Dietmar Drummer
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Plastics Handbook

The Resource for Plastics Engineers



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Drummer / Osswald / Rudolph / Baur
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6th Edition

HANSER



Print-ISBN: 978-1-56990-176-2
E-Book-ISBN: 978-1-56990-373-5

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Bibliographic information of the German National Library:
The German National Library lists this publication in the German National Bibliography; detailed bibliographic data are available on the Internet at http://dnb.d-nb.de.

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Vilshofener Straße 10 | 81679 Munich | info@hanser.de
www.hanserpublications.com
www.hanser-fachbuch.de
Editor: Dr. Mark Smith
Production Management: Der Buchmacher – Arthur Lenner, Windach
Cover concept: Marc Müller-Bremer, www.rebranding.de, Munich
Cover design: Thomas West
Cover picture: © Tim A. Osswald
Typesetting: Eberl & Koesel Studio, Kempten
Druck: Elanders Waiblingen GmbH, Waiblingen
Printed in Germany

Preface

This 6th edition of the Plastics Handbook is a completely reworked version of a reference that traces its origins to the German Saechtling Kunststoff Taschenbuch, first published in 1936 and now in its 32nd edition. Since the previous edition, the German and English versions have been fully synchronized, while continuing to address the needs of their respective markets. In this edition, we have added a new chapter on Material- and Processing-Oriented Design and Simulation to reflect the updates introduced in the latest German edition. The plastics industry continues to evolve rapidly, shaped by major factors such as energy efficiency, the development of new materials, and emerging technologies like additive manufacturing. For that reason, we view the Plastics Handbook as a living project—one that will continue to adapt and grow alongside the industry. We look forward to the innovations the coming years will bring and to the opportunity of incorporating them into future editions. This edition would not have been possible without the invaluable contributions of Nicole Janke, who reworked some of the figures with dedication and precision. We are also grateful to Dr. Mark Smith for his careful review of the manuscript and to Rebecca Wehrmann for her translation and production work, which ensured a result both accurate and visually pleasing. Finally, our deepest thanks go to our families for their unwavering love and support.

Fall 2025

Dietmar Drummer, Tim A. Osswald, and Natalie Rudolph

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1
Common Abbreviations and Acronyms in Plastics Technology

The plastics industry typically categorizes plastic materials by their chemical family and assigns material abbreviations (or acronyms) with respect to this family. While this is common practice, it does not reflect reality in the plastics industry, because the materials are sold under their trade names, each with a very specific property spectrum. In fact, the trade name is the only criterion for identification (similar to an order number). Standards defining the properties of specific material classes, such as are common practice for metals, have been introduced for thermosetting materials only. The materials within one family typically exhibit a wide range of properties.

However, in order to structure our knowledge of these materials, it is necessary to categorize them in a logical and comprehensible way.

We will introduce the common method of assigning abbreviations in this book. Here, a compromise needs to be struck between an unambiguous classification that follows strict rules and the popular notations commonly used. Although there are several standards regarding plastic material notations, they are inconsistent and contradictory, sometimes even within the same standard.

In Section 1.1 the abbreviations of the plastic materials covered in this book are summarized, preferably considering the chemical composition of the polymers and avoiding additional specifications that relate to physical properties or processing technologies. However, in light of the fact that notations such as “A” for amorphous or “B” for block copolymers are often used in the literature, they are used here at times as well. We discourage using them though because they lack general validity and often cause contradictions.

Table 1.1 contains bold listings, indicating that they are standardized. They are based on suggestions made in connection with the plastics database CAMPUS. Here, the current ISO-standards are reflected; however, exceptions are permitted as long as they are widely used. This approach allowed for CAMPUS to define a list of so-called base

polymers that covers almost the entire plastic materials market. This list is routinely reviewed and expanded when necessary.

Table 1.1 provides the abbreviations for plastics and rubbers, whereas Table 1.2 provides abbreviations for *plasticizers*.

1.1 Alphabetical List of Plastics Name Abbreviations, Chemical Notation

Table 1.1 Plastics and Rubbers

Abbreviation	Chemical notation	Section
*	Pyrrone	6.16
*	Polycyclone	6.16
*	Polyphenylene (polyarylene)	6.16
*	Polytriazine	6.14.1.4
ABS	Acrylonitrile-butadiene-styrene copolymer	6.3.2
ACM	Acrylate rubber (AEM, ANM)	6.23.4
ACS	Acrylonitrile-chlorinated polyethylene-styrene	6.3.2
AECM	Acrylic ester-ethylene rubber	6.23.4
AEM	Acrylate ethylene polymethylene rubber	6.23.4
AES	Acrylonitrile ethylene propylene diene styrene copolymer	6.3.2
AFMU	Nitroso rubber	6.23.8
AMMA	Acrylonitrile methyl methacrylate	6.6.2.2
APE-CS	see ACS	
ASA	**Acrylonitrile styrene acrylic ester copolymer**	6.3.2
AU	Polyester urethane rubber	6.23.8
BIIR	Bromobutyl rubber	6.23.3
BR	Butadiene rubber	6.23.3
CA	Cellulose acetate	6.18.1
CAB	Cellulose acetobutyrate	6.18.1
CAP	Cellulose acetopropionate	6.18.1

Abbreviation	Chemical notation	Section
CF	Cresol formaldehyde	6.21
CH	Hydrated cellulose, cellulose film	6.18.1
CIIR	Chlorobutyl rubber	6.23.3
CM	Chlorinated polyethylene rubber	6.23.4
CMC	Carboxymethyl cellulose	6.18.1
CN	Cellulose nitrate, celluloid	6.18.1
CO	Epichlorohydrin rubber	6.23.5
COC	**Cyclic polyolefin copolymers**	6.2.4
COP	COC copolymer	6.2.4.6
CP	Cellulose propionate	6.18.1
CR	Chloroprene rubber	6.23.3
CSF	Casein formaldehyde, artificial horn	6.18.3
CSM	Chlorosulfonated polyethylene rubber	6.23.4
CTA	Cellulose triacetate	6.18.1
E/P	**Ethylene propylene copolymer**	6.2.4
EAM	Ethylene vinyl acetate rubber	6.23.4
EAMA	Ethylene acrylic acid ester maleic acid anhydride copolymer	6.2.4
EB	Ethylene butene	6.2.4
EBA	Ethylene butyl acrylate	6.2.4
EC	Ethyl cellulose	6.18.1
ECB	Ethylene copolymer bitumen blend	6.2.4
ECO	Epichlorohydrin rubber	6.23.5
ECTFE	Ethylene chlorotrifluoroethylene	6.2.4
EEA	Ethylene ethyl acrylate copolymer	6.2.4
EIM	Ionomer copolymer	6.2.4
EMA	Ethylene methacrylic acid ester copolymer	6.2.4
EP	**Epoxy resin**	6.21
EP(D)M	see EPDM	
EPDM	Ethylene propylene diene rubber	6.23.4

Table 1.1 Plastics and Rubbers *(continued)*

Abbreviation	Chemical notation	Section
EPM	Ethylene propylene rubber	6.23.4
ET	Polyethylene oxide tetrasulfide rubber	6.23.7
ETER	Epichlorohydrin ethylene oxide rubber (terpolymer)	6.23.5
ETFE	Ethylene tetrafluoroethylene copolymer	6.5.2
EU	Polyether urethane rubber	6.23.8
EVAC	**Ethylene vinyl acetate copolymer**	6.2.4
EVAL	Ethylene vinyl alcohol, old abbreviation EVOH	6.2.4
FEP	Polyfluoroethylene propylene	6.5.2
FF	Furan formaldehyde	6.21
FFKM	Perfluoro rubber	6.23.4
FKM	Fluoro rubber	6.23.4
FPM	Propylene tetrafluoroethylene rubber	6.23.4
FVMQ	Fluorosilicone rubber	6.23.6
HCR	High consistency rubber (high temperature vulcanizing silicone rubber)	6.23.6
HNBR	Hydrated NBR rubber	6.23.3
HTV	see HCR	
ICP	Intrinsically conductive polymers	6.19
IIR	Butyl rubber (CIIR, BIIR)	6.23.3
IR	Isoprene rubber	6.23.3
LCP	**Liquid crystal polymer**	6.15
LSR	Liquid silicone rubber	6.23.6
MABS	**Methyl methacrylate acrylonitrile butadiene styrene**	6.6.2
MBS	**Methacrylate butadiene styrene**	6.6.2
MC	Methylcellulose (cellulose derivate)	6.18.1
MF	**Melamine formaldehyde**	6.21
MFA	Tetrafluoroethylene perfluoromethyl vinyl ether copolymer	6.5.2.7
MMA-EML	Methyl methacrylate-exo-methylene lactone	6.6.3.3

Abbreviation	Chemical notation	Section
MPF	**Melamine phenolic formaldehyde**	6.21
MQ	Polydimethyl silicone rubber	6.23.6
MS	see PMS	
MUF	Melamine urea formaldehyde	6.21
MUPF	Melamine urea phenolic formaldehyde	6.21
NBR	Acrylonitrile butadiene rubber	6.23.3
NCR	Acrylonitrile chloroprene rubber	6.23.3
NR	Natural rubber	6.23.3
PA	Polyamide	6.8
PA 11	**Polyamide from aminoundecanoic acid**	6.8.1
PA 12	**Polyamide from dodecanoic acid**	6.8.1
PA 46	**Polyamide from polytetramethylene adipic acid**	6.8.1
PA 6	**Polyamide from ε-caprolactam**	6.8.1
PA 610	**Polyamide from hexamethylene diamine sebacic acid**	6.8.1
PA 612	**Polyamide from hexamethylene diamine dodecanoic acid**	6.8.1
PA 66	**Polyamide from hexamethylene diamine adipic acid**	6.8.1
PA 69	**Polyamide from hexamethylene diamine azelaic acid**	6.8.1
PAA	Polyacrylic acid ester	6.6.1
PAC	Polyacetylene	6.19
PAEK	**Polyarylether ketone**	6.13.1
PAI	Polyamide imide	6.14.2
PAN	Polyacrylonitrile	6.6.1
PANI	Polyaniline, polyphenylene amine	6.19
PAR	Polyarylate	6.9.3.1
PARI	Polyarylimide	6.14.2
PB	Polybutene	6.2.8
PBA	Polybutyl acrylate	6.6.1
PBI	Polybenzimidazole	6.14.1.3
PBMI	Polybismaleinimide	6.14.1.2

Table 1.1 Plastics and Rubbers *(continued)*

Abbreviation	Chemical notation	Section
PBN	Polybutylene naphthalate	6.9.3.2
PBO	Poly(p-phenylene-2,6-benzobisoxazole)	6.14
PBT	**Polybutylene terephthalate**	6.9.2.2
PC	**Polycarbonate (from bisphenol-A)**	6.9.1.1
PCTFE	Polychlorotrifluoroethylene	6.5.1
PDAP	Polydiallylphthalate resin	6.21.4.5
PDCPD	Polydicyclopentadiene	6.2.9.2
PE	**Polyethylene**	6.2.1
PE-HD	Polyethylene-high density	6.2.1
PE-HMW	Polyethylene-high molecular weight	6.2.1
PE-LD	Polyethylene-low density	6.2.1
PE-LLD	Polyethylene-linear low density	6.2.1
PE-MD	Polyethylene-medium density	6.2.1
PE-UHMW	Polyethylene-ultra high molecular weight	6.2.1
PE-ULD	Polyethylene-ultra low density	6.2.1
PE-VLD	Polyethylene-very low density	6.2.1
PE-X	Polyethylene, cross-linked	6.2.2
PEA	Polyester amide	6.15
PEDT	Polyethylenedioxythiophene	6.19
PEEEK	Polyether ether ether ketone	6.13.1
PEEK	Polyether ether ketone	6.13.1
PEEKEK	Polyether ether ketone ether ketone	6.13.1
PEEKK	Polyether ether ketone ketone	6.13.1
PEI	**Polyetherimide**	6.14.2.2
PEK	Polyether ketone	6.13.1
PEKEKK	Polyether ketone ether ketone ketone	6.13.1
PEKK	Polyether ketone ketone	6.13.1

Abbreviation	Chemical notation	Section
PEN	**Polyethylene naphthalate**	6.9.3
PEOX	Polyethylene oxide	6.12
PESI	Polyester imide	6.15
PES	Polyether sulfone	6.10.2
PESU	see PES	
PET	**Polyethylene terephthalate**	6.9.2.1
PET-G	**Polyethylene terephthalate, glycol modified**	6.9.2.1
PF	**Phenolic formaldehyde resin**	6.21.3.2
PFA	Perfluoroalkoxy	6.5.2.4
PFMT	Polyperfluorotrimethyl triazine rubber	6.23.10
PFU	Polyfuran	6.19
PHA	Polyhydroxyalkanoate	6.18.2
PHB	Polyhydroxybutyrate	6.18.2
PHV	Polyhydroxy valeric acid	6.18.2
PI	**Polyimide**	6.14
PIB	Polyisobutene	6.2.8
PISO	Polyimide sulfone	6.14.2.3
PK	**Polyketone**	6.13.2
PLA	Polylactide	6.18.4
PMA	Polymethylacrylate	6.6.1
PMI	Polymethacrylimide	6.14.2
PMMA	**Polymethylmethacrylate**	6.6.2
PMMI	Polymethacrylmethylimide	6.6.3.1, 6.14.2
PMP	Poly-4-methylpentene-1	6.2.9.1
PMS	Poly-α-methylstyrene	6.3.1.1
PNF	Fluoro-phosphazene rubber	6.23.9
PNR	Polynorbornene rubber	6.23.3
PO	Polypropylene oxide rubber	6.23.5

Table 1.1 Plastics and Rubbers *(continued)*

Abbreviation	Chemical notation	Section
PO	General notation for polyolefins, polyolefin derivatives and copolymers	6.2
POM	**Polyoxymethylene (polyacetal resin, polyformaldehyde)**	6.7
PP	**Polypropylene**	6.2.5
PPA	Polyphthalamide	6.8.3.1
PPB	Polyphenylene butadiene	6.19
PPE	**Polyphenylene ether, old notation PPO**	6.11
PPMS	Poly-para-methylstyrene	6.3.1.1
PPOX	Polypropylene oxide	6.12
PPP	Poly-para-phenylene	6.19
PPS	**Polyphenylene sulfide**	6.10.1
PPSU	**Polyphenylene sulfone**	6.10.2
PPTA	Poly-p-phenylene terephthalamide	6.8
PPV	Polyphenylene vinylene	6.19
PPY	Polypyrrole	6.19
PPYR	Polyparapyridine	6.19
PPYV	Polyparapyridine vinylene	6.19
PS	**Polystyrene**	6.3.1.1
PSAC	Polysaccharide, starch	6.18.1
PSU	**Polysulfone**	6.10.2
PT	Polythiophene	6.19
PTFE	**Polytetrafluoroethylene**	6.5.1
PTHF	Polytetrahydrofuran	6.12
PTT	Polytrimethylene terephthalate	6.9.2.4
PUR	**Polyurethane**	6.17
PVAC	Polyvinyl acetate	6.4.5
PVAL	Polyvinyl alcohol	6.4.5
PVB	Polyvinyl butyral	6.4.5

Abbreviation	Chemical notation	Section
PVC	**Polyvinyl chloride**	6.4.1, 6.4.2
PVDC	Polyvinylidene chloride	6.4.5
PVDF	**Polyvinylidene fluoride**	6.5.1
PVF	Polyvinyl fluoride	6.5.1
PVFM	Polyvinyl formal	6.4.5
PVK	Polyvinyl carbazole	6.4.5
PVME	Polyvinyl methyl ether	6.4.5
PVMQ	Polymethylsiloxane phenyl vinyl rubber	6.22.6
PVP	Polyvinyl pyrrolidone	6.4.5
PZ	Phosphazene rubber with phenoxy groups	6.23.9
RF	Resorcinol formaldehyde resin	6.21, 6.22.1
RTV	Room-temperature-vulcanizing silicone rubber	6.23.6
SAN	**Styrene acrylonitrile copolymer**	6.3.2
SB	**Styrene butadiene**	6.3.2
SBMMA	Styrene butadiene methyl methacrylate	6.3.2
SBR	Styrene butadiene rubber	6.23.3
SBS	Styrene butadiene styrene	6.3.2
SCR	Styrene chloroprene rubber	6.23.3
SEBS	Styrene ethene butene styrene	6.3.2
SEPS	Styrene ethene propene styrene	6.3.2
SI	Silicone, silicone resin	6.21
SIMA	Styrene isoprene maleic acid anhydride	6.3.2
SIR	Styrene isoprene rubber	6.23.3
SIS	Styrene isoprene styrene block copolymer	6.3.2.1
SMAB	Styrene maleic acid anhydride butadiene	6.3.2
SMAH	**Styrene maleic acid anhydride**	6.3.2
TCF	Thiocarbonyldifluoride copolymer rubber	6.23.7
TFEHFPVDF	Tetrafluoroethylene hexafluoropropylene vinylidene fluoride	6.5.2
TFEP	Tetrafluoroethylene hexafluoropropylene	6.5.2

Table 1.1 Plastics and Rubbers *(continued)*

Abbreviation	Chemical notation	Section
TOR	Polyoctenamer	6.23.3
TPA	**Thermoplastic elastomers based on polyamide**	6.20
TPC	**Thermoplastic elastomers based on copolyester**	6.20
TPE	Thermoplastic elastomers	6.20
TPE-A	see TPA	6.20
TPE-C	see TPC	6.20
TPE-O	see TPO	6.20
TPE-S	see TPS	6.20
TPE-U	see TPU	6.20
TPE-V	see TPV	6.20
TPO	**Thermoplastic elastomers based on olefins**	6.20
TPS	**Thermoplastic elastomers based on styrene**	6.20
TPU	**Thermoplastic elastomers based on polyurethane**	6.20
TPV	**Thermoplastic elastomers based on cross-linked rubber**	6.20
TPZ	**Other thermoplastic elastomers**	6.20
UF	Urea formaldehyde resin	6.21
UP	**Unsaturated polyester resin**	6.21
VCE	Vinyl chloride ethylene	6.4.3
VCEMAK	Vinyl chloride ethylene methyl methacrylate	6.4.3
VCEVAC	Vinyl chloride ethylene vinyl acetate	6.4.3
VCMAAN	Vinyl chloride maleic acid anhydride acrylonitrile	6.4.3
VCMAH	Vinyl chloride maleic acid anhydride	6.4.3
VCMAI	Vinyl chloride maleic imide	6.4.3
VCMAK	Vinyl chloride methacrylate	6.4.3
VCMMA	Vinyl chloride methyl methacrylate	6.4.3
VCOAK	Vinyl chloride octylacrylate	6.4.3
VCPAEAN	Vinyl chloride acrylate rubber – acrylonitrile copolymer	6.4.3
VCPE-C	Vinyl chloride-chlorinated ethylene	6.4.3

Abbreviation	Chemical notation	Section
VCVAC	Vinyl chloride vinyl acetate	6.4.3, 6.4.4
VCVDC	Vinyl chloride vinylidene chloride copolymer	6.4.3
VCVDCAN	Vinyl chloride vinylidene chloride acrylonitrile copolymer	6.4.3
VDFHFP	Vinylidene chloride hexafluoropropylene copolymer	6.4.3
VE	Vinyl ester resin	6.21
VF	Vulcanized fiber	6.18.1
VMQ	Polymethylsiloxane vinyl rubber	6.23.6
VU	Vinyl ester urethane	6.21.1.3
XBR	Butadiene rubber, containing carboxylic groups	6.23.3
XCR	Chloroprene rubber, containing carboxylic groups	6.23.3
XF	Xylene formaldehyde resin	6.21.1.1
XNBR	Acrylonitrile butadiene rubber, containing carboxylic groups	6.23.3
XSBR	Styrene butadiene rubber, containing carboxylic groups	6.23.3
* There are no known acronyms for these plastic materials.		

Table 1.2 Common Plasticizers

Abbreviation	Chemical notation	Abbreviation	Chemical notation
ASE	Alkylsulfone acid ester	DODP	Dioctyldecyl phthalate
BBP	Benzyl butyl phthalate	DOP, DEHP	Dioctyl phthalate
DBA	Dibutyl adipate	DOS	Dioctyl sebacate
DBP	Dibutyl phthalate	DOZ	Dioctyl azelate
DBS	Dibutyl sebacate	DPCF	Diphenyl cresyl phosphate
DCHP	Dicyclohexyl phthalate	DPOF	Diphenyl octyl phosphate
DEP	Diethyl phthalate	DPP	Dipropyl phthalate
DHXP	Dihexyl phthalate	ELO	Epoxidized linseed oil
DIBP	Diisobutyl phthalate	ESO	Epoxidized soybean oil
DIDP	Diisodecyl phthalate	ODA	Octyl decyl adipate
DINA	Diisononyl adipate	ODP	Octyl decyl phthalate

Table 1.2 Common Plasticizers *(continued)*

Abbreviation	Chemical notation	Abbreviation	Chemical notation
DMP	Dimethyl phthalate	PO	Paraffin oil
DMS	Dimethyl sebacate	TBP	Tributyl phosphate
DNA	Dinonyl adipate	TCEF	Trichloroethyl phosphate
DNODP	Di-n-octyl-n-decyl phthalate	TCF	Tricresyl phosphate
DNOP	Di-n-octyl phthalate	TIOTM	Tri-iso-octyl trimellitate
DNP	Dinonyl phthalate	TOF	Trioctyl phosphate
DOA (DEHA)	Dioctyl adipate, also diethylhexyl adipate, DEHA no longer used	TPP	Triphenyl phosphate

1.2 Common Units, ISO- and US-Units

Length

	mm	m	km	in	ft	yd	mile
1 mm =	1	10^{-3}	10^{-6}	0.0394	0.0033	–	–
1 m =	10^{3}	1	10^{-3}	39.37	3.281	1.094	–
1 km =	10^{6}	10^{-3}	1	39,370	3281	1094	0.6214
1 inch =	25.40	0.0254	–	1	0.0833	0.0278	–
1 foot =	304.8	0.3048	–	12	1	0.3333	–
1 yard =	914.4	0.9144	–	36	3	1	–
1 statute mile =		1609	1609	–	5280	1760	1

Area

	cm^2	m^2	a	ha	km^2	in^2	ft^2	yd^2
1 cm^2 =	1	10^{-4}	–	–	–	0.155	–	–
1 m^2 =	10^4	1	0.01	10^{-4}	10^{-6}	1550	10.76	1.196
1 a =	–	100	1	0.01	10^{-4}	–	1076	119.6
1 ha =	–	10^4	100	1	0.01	–	–	–
1 km^2 =	–	10^6	10^4	100	1	–	–	–
1 square inch =	6.452	–	–	–	–	1	–	–
1 square foot =	929	0.0929	–	–	–	144	1	0.1111
1 square yard =	8361	0.8361	–	–	–	1256	9	1

Volume

	cm^3	dm^3	m^3	in^3	ft^3	yd^3	gal (US)
1 cm^3 =	1	10^{-3}	10^{-6}	0.061	–	–	–
1 dm^3 [1)] =	10^3	1	10^{-3}	61.02	0.0353	–	0.2642
1 m^3 =	10^6	10^3	1	61023	35.31	1.308	264.2
1 cubic inch =	16.39	0.0164	–	1	–	–	–
1 cubic foot =	–	28.32	0.0283	1728	1	0.037	7.841
1 cubic yard =	–	764.6	0.7646	46656	27	1	202
1 gallon (US) =	3785	3.785	–	281	0.1337	–	1

[1)] 1 Liter (1) = 1.0 dm^3

Force

	N	dyn^2	kp	
Newton 1 N =	1	10^5	0.101972	
Kilopond[1)] 1 kp =	9.80665	980 665	1	
Pound-force 1 lbf =	4.44822		0.4536	kilogram-force (kgf) = kp

[1)] Unit no longer approved

Mass

	g	kg	t	oz	lb
1 g =	1	10^{-3}	10^{-5}	0.0353	
1 kg =	10^{3}	1	10^{-3}	35.27	2.205
1 t =	10^{6}	10^{3}	1	–	2205
1 ounce (oz) =	28.35	0.0284	–	1	0.0625
1 pound (lb) =	453.6	0.4536	–	16	1
Metric carat 1 ct = 0.200 g for gemstones. For gold alloys, 1 carat represents $^{1}/_{24}$ mass fraction gold; grain 1 gr = ($^{1}/_{700}$) lb = 0.0648 g					

Pressure

Rounded values. The unit for pressure is Pascal (Pa)

	Pa = N/m²	bar	kp/cm² = at	atm	Torr	lbf/in²	
1 Pa = 1 N/m² =	1	10^{-5}	$10.2 \cdot 10^{-6}$	$9.869 \cdot 10^{-6}$	$7.5 \cdot 10^{-3}$	$145.05 \cdot 10^{-6}$	–
1 bar =	10^{5}	1	1.02	0.987	750	14.505	1 µbar = 1 dyn/cm² [1)]
1 kp/cm² = 1 at = (techn. atmosph.)[1)]	98 100	0.981	1	0.968	735.5	14.224	1 at = 10 m WS (4 °C)
1 atm = (phys. atmosph.)[1)]	101 325	1.013	1.033	1	760	14.7	1 Torr = 1/760 atm
1 Torr [1)] =	133.32	$1.333 \cdot 10^{-3}$	$1.36 \cdot 10^{-3}$	$1.316 \cdot 10^{-3}$	1	0.01934	1 Torr = 1 mm Hg (0 °C)
1 lbf/in² =	6894.8	0.6895	0.0703	0.06804	51.715	1	–
[1)] Unit no longer approved							

Energy (work, heat)

	J	kWh	kpm	PSh	kcal	Btu	Details
1 J = 1 Ws = 1 Nm = 1 kg m^2/s^2	1	$277.8 \cdot 10^{-9}$	0.101972	$377.5 \cdot 10^{-9}$	$238.8 \cdot 10^{-6}$	$984 \cdot 10^{-6}$	1 J = 1 Nm = 10^7 erg 1 eV = $1.602 \cdot 10^{-19}$ J
1 kWh =	$3.6 \cdot 10^6$	1	$367 \cdot 10^3$	1.360	859.8	3412	
1 kpm [1] =	9.80665	$2.724 \cdot 10^{-6}$	1	$3.704 \cdot 10^{-3}$	$2.342 \cdot 10^{-3}$	$9.294 \cdot 10^{-3}$	
1 PSh [1] =	$2.648 \cdot 10^6$	0.7355	$270 \cdot 10^3$	1	632.4	2509	
1 kcal [1] =	4186.8	$1.163 \cdot 10^{-3}$	426.9	$1.581 \cdot 10^{-3}$	1	3.968	
1 Btu = (British Thermal Unit)	1055	$293 \cdot 10^{-6}$	107.6	$398.5 \cdot 10^{-6}$	0.252	1	

[1] Unit no longer approved

Power

	W	kW	kpm/s	PS	hp	
1 W =	1	10^{-3}	0.101972	$1.36 \cdot 10^{-3}$	$1.341 \cdot 10^{-3}$	1 W = 1 J/s = 10^7 erg/s
1 kW =	10^3	1	101.975	1.36	1.341	
1 kpm/s [1] =	9.80665	$9.80665 \cdot 10^{-3}$	1	0.0133	0.0131	
1 PS [1] =	735.5	0.7355	75	1	0.986	
1 hp (horsepower) =	745.7	0.746	76.04	1.014	1	1 hp = 550 ft lbf/s

[1] Unit no longer approved

2
Introduction

2.1 Economic Significance of Plastics

As an independent group of materials alongside metals and ceramic materials, plastics have achieved a very high level of technological and economic importance. The considerable growth of this group of materials has meant that plastics now have a larger production volume worldwide production volume than, for example, steel and aluminum (Figure 2.1).

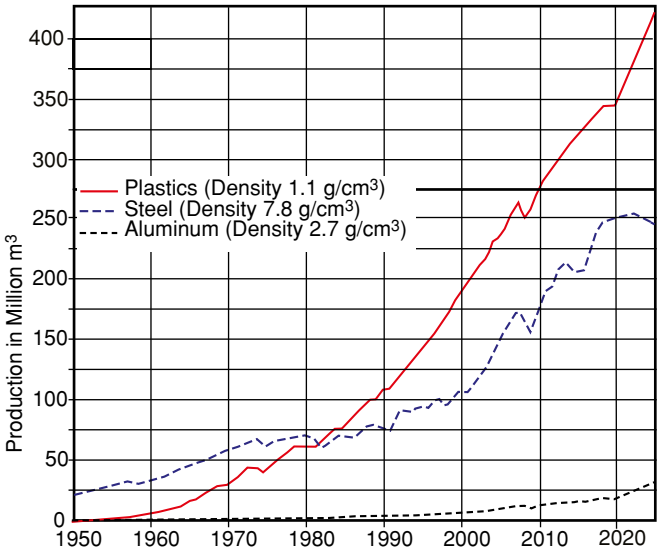


Figure 2.1 Production volume of different materials
[Source: Plastics Europe, World Steel Association, The International Aluminum Institute]

Figure 2.2 shows the rapid growth in plastics production in the various regions of the world between 1990 and 2023. We have indisputably arrived in the "plastics era" in the 21st century. This group of materials is an essential basis for technological development and an indicator of the economic growth of an industrialized society. There is a clear correlation between the production of this material and the economic and technological performance of a region.

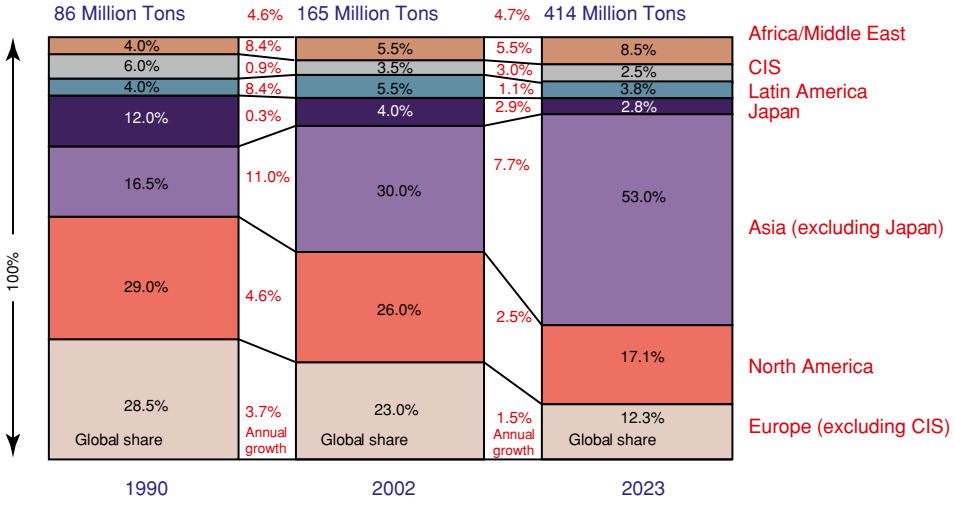


Figure 2.2 World plastics production since 1990
[Source: Plastics Europe]

An analysis of the main areas of application for this group of materials using as an example Europe in 2022 (Figure 2.3) illustrates the diversity of applications. The share of other applications at 24.0% in Figure 2.3 includes applications in agriculture, furniture, household, leisure, sport, medicine, and mechanical engineering. Although medical applications are increasing rapidly, their share is still only around 1% of the total amount of plastics used. Plastics have found their way into all areas of industrial production. However, it is not always the special properties of this group of materials, such as their lightweight construction potential or good insulating properties that make their use worthwhile. Probably the most important property of this group of materials is the economic processing methods available for them. Injection molding, for example, allows the production of highly complex shaped components with a cycle time of a few seconds to a few minutes. The main costs for such production arise from the depreciation of the production equipment (machine and tools) as well as the costs for raw materials and energy. With increasing quantities, even complex production facilities become highly profitable.

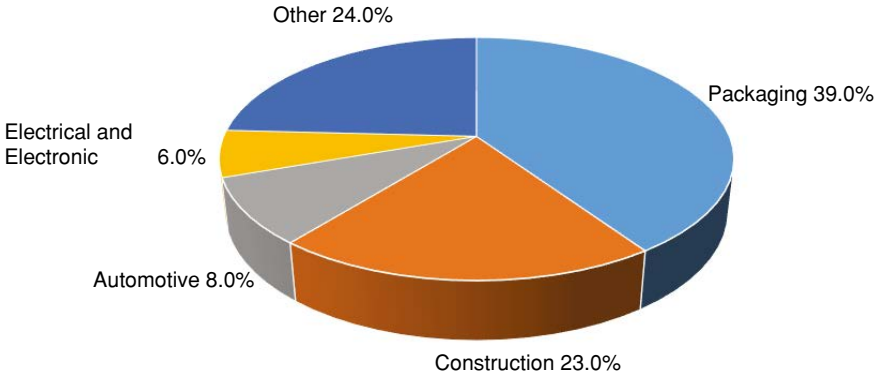


Figure 2.3 Main areas of application for plastics in Europe (2022)
[Source: Plastics Europe]

If we look at the industry working with plastics materials, it can be divided into the following three areas:

- Plastics production,
- Plastics processing, and
- Manufacture of machines for the above.

The plastics industry makes a significant contribution to the well-being of the European economy. More than 1.5 million people work in almost 52,000 companies that generate an estimated annual turnover of 365 billion euros in the EU27+3 countries.

2.2 Classification of Plastics

Polymers are organic or semi-organic materials with high molecular mass (molecular weight), *i. e.,* they are composed of very large molecules (macromolecules), which significantly determine the distinct characteristics of these materials. Figure 2.4 reflects the classification of plastic materials in the general field of material science. Here, distinguishing characteristics are chemical structure, type of polymerization, and the processing and service properties.

In this book, the focus will be on thermoplastic materials, reflecting their economic importance. However, many statements made for thermoplastics are valid for all polymeric materials. A clear definition of the terminology used is missing in many texts, *e. g.,* the terms plastic and polymer are often used synonymously. In our view, the term *polymer* is applicable to all materials with a macromolecular structure, whereas the term *plastics* only describes polymers that are modified with additives to meet the requirements of industrial processing technologies, such as processing aids, stabilizers, pigments, fillers, and others.

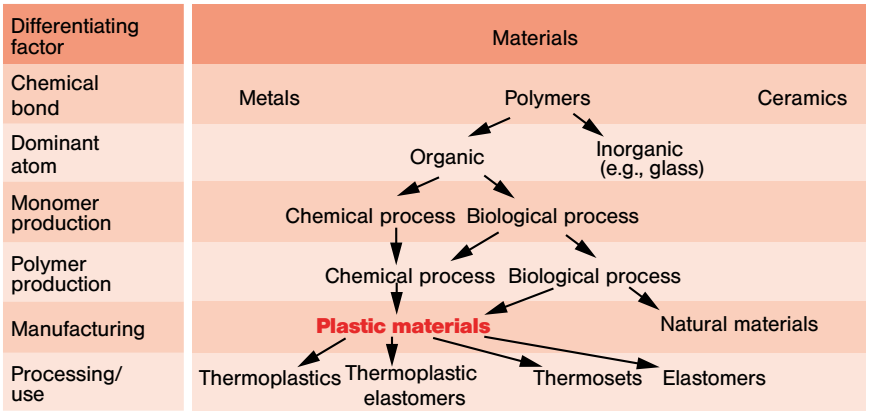


Figure 2.4 Classification of plastic materials in the general field of material science

Despite this clear definition, we were not always able to strictly adhere to this terminology. One reason for this shortcoming is the fact that even in the language of science and in economic statistics the differentiation is not consistent. Even in material standards, the term polymer is often used when in fact they cover plastic materials. In these cases, it is not an option to change the term *polymer* to *plastics*, because that would make it impossible to retrieve the standard.

The following general statements can be made for plastic materials:

- The variety of plastic material classes and types is unparalleled by any other material class. Plastics represent an extremely large span of property profiles, and the slogan of the early days of plastic material development that euphorically declared them "**tailored materials**" has become reality. In almost every area of modern life plastic materials have established themselves as manufacturing materials of choice or as materials with specific functionalities.
- Their complex chemical and morphological structures together with their wide variety in terms of composition and modifiability result in highly complex **material behaviors** that strongly determine service and processing conditions. Examples of properties to be considered include their visco- and entropy elasticity, non-Newtonian flow, complex aging characteristics, semi-crystallinity, liquid crystallinity, orientation- and modification-dependent anisotropy, stress cracking, and many others. A variety of test procedures is necessary to comprehensively describe plastic properties and to provide meaningful characteristic values (single-point data) or property functions (multiple-point data) (see Chapter 3).
- Plastics technology provides a large number of different **processes** for the compounding, processing, and post-processing of plastic materials. The molding and shaping processes play a dominant role because they offer highly productive and energy efficient material utilization within a minimal number of process steps. In

some cases, material shaping and conversion (*e. g.*, tempering, vulcanization) happen simultaneously during processing. The properties of the final product are significantly influenced by the processing conditions. Therefore, process optimization and quality control have to be emphasized appropriately in plastics manufacturing operations (see Chapter 4).

- It is not possible to efficiently **design** plastic components without considering the constraints introduced by material properties and manufacturing processes. This fact, together with the high degree of material and geometry specialization of many manufacturing technologies, requires the consideration of the close interdependence of design, material, and process decisions.
- The manufacturing costs of plastic parts are significantly determined by **material costs**. In addition to economic goals, ecological requirements are increasingly considered during material selection (see Chapter 6). Appropriate material selection and material-saving designs are effective approaches to achieve economic production and ecologically expedient plastic applications. Integration of functionalities also facilitates the reduction of processing steps and thus processing costs. Component design that allows for easy recycling offers additional benefits.

The majority of plastic materials are used in systems in which they perform structural, protective, or separating roles. Here, the mechanical properties of plastics materials play a dominant role.

Plastic materials are increasingly used as functional materials, *e. g.*, they are selected for specific applications because of their optical, electrical, or specific mechanical properties. These materials include UV-curing resins, photo-addressable macromolecules, and electrically switchable polymers. Generally, these materials are referred to as functional polymers (more precisely: functional plastics). They are locally placed in the component, *e. g.*, in layers or punctiform arrangements, and assume specific functions (*e. g.*, data storage). Growing importance is predicted for this group of materials in the future. Because they are currently used only in rather specific applications, these materials will not be covered in this book.

Historically, textiles are not covered in the field of plastics, because textile manufacturing traditionally utilized natural materials only. However, over the course of time, textile technology adapted manufacturing technologies geared towards plastic materials.

Also historically based is the differentiation between thermoplastic and thermoset materials on the one hand and elastomers on the other. However, the development of thermoplastic elastomers revealed that there was no technical rationale for this differentiation

In plastic processing we distinguished between three characteristic phases:

- Compounding,
- Processing,
- Post-processing and finishing.

During the compounding phase, the plastic raw materials or precursors are transformed into processable molding compounds. If a chemical reaction occurs during the processing phase, the molding material is a reactive precursor and fundamentally different from the final molding material. A second processing step is used, if necessary, to shape, machine, or weld semi-finished plastic parts into final products or to assemble components and/or semi-finished parts into finished products. During post-processing the parts may be finished (*e. g.,* by deflashing), surface treated (*e. g.,* by printing, flocking, metal coating), or their material properties may be changed (conditioning, tempering), depending on application requirements. Molding compounds are available in different types and conditions: powder, chips, dry blends, agglomerates, pellets, prepregs, premix, paste (plastisol), solution, suspension, emulsion, and latex, among others.

2.3 Composition of Plastics

A material's properties are defined by its structure. Plastic materials offer the most structural variety of all materials used by man. Both synthetically produced plastics, plastics resulting from material conversion, as well as bio-plastics, such as proteins and carbohydrates, follow the same structural principles. Elementary knowledge of polymeric structure is necessary in order to navigate the field of plastics and rubbers and to assess material properties. In the following, we will present this knowledge in a concise but simple way that does not claim to be complete or go into academic depth. In the subsequent chapters, more detailed information on structure-property relationships will be provided.

2.3.1 Chemical Structure (Constitution and Configuration of Macromolecules)

Polymers are organic macromolecules consisting of many repeating units. They are synthesized from low-molecular units *(monomers)* by different polymerization reactions. The predominant types of chemical bonds in polymers are atomic bonds (covalent bonds). In very few cases we also see ionic bonds (electrovalence). If the concentration of ions results in water-soluble polymers, the ionic polymers are called

polyelectrolytes; they are called ionomers if the concentration of ionic dissociated bonds leads to non-water-soluble polymers.

The atomic building blocks of polymers are primarily the non-metallic elements carbon (C), hydrogen (H), and oxygen (O). Nitrogen (N), chlorine (Cl), fluorine (F), and sulfur (S) *(heteroatoms)* are also recurrent elements in polymers. The so-called semi-organic polymers contain the metalloid elements silicon (Si) (in silicone and polysiloxane) and boron (B). Although other elementary compositions can sometimes be found in polymers, we will not discuss them in more detail here because of their very specific nature. The structural characteristics of the mentioned elemental building blocks define the properties common to all organic polymers:

- Low electrical conductance (electrical insulators),
- Low thermal conductance (thermal insulators),
- Low specific weight (density 0.8 to 2.2 g/cm^3),
- Limited thermal resistance, because the splitting of covalent bonds is irreversible.

In addition, the properties of final plastic parts and components are significantly influenced by the conformation configuration of the macromolecules.

2.3.1.1 Conformation

The conformation describes the preferential spatial positions of the atoms in a molecule, which is described by the polarity, flexibility, and regularity of the macromolecule. Typically, carbon atoms are tetravalent, which means that they are surrounded by four substituents in a symmetric, tetrahedral geometry.

The arguably best known example of a molecule with tetrahedral geometry is methane, CH_4, schematically shown in Figure 2.5. The figure shows that the tetrahedral arrangement of the substituents (here hydrogen) creates a bond angle of 109.5°. This angle is maintained between the carbon atoms in the macromolecule, as illustrated in Figure 2.5, right. The figure also shows that each axis of the carbon chain is able to freely rotate.

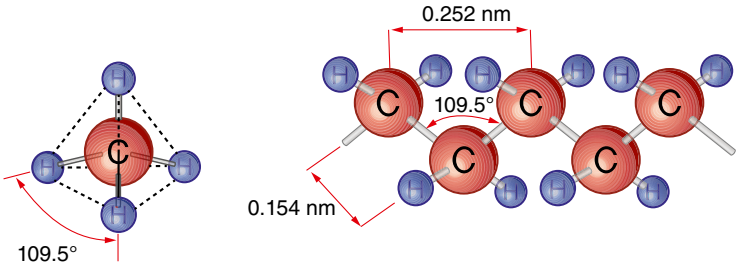


Figure 2.5 Left: schematic illustration of methane (CH_4); right: detail of a polyethylene molecule

2.3.1.2 Configuration

The configuration provides information about the distribution and spatial organization of the molecule. For polymers composed of asymmetric monomers it is possible to place the side groups on the carbon-carbon backbone in different directions during polymerization. The order in which they are arranged is called the tacticity. The polymers whose side groups are all on the same side are called isotactic and are assigned the suffix "I" as in polypropylene: PP-I. The polymers whose side groups are regularly alternating on both sides are called syndiotactic (*e. g.*, PP-S). Irregular arrangement of the side groups is called atactic or random configurations (*e. g.*, PP-R).

Figure 2.6 illustrates the three different tacticity cases for polypropylene. A polymer's tacticity determines the degree of crystallinity that it can reach. For example, polypropylene with a high isotactic content will reach a high degree of crystallinity, and as a result will be stiff, strong, and hard.

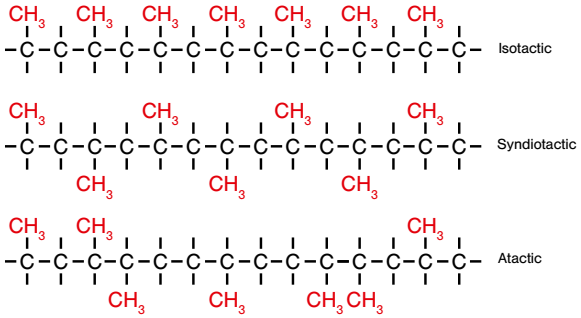


Figure 2.6 Different polypropylene configurations

Another type of geometric arrangement arises with polymers that have double bonds between carbon atoms. Double bonds restrict the rotation of the carbon atoms about the backbone axis, causing the formation of different, so-called stereoisomers. The side groups may be on the same side (cis-) or on opposite sides (trans-) of the chain, as schematically shown in Figure 2.7. The arrangement in a cis-1,4-polybutadiene results in a very elastic rubbery material, whereas the structure of the trans-1,4-polybutadiene results in a leathery and tough material. A cis-1,4-polybutadiene can be used to manufacture the outer tread of an automotive tire. A trans-1,4-polybutadiene can be used to make the outer skin of a golf ball. The same geometric arrangement is found in natural rubber, polyisoprene. The cis-1,4-polyisoprene is the elastic natural rubber used for the body of a tire, and the latex used to manufacture "rubber" gloves and condoms.

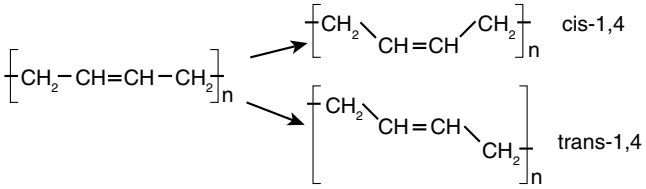


Figure 2.7 Chemical structure of cis-1,4- and trans-1,4-polybutadiene molecules

2.3.1.3 Constitution

Chemical reactions cause chain branching, and the type and length of the branches are determined by the type of polymerization reaction chosen. The chain branches influence the final structure, crystallinity, and thus the properties of the plastic material. Figure 2.8 schematically compares different molecular structures of polyethylene (PE).

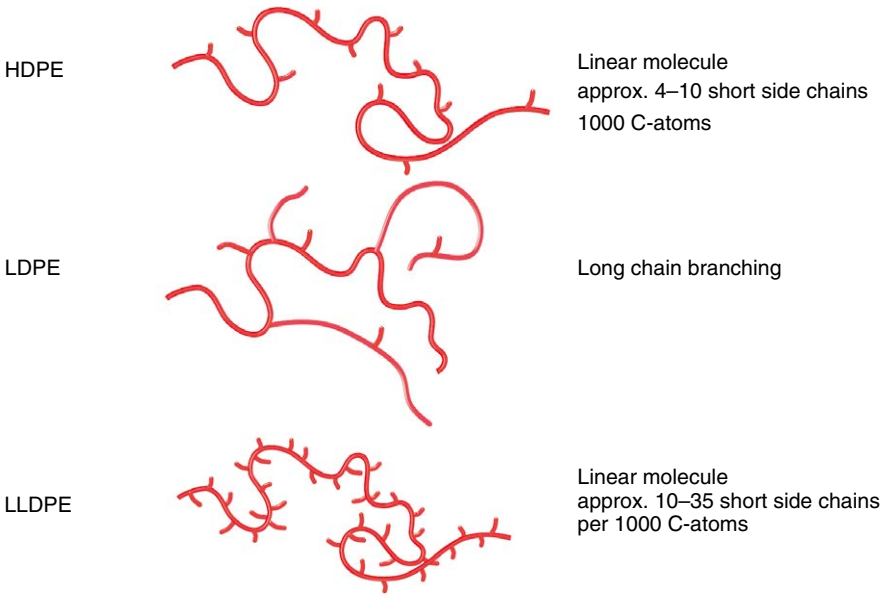


Figure 2.8 Molecular structure of various polyethylenes (schematic)

High density polyethylene (PE-HD) features between 4 and 10 short side chains per 1000 carbon atoms. Low density polyethylene (PE-LD) has the same number of side chains; however, they are significantly longer and often branched themselves. Linear low density polyethylene (PE-LLD) features between 10 and 35 short side chains per 1000 carbon atoms. Molecular chains with less and shorter side chains will crystallize more easily and therefore exhibit higher densities.

Other than by their structure, the properties of plastic materials are also determined by the molecular weight of the chains. For example, polystyrene (PS) with a polymerization degree of 1000 (number of monomer units in the polymer) is stiff and brittle. With a polymerization degree of 10, PS is soft and tacky. Figure 2.9 illustrates the dependence of mechanical and rheological properties on molecular weight. The size of the molecular chains significantly influences the ability of a plastic material to flow in the molten state or in solution. Therefore, there are material characteristic values and functions describing the flow behavior of polymers that are directly correlated to molecular weight.

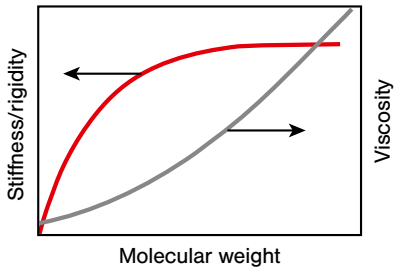


Figure 2.9
Influence of molecular weight on mechanical and rheological properties

High molecular mass imparts higher tensile strength to plastic materials, in particular under impact load. However, this effect is accompanied by higher viscosity, which reduces the material's ability to flow. Therefore, often compromises have to be found between processability (flow behavior) and service properties. In addition, certain processing technologies (*e. g.*, injection molding) require rather narrow molecular weight distributions in order to control the viscosity. Special molding compounds have been developed to meet these requirements.

The size of a macromolecule is an important structural parameter. The polymerization reactions of most synthetic linear polymers result in molecular chains of varying lengths. They consist of molecular fractions of different sizes, also called *polymolecular ("polydisperse") material systems*. There is no uniform molecular size; therefore, the specification of molecular mass (here: relative molecular mass) is always a statistical mean, or average value that depends on the distribution spectrum of the individual molecules and on the way the average value was determined. With the exception of some natural polymers, most polymers exhibit a molecular weight distribution similar to the one shown in Figure 2.10.

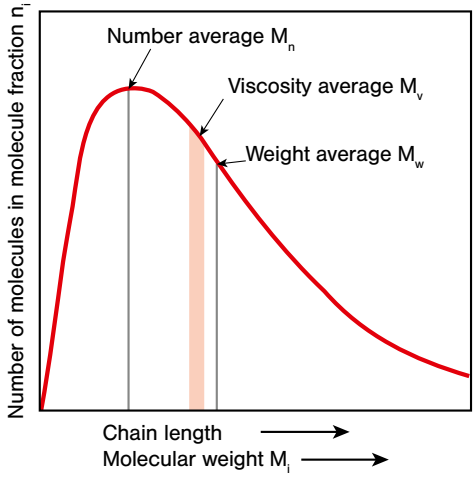


Figure 2.10
Molecular weight distribution of a typical thermoplastic material

For such a distribution function, we can define a number-, weight-, and viscosity average. In practical applications, the weight average (M_w) is more meaningful when investigating property correlations. The number average (M_n) is used when investigating the heterogeneous nature of polymers. It is defined as

$$\overline{M}_n = \frac{\sum m_i}{\sum n_i} = \frac{\sum n_i \cdot M_i}{\sum n_i}$$

Where:
m_i = the total mass of all molecules
M_i = molecular weight
n_i = number of molecules with i repeat units

The weight average (M_w) is defined as

$$\overline{M}_w = \frac{\sum n_i \cdot M_i^2}{\sum n_i \cdot M_i} = \frac{\sum m_i \cdot M_i}{\sum m_i}$$

The viscosity average (M_v) is calculated by

$$\overline{M}_v = \left(\frac{\sum m_i \cdot M_i^{\alpha+1}}{\sum m_i} \right)^{1/\alpha}$$

Where:
α = material constant that relates the *intrinsic viscosity* [η] to the molecular weight

This correlation is sometimes identified as the *Mark-Houwink Equation*, written as

$$[\eta] = k\overline{M}_v^{\alpha}$$

For low molecular weight polymers or short chains, this relationship is linear with $\alpha = 1$, and for high molecular weight polymers, which exhibit increasing numbers of entanglements, this relationship follows a Power Law ($\alpha = 3.4$). As seen in Figure 2.10, most plastic materials consist of chains of different lengths, *i. e.*, they are polydisperse and can be described as follows:

$$\overline{M}_w > \overline{M}_v > \overline{M}_n$$

In the few cases in which a polymer consists of chains of equal lengths (monodisperse polymers), we can say

$$\overline{M}_w = \overline{M}_v = \overline{M}_n$$

A measure of the broadness of a polymer's molecular weight distribution – or the uniformity of its chain lengths – is the polydispersity index defined by

$$PI = \frac{\overline{M}_w}{\overline{M}_n} - 1$$

The broadness of the molecular weight distribution significantly influences the mechanical and rheological properties of plastic materials. Plastic material grades with low polydispersity index values typically exhibit higher strength and better flowability. Table 2.1 provides an overview of the polydispersity of various plastic materials.

Table 2.1 Molecular Dispersity as a Function of Polymerization Method

Polymer	$\frac{\overline{M}_w}{\overline{M}_n}$
Polymers with consistent molecular weight	1
Polycondensation and polyaddition products	2
Vinyl polymers	2–5
Highly branched polymers	20–50

What is the molecular mass that defines a polymer? Considering the minimum molecular size at which entanglements in melts and solutions can be detected, the lower limit for the molecular weight of a polymer can be determined as approx. 10^4 g/mol. Molecular entanglements represent temporary physical cross-links that create qualitatively new material properties (*e. g.*, entropy elasticity) not seen in lower molecular materials. An upper limit to the molecular mass of polymers cannot be determined. Plastics used in technical applications have molecular weights ranging from 10^4–10^7, and typically from $5 \cdot 10^4$–$5 \cdot 10^5$ g/mol. Macromolecules with weights in a transitional range of 10^2–10^4 g/mol are also called oligomers.

For a visual representation of the macromolecules of engineering plastics in a disentangled, stretched state, envision 1 mm thick threads with lengths ranging from 2 to 200 m. Specific biopolymers may contain macromolecules with lengths exceeding this by several orders of magnitude.

The different polymerization reactions will be covered in the following. The reactions forming macromolecules are controlled by suitable reaction conditions (temperature, pressure, monomer concentration, reaction medium) and by either activating or inhibiting and structure-controlling additives (catalysts, activators, accelerators, inhibitors). During *polymerization* the monomers connect through a chain reaction by either splitting of multiple bonds or by ring opening to form *polymers*. Here, *polycondensation* reactions are step reactions during which monomers are polymerized by the elimination of reaction products (*e. g.,* water). In *polyaddition* reactions, intermolecular migration of hydrogen atoms without the elimination of any reaction products creates *polyadducts*. An example of this reaction is the urethane reaction. There are a number of other polymerization reactions; however, they will not be discussed in detail. It is not possible to unambiguously relate polymers to specific reaction types, because polymer synthesis may occur in a number of different ways. Polyacetal (POM), for example, can be synthesized by each of the above mentioned reaction mechanisms. Other polymers, such as polyamide (PA), are synthesized in several steps using different reaction mechanisms, such as condensation and addition polymerization.

From a technical point of view, polymerization reactions can be categorized with respect to the reaction medium into bulk-, suspension-, emulsion-, and solution polymerizations. When the type of polymerization reaction is relevant for the material properties of the polymer, an appropriate designation will be added to the polymer acronym.

Appropriate reaction control (*e. g.,* stereo-catalysis; metallocene catalysts) allows tailoring of the structure of engineering polymers, which explains why it is possible for plastic materials with identical elemental compositions to exhibit a wide range of properties. For example, the soft, rubber-like, amorphous, atactic (random) PP-R is of very little practical interest, while the harder, semi-crystalline, isotactic PP-I has found wide-spread applications. The so-called impact-modified polypropylenes are a blend of these two structures.

The technical synthesis of 100% PP-I is not achievable. The atactic content can be determined as a heptane-soluble phase and is declared in form of the “isotacticity index” as a material characteristic.

2.3.1.4 Major Plastic Material Groups

In this section we will introduce the major groups of plastic materials currently in use. In Chapter 6 many of these materials are covered in more detail regarding their properties and processing options.

Linear homopolymers should also be mentioned here; they are either polymerized directly from unsaturated monomers or created by polymer-analogue conversions. The latter are represented by polyvinyl alcohol and by polyvinyl acetals, which are chemically derived from polyvinyl acetate. The many possible combinations of monomers result in the respective variety of copolymers.

Often, these plastic materials are categorized by different attributes. For example, all plastic materials based on olefinic precursors are categorized as polyolefins (PO): PE, PP, PB, PMB, and PIB.

Polyacetals and polyether result when heteroatoms, such as oxygen, are part of the backbone. When additional "bulky" aromatic units are incorporated (polyaryl ether, polyaryl ether ketone), the stiffer macromolecules cause a significant increase in heat distortion temperature of these plastic materials.

In the early days of plastic material development, natural products, such as cellulose, were subjected to conversion reactions that resulted in plastic materials suitable for technical applications, some of which are still (or again) in use today. The stiff cellulose molecule impedes thermoplastic processing so that these materials are blended with plasticizers or other polymers. The high polarity of these blends results in high levels of water absorption, and in some cases even in water solubility, such as in carboxy methyl(ated) cellulose (CMC) used as wallpaper paste.

Polyamides are linear polycondensation products that are widely used as structural materials, fibers, and films, among other applications. Some of these polymers are highly heat resistant because of their hydrogen bridges and aromatic groups; however, they are also hydrophilic and exhibit relatively high water absorption rates. Varying the non-polar methylene groups [—CH_2—] allows the creation of almost all transitional phases between polyolefins and polyamides with high levels of amide group concentration [—NHCO—]. As a result, a variety of copolyamides makes up the wide property palette.

Linear polyesters are also polycondensation products; however, they have gained technical importance only in the form of aromatic polyaryl esters. Specific copolyesters contain extremely stiff molecular segments (mesogens) that render them anisotropic even in the molten state; they represent liquid crystalline, self-reinforced polymers (LCP).

The chemical structure of polyimides provides the highest level of molecular stiffness. Some of these materials, such as PPI, PBI, PBMI, can no longer be processed like thermoplastic materials. They exhibit very high heat aging and heat distortion resistance and are typically used as conductive or semi-conductive polymers.

Polyaryl ether sulfones and polyaryl sulfides represent a group of technically important thermoplastic materials. Their well-balanced properties are based on their chemical structure, in particular the combination of aromatic and sulfuric chain units, which makes them uniquely suitable for structural applications.

All plastic materials described so far are linear polymers that can be processed in their molten state by molding or shaping methods; if they are infusible, they are processed as solutions, dispersions, or powders by coating or sintering technologies. Polymers with double bonds in their macromolecules can be chemically crosslinked to form elastomers (*e.g.,* by sulfur vulcanization), representing typical rubbers. Recently, polycyclic olefins have gained importance as particularly heat resistant thermoplastic materials.

The production of crosslinked plastics (thermosets) or elastomers (rubbers) requires soluble or melt-processable molding materials that are composed of largely linear or partially crosslinked macromolecules or of low-molecular compounds. The actual molding compound is generated only during the crosslinking reaction *(curing, vulcanization)*. The starting materials must contain tri- or higher functional molecules in order to facilitate the crosslinking reaction. Here, the plastics manufacturer needs to control not only the molding operation, but also the chemical synthesis. If it is not possible to initiate the reaction with low molecular, reactive compounds, the use of "prefabricated" macromolecules *(prepolymers)* is an option. These are typically oligomers in terms of their molecular mass. Potential crosslinking reactions include all types of polymerization reactions discussed so far. The most important crosslinked plastics are phenolic plastics (PF), aminoplastics (UF, MF), unsaturated polyester resins (UP), epoxy resins (EP), polyurethane thermosets and -elastomers (PUR), and silicone resins and -elastomers. With appropriate chemical modifications each represents a wide variety of types. A more detailed description of crosslinked plastics can be found in Chapter 6.

2.3.2 Morphological Structure (Conformation and Aggregation of Macromolecules)

Now that we have covered chemical composition and molecular architecture of macromolecules, we will investigate the state of motion and order in macromolecules under varying external conditions, *e.g.,* changes in temperature or deformation under load.

Amorphous structures lack a continuous, long-range order of their molecules. The molecules assume the lowest state of energy in a statistical intertwined coil. Therefore, a certain short-range order is only detectable in a range of approx. 1 nm, and it depends on intermolecular forces and the shape of the molecule. If the intermolecular forces are weakened, *e.g.,* by increasing temperatures or through adsorption of

solvent molecules (solvation), micro-Brownian motion is released and all polymers assume this amorphous intertwined state, independently of their specific structure in the solid state.

The amorphous solid state resembles the state of solidified glass and is therefore often referred to as "*glassy state*". Because of their random structure, the characteristic size of the largest ordered region of amorphous materials is on the order of a carbon-carbon bond. This dimension is much smaller than the wavelength of visible light, and thus amorphous thermoplastics are generally transparent. Figure 2.11 shows the shear modulus G' (a measure for the linear elastic deformation of a plastic material) of polystyrene as a function of temperature. Polystyrene is one of the most commonly used amorphous plastic materials. We distinguish two major regions: for low temperatures or in the glassy state the modulus is relatively constant; with increasing temperatures the modulus decreases significantly. At high temperatures, the modulus is negligible – the material is soft enough to flow. Although amorphous materials do not exhibit a sharp transition between the "solid" and the "fluid" state, we identify the temperature range separating these two states as the *glass transition range or glass transition temperature* T_g. For the polystyrene in Figure 2.11 the glass transition temperature is approx. 110 °C. At temperatures below T_g the material behaves like a viscoelastic solid, identified as the *energyelastic zone* in the figure. Once the material is heated above its T_g, it enters the *entropy-elastic zone,* where it can be readily molded, *e. g.,* utilizing thermoforming processes. However, in order for the material to flow, the temperature has to be increased beyond the *softening temperature* T_s. Then the material behaves like a viscoelastic fluid. The softening temperature is also characterized as the point at which the viscous parts of the deformation (the loss modulus) outweigh the elastic parts of the deformation (the storage modulus). For amorphous materials, this zone is typically 50 K above the glass transition temperature. The exact determination of *glass transition* and *softening temperatures* relies on the testing method and also depends on the type and duration of the load during testing. There is a delay between the "load" exerted by the test method and the "molecular response". Therefore, dynamic-mechanical tests with high load cycle frequencies result in significantly higher glass transition temperatures (dynamic glass transition temperature $T_{g\ dyn}$) than calorimetric or dilatometric (elongation) tests with slow temperature changes (static glass transition temperature $T_{g\ stat}$). Depending on type of plastic and level of glass transition temperature, differences of up to 50 K are to be expected. A descriptive way to explain this phenomenon is the statement that plastic materials are the more rigid or stiff the faster the load cycle during testing.

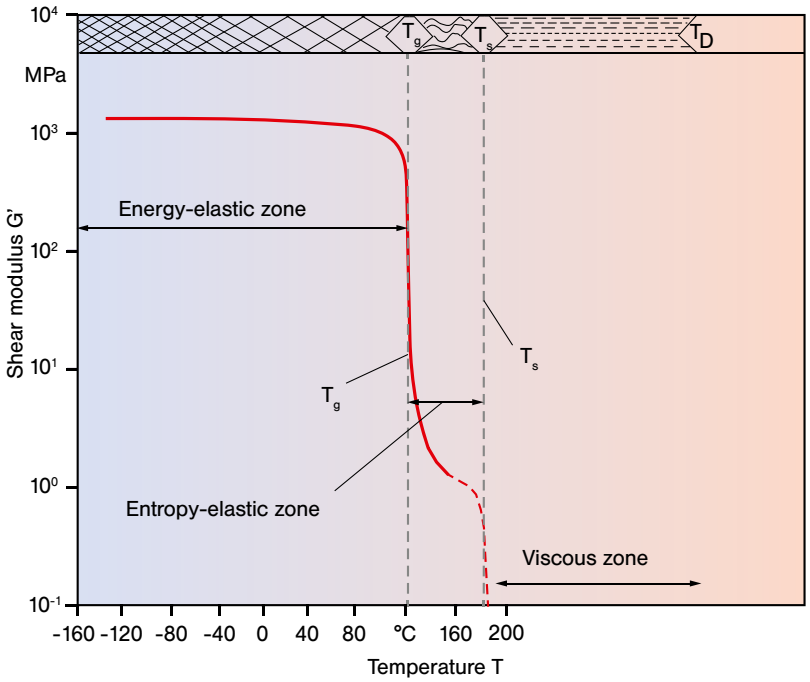


Figure 2.11 Shear modulus of PS as a function of temperature

When plastic materials are exposed to loads or deformations, we observe a time-dependent increase in strain at constant stress *(creep, retardation)* and a time-dependent decrease in stress after being deformed *(relaxation)*. This behavior, also called *viscoelasticity*, is determined by the simultaneous effect of three deformation mechanisms:

- Energy-elastic (also spontaneous-elastic) deformation,
- Entropy-elastic (also rubber-elastic) deformation, and
- Plastic (also viscous) deformation.

The difference in behavior between plastic materials and rubbers is determined only by the gradually different deformation mechanisms in the respective thermal state. The different mechanisms of molecular motion allow for widely different deformations, ranging from approx. 0.1% for energy-elastic deformations, to almost 100% for rubber-elastic deformations, to deformations of up to 10^4% for plastic melts. The *non-Newtonian flow* behavior (*e.g.*, shear thinning) of plastic melts and solutions is also attributed to these deformation mechanics, see Chapter 3.

The amorphous coil structure is a well-suited example to explain the main structure-property relationships encountered in plastic materials. In very uniformly structured

macromolecules in which configuration and intermolecular forces allow for a denser packing of the molecules, we observe the formation of *crystallites*, because the increase in order creates, at least partially, a larger energy gain than the entropy increase.

Because structure formation during the crystallization of organic polymers is such a complex phenomenon, we will provide only a very simplified description. Similar to lower molecular weight materials, crystallization is determined by two distinct stages: nucleation and crystal growth. The variety of conformations together with the macromolecules' tendency towards increase in entropy (coiling of molecules) do not allow for complete crystallization during manufacturing and processing. As a result, plastic materials are typically *semi-crystalline*. Their morphological structure is characterized by a mix of amorphous and crystalline phases whose boundaries on the molecular level cannot be determined easily. Specific sections of the same macromolecule may be part of either an amorphous or a crystalline phase.

In general, the lamellar or micellar crystallites aggregate to form *crystalline superlattices* (Figure 2.12), such as *spherulites*, one of their most common representatives. The degree of crystallization is a quantitative measure of the crystalline part in a macromolecule. In plastic materials that crystallize particularly easily this degree can reach 60 to 80%. Under laboratory conditions higher values are possible, even reaching *polymeric mono-crystals*.

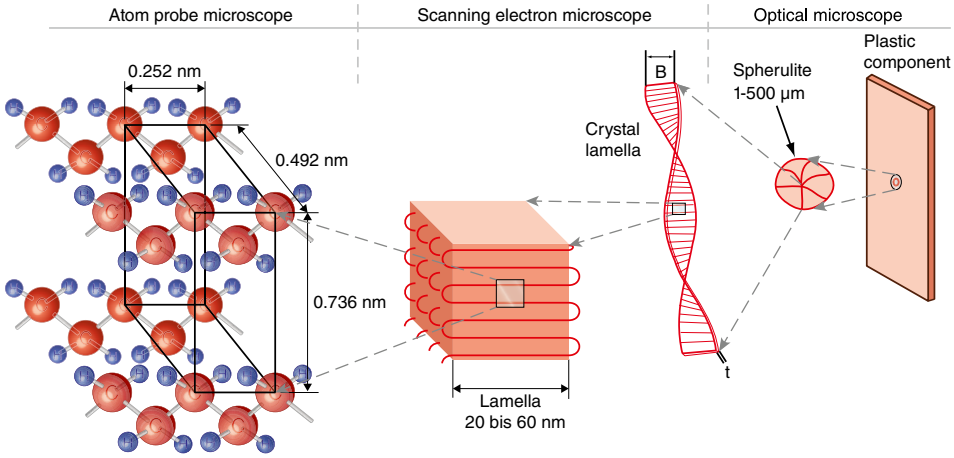


Figure 2.12 Morphology of a semi-crystalline thermoplastic material

Figure 2.13 shows the dynamic shear modulus as a function of temperature for a PE-HD, the most common semi-crystalline plastic material. This curve presents data measured at one test frequency. The figure clearly shows two distinct transitions: one at about −110 °C, the *glass transition temperature*, and one near 140 °C, the melting

temperature. Above the *melting temperature*, the shear modulus is negligible and the material will flow. Crystalline arrangement begins to develop as the temperature decreases below the melting point. Between the melting and glass transition temperatures, the material behaves as a leathery solid. Once the temperature decreases below the glass transition temperature, the amorphous regions between the crystalline structures vitrify, resulting in stiff and often also brittle material behavior.

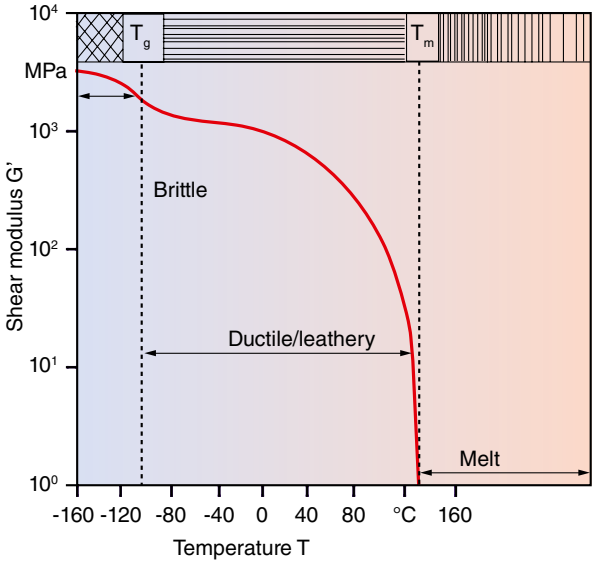


Figure 2.13 Shear modulus of PE-HD as a function of temperature

During processing of plastic materials, inhomogeneous crystal nucleation or differential cooling rates in the material may create locally different crystalline structures, *e.g.*, the fine spherulitic surface layers in injection molded components. This in turn results in anisotropic material properties. The particular characteristics of the molecular structure of semi-crystalline plastics have been tailored in various ways in order to create desired properties:

- Stretching or shearing of macromolecules are used to create molecular rearrangement and the formation of new oriented, crystalline structures, respectively. This results in a significant increase in stability and stiffness, in particular in a desired direction. Examples of such crystalline structures are the fibrils and shish-kebab structures shown in Figure 2.14. A number of processing variations are common in the chemical fiber industry and in plastic engineering, including fiber stretching, biaxial film stretching, and injection- and compression molding stretching. These manipulations result in anisotropic structures with unidirectional or orthogonal orientation.

- Highly homogeneous and fine-grained crystallite structures are obtained by controlling the cooling conditions and/or adding finely dispersed nucleating agents. These structures are advantageous in particular for dimensionally stable and wear resistant components.

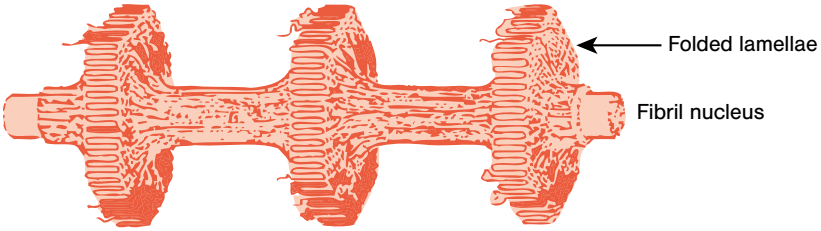


Figure 2.14 Shish-kebab structure

Under common solidification conditions, some polymers are not able to crystallize because of their specific molecular configuration. However, stretching facilitates a partial crystallization by aligning and denser packing of molecular segments *(elongation-induced crystallization)*. This type of structure formation requires a certain level of micro-Brownian molecular mobility, because crystallites can form only by molecular rearrangement during stretching. Elongation-induced crystallization is often seen with rubbers (*e. g.*, NR, IR, IIR, CR). However, the corresponding increase in hardness is not necessarily a welcome side effect in rubber applications.

Crystalline structures in polymers represent the state of highest molecular order in terms of dense molecular aggregation and the corresponding stronger intermolecular forces. Yet, they are still imperfect results of a "frozen" crystallization imbalance so that an increase in temperature will cause melting over a varying temperature interval rather than at a specific melting point. Melting requires additional latent thermal energy in the form of *melting heat*. During rapid solidification, crystallization sets in at temperatures that may be up to 20 to 40 K below the melt temperature range. The use of nucleating agents may decrease this difference. Crystalline regions increase hardness, stiffness, and wear resistance in plastic materials. They also decrease permeation, diffusion, solubility, and swelling. In many respects, the effects of crystallization on the properties of plastic materials are similar to those seen after chemical crosslinking. Therefore, crystalline structures can be described as thermally reversible *physical cross-linking points*.

Extremely stiff macromolecules, *e. g.*, ladder polymers (double-strand polymers with a ladder-like structure), are neither able to form an amorphous coil structure, nor can they be arranged in crystal lattices. The molecules can be compared to rather inflexible rods *(mesogens)* with limited micro-Brownian mobility. If macro-Brownian motion is possible, they form anisotropic parallel structures (model: tree trunks in a river) that are called *mesophases*. Although there are intermolecular forces between the

mesogens, their strength is far smaller than those in crystal lattice structures. In other words, this is a quasi-crystal degree of order with a low energy level. In a liquid-like state, the mesophase structure is typically retained, and polymers exhibiting such structures are called *liquid crystal polymers (LCP)*. Because even minimal macro-Brownian molecular motion will cause a unidirectional orientation of the mesogens in the direction of stretching or flow, the result are anisotropic structures with excellent mechanical properties, also called *self-reinforcing polymers*. The mesophase structure is considered an intermediate between amorphous and crystalline structure and such materials are called *mesomorphous*.

Continuous ladder polymers (*e. g.*, aramids) cannot be plasticized by heating; a liquid-like state can only be achieved in solution *(lyotropic LCP)*. In order to obtain *thermotropic* LCPs, the ladder structures have to be combined with flexible molecular segments, so-called *spacers*. In these polymers the mesophase structure is limited to the mesogens. The mesogens in the solid phase are arranged differently than in the melt, which leads to a variety of mesophase structures (*e. g.*, nematic, smectic) that exhibit different orientation and packing symmetries. Mesophase transitions occur at certain temperatures without general changes in the mesomorphous (anisotropic) structure of the LCPs. Above a certain temperature (as long as there is no thermal degradation), the mesophase structure is transformed to an un-ordered, isotropic structure. All these transitions require only low levels of heat of transformation. The spacer segments in the macromolecules may exhibit any kind of polymeric morphology (amorphous, crystalline).

2.3.2.1 Different Classes of Plastic Materials

Figure 2.4 explained the classification of plastic materials in thermoplastic, thermosetting, elastomeric, and thermoplastic elastomeric materials based on a qualitative differentiation of their molecular mobility at room temperature (RT). Here, the identification as a thermoplastic material indicates only the potential, not the imperative for a thermoplastic state. Figure 2.15 relates the classes of plastic materials introduced in Figure 2.4 to their respective macro- and micro-Brownian molecular mobility.

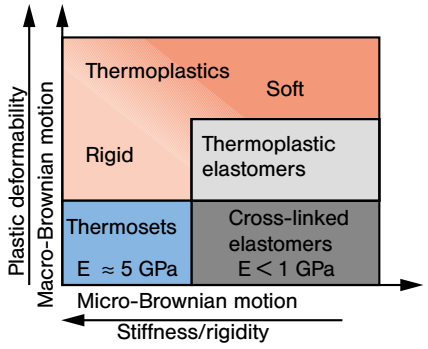


Figure 2.15
Classification of plastics according to their molecular mobility at room temperature (RT)

The materials classified here are end product materials, not resins or precursors. Compared to thermoplastics and thermoplastic elastomers, thermosets and crosslinking elastomers exhibit lower macro-Brownian mobility (free mobility of complete molecular chains: sliding of chains past each other, formation and releasing of entanglements) because of their covalent (chemical) crosslinks. Therefore, plastic deformation of thermosets and rubbers is typically not observed; only incomplete crosslinking allows for a limited degree of plastic deformation.

The differentiation between thermosets and rubbers is a question of convention and typically refers to differences in hardness and stiffness. This approach to a classification is directly related to micro-Brownian molecular mobility (rotational and translational movement around the bond axis of atoms or small chain segments) of the material. Materials covered by this include rigid rubber, flexible EP-, UP-, PUR-X-, SI-X-resins, and others.

Following this categorization, thermosets and thermoplastic elastomers are identified as non-crosslinked plastic materials, *i. e.,* they consist of either linear or branched macromolecules. Only this type of structure allows for a thermoplastic state with highest macro-Brownian molecular mobility. Plastic materials that combine rubber-like properties with the ability to be processed like thermoplastics have gained increasing importance since approx. 1990. This class of materials is identified by the term *thermoplastic elastomers*. The current efforts regarding the nomenclature of these plastic materials are yet another example of the long struggle with classification systems in the plastics technology community. It also sheds light on the fact that the physical composition of thermoplastic elastomers represents a complex problem. In essence, these materials are supposed to be ideal rubber materials that can be processed like thermoplastics. This demand means that the highest possible micro-Brownian molecular mobility has to be combined with sufficient rubber-elastic (entropy-elastic) deformability and low macro-Brownian mobility (little plastic deformation). This requires a loosely crosslinked plastic material with low intermolecular forces and thermally reversible crosslinks. Such *physical crosslinks* can be realized in a number of different ways.

The entanglements of the molecules in thermoplastic materials represent a certain “rubber potential”. In fact, soft polyvinyl chloride (PVC-P, PVC plasticized), polyisobutene (PIB), and other soft-elastic thermoplastic materials have been widely used as rubber-like substitutes in a range of applications until they were substituted by modern thermoplastic elastomers.

However, Figure 2.15 also shows that the ideal rubber material is reached only when the physical crosslinks attain the bond strength of covalent crosslinks. Perfecting the ionic structures may offer a promising approach.

In the context of these structural considerations, we will provide a characterization of the most important classes of plastic materials (except LCPs):

- *Amorphous Thermoplastics.* Linear and branched macromolecules with amorphous structure. Thermo-plastically softening (*e. g.,* PMMA molding compounds) or for extremely high molecular mass materials only thermo-elastically softening (*e. g.,* PMMA cast semi-finished products). Generally soluble in suitable solvents. T_g < RT for low intermolecular forces (*e. g.,* non-polar PIB) or when intermolecular forces are decreased by solvation (*e. g.,* addition of plasticizers, PVC-P) and flexible macromolecules. These plastic materials are soft-elastic at RT and increasingly rubber-like with higher molecular mass. Stronger intermolecular forces and stiffer molecules result in T_g > RT, *i. e.,* at RT they are rigid-elastic plastic materials. In extreme cases (*e. g.,* ladder polymers) thermal degradation will set in prior to softening.
- *Semi-crystalline Thermoplastics.* General characteristics of the molecules are similar to those of amorphous plastics. In addition, semi-crystallinity causes higher hardness and lower solubility. When T_g < RT, the crystalline phase results in horn-like, ductile-rigid behavior at RT. A thermoplastic state is attainable only above T_m. If T_m is much higher than T_g, materials reach a thermoplastic state immediately after the crystallites melt (*e. g.,* polyamides). When this is not the case or for materials with very high molecular mass (*e. g.,* high-molecular polyamides), the material reaches a thermo-elastic state. Extreme reduction of molecular mobility may prevent both thermo-elastic softening (*e. g.,* anhydrous cellulose with T_g = 225 °C) and a thermoplastic state (*e. g.,* PE-UHMW, ultra-high molecular weight PE) prior to degradation. The solubility at RT of such materials may be severely limited, and for some there is no currently known solvent (*e. g.,* polytetrafluoroethylene, PTFE).
- *Thermoplastic Elastomers.* Thermally reversible crosslinked macromolecules with low crosslinking density created by amorphous and semi-crystalline rigid segments (domains) or by ion clusters. Also blends of thermoplastic materials with high contents of crosslinked and non-crosslinked elastomer phases. Thermo-plastically softening and soluble, elastomer-like plastic materials.
- *Crosslinked Elastomers (Rubber).* Thermally irreversibly (covalently) crosslinked macromolecules with predominantly amorphous structure and typically low crosslinking density (low hardness). Thermo-plastic softening not possible. Generally not soluble, but suitable media cause high levels of swelling. Pronounced rubber-elasticity (entropy elasticity) without plastic deformation in service temperature range. Stretching-induced crystallization relatively common.
- *Thermosets.* Thermally irreversibly (covalently) crosslinked macromolecules with amorphous structure and high crosslinking density. Thermo-elastic softening more or less pronounced depending on the strength of the intermolecular forces and crosslinking density. For very high crosslinking densities of no practical interest. Generally not soluble, but depending on the degree of crosslinking more or less swelling in suitable media.

2.4 Effects of Processing on Material Properties

The properties of a plastic material in a manufactured component are determined by the processing and its many variable parameters together with component geometry, material properties, and other factors (Figure 2.16). Because of these typically complex interdependencies, it has become common practice in plastics technology to define "intrinsic characteristics". These characteristics are attributes describing the state of a plastic material, which include:

- Morphology,
- Orientation,
- Residual stresses,
- Crystallization (crystallization parameter),
- Molecular composition (average molecular weight, molecular weight distribution),
- Change in additives/reinforcements (*e. g.*, stabilizer content, fiber length).

The intrinsic characteristics describe the change in properties during use and allow the determination of processing conditions on component properties.

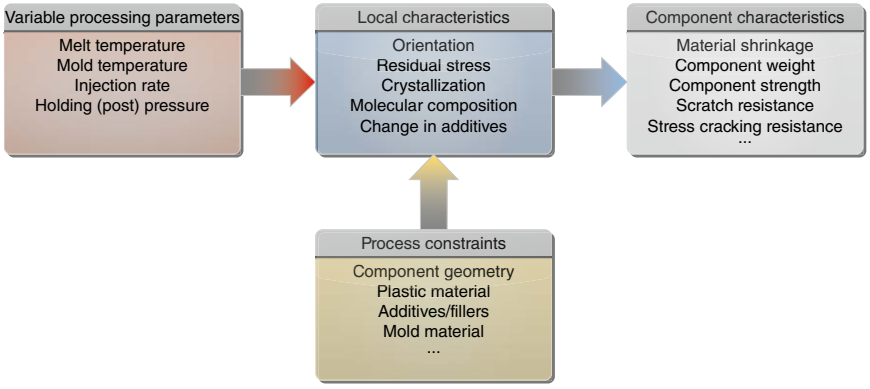


Figure 2.16 Factors influencing intrinsic properties

2.4.1 Residual Stress

Residual stresses are the direct result of pressure and temperature control during the solidification process (Figure 2.17). Internal stress will increase with:

- A heterogeneous temperature distribution in the component,
- High cooling rates,

- High coefficients of thermal expansion, and
- High Young's modulus of the material.

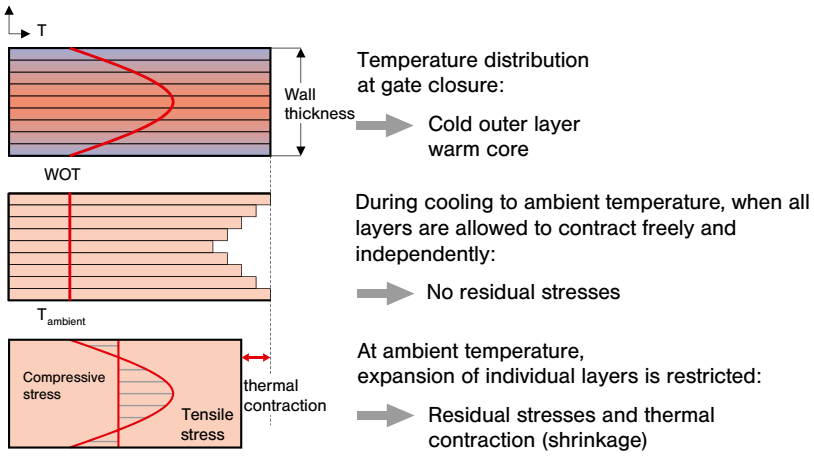


Figure 2.17 Layer model: formation of residual stresses during cooling

Residual stresses represent mechanical loads that act on the component just like external stresses and need to be considered during strength analysis (in a first approximation by reducing the strength parameter).

Differences in coefficients of thermal expansion in composite materials may also cause residual stresses subject to the temperature interval experienced (bi-metal effect). Tempering (heating over a long period of time) to just below the melting temperature and subsequent slow cooling allow for a release of these stresses. In components made from materials that are prone to stress cracking, even small external loads or exposure to crack-inducing media may cause crack formation.

The effects of processing, and in particular those of residual stresses, on the component properties are most pronounced in characteristics such as shrinkage and warpage. They will be covered in more detail in Sections 3.2.2.2 and 3.2.2.3.

2.4.2 Molecular Orientation

In a stationary plastic melt, the molecular chains are in an unordered, coiled state (LCPs are the only exception), while in a moving melt stream the molecules align in a preferred direction, an effect that is also called molecular orientation. Figure 2.18 schematically shows how a circular melt element turns into an oriented element during flow. Molecular orientation is based on two distinct phenomena:

- Local stretching of a melt element, *e. g.*, in a narrowing flow channel or when a melt front expands similar to a balloon being inflated; this effect is also seen during blow molding and thermoforming.
- Shearing of adjacent melt layers in flows with velocity gradients, *e. g.*, during injection molding or extrusion when the melt adheres to the channel walls.

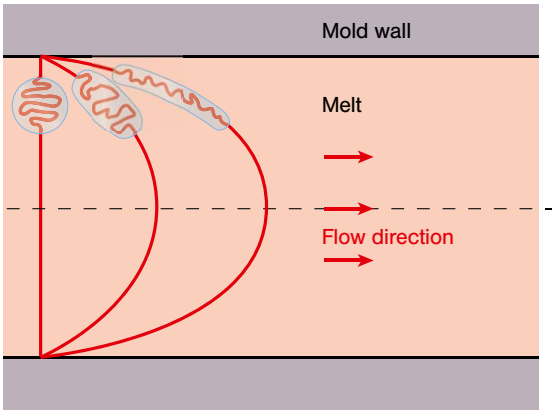


Figure 2.18
Formation of molecular orientation

Determining the level of orientation may be difficult, and in particular for complex components it takes a certain level of experience and the help of simulation programs. Stretching of the flow front and its sudden solidification on contact with the mold wall typically result in a thin, highly bi-axially oriented layer at the component surface. During filling, the high shear differential below the surface results in a layer that is primarily oriented in flow direction. The center of the component wall experiences low shear differentials and thus little orientation.

Because of molecular Brownian motion, orientations in the melt quickly decrease, the molecules relax. Under the conditions prevalent during injection molding, relaxation takes only a few seconds; however, because the mold also cools very fast, orientation is partially frozen in the plastic component. The degree to which orientation is frozen-in depends on the melt temperature, the level of stretching and shear flow, the solidification behavior of the melt, the temperature at the mold wall, and the thickness of the component wall. Although high injection rates during injection molding will cause high levels of orientation, they also result in longer residence times at higher temperatures, which in turn allow for higher levels of relaxation. In consequence, the level of frozen-in orientation may be lower than at slower injection rates. Low melt temperatures, cool molds, and thinner component walls result in higher levels of orientation.

Once at room temperature, the frozen-in orientations will no longer relax. However, if the component experiences elevated service temperatures for longer periods, these

orientations may relax, causing shrinkage or warpage, unless this deformation is prevented by suitable constraints, similar to the mold constraint during injection molding, see Sections 3.2.2.2 and 3.2.2.3.

Orientation always results in anisotropic properties: parallel to the direction of orientation strength, stiffness, thermal expansion, and mold shrinkage will increase.

Orientations in transparent materials can be qualitatively evaluated by optical polarization methods, because oriented regions are birefringent, see Section 3.6. X-ray diffraction analysis is particularly suited for a quantitative evaluation of semi-crystalline plastic materials. Measuring shrinkage is another quantitative approach. Here, complete components, sections, or microtome cuts are stored at elevated temperatures so that orientations can relax and cause deformations. The degree of deformation is a measure for the frozen-in orientation.

2.4.3 Crystallization Behavior

The intrinsic properties of semi-crystalline thermoplastic materials are also determined by the level of crystallinity. The degree of crystallinity together with general structural properties (*e. g.*, the diameter of the spherulites) are crystallinity characteristics.

- The higher the degree of crystallinity, the stiffer, stronger, but also the more brittle the component. The density of the plastic material is directly correlated to its degree of crystallinity. Low degrees of crystallinity or very fine crystal structures result in opaque to transparent parts. The degree of crystallinity is determined by the chemical structure of the plastic material, the type of nucleation, the processing technique, and also potential heat treatment (tempering). Lower tool temperatures and high rates of cooling result in low degrees of crystallinity and fine crystalline structures. A typical example is bottles made from PET. They are cooled so rapidly that the normally white material solidifies into transparent bottles. The same effect is seen for components with thin walls and on the surfaces of components. Long melt residence times at high temperatures result in high degrees of crystallization and coarser crystalline structures, which will occur in particular in the interior of thick-walled components. In injection molded parts, heat is conducted through the component surface to the tool. The low thermal conductivity of plastic materials causes a temperature gradient in the component, which in turn results in a layer-specific degree of crystallinity, Figure 2.19.
- Post-crystallization is observed with extended use of molded components, in particular at elevated temperatures. It causes a decrease in volume that may cause warpage or clearance problems. Tempering or annealing, *i. e.*, exposure to elevated temperatures for a certain period, may preempt post shrinkage. During processing, the spherulites can be aligned by shearing – similar to the macromolecules –

and subsequently cause anisotropic behavior of the component. The higher the degree of order of the macromolecules in the melt (orientation), the easier they are able to crystallize (shear-induced crystallization).

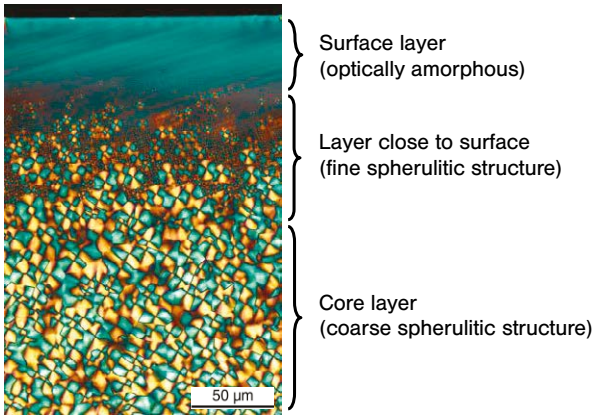


Figure 2.19 Structure of an injection molded component made of PA 66 [1)]

The crystalline portion in a given polymeric material can be identified by X-ray diffraction, differential scanning calorimetry (DSC), or by nuclear resonance spectroscopy. When a calibration curve is available, the direct relationship between density and the degree of crystallinity allows the inference of crystallinity from density.

2.5 Modifications of Plastic Materials

In the context covered here, material modifications will include blending of homopolymers and the addition of fillers and other additives for a variety of specific functions. This field is rather complex and we will give only a general overview here. More detailed information is provided in the following chapters.

2.5.1 Copolymers and Polymer Blends

Copolymers are plastic materials containing two or more types of monomers within their chain. A copolymer consisting of two different monomers is also called a *bi-polymer*. Copolymers consisting of three different monomer units are called *ter-polymers*.

[1)] C. M. Dallner, M. O. Kobes, R. W. Feulner, E. Schmachtenberg: Influence of the morphology on the tribological behaviour of assembly injection moulded Microdrives, PPS-23, May 27–31, 2007, Salvador, Brazil (2007)

Depending on the arrangement of the different monomer units within the chain, we distinguish between four different types of copolymers: *statistical*, alternating, *block-* and *graft-copolymers*. Ethylene-propylene is a typical example of a copolymer. Although both monomers are semi-crystalline thermoplastics, blends with ratios between 35/65 und 65/35 do not exhibit a melting temperature: the material is an elastomer. These so-called EDM-materials (ethylene propylene-diene rubbers) are increasingly utilized for industrial applications because of their good weather resistance. In contrast, all ethylene-propylene block copolymers exhibit a melting temperature, independent of their blend ratios.

Plastic mixtures, blends, and alloys are created by mixing or blending two or more plastic materials. The goal is to create a material with improved properties compared to those of its components. The most common polymer blends include PP-PC (polycarbonate), PVC-ABS (acrylonitrile butadiene styrene), and PE-PTFE. The miscibility of polymers is generally rather limited (disadvantageous energy states), and on a molecular level homogeneous mixtures (blends) are an exception.

The formation of a morphological multi-phase system may be advantageous, because many useful properties of the initial components can be retained. A prerequisite for high-value blends is a stable blend morphology. Dispersed phase and matrix must be uniformly distributed and exhibit good phase adhesion. With current state-of-the-art mixing and compounding technology “phase droplets” below the wavelength of visible light can be achieved (transparent blends). A variety of methods and technologies is used to improve miscibility and adhesion:

- Matching of initial compatibility,
- Matching of quantitative composition and compounding temperature control,
- Chemical modification by ionic bonds, dynamic crosslinking of dispersed phases, partial graft copolymerization and others. Here, the reactions may take place during blending,
- Addition of compatibilizers, and
- Formation of interpenetrating networks (IPN) for crosslinked polymer structures, which result in particularly good mechanical properties.

Originally, blending was used to improve processability and achieve impact modification, in particular for thermoforming applications, typically using rubbers as blend components (elastomer modified plastics). Today, polymer blends are used to improve any given property, including increasing the heat distortion temperature, decreasing stress crack formation, improving coated and plated surfaces, and reducing flammability. Utilizing blend technologies for thermoplastic elastomers should be particularly noted. The increasing trend for material recycling has proven to be an additional incentive for blend technology.

2.5.2 Plastic Composites

Plastic composites represent a form of property and/or material modification that can be classified by the type of bonding:

- Multi-layer composites and
- Reinforced composites.

Multi-layer composites consist of geometrically distinct layers of different materials. They include *multi-layer films, sheets, pipes, hoses, and sandwich designs* consisting of light plastic, honey comb, or homogenous cores with relatively thin-walled surface layers, *multi-component parts* manufactured by multi-component and/or multi-color injection molding, back-injection molding, and by *insert- and outsert methods*. Multi-layer structures allow the development of composite films with clearly defined permeation behavior and of light yet very rigid sandwich designs for aeronautical and automotive applications. They also facilitate a variety of other property combinations with regard to strength, stiffness, gas permeability, flammability, decorative appearance, thermal insulation, ease of assembly, among others. Multi-layer composites can be formed by the combination of different plastic materials as well as by combinations with other materials (metals, wood, etc.). A technological focus of this material modification is to achieve sufficient adhesion between the layers using chemical and/or mechanical bonding principles.

Reinforced composites consist of a polymer matrix into which fillers have been incorporated for reinforcement or to improve specific properties. The distribution of these fillers determines whether the composites exhibit isotropic or anisotropic behavior. Typical examples are *high-performance fiber composites* made from high-tensile and/or high-modulus fibers or textiles and a plastic matrix. In addition, this class of materials also includes plastic/concrete composites, laminated materials (fabric-, paper-, and glass mat based laminates), long-fiber reinforced thermoplastics, and the wide range of filled and reinforced thermosets and laminates. Chapter 6 will discuss these materials in more detail.

However, plastic components reflect the excellent mechanical properties of fiber-reinforced materials only if they contain high ratios of well-ordered fibers, which requires special, high-cost manufacturing methods (see Chapter 4).

The majority of plastic materials is shaped/molded using flow processes. To ensure the flowability of the plastic material, the reinforcing fibers must not exceed certain lengths. The type and ratio of reinforcing material determines the applicable manufacturing process (see Figure 2.20). Plastic manufacturing processes suitable for large-scale production typically allow for fiber lengths of approx. 10 mm. It should be noted that fiber lengths typically decrease during manufacturing so that the fiber length in the component is always smaller than in the original molding compound.

Manufacturing process	Injection molding	Compression molding	Resin injection and transfer molding, autoclave processes
Pellets	Pellets	Sheet and bulk molding compounds, long fiber reinforced thermoplastics	Textile semi-finished products, preforms, prepregs
Characteristics	Short fibers: $L < 4.5$ mm $\Phi < 25\%$	Short fibers: $4.5 < L < 40$ mm $\Phi < 25\%$	Continuous fibers: $L \approx$ component size $\Phi > 30\%$
Fiber orientation in component			

Suitable for mass production ← → Mechanical properties

Figure 2.20 Correlation between manufacturing process and achievable fiber length

In general, a wide range of fillers can be incorporated into plastic materials in order to tailor the material's properties. Figure 2.21 shows matrix reinforcement (*i. e.,* the change in Young's modulus as a result of the filler) as a function of type, shape, and orientation of the filler particles at different filler contents.

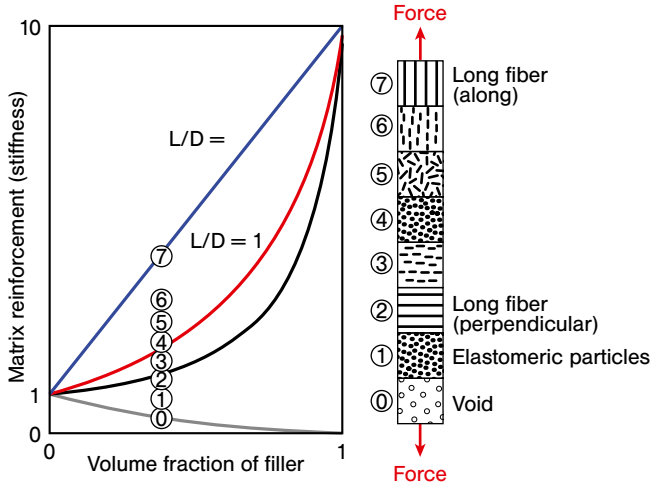


Figure 2.21 Relationship between stiffness and type, shape, and orientation of filler particles

3
Material Properties and Testing Methods

In this chapter we will introduce the characteristic properties of plastics and the testing methods required to determine them. It is our goal to develop and improve a general understanding of this group of materials. Our descriptions will be general and qualitative and the diagrams displaying material characteristics are meant to help gain insight into the behavior of this group of materials. Some tables and figures provide a comparison of selected plastics; however, these comparisons are also only means to foster a general understanding.

It should be noted that plastics are almost always modified by functional or other additives. The properties of commercially available plastic materials may vary from the "average values" provided here. Before selecting a specific plastic material, it is recommended to verify properties through the manufacturer. Another highly recommended source of material property information is CAMPUS, a free database provided by 30 plastic material producers. This database contains material data for materials under their respective tradenames. Both space and timeliness are prohibitive factors for a printed work to provide the plethora of information available. More detailed information regarding the CAMPUS database and free downloads can be found at *www.CAMPUSplastics.com*.

Figure 3.1 compares the stress/strain diagrams of unfilled PBT grades to exemplify the wide variation of plastic characteristics (data according to CAMPUS). Large differences in property profiles can be found even within one plastic class.

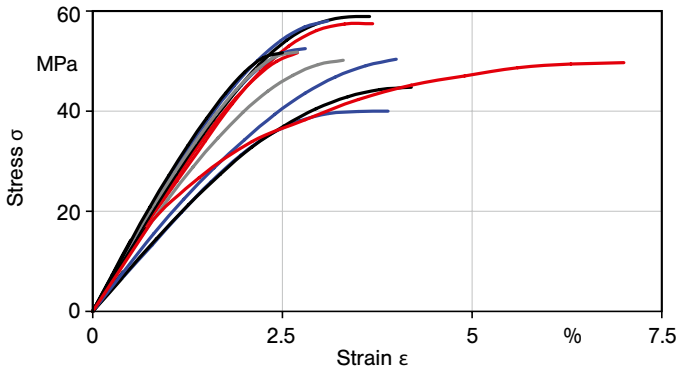


Figure 3.1 Range of stress-strain diagrams for PBT at 23 °C

3.1 Significance of Characteristic Values

Material characteristics are the determining factors during all phases of development and design. They affect the initial, conceptual design steps, material selection, and dimensioning of molded components. In order to meet these requirements, material characteristics have to be

- comparable,
- meaningful, and
- determined by a rational process.

Databases and material data sheets provide up to 200 different characteristics of a product. This large amount of information makes it difficult if not impossible to gain and maintain a comprehensive overview.

In order to select meaningful characteristics here, we refer to a globally respected source: ISO 10350: “Plastics – Acquisition and presentation of comparable single-point data, molding materials” (see Table 3.1). The reference to this standard will also determine the order in which we will describe specific characteristics in this chapter. Another important standard is ISO 11403: “Plastics – Acquisition and presentation of comparable multipoint data, mechanical properties” (see Table 3.2).

Table 3.1 CAMPUS Characteristic Data Catalog According to ISO 10350

Property	Symbol	ISO-(IEC)-standard	Specimen (in mm)	Unit	Notes
Rheological characteristics					
Melt volume rate	MVR	1133	Compound	cm^3/10 min	
Mold shrinkage *parallel*	S_{Mp}	294-4 (thermoplastics) 2577 (thermosets)	60 · 60 · 2	%	See ISO 294-3, thermoplastics and ISO 10724-2, thermosets
Mold shrinkage *normal*	S_{Mn}				
Mechanical characteristics, 23 °C					
Tensile modulus	E_t	527-1/2	ISO 3167 (multi-purpose specimen)	MPa	Elongation 0.05 to 0.25%
Yield stress	σ_y			MPa	
Yield strain	ε_y			%	
Nominal strain at break	ε_{tB}			%	After yield
Stress at 50% strain	σ_{50}			MPa	For specimens without σ_y up to $\varepsilon = 50\%$
Stress at break	σ_B			MPa	For specimen without yield
Strain at break	ε_B			%	For specimen without yield
Tensile creep modulus: 1 h	E_{tc} 1	899-1		MPa	Elongation 0.5%
Tensile creep modulus: 1000 h	E_{tc} 10^3				
Charpy impact strength, unnotched at +23 °C	a_{cU} +23	179/1eU	80 · 10 · 4 (general purpose specimen)	kJ/m^2	
at −30 °C	a_{cU} −30				
Charpy impact strength, notched at +23 °C	a_{cA} +23	179/1eA			
at −30 °C	a_{cA} −30				

Table 3.1 CAMPUS Characteristic Data Catalog According to ISO 10350 *(continued)*

Property	Symbol	ISO-(IEC)-standard	Specimen (in mm)	Unit	Notes
Tensile impact strength at +23 °C	a_t 1	8256/1	80 · 10 · 4 (multi-purpose specimen) with double V-notch	kJ/m^2	When Charpy impact strength cannot be determined
Puncture impact properties at +23 and −30 °C	F_M	6603-2	60 · 60 · 2	N	
Max. force at +23 and −30 °C	W_P			J	
Thermal characteristics					
Melting temperature	T_m	11357-1 and -3	Material	°C	Temperature increase 10 K/min
Glass transition temperature	T_g	11357-1 and -2			
Temperature of deflection under load at 1.8 MPa	T_f 1.8	75-1/2	80 · 10 · 4 (multi-purpose specimen)	°C	Select 1.8 MPa and a second load level
at 0.45 MPa	T_f 0.45				
at 8.0 MPa	T_f 8.0				
Vicat softening temperature	T_v 50/50	306	≥ 10 · 10 · 4 (multi-purpose specimen)	°C	Temperature increase 10 K/min, load increase 50 N
Coefficient of linear thermal expansion, parallel	α_p	11359-1/2	Center of 80 · 10 · 4 (multi-purpose specimen)	E^{-6}/K	Increase in elongation between 23 and 55 °C
Normal	α_n				
Burning behavior, 1.5 mm thickness	B50/1.5 B500/1.5	60695-11-10	125 · 13 · 1.5 ≥ 150 · 150 · 1.5	Class	Classes for B50: V-0, V-1, V-2, HB Classes for B500: 5VA, 5VB, N
-.- mm thickness	B50/-.- B500/-.-	60695-11-10/-20	125 · 13 · 1.5 ≥ 150 · 150 · 1.5		
Oxygen index	OI23	4589-1/2	80 · 10 · 4 (multi-purpose specimen)	%	Method A: Ignition at upper surface

Property	Symbol	ISO-(IEC)-standard	Specimen (in mm)	Unit	Notes
Electrical characteristics					
Relative permittivity 100 Hz 1 MHz	 ε_r100 ε_r1M	IEC 60250	60 · 60 · 2 (60 · 60 · 1)	E^{-4}	
Dissipation factor 100 Hz 1 MHz	 tan δ100 tan δ1M				
Specific volume resistivity	ρ_e	IEC 60093	60 · 60 · 2 (60 · 60 · 1)	Ω · m	1-minute values
Specific surface resistivity	σ_e			W	1-minute values, 500 V
Electric strength	E_B1	IEC 60243-1	≥ 60 · ≥ 60 · 1	kV/mm	Voltage increase 2 kV/s
Comparative tracking index	CTI	IEC 60112	≥ 15 · ≥ 15 · 4 (multi-purpose specimen)		Testing medium A
Other characteristics, 23 °C					
Water absorption	W_W	62 and 15512	Thickness ≥ 1	%	Saturation value in water, 23 °C
Moisture absorption	W_H				Saturation value at 23 °C/50% r.h.
Density	ρ	ISO 1183	(Multi-purpose specimen)	kg/m^3	
Resin-specific characteristics					
Viscosity number	VN		Material	cm^3/g	
Characteristic density	ρ_I	1872-1		kg/m^3	Only for PE
Luminous transmission index	τ_t	13468-1/ -2	60 · 60 · 2	%	
Processing conditions for testing specimens					

Table 3.1 CAMPUS Characteristic Data Catalog According to ISO 10350 *(continued)*

Property	Symbol	ISO-(IEC)-standard	Specimen (in mm)	Unit	Notes
Injection molding of thermoplastics					Where: P = Thermoplastics S = Thermosets I = Injection molding C = Compression molding R = Cooling rate M = Molding $_c$ = Cure
Compound temperature	T_M IP	294-1 and 3		°C	
Mold temperature	T_C P				
Injection rate	v_I P			mm/s	
Holding pressure	P_H			MPa	
Injection molding of thermosets					
Temperature of the plasticized compound	T_M IS	10724		°C	
Mold temperature	T_C S				
Injection rate	v_I S			mm/s	
Curing time	t_C I			min	
Compression molding of thermoplastics					
Mold temperature	T_MCP	293		°C	
Cooling rate	R_C			K/min	
Compression time	t_M			min	
Demolding temperature	T_D			°C	
Compression molding of thermosets					
Mold temperature	T_MCS	295		°C	
Curing time	t_CC			min	

These two standards form the basis for the international database of plastic characteristics (CAMPUS). It provides the characteristic values for specific products according to Table 3.1 and Table 3.2.

Table 3.2 CAMPUS Characteristic Diagrams According to ISO 11403

Diagrams	Parameter	ISO Standard
Viscosity/Shear rate	Temperature	11443
Shear modulus/Temperature		6721-1,2,7
Stress/Strain	Temperature	527-1,2
Secant modulus/Strain	Temperature	
Stress/Strain (isochronous) T1 to T6	Temperature, time	899-1
Creep modulus/Time T1 to T6	Stress	
Specific volume/Temperature (p-v-T)	Pressure	17744
Specific enthalpy per mass/Temperature (DSC)		11357-1 and 4

Each characteristic value is determined using standardized testing methods that are defined by ISO standards. The manufacture of testing specimens also follows standardized rules, which is important to ensure that the values are comparable, in particular because the characteristic values depend strongly on the processing conditions during injection molding of the specimens. Although the CAMPUS database was designed predominantly for thermoplastics, the data can also be applied to elastomers, thermoplastic elastomers, and thermosets.

In the following we will provide more detail with regard to the characteristics used to evaluate the behavior of plastics during processing. This includes the molding of components, their intended use, and component overload. In general, it is important to note that characteristic material values do not represent universal material constants. Similar to characteristics of other materials they depend on the following influencing factors:

- Temperature,
- Duration and rate of load,
- Load frequency,
- Environmental influences,
- Material inhomogeneities, such as flow lines, notches, etc., and
- Manufacturing conditions of components and the resulting shrinkage and warpage.

The following sections will provide specific examples.

3.2 Processing Characteristics

Thermoplastic and thermoset components are manufactured by molding at elevated temperatures. For thermoplastics this process can be repeated several times. Thermosets, on the other hand, cure during molding and cannot be fused repeatedly. Cast resin components, also considered thermosetting materials, are manufactured using special processes, see Section 4.6.

The manufacturing process determines both properties and costs of a molded component. Therefore, knowledge of the following properties is important for material selection and preparation for production.

3.2.1 Rheological Behavior

The number and arrangement of gates in an injection mold is determined by the flowability of the plastic melt at processing temperature. Together with the material's solidification behavior it also determines the achievable wall thickness of the component. The minimal wall thickness is a measure for the required material input. **Viscosity** is the measure for the flowability of a material. The rheology of plastics is a complex field because of the numerous influencing factors (plastic melts are shear thinning, visco-elastic, and flow behavior is temperature and pressure dependent). Shear viscosity plays a determining role in the majority of manufacturing processes. Therefore, viscosity is generally measured by devices in which the melt flows under shear load.

3.2.1.1 Flow Behavior, Viscosity

The rheological behavior of thermoplastics is described by flow curves that are determined by capillary rheometers. They characterize the correlation between shear viscosity in Pa · s and the shear rate in s^{-1}.

The shear viscosity is a measure for the relation between shear stress and shear rate in a flowing substance and thus a measure for the resistance of the melt to flow. Figure 3.2 shows the change in viscosity with increasing shear rate for different thermoplastics. At low shear rates, plastics exhibit Newtonian behavior, *i. e.*, the viscosity is independent on the shear rate and exhibits a so-called Newtonian plateau. This is also referred to as zero-viscosity. It is possible to reach a second Newtonian plateau at very high shear rates. In other words, here the viscosity is again shear rate independent. This phenomenon can be explained by the fact that at high shear rates, all molecular chain entanglements are relaxed and the chains cannot slip any further.

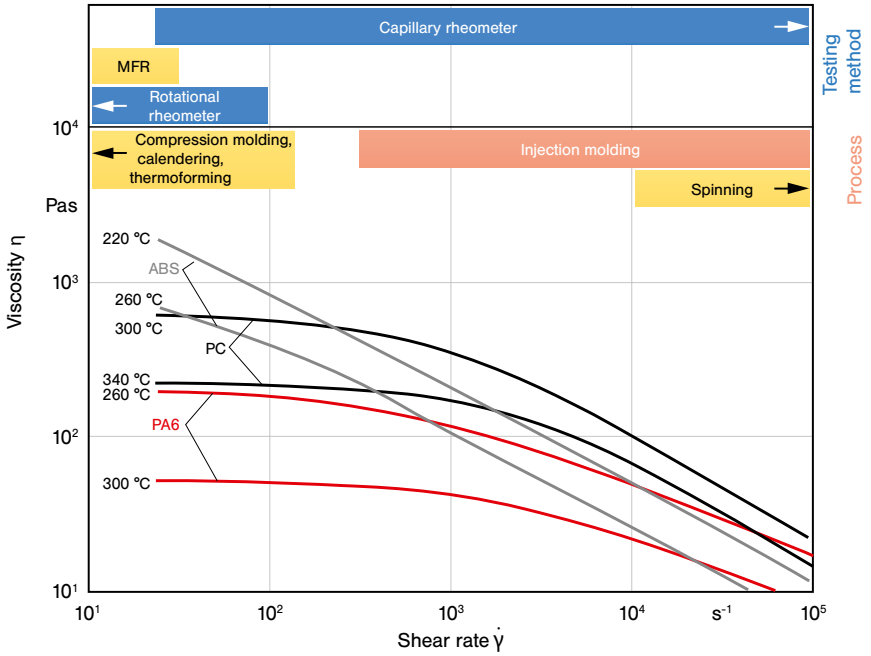


Figure 3.2 Melt viscosity of selected thermoplastics at normal upper and lower permissible melt temperature, respectively

Temperature also influences viscosity: with decreasing temperature the viscosity will increase. Figure 3.2 also shows the shear rate ranges encountered in different processing technologies and identifies the testing methods used for their determination. Figure 3.3 shows the order of magnitude of possible variations in the viscosity curves for ABS at constant temperature. Flow path calculations based on these viscosity curves resulted in variations of up to 30%. This example shows that caution is warranted when operating with averaged values for rheological data. They should be used exclusively for comparisons between material classes – never as the basis for design or dimensioning.

Figure 3.4 shows the two most commonly used rheometer designs and their areas of application. Rotational rheometers, such as the depicted cone-plate system, facilitate measurements at low shear rates. These typically complex measurements allow for the fundamental analysis of rheological phenomena, such as principal stress differences and the derivation of rheological models, because they detect changes on the molecular level. Shear viscosity, which is a processing relevant parameter, is typically measured using capillary rheometers. It is determined at constant temperature by measuring the material exiting a capillary at a specific pressure.

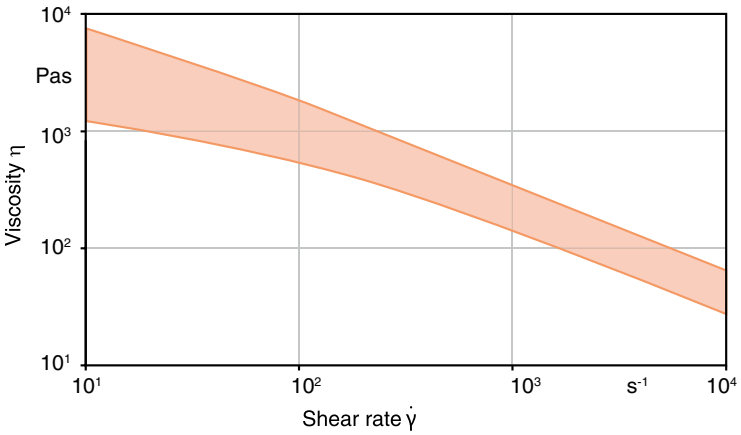
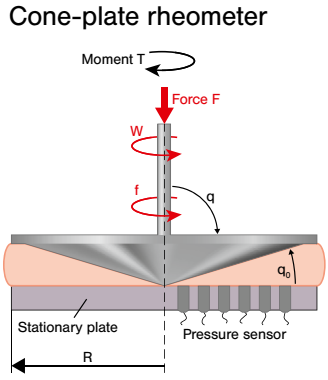
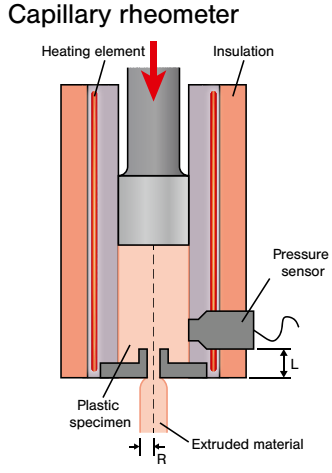


Figure 3.3 Viscosity curve range for ABS at 240 °C





Shear rate range that can be experimentally measured	Material functions to be determined
$(10^{-6}$ to $10^{2})s^{-1}$	Rotating operation: $\tau, \eta = f(T, p, \dot{\gamma}, t)$ Oscillating operation: $\eta', \eta''; G', G''$
$(10^{1}$ to $10^{6})s^{-1}$	$\tau, \eta, \sigma = f(p, T, \gamma)$

T	=	Temperature	°C
t	=	Time	s
p	=	Pressure	Pa
σ	=	Tensile stress	Pa
τ	=	Shear stress	Pa
γ	=	Shearing	m
$\dot{\gamma}$	=	Shear rate	$m \cdot s^{-1}$
η	=	Viscosity	$Pa \cdot s$
G	=	Shear modulus	Pa
η'; G'	=	Elastic part	$Pa \cdot s$
h''; G''	=	Viscous part	$Pa \cdot s$

Figure 3.4 Rheometer types

Online- and inline rheometers help monitor both injection molding and extrusion processes. While in the past partial flows were sampled from the volume flow (bypass principle), today viscosity is measured directly in the main volume flow. In order to do this, pressure and temperature sensors are placed along the flow length that allow to calculate the viscosity taking into consideration the time of contact with the flow front, the pressure drop, and the geometric dimensions of the cavity. However, this approach is possible only at the shear rate predetermined by the process.

Figure 3.5 shows the flow curves of different plastics with Figure 3.5 a) showing the viscosity curves of polyolefins with different flow behaviors. The easy flowing grades exhibit lower viscosities. Many plastics contain additives, such as flow promoters or color pigments, which affect processing behavior as well as product properties (*e. g.*, color). As seen in Figure 3.5 b), the addition of white pigments (TiO_2) increases the viscosity of the compound [1]. The data also indicate that this effect is more pronounced for particles with larger diameters. The increase in viscosity caused by the addition of fillers is also dependent on the viscosity of the plastic itself: the lower the viscosity, the higher the increase in viscosity. This is further illustrated in Figure 3.5 c) in the case of an easy flowing PE-LD [1]. The viscosity of plastic grades that are offered by the manufacturer already compounded with color pigments typically matches that of the base (uncolored) grade. For master batches however, the processing conditions have to be adjusted accordingly by the processor. Figure 3.5 d) illustrates the effect of fillers with even larger particles, such as fibers or the copper platelets shown here, as a function of temperature [2]. At high temperatures the filler content has less influence than at lower temperatures.