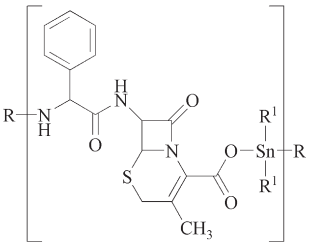
Much of the recent activity with organotin compounds, including polymers, involves their use to inhibit a wide variety of microorganisms at low concentrations. These microorganisms include a variety of cancers, bacteria, yeasts, and viruses. Some simple organotin polyethers **18** based on hydroxyl-terminated poly(ethylene glycols) inhibit a wide variety of cancers including ones associated with bone, lung, prostate, breast, and colon [354, 355].



18

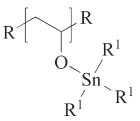
Some of these organotin polymers are water-soluble, and this allows for medical applications utilizing the material in simple pills.

A wide variety of organotin compounds developed on the basis of known antiviral drugs such as acyclovir and known antibacterial agents such as ciprofloxacin, norfloxacin, cephalexin (**19**), and ampicillin inhibit a wide variety of viruses including those responsible for many of the common colds, chicken pox, small pox, shingles, and herpes simplex [355].



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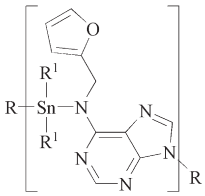
Some of the organotin-containing polymers inhibit *Candida albicans*, the yeast responsible for yeast infections in humans, better than commercially available applications while leaving the normal flora unharmed [353, 358]. Others, such as **20** inhibit methicillin-resistant *Staphylococcus aureus* (MRSA) preferentially [359, 360].



20

Organotin polyamines containing the plant growth hormone kinetin (**21**) increase the germination of damaged seeds and thus is may help in providing food in third-world countries [361]. It also increases the germination rate of sawgrass seed from about 0 to over 50 % and is an important agent in replacing the "sea of grass"

(actually sawgrass) in the Everglades.

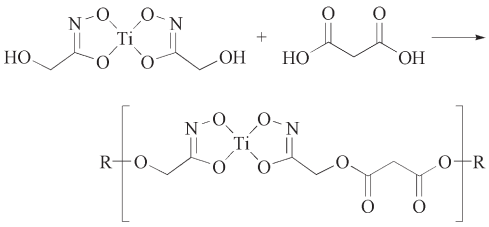


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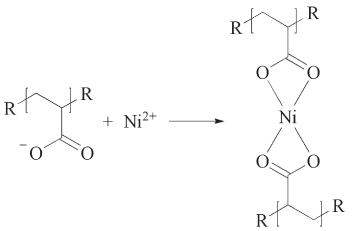
Coordination Polymers. The drive for the synthesis and characterization of synthetic coordination polymers was catalyzed by work supported and conducted by the U.S. Air Force in a search for materials which exhibit high thermal stability [362]. Attempts to prepare highly stable, tractable coordination polymers were disappointing. Typically, only oligomeric products were formed and the monomeric versions were often more stable than their polymeric counterparts.

Coordination polymers can be prepared by a number of routes, with the three most common being

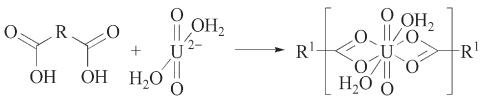
1. Preformed metal coordination complexes polymerized through functional groups where the actual polymer-forming step may be a condensation or addition reaction.



2. Reaction with polymer-containing ligands.



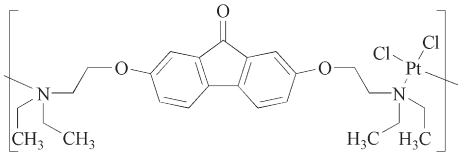
3. Polymer formation through chelation.



The last two processes were employed to recover the uranyl ion [19], the natural water-soluble form of uranium oxide, which acts as a heavy-metal toxin. By using salts of dicarboxylic acids and poly(acrylic acid) the uranyl ion was removed to 10^{-5} M and the resulting product was much less toxic and convertible to uranium oxide by heating.

Many of the organometallic polymers are semiconductors with bulk resistivities in the range of 10^3 to $10^{10}\Omega$ cm suitable for specific semiconductor use [18]. Further, some exhibit interesting photoproperties.

In 1964, Rosenberg and co-workers found that bacteria failed to divide but continued to grow. After much effort they found that the cause of this anomalous growth was a broken electrode and eventually identified the chemical as *cis*-dichlorodiammineplatinum(II). This compound is now licensed under the name Platinol and is also known as cisplatin. Cisplatin is the most widely used anticancer drug. The toxic effects of cisplatin have been reduced though placement of the platinum moiety into various platinum coordination polymers [17]. Some of these polymers inhibit various cancer growths with much less toxic effects. Many of them are also very active antiviral agents and some are able to prevent the onset of virally related juvenile diabetes in test animals [17]. Cisplatin derivatives formed from reaction of tetrachloroplatinum(II) and methotrexate [27, 363] inhibited a wide range of viruses in the nanograms per milliliter range. Similar results were found for the analogous product formed from reaction with tilorone (**22**) [27, 364].



22

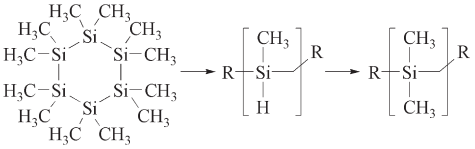
Addition Polymers. Many of the addition polymers are discussed elsewhere in this article. These include sulfur nitride polymers, polyphosphanes, and polysilanes.

One area of active interest in ceramics is the formation of ceramics that may contain some fiber structure. Currently, ceramics, while very strong, are very brittle. Introduction of thermally

Table 2. Nonoxide ceramics produced from the pyrolysis of polymeric materials

Polymer(s)	Resultant ceramic
Poly(phosphonitric chlorides)	PN
Polysilanes, polycarbosilanes	SiC
Polyphenylborazole	BN
Polytitanocarbosilanes	Si – Ti – C
Polysilazanes	Si_3N_4, Si – C – N

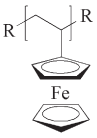
stable fiberlike materials may impart the ceramics with some flexibility before cleavage. Such materials can be considered as ceramic composites in which the matrix is the ceramic portion and the fibers are the thermally stable fibers. Introduction of the fibers during the ceramic-forming step is a major obstacle that must be overcome. Carbon fibers have been investigated, as have other high-temperature materials such as polysilanes. Polysilanes are formed from a six-membered ring by extended heating at 400 °C.



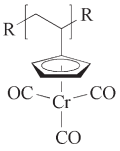
Further heating gives silicon carbide.

Table 2 lists a number of nonoxide ceramics that have been produced from the pyrolysis of polymers.

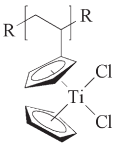
The landmark discovery of ferrocene by Kealy and Paulson in 1951 marked the beginning of modern organometallic chemistry [365]. The first organometallic addition polymer was polyvinylferrocene, synthesized by Arimoto and Haven in 1955 [366, 367], but it was about another decade until the work of Pittman [368], Hayes and George [368], and Baldwin and Johnson [370] allowed the launch of ferrocene-containing polymers.



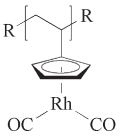
A large number of vinyl organometallic monomers have been prepared, homopolymerized, and copolymerized with classic vinyl monomers [368]. These include polymers containing Mo, W, Fe, Cr (**23**), Ir, Ru, Ti (**24**), Rh (**25**), and Co.



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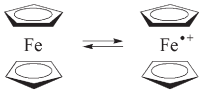


24



25

Neuse acted as an early catalyst in the development of metal-containing polymers including the use of ferrocene-containing polymers to fight cancer [371]. One key feature of ferrocene is its ability to donate an electron from a nonbonding high-energy MO resulting in the transformation of a neutral, diamagnetic site into the paramagnetic ferricenium radical cation. This occurs within a typical chemical environment and within selected biological environments.



This ferricenium radical cation, as do other free radicals, readily recombines with other free radicals. Neuse and others have successfully inhibited a wide variety of cancers using ferrocene-containing polymers [372]. Often the employed compounds are elaborately designed with special backbones and a ferrocene-containing unit as a tether dangling from the polymer backbone.

9. Sol – Gel Inorganic Polymers

In the 1980s, several symposia were devoted to sol – gel inorganic polymer preparation,

indicating the explosive growth in this field [373–375]. This field has continued explosive growth under additional "titles" such as organic/inorganic composite materials. Reviews are given in [376–384].

In sol – gel processes, ceramic polymer precursors are formed in solution at ambient temperature; shaped by casting, film formation, or fiber drawing; and then consolidated to furnish dense glasses or polycrystalline ceramics [385]. The most common sol – gel processes employ alkoxides of elements such as silicon, boron, titanium, and aluminum. In alcohol – water solution, the alkoxide groups are removed stepwise by hydrolysis under acidic or basic catalysis and replaced by hydroxyl groups, which then form $-M-O-M-$ linkages. Thus, branched polymeric chains grow and interconnect, as illustrated below for a silicate sol. Gelation eventually occurs as the growing polymers link together to form a network that spans the entire solution volume. At this point (the gel point), both the viscosity and the elastic modulus increase rapidly.

$$Si(OR)_4 + H_2O \rightleftharpoons (RO)_3Si-OH + ROH$$

$$2\,(RO)_3Si-OH \rightleftharpoons (RO)_3Si-O-Si(OR)_3 + H_2O$$

$$(RO)_3Si-O-Si(OR)_2OH \overset{+H_2O}{\underset{-H_2O}{\rightleftharpoons}} (RO)_3SiO\underset{\displaystyle OR}{\overset{\displaystyle OR}{Si}}O\underset{\displaystyle OR}{\overset{\displaystyle OR}{Si}}OSi(OR)_3$$

$$\overset{-ROH}{\updownarrow}$$

$$SiO_2\ (\text{glass or ceramic}) \xleftarrow{\Delta H} \text{Chain extension and cross-linking}$$

The gel can be viewed as a viscoelastic material composed of interpenetrating liquid and solid phases. The solid network retards the escape of the liquid and prevents structural collapse. Gelation is advantageous in processing because the gel freezes in shapes. Thus, the sudden increase in viscosity locks in place the shapes formed by casting, drawing of fibers, or film formation. Some sols and gels may be oriented or modified by drawing or shearing. The gel can then be dried by evaporation to form a *xerogel* or by supercritical fluid extraction to give an *aerogel*. Consolidation to dense glasses or ceramics is finally carried out by thermal treatment and sintering. Figure 3 gives some generalized sol –gel processes for ceramic or glass preparation.

Both aerogels and xerogels have high surface area (>500 m^2/g) and small pore diameter (<20 nm). They have been used as ultrafiltration media, antireflective coatings, and catalyst supports. Final densification is accomplished by viscous sintering in which the viscosity exceeds 10^{12} Pa · s.

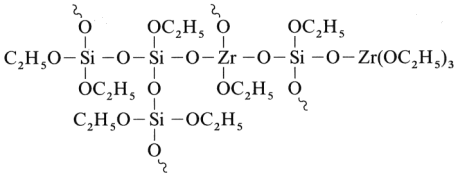
The rate of silicate sol and gel formation is exceptionally sensitive to pH and to the water – alcohol molar ratio in the reaction medium, as is the solubility of the amorphous silica that is formed. Silica networks are based on $[SiO_4]^{4-}$ tetrahedra modified by $[O_3Si-O^-M^+]$ units. Addition of B_2O_3, Al_2O_3, TiO_2, ZrO_2, and related network-forming units can result in the formation of mixed glasses and ceramics. The sol – gel approach uses the corresponding metal alkoxides, as illustrated below, for the formation of borosilicate glasses:

$$NaOR + B(OR)_3 + Si(OR)_4 \xrightarrow[-HOR]{H_2O}$$

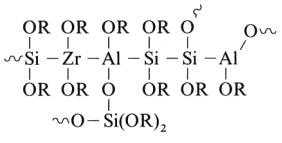
$$NaOH + B(OH)_3 + Si(OH)_4 \xrightarrow[\text{via sol and gel}]{-H_2O}$$

$$(Na_2O \cdot B_2O_3 \cdot SiO_2) \cdot H_2O \xrightarrow[\Delta]{-H_2O} Na_2O \cdot B_2O_3 \cdot SiO_2$$

The chemistry of the sol – gel process can thus be tailored to design new polymeric glasses or ceramics. For example, two or more metal alkoxides can be mixed in varying ratios to form mixed sol – gel polymers. Mixing $Zr(OEt)_4$ with $Si(OEt)_4$ could lead to a gel with structure **26**. Similarly, a zirconia – alumina – silicate gel polymer of structure **27** could be obtained from $Zr(OR)_4$, $Al(OR)_3$, and $Si(OR)_4$.



26



27

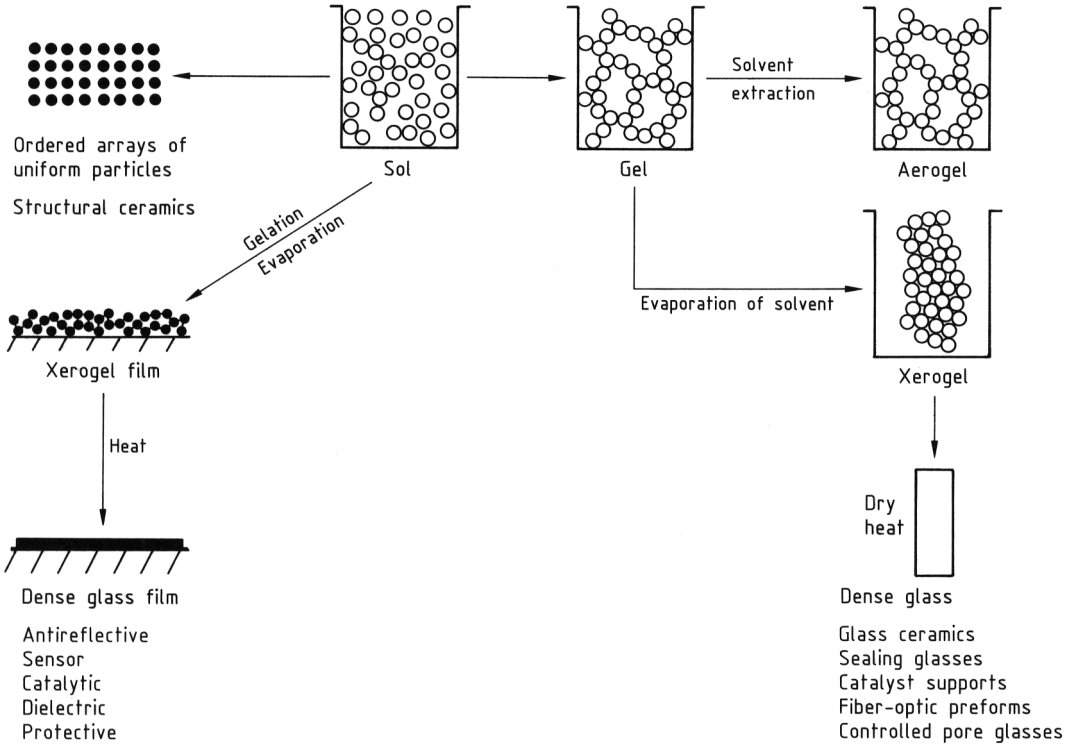
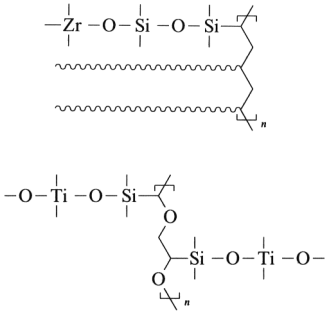


Figure 3. Schematic of the sol – gel process

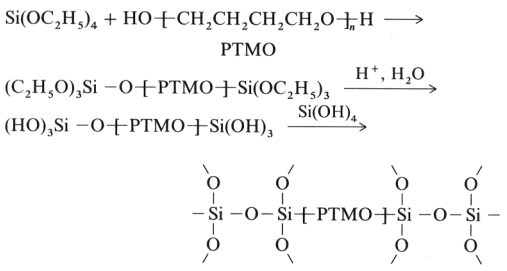
The development of organically modified silicates (ceramers) has resulted in a variety of new materials [386]. Thus, vinyl groups, epoxides, and methacrylate functions have been polymerized to give interpenetrating networks with a wide variety of structures and properties [387–389]:



Applications of ceramers include adhesives for glass surfaces [387], protective coatings for medieval stained glass [390], and scratch-resistant coatings for plastic eyeglass lenses.

Sol – gel preparations of tetraethoxysilane – water – alcohol – HCl can be spun into fibers once the appropriate viscosity has been reached. These fibers are only slightly weaker than silica-glass fibers; ZrO_2-SiO_2 fibers have also been made in this way. Sol – gel processing of Ti(i-$C_3H_7O)_4 - H_2O$ – ethanol – HCl gives thin film coatings of controlled thickness which exhibit interference colors that vary with film thickness and they are n-type semiconductors [391].

Hybrid materials have been made by incorporating end-capped poly(tetramethylene oxide) (PTMO) blocks of molecular mass 650 – 2000 into tetraethoxysilane sol – gel glasses [392].



These materials exhibit high extensibility. They contain interdispersed organic polymer and inorganic polymer regions. Although the PTMO blocks are well dispersed, some degree of local phase separation occurs. Titanium isopropoxide has been used to incorporate TiO_2 into these block systems [392].

Thus, although sol – gel chemistry has been extensively investigated since the early 1960s [394, 395], only now is it rapidly becoming important in material synthesis.

Uses. Sol – gels offer properties between those of organic polymers and inorganic materials. They are particularly useful in areas where they can replace materials to give better properties, better processability, and/or lower cost. Thin-film applications are promising, and the production of numerous nonlinear optical materials has been reported [376]. Thin-film protective coatings are being considered in a number of areas. Hot-melt adhesives for glass containers have been developed [377]. Hard contact lens materials have also been developed [377]. Another area of practical application is the reinforcement of plastics and elastomers [377]. Recent production of sol – gels with nanoscale pores allows their potential use as catalysts, porous supports, and as selective absorbents [377].

Aerogels. The topic of aerogels has reviewed [396, 397] (see also → Aerogels). Aerogels are highly porous materials in which the pore sizes are truly on a molecular level, less than 50 nm in diameter. This gives a material with the highest known internal surface area per unit weight, over 1000 m^2/g.

Porous materials can be either open-pored such as a common sponge, or closed-pored such as the bubble-wrap packaging. Aerogels are open-pored materials such that unbonded material can move from one pore to another.

While in the gel state the pre-aerogel has some flexibility, but solid aerogels behave as a fragile glass. It may be very strong in comparison to its weight, but it is very light. Aerogels are more durable when under compression. Compression can be simple such as sealing the aerogel sample in a typical food sealer packing. Aerogels are best cut using a diamond-coated saw similar to that used to slice rocks.

When handled, aerogel samples initially appear to exhibit some flexibility but then burst into millions of pieces. As force is applied, there is little bond flexing, so that the applied kinetic energy results in the collapse of the network with the force of impact spread over a large part of the aerogel and over some time because of the time required to transfer this energy from one cell to another within the aerogel matrix. Because the aerogel is open-pored, gas contained within the solid is forced outwards as collapse occurs. The frictional forces caused by the gas passing through a restricted opening are indirectly proportional to the square of the pore diameter. Because the pore sizes are so small, the rapidly moving gas also absorbs a lot of the energy. Thus, energy is absorbed by the aerogel through both collapse of the solid network structure and release of the gas within the aerogel.

Aerogels that are about 2 – 5 nm in diameter have large surface to volume ratios on the order of 10^9 m^{-1} and high specific surface areas approaching 1000 m^2/g. Such large surface to volume ratios makes the surface particularly active with potential in catalysts, absorbents, and catalyst substrates.

The precise chemical makeup of the surface depends on the materials used to make the aerogel and method of processing. Typical aerogel sequences produce products whose surfaces are rich in hydroxyl groups. Because of the high surface area, SiOH groups act as weak acids and are reactive in typical Lewis acid–base reactions. The many hydrogen-bonding hydroxyl groups at the surface make aerogels extremely hygroscopic. Dry aerogel materials will increase their weight by 20 % through uptake of moisture from the air. This absorption is reversible and appears to have little or no effect on the aerogel. Water is removed by heating to 100–120 °C.

While adsorption of water vapor has little effect on aerogels, contact with liquid water has devastating effects. When water enters the nanometer-sized pores, the surface tension of the water exerts capillary forces sufficient to fracture the silica backbone, resulting is a collapse of the complex matrix structure. This tendency to be attacked by water is overcome through conversion of the surface polar OH groups to nonpolar OR groups, where R is typically a

trimethylsilyl group, though any aliphatic group would work. Conversion can be accomplished within the wet stage (pre-aerogel) or after supercritical drying. These treatments result a "hydrophobic" aerogel which is stable in water.

The pore size of aerogels varies. IUPAC classifies materials with pore sizes of less that 2 nm as "microporous", 2 – 50 nm as "mesoporous", and greater than 50 nm in diameter as "macroporous". While aerogels have some pores that fall within the micropore range, the majority of pores are in the mesopore region.

The good visible-light transmission and good insulting power make aerogel materials of interest in window manufacturing. The visible transmission spectra of light shows little absorption in the range of about 300–2700 nm, and the good visible-light "window" makes aerogels attractive for day-lighting applications. Aerogels provide about 40 times more insulation than fiberglass. While aerogels may eventually be used as the entire window component, for the present time they act as the material sandwiched between two pains of clear plastic or glass. Thermoglass is generally simply glass sheets that are separated by a vacuum. The seals on such thermoglass often spring small leaks causing diminished insulation properties. Aerogel inner cores will not suffer from this problem. Currently, about 40 – 50 % of a house's heating bill literally goes out the window because of heat lost through windows. A single one-inch thick glass pane of aerogel offers the insulation equivalent to over 30 windowpanes of R-20 insulation rated glass.

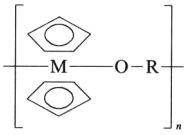
Another commercial area that is being considered is the use of aerogels as nanocomposite materials. In one approach, material is added to the silica sol before gelation. The material can be inorganic, organic, polymeric, bulk fibers, woven cloths, etc. The additional material must be able to withstand the subsequent processing steps including carbon dioxide drying. The added material must be present in a somewhat homogeneous manner throughout the system. Gentle agitation appears to be sufficient to give a product with decent homogeneity. Aerogels may be good materials for optical sensors. They have good visible transparency, high surface area, good temperature and chemical stabilities, and facile transport of gases through their pores.

10. Inorganic Fibers and Whiskers

Inorganic fibers have been important materials for over 50 years. Asbestos, glass, and carbon fibers are particularly well known. Many of the materials described herein are discussed in more detail under → Fibers, 11. Inorganic Fibers, Survey.

Many inorganic fibers exhibit very high tensile strength and thermal stability (>1000 °C) but suffer from high density and, high cost. This chapter discusses the preparation and properties of some inorganic fibers which are of interest in the production of high-performance materials, particularly advanced resin-matrix, ceramic-matrix, and metallic-matrix composites. The patent literature on inorganic fibers and composites is extensive and growing rapidly [392].

Asbestos, once widely used as insulation, now has more limited applicability because of its health hazard. Small fibers lodge in the lungs and can cause lung cancer and other lung damage. Asbestos-containing shingles, paper, welding rods, floor tiles, and brake linings are, however, still manufactured. These products avoid fibers of length 5 – 20 μm, which are the most dangerous. *Glass fibers* are used widely as insulation and in fiber-reinforced plastics. *Carbon fibers* are of increasing importance in high-performance composites. Several metallocene-type condensation polymers (e.g., **28**) exhibit fiber formation directly upon polymerization or upon application of stress [399].



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Inorganic fibers composed of alumina, silica, titania, zirconia, aluminum silicate, boron, boron carbide, boron nitride, silicon boride, silicon carbide, silicon nitride and others are known. Polymeric *alumina, titania*, and *zirconia fibers* are produced industrially [400–403]. Zirconia textiles are produced by Union Carbide under the trade name Zircar.

Alumina fibers with a high Al_2O_3 content have high temperature stabilities and high moduli.

They have been made by dispersing aluminum salts on rayon fiber, heating to burn off the organic material, and sintering. Alternatively, slurries of hydrated alumina can be extruded, dried, and heated to give polycrystalline filaments [404, 405]. Fibers may also be extruded and drawn from a viscous organic solution, followed by heating to high temperature [406]. Polyaluminoxanes are spun into fibers and sintered to give Al_2O_3 fibers, or mixed with silicon compounds, spun, and calcined at 1000 – 1200 °C to give aluminosilicate fibers.

High-purity *silicon dioxide fibers* can be used up to 1100 °C and are of interest for advanced composites [407]. They are made by melting a glass composed of 75 % SiO_2 and 25 % Na_2O, and then spinning and stretching the fiber simultaneously at 1100 °C. The fibers are then acid-leached to remove Na_2O and dried above 300 °C [408]. In another process, silicon alkoxide polymers are spun by a sol – gel process to make high-purity SiO_2 fibers. The fibers are heated to 1000 °C to give a 99.999 % pure quartz fiber which is stable at 1000 °C [409].

A variety of *metal oxide fibers* are now available. Du Pont has developed an alumina – zirconia fiber with a tensile strength >2100 MPa and a modulus of 380 GPa for use in high-performance composites [410]. Even after exposure to 1400 °C for 100 h, its tensile strength was 1400 MPa and its modulus remained unchanged. Stabilized zirconia and alumina – silica – boria fibers have also been produced [408]. The patent literature reports fibers of such materials as alumina – chromia, thoria (thorium oxide), titania, titania – silica, thoria – silicate, zirconia – alumina, zirconium silicate, and zirconia – yttria, as well as whiskers of these and many other metal oxides [411].

Boron – tungsten fibers have densities of 2.4 – 2.6 g/cm^3 and elastic moduli as high as 390 GPa. However, they lose both tensile strength and modulus at high temperature. When coated with silicon carbide and boron carbide, they retain about half their initial strength in air up to 800 – 1000 °C. *Boron fibers* are much less dense and are, therefore, useful in the construction of lightweight composites [411] found in tennis racket frames and aircraft. However, their cost is high because of production complexities. Processes involve chemical vapor deposition of boron onto carbon fiber and other cores, followed by a variety of treatments [412]. *Boron carbide fibers* are made from mixtures of methane and boron trichloride by using CVD to create a boron carbide layer on tungsten core filaments [392]. *Boron nitride fibers* are used with boron nitride matrices to give composites that are employed as electrical insulators which are also good thermal conductors. Boron nitride fiber mats are useful as electric cell separators in lithium sulfide batteries [392]. The fibers are made from boric oxide fibers that are nitrided by ammonia at ca. 800 °C followed by stretching at 2000 °C. They have a tensile strength of 2100 MPa and a modulus of 345 GPa.

Silicon carbide can withstand 1800 °C under oxidizing conditions. Two methods of production are employed. In the first, CVD is used to deposit silicon carbide on tungsten filaments. In the second method, polysilanes are melt-spun to give a precursor fiber, which on heat treatment yields fibers 10 – 30 μm in diameter (see Chap. 2), [135, 413, 414]. Silicon carbide fibers are more resistant to oxidation at high temperature than carbon fibers and have greater compressive strength and electrical resistance. *Silicon carbide – carbon* fibers, can be spun from mixtures of pitch and a poly(dimethylsilane), followed by vacuum heating at 1400 °C [415]. In a similar fashion, melt-spinning of a polycarbosilazane followed by high-temperature treatment gives *silicon carbide – nitride* fibers with a tensile strength of 1.2 MPa and a modulus of 187 MPa, which resist oxidation up to 1200 °C [416].

Silicon nitride fibers are used in advanced composites for aircraft, radomes, and electrical components. They are prepared either by reduction of silica in the presence of nitrogen in an electric furnace [408] or by nitriding polycarbosilane precursor fibers with ammonia [418].

Sol – gel *polytitanocarbosilanes* have been prepared and used to melt-spin a precursor fiber which, on pyrolysis in nitrogen at 800 – 1500 °C, gives Si – C – Ti – O fibers. At 1300 °C, a tensile strength of 3.0 GPa and a modulus of 220 GPa were achieved [419]. Polycarbosilanes can be treated with titanium tetrabutoxide to give a polymer from which fibers may be spun. After heat treatment, Si –

C – Ti – C fibers with a Young's modulus of 75 – 150 GPa and tensile strength of 0.1 – 11 GPa were obtained [420].

More recently, a number of inorganic materials have also been produced as whiskers (see also → Whiskers). In general, the tensile strengths of whiskers are greater than those of fibers. For instance the approximate tensile strength of graphite in the bulk form is 1000 MPa, for fibers it is 2800 MPa, and for whiskers it is 15 000 MPa. Carbon whiskers are produced by depositing a layer of pyrocarbon from the vapor phase on a catalytically grown carbon filament [421].

Inorganic fibers and whiskers exhibit some of the highest tensile strengths recorded. They are useful when light weight and high strength are needed. Uses include turbine blades, heat-resistant re-entry vessels, golf club shafts, automotive radio aerials, fishing poles, dental fillings, and parts of aircraft, including stealth aircraft [422]. Many of these inorganic fibers and whiskers are used as reinforcing agents in composites [422].

11. Biomedical and Antimicrobial Polymers

Parts of this topic are covered in Chapter 8.

Silicones. Silicones (polysiloxanes) are polymers having a silicon – oxygen backbone. Among the numerous materials having biomedical applications, silicone polymers play an important and versatile role. Medical devices made from polysiloxanes include artificial wrist, toe, and finger joints; hip implants; oviductal plugs [423, 424]; brain membranes; mammary implants; tracheotomy vents; and artificial hearts. For a detailed description of polysiloxanes, see → Silicones [412, 426–428]. This chapter deals with their biomedical applications [416]. Polysiloxanes are widely applied in medicine for numerous reasons including their generally extremely low toxicity, high gas permeability, good mechanical properties, and the wide range of fabrication processes that can be used (e.g., coating, encapsulation, casting, molding, sealing, and extrusion). Furthermore, they are generally inert to the body and to the immune system. The biomedical applications of polysiloxanes are reviewed in [290]. Monomeric and oligomeric siloxanes are generally not sold as medical-grade materials and may contain toxic trace contaminants that are not important in industrial applications but may be critical in biomedical applications. Proper procedures must be adopted to ensure quality control and absence of contaminants that may be toxic and may adversely affect long-term, repeated use of the end product.

Polysiloxanes are extensively employed in biomedical devices as specialty surface treatments [416, 429, 430]. For example, octadecylpolysiloxane (Siliclad, Glassclad 18) is applied to hydrophilic surfaces to reduce blood – surface interactions and protein adsorption [430, 420]. Other polysilane-derived surface treatments are sold under tradenames such as Glassclad HP, D.C. 5700, Glassclad 6C, Dri-Film, and Glassclad IM [290, 297]. Silicone membranes play critical roles in oxygenation and dialysis. Polysiloxanes are about ten times more permeable to oxygen than low-density polyethylene and a hundred times more permeable than nylon or butyl rubber [431]. Therefore, poly(dimethylsiloxane) [1646-73-7] soft lenses and poly(dimethylsiloxane-*co*-methacrylate) hard lenses constitute a major portion of the contact lens market. Silicone-based interpenetrating polymer networks give clean, resilient gels with cohesive properties, which are used in breast implants [432–434, 290]. Bilayer membranes employing a top layer of cured silicone polymer are used as artificial skin [442, 443].

Low-consistency, room-temperature vulcanizing silicones cure to give low modulus mechanical plugs when injected into the fallopian tubes [423, 424]. This blocks the ovum from reaching the uterus and serves to prevent conception. A retrieval ring at the uteral end makes the procedure reversible. Silicone polymers are used to make dental impression materials [436–439]. Vinyl addition cured systems are used in biomedical encapsulation and mold making [440] and in maxillofacial prostheses. High-consistency elastomers are used in compression molding of shunts, flexing joints, and catheter tubing [441]. Silicone – urethanes (e.g., cardiothane 51) are used in blood pumps, intraaortic balloons, and artificial hearts because of their good fatigue strength, flexibility, toughness, and retarded interaction with plasma proteins [442].

Silicone – polycarbonate block copolymers can be injection-molded, extruded, and cast into films. Their synthesis is described in [443, 423, 424]. They have high tear strength as well as high oxygen and water permeability. Applications include blood oxygenation, dialysis, and microelectrode materials [444–446].

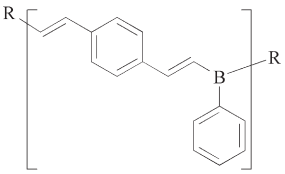
Metal-Containing Polymers. A few metal-containing polymers are used as therapeutic agents in the treatment of cancer [447–451], juvenile diabetes [452–454], Cooley's anemia [455, 456], and in the control of bacteria [451, 457–459] and viruses [451–454]. The polymer derived from the reaction of tetrachloroplatinate and methotrexate can inhibit the virus that causes juvenile diabetes-like symptoms [452, 453].

Tin-containing compounds are inhibitory to certain bacteria. A variety of methyl-, ethyl-, and propyl-substituted organotin polymers effectively inhibit *Pseudomonas aeruginosa* strains which are responsible for about one-half of the deaths of burn patients. Some suggested uses are as additives to paints, insulation, bandages, and clothing [461]. Degradation resistance has been obtained by in situ polymerization of tin-containing esters in wood [458, 459]. Impregnated poles and planks show total stability when exposed to seaside environment or seawater for more than five years [462, 463]; untreated wood is destroyed within a year. Similar results have been obtained for tin-containing cross-linked coatings in the control of ship hull fouling. Nevertheless, plants and sea creatures survive within centimeters of test objects, suggesting that the use of tin-containing polymers might be environmentally acceptable. Tin-containing polymers have been examined in the United States and Japan as antifouling coatings [464–467, 462, 463] and mildew-resistant paints [298]. Commercial products are available; however, environmental concerns in harbor areas remain.

12. Boron Polymers

The topic of boron polymers has been reviewed [299, 22, 468].

Organoboron has been incorporated into polymers by a variety of techniques. In the 1920s Stock first created a boron hydride polymer during his work on boron hydrides. Much of the current interest in boron-containing polymers is a consequence of three factors. First, the presence of a low-lying (low-energy) vacant p orbital allows its use in moving electrons in a conjugated system. This is being taken advantage of through the synthesis of various π-conjugated systems and their use in optical and sensing applications. This includes use in light-emitting diodes (LEDs), nonlinear optical systems, energy storage in batteries, and the construction of sensing devices. One such polymer structure is **29**.



29

These polymers are mainly synthesized employing the hydroboration reaction, that is, the addition of a boron hydride to a double or triple bond.



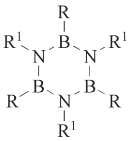
This low-lying vacant p orbital also allows boron-containing polymers to be luminescent with potential optical applications. Many of these luminescent materials are NLO materials.

The second reason for interest in boron polymers involves their use as catalysts. While the boron atom can be used as the site of catalytic activity, more effort has involved the use of boron-containing materials as blocking and protecting agents and as cocatalysts. They are increasingly being used in catalytic asymmetric syntheses.

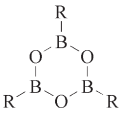
The third reason for interest in boron polymers involves the ability of many boron compounds to form cocoons about objects, which provides a ready method for coating wires and fibers [469]. Thus boron-containing polymers and monomers have been employed to form a surface layer of intumescent protective char that acts as a barrier to oxygen, protecting the wires and fibers from ready oxidation. These coatings also provide flame retardancy to the coated materials. Boron-containing units have been

incorporated into polymers to give materials that have added flame resistance through char formation. Somewhat related to this is the use of boron-containing polymers in forming high-strength fibers and whiskers for use in composites. Finally, boron has a high capture cross section for neutrons so effort has gone into using this nuclear characteristic.

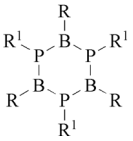
Today there exist a wide variety of boron-containing polymers including ring systems such as borazines, boroxines, and triphosphatoborins



Borazine



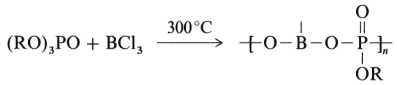
Boroxine



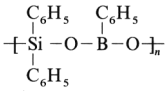
Triphosphatoborin

as well as metal-, metalloid-, and ferrocene-containing polymers, each offering their own potential for exhibiting desired properties.

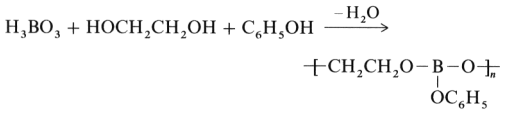
A variety of boron-containing polymers have been made by heating trialkyl phosphates with boron trichloride at 300 °C [300, 470]. At 900 °C this reaction produces boron phosphate glass. The boron polymers form networks prior to glass formation.



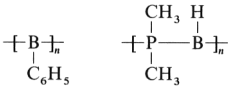
Reaction of benzene boronic acid with diphenylsilane gives transparent, film-forming, polymeric borosiloxanes which can be drawn into fibers [471]. Similar materials resulting from boronic esters and chlorosilanes form electrically insulating films when baked on copper plates [472]. A variety of polymers containing Si–O–B units have been reported [473]:



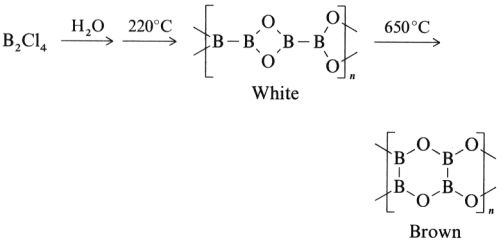
Boric acid forms condensation polymers with polyhydroxy compounds. With ethylene glycol and phenol, a tacky polymer is formed that is hydrolyzed readily by water [474]. Many such compositions have been studied as adhesives, binders, coatings, and resins.



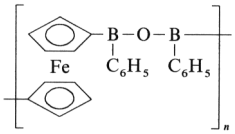
Polymers with all-boron backbones [475] or alternating boron – phosphorous backbones [301] have been reported. Pyrolysis of dimethylphosphineborane in the presence of a base gives linear high molecular mass polymers [476]. In many cases, ring systems form instead of linear polymers, with cyclic trimers and tetramers predominating. Use of triethylamine as a chain end blocking group favors the formation of linear polymers.



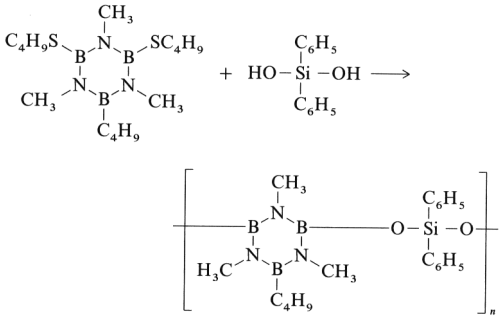
The action of water on diboron tetrachloride gives subboric acid, $B_2(OH)_4$, which when heated at 220 °C loses water to yield a white boron monoxide polymer [477]. This remains unchanged up to 500 °C, but at 650 °C is transformed into brown boron monoxide which has lower solubility in water.



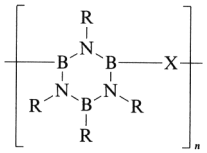
Low molecular mass polymers result from the reaction of 1,1′-dilithioferrocene with phenylboron dichloride, followed by treatment with water [478]:

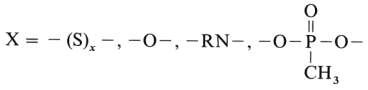


A large number of polyborazines have been prepared, and many are reviewed in [479]. The condensation of bis(alkylthio)borazines with diphenylsilicondiol gives borazine – siloxane polymers [480]. Cross-linked materials result from the corresponding reactions with trialkylthioborazines:

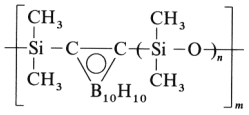


Reaction of β-chloroborazines with sodium sulfide, sodium disulfide (Na_2S_2), or sodium tetrasulfide (Na_2S_4) leads to polyborazines with sulfur linkages between the rings and molecular masses up to 53 000 [481]. Other polyborazines with oxygen [482], nitrogen [483], and phosphite bridges [484]between rings have also been prepared.



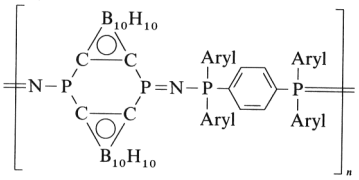


Carborane polymers with a variety of structures have been made from the $C_2B_{10}H_{10}$ icosahedral cage systems, in which the carbon atoms are located ortho, meta, or para to one another. The best known examples are the Dexsil polymers of the Olin Corporation [485, 486]. This series has siloxane groups attached to the carbon atoms of *ortho*-carborane ($1,2\text{-}C_2B_{10}H_{12}$) and varying numbers of dimethylsiloxane groups between adjacent cages:

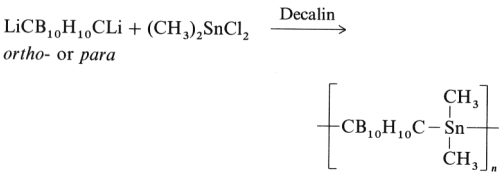


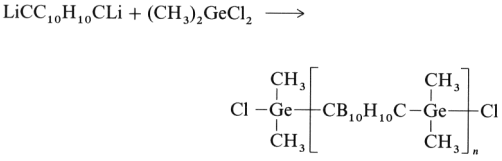
$n = 2$, Dexsil 200
$n = 3$, Dexsil 300
$n = 4$, Dexsil 500

Many other groups have been used to connect carborane cages. Treatment of dilithiocarborane with phosphorus trichloride and sodium azide leads to the very unusual structure [487]:



Dilithiocarboranes are reacted with dialkyl metal dihalides to introduce metal functions between the cages. For example, reaction of *ortho*- or *para*-dilithiocarborane with dimethyldichlorostannane introduces dimethyltin bridges between the cages. Dimethylgermanium bridges are introduced in a similar manner [488, 489].

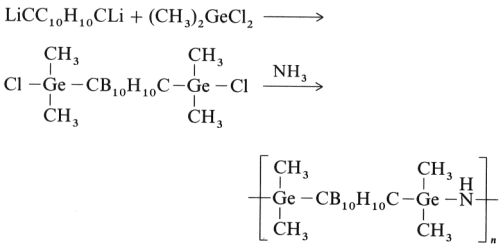




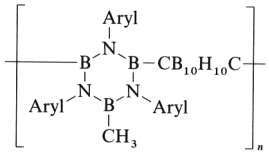
The dimethyltin-bridged *para*-carborane polymer softens only above 420 °C and decomposes

at 425 °C, whereas its ortho analogue melts at 250 – 255 °C. Random mixtures of *meta*-carborane (1,7-$C_2B_{10}H_{12}$) and *para*-carborane (1,12-$C_2B_{10}H_{12}$) have been used to prepare dialkyltin-bridged polymers.

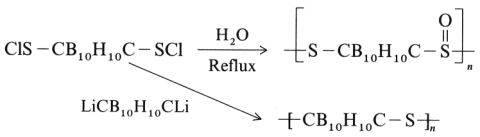
A polymer bridged by $-Ge(CH_3)_2NH-$ units was prepared from dilithiocarborane by using excess dimethyldichlorogermane and then ammonia:



Borazine bridges have also been introduced [490]:



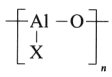
Refluxing the bis(sulfinyl chloride) of *meta*-carborane in water gives a poly(carboranethiosulfinate), whereas treatment with dilithiocarborane gives the corresponding poly (carboranesulfide) (*mp* 219 – 222 °C) [491]:



The functionalization of polymers with Lewis acidic boron sites has allowed the synthesis of many materials, some of which are being studied as catalysts, luminescent materials, and for the design of sensor systems for nucleophiles [492].

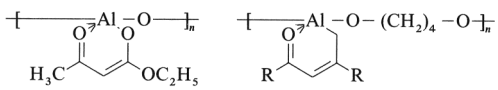
13. Aluminum Polymers

Polymers containing only aluminum atoms in the backbone are unknown. Aluminum – oxygen and aluminum – nitrogen backbones are known, but they are hydrolyzed readily by aqueous acid and alkali. Polymers with an aluminum – oxygen backbone are usually obtained by reaction of aluminum alkoxides with water, diols, organic acids, or amides. They occur as gums to brittle solids; applications include use as cross-linking agents, drying agents, gelling agents, fuel additives, water repellents, paints, varnishes, linoleum, and inks [493–497]. An idealized linear structure is

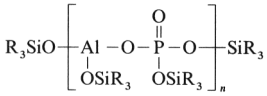


where X can be RO– [498], RCOO– [499], R_3SiO- [498, 500], or R(RO)P(O)O– [501]. These polymers are highly cross-linked, and the aluminum is actually four-coordinate; cyclic structures often predominate.

To increase the hydrolytic stability of Al–O bonds and permit the synthesis of linear polymers, four-coordinate aluminum ethyl acetoacetate complexes have been made as chelate rings along the chain [502]. The use of diols gives hydrolytically unstable polymers [503].

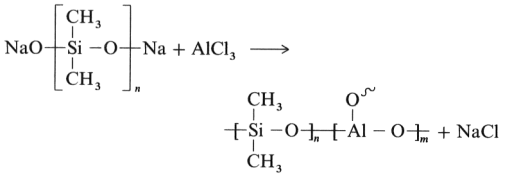


A variety of coordination polymers involving aluminum chelates have been made, but these are considered true organometallic polymers and are not discussed here. ANDRIANOV pioneered the use of R_3SiO- blocking groups to prevent formation of three-dimensional networks. Although oligomers such as



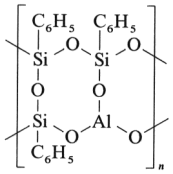
have been prepared [500], useful higher polymers remain elusive.

Poly(aluminosiloxanes) are polymers containing an Si–O–Al–O backbone. A typical example results from the reaction of the sodium salt of a poly(dimethylsiloxane) with aluminum chloride.

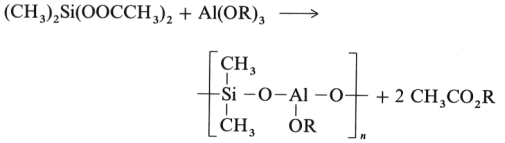


Polymers with silicon – aluminum ratios of 0.8 – 23 have been made [504, 505]. Polymers with low silicon – aluminum ratios are brittle and insoluble, indicating a three-dimensional structure; those with silicon – aluminum ratios of 7 – 23 are soluble and stable in both polar and nonpolar solvents even at 150 °C.

The poly(aluminophenylsiloxane) having a silicon – aluminum ratio of 4 is completely infusible but very soluble in organic solvents; it can be plasticized. A ladder structure has been assigned:



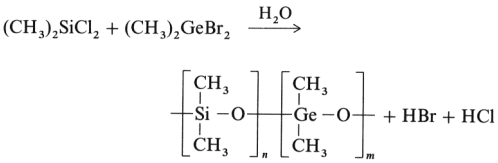
Regular poly(aluminosiloxane) structures are prepared by polycondensation of dialkyldiacetoxysilanes with aluminum alkoxides.



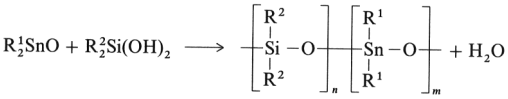
14. Polymers with −Si−O−M−O− Backbones

The early driving force in preparing poly-(metallosiloxanes) was to enhance thermal stability. The group 13 elements boron and aluminum have been incorporated into siloxane chains (see Chaps. 12 and 13). The metal can also be from group 14 (Ge, Sn, Pb), 15 (P, As, Sb), or 16 (S), or a transition metal (Ti, V, Cr, Fe, Ni, Zr, Hf). The thermal and hydrolytic stabilities of these polymers are usually inferior to those of the parent poly(organosiloxanes), but a variety of property modifications have been achieved. The hydrolytic stability (to HCl) of poly(titanoxane –phenylsiloxane) was shown to be greater than that of its aluminum analogue poly(aluminoxane – phenylsiloxane), but less than that of poly(diphenylsiloxane). Thus, the order of stability with respect to cleavage by hydrochloric acid at 90 °C is −Si−O−Si−O−>−Si−O−Ti−O−>−Si−O−Al−O−.

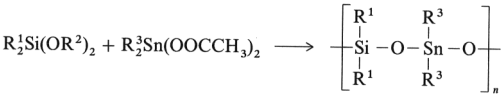
Random −Si − O − Ge − O − and − Si − O − Sn − O − polymers can be made by the cohydrolysis of dialkyldichlorosilanes with dialkyldihalogermanes or dialkyldihalostannanes [506]. Low molecular mass components are treated further with sulfuric acid to give rubberlike materials.



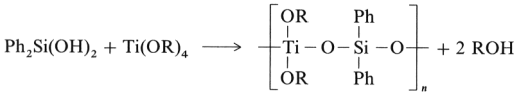
The random incorporation of tin is achieved by cohydrolysis of dihalostannanes with dihalosilanes [507] or by reaction of dialkyltin oxides with a silanediol [508].



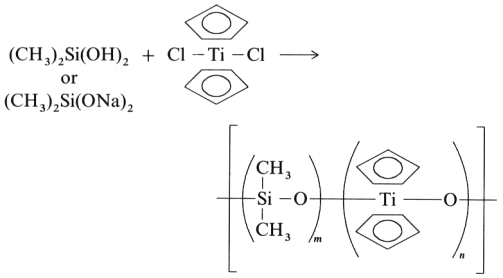
The most stable polymers in this series have high silicon: tin ratios. Regular alternating structures are achieved by reaction of dialkyldiacetoxystannanes with dialkyldialkoxysilanes [509]:



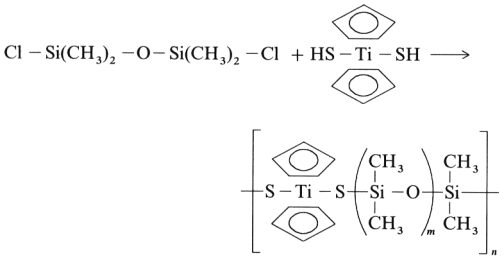
Poly(titanosiloxanes) can be prepared by cohydrolysis of dichlorosilanes with titanium alkoxides to give random incorporation of $-Si(R)_2O-$ and $-Ti(R)_2O-$ units. Alternatively, diphenylsilanediol can react with titanium alkoxides [510]. The resulting polymers are hard coatings, which are opaque to UV light and suitable for use as refrigeration enamels [510].



Partial hydrolysis of alkylalkoxysilanes with titanium alkoxides, acylates, or alkylamides gives copolymers that can be used to help catalyze the drying of printing inks [511, 512]. Similar silicon – zirconium (−Si−O−Zr−O−) preparations have also been reported [513]. A different type of titanium unit is represented by the titanocene fragment. Condensation of dimethylsilanediol [514] or its disodium salt [515] with titanocene dichloride results in the incorporation of titanocene units into the polymers.

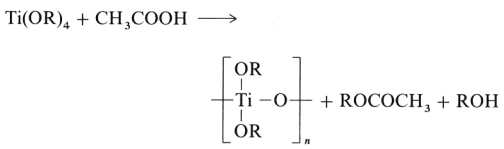


A related polymer containing −O−Si−S−Ti−S−Si− units in the backbone is made by polycondensation of dimercaptotitanocene [516]:

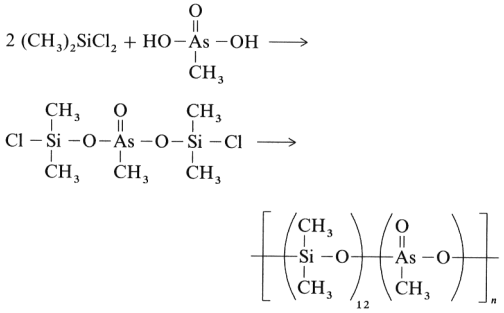


Reactive silicones and titanium alkoxides give polymers with −Si−O−Ti−O− backbones when heated in petroleum solvents. These are said to be suitable for making waterproof leather and textiles [517, 518].

Polymers with titanium – oxygen backbones, related to siloxanes, are prepared by heating trialkoxytitanium acylates and dialkoxytitanium diacylates at 75 °C. These materials have low molecular mass, and whether they are linear polymers or cyclic oligomers is as yet unresolved. Titanium alkoxides polymerize on treatment with acetic acid, but problems with cross-linking and three-dimensional network formation complicate this method.

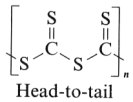


Incorporation of a group 15 element is illustrated by the preparation of −Si−O−As−O− chain polymers. Condensation of dimethyldichlorosilane with $CH_3AsO(OH)_2$ gives a transparent, rubbery polymer that is used as an impregnation rubber additive [519]. The arsenic content inhibits the growth of molds.

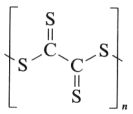


15. Poly(Carbon Disulfide), Poly(Carbon Diselenide), and Polythiocyanogen

The delocalized chalcogen-based polymers are of special interest due to the observation of superconductivity in $[SN]_n$ [520] and $[Se]_n$ [521]. BRIDGMAN first showed that carbon disulfide can be polymerized under high pressure (>4.5 GPa) at 175 °C to give a black semiconducting solid [522]. The $(CS_2)_n$ prepared under high pressure was later assigned a head-to-tail linear structure [523]. The head-to-head structure is 16.3 kJ/mol lower in energy and, by analogy to $(CSe_2)_n$, might be the more likely structure [524].



Head-to-tail

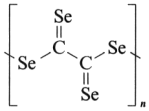


Head-to-head

Reaction products vary with experimental conditions. CHAN and JONSHER isolated a low-conductivity material ($<10^{-13}$ S/cm) and a semiconducting material (10^{-3} S/cm) which consisted of free sulfur in a (CS_{2-x}) matrix [525]. They also proposed a cross-linked structure.

Anionic polymerization of carbon disulfide, initiated by sodium dispersed in dipolar aprotic solvents, results in polymers with less than two sulfur atoms per carbon [524, 526]. Poly(carbon disulfide) has also been prepared by photolysis [527], irradiation [528], and plasma deposition [529] to give structures described as $[C_3S_2]_n$, $[CS(S)_m]_n$, or mixtures [530].

Unlike carbon disulfide, carbon diselenide can be polymerized both at high pressure and under ambient conditions. The products obtained range from insulators to metals and superconductors. Carbon diselenide polymerizes at a rate of about 1 wt % per month at ambient temperature and pressure [531, 532]. When dissolved in solvents such as methylene chloride and dioxane, it polymerizes readily under high pressure (ca. 0.5 GPa) at 100 °C [533]. This polymer is an amorphous insulator. When the polymer is heated to 130 – 160 °C, a black semiconducting (10^{-3} S/cm) material results. After high-pressure polymerization and annealing at 130 °C, a crystalline product is obtained with a room-temperature conductivity of 50 S/cm; it has been assigned a two-dimensional sheet structure [534–536]. The polymer is thought to have a head-to-head structure [531, 532], which is significantly more stable than the head-to-tail structure [524]:



It is typically contaminated with trigonal selenium domains, depending on annealing and polymerization conditions. The observed crystallinity is due to both small and large trigonal selenium crystallites within the polymer matrix, and this selenium is the reason for the high conductivity [524]. As selenium crystallites form, the polymer becomes highly disordered, with the formation of −C−C−, −C=Se−, and −C−Se−Se−C− units.

Carbon selenosulfide (CSeS) does not polymerize in solution under conditions similar to those used to polymerize carbon diselenide [524]. Polymerization of carbon diselenide in the presence of excess carbon disulfide gives only the selenium-containing product. The slow polymerization of carbon diselenide at atmospheric pressure and 25 °C gives a black product with an electrical conductivity $<10^{-6}$ S/cm, consistent with a band gap of ca. 2 eV [524].

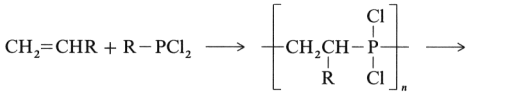
Polythiocyanogen. Polythiocyanogen or parathiocyanogen is formed by the spontaneous polymerization of thiocyanogen $(SCN)_2$ [537]. While a number of structures are possible, a linear structure with the SCN atoms connected with a bond order of 1.5 is currently preferred [538]. The polymer is a semiconductor that can be doped with halogens [538].

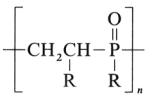
A more recent synthesis and study of thiocyanogen polymers were reported [539]. These materials have mainly a sulfur – carbon – nitrogen repeat unit. Related compounds except including materials containing selenium – carbon – nitrogen repeat units were prepared from reaction of AgNCS with bromine and AgNCSe with iodine, which led to spontaneous formation of polymer [540]. Another new class of sulfur-containing polymers was synthesized from sulfur dicyanide. These polythiocyanogens are easily formed in the absence of water under moderate heating [541].

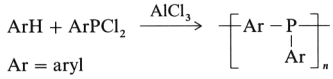
16. Phosphorus-Containing Polymers

Phosphorus-containing polymers are among the three most important basic blocks of life. They serve as the building blocks of the critical nucleic acids, DNA, RNA, phosphosaccharides, phosphoproteins, and related biomaterials.

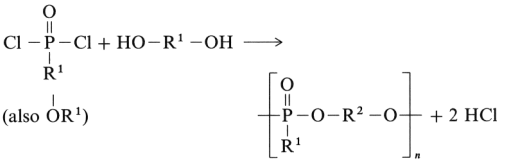
Here, we will focus only on synthetic phosphorus-containing polymers. Reviews are given in [544–549]. Reviews deal with organic derivatives of pentavalent phosphorus [550], phosphorus-based flame retardants [551], organic phosphites as polymer stabilizers [552], and phosphorus-containing polymers for drug delivery [553]. The reviews cover the synthesis and uses of organic and inorganic phosphorus polymers having a wide variety of compositions and structures. Polymer chains containing phosphorus can be made by a variety of approaches, including those summarized below:



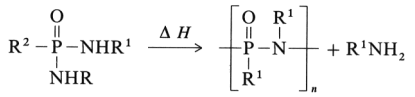




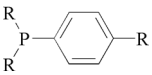
Ar = aryl



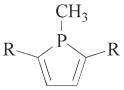
R = alkyl, aryl, alkoxy, dialkylamido, diarylamido



Organophosphorus π-conjugated polymers have been reviewed [555]. While vinyl polymers such as polyacetylene, polypyrrole, and polythiophene are widely known as conductors after they are doped, a variety of phosphorus-containing structures are also capable of forming such π-conjugated structures. The focus is on phosphorus-containing moieties with an unbonded electron pair on the phosphorus atom. The unbonded electron pair is capable of bridging the electron gap between conjugated units, creating increased electrons that can promote conductivity when doped. Structures of some of these central units are shown below.



Arylphosphane



Phosphole

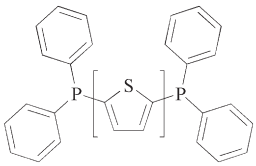


Phosphalkene



Diphosphene

Some of the arylphosphanes have exhibited nonlinear optical behavior. They show potential application in constructing organic light-emitting diodes (OLEDs). Efforts are underway to employ unbonded-electron phosphorus-containing units as end groups for organic conducting polymers such as polythiophenes (**30**) with the intent to used these unbonded electron sites as metal-chelating units to materials with possible conductivity, luminescence, and interesting optical and magnetic properties.

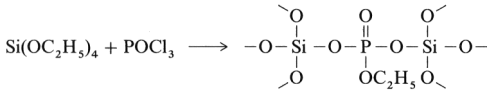


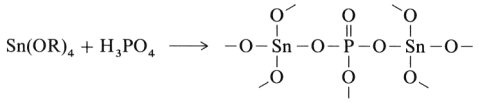
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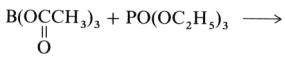
Complexes with a wide variety of metals and organometallics have been made and show promise in a variety of application areas including light-induced conductors. This is an area of great promise in a wide variety of areas including communications, electronics, solar energy conversion, and catalysis.

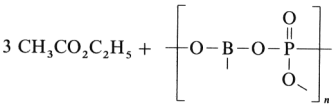
Polymers with a glasslike structure are formed by cocondensation of metal alkoxides

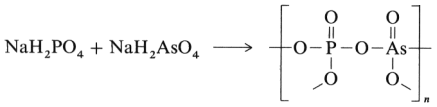
or metal acetates with phosphorus oxychloride or phosphoric acid:





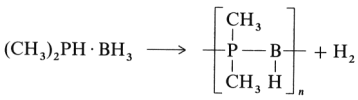




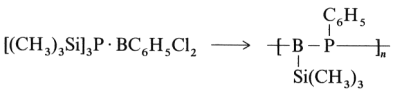


Such reactions can be used to prepare artificial glass, paint and lubricant additives, plasticizers, and adhesives.

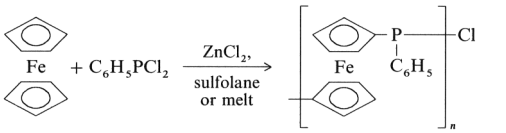
An interesting class of linear phosphorous – boron backbone polymers has been reported [543]. When the dimethylphosphine – borane complex is pyrolyzed, a linear polymer with $n = 80$ is obtained which is soluble in hot benzene:

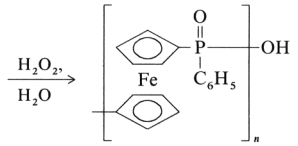


A similar process yields borophane polymers from tris(trialkylsilyl)phosphines [543]:

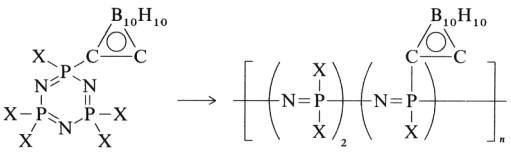


An interesting application of electrophilic substitution involves the incorporation of phosphorus bridges between ferrocene units [544, 556]. However, this route only gives low molecular mass materials.





Polyphosphazenes are discussed in Chapter 4. However, a few carboranylphosphazene polymers have been reported [557]. Ring-opening polymerization of the carboranyl-substituted phosphazene ring proceeds without complications to yield a high molecular mass polymer:



17. Traditional and Metal-Matrix Composites

The topic of metal-matrix composites has been recently reviewed [558–562] (see also → Metal-Matrix Composites). Space age or advanced composites were front stage in the early 1960s with the development of high-modulus whiskers and filaments. These whiskers and filaments continue to be developed. Many fibers for both traditional and metal-matrix composites are inorganic polymers and are among the strongest materials made. They have tensile strengths on the order of 4 GPa and tensile strength/density ratios of about one thousand.

For polymer-intense composites, the matrix materials are organic polymers. For metal-matrix composites (MMCs), the matrix materials are typically a metal or less likely an alloy. Often employed metals include aluminum, copper, copper alloys, magnesium, titanium, and superalloys.

In polymer-matrix composites the non-continuous phase or reinforcement material is

a fiber such as glass, carbon fibers (graphite), aromatic nylons, and a number of inorganic fibers including tungsten carbide (WC), titanium carbide (TiC), zirconia (ZrO_2), and alumina (Al_2O_3). For the metal-matrix composites, the discontinuous phase generally exists as fibers, wires, whiskers, and particulates. Some of the discontinuous-phase materials overlap with the listing given for polymer-intense composites including tungsten carbide, titanium carbide, alumina, and graphite, but there are a number of other materials whose fibers and whiskers are employed, including silicon carbide and boron carbide. By volume, the amount of whiskers, wires, and particulates is greater for the metal-matrix composites.

As in the case with polymer-intense composites, the matrix and fiber must be matched for decent properties. Below is a listing of typical matrix/fiber mixes.

In comparison to single-metal materials such as aluminum, copper, and iron, MMCs generally have

- Higher strength-to-density ratio
- Better fatigue and wear resistance
- Better high temperature strength
- Lower creep related to lower coefficients of thermal expansion
- Greater stiffness

In comparison to polymer-intense composites, MMCs offer

- No moisture absorption
- Greater fire resistance
- Higher use temperatures
- Greater radiation resistance
- Greater stiffness and strength
- Higher thermal and electrical conductivities

MMCs also have some disadvantages in comparison to polymer-matrix composites. These include

- Higher cost
- Newer and less developed technology and scientific understanding
- Generally more complex fabrication
- Greater weight

Table 3. Typical metal/composite matches

Matrix material	Discontinuous phase	
	Form	**Material**
Aluminum	fibers	boron
		alumina
		graphite
		alumina – silica
		silicon carbide
	whiskers	silicon carbide
	particulates	silicon carbide
		boron carbide
Titanium	fibers	boron (coated)
	particulates	silicon carbide
Titanium carbide		
Copper	fibers	graphite
		silicon carbide
	particulates	boron carbide
		silicon carbide
		titanium carbide
Magnesium	fibers	alumina
		graphite
	particulates	boron carbide
		silicon carbide
	whiskers	silicon carbide

As noted above, the range of fibers employed does not precisely overlap with those employed for organic composites. Because the formation of the metal-matrix composites generally requires melting of the metal matrix the fibers must have some stability to relatively high temperatures. Such fibers include graphite, silicon carbide, boron, alumina – silica, and alumina fibers. Most of these are available as continuous and discontinuous fibers.

As with organic-matrix composites, the orientation of the reinforcing material determines whether the properties will be isotropic or oriented in a preferential direction, so that the strength and stiffness are greater in the direction of the fiber orientation.

There are a number of differences between traditional and metal-matrix composites. First, the metal matrix can also have considerable strength itself, so its contribution to the overall strength is more important than for organic-matrix composites. Second, the difference in the coefficient of expansion between the reinforcing material and metal-matrix is often greater. Because of the wider ranges of use temperature that are often required for metal-matrix composites, these differences become more important. They can result in large residual stresses in metal-matrix composites that may

result in yielding. A third difference is related to the relative lower flexibility of metal-matrix composites. This leads to greater concerns in the marrying or joining of such composite parts. Many methods of joining these composite parts have been developed. A fourth difference is the possible greater reactivity between the matrix and fiber for metal-matrix composites. This limits combinations but has been overcome in many situations. One major approach is to place a barrier coating on the reinforcement. For example, application of boron carbide as a barrier coating on boron fibers allows their use to reinforce titanium. Because these coatings can be "rubbed" off by usage, composites made from these coated reinforcements should be monitored more closely and more often.

Metal-matrix composites are finding use in the military and in the aerospace industry as high-strength materials [558–562].

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