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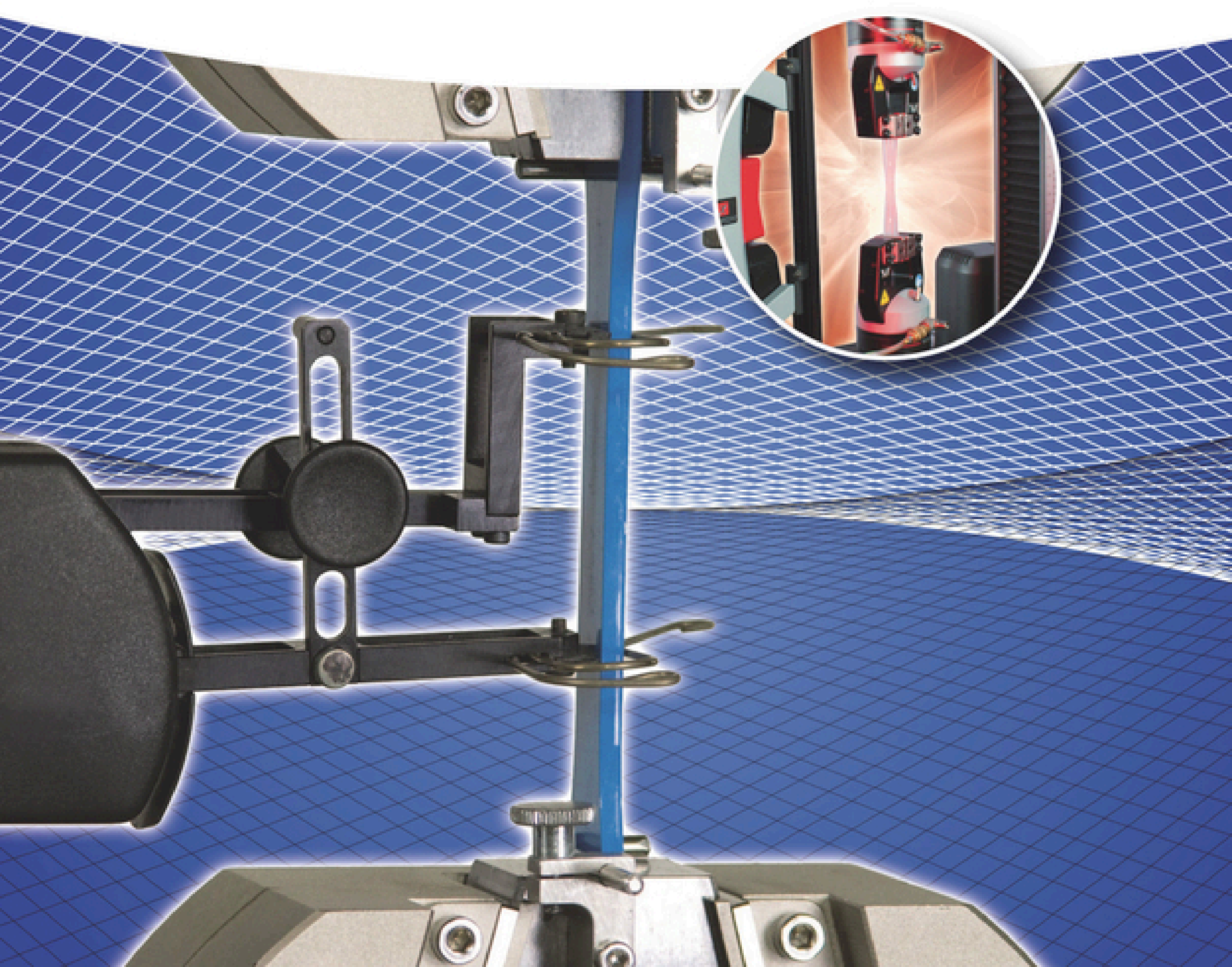

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Authors
Professor Dr.-Ing. Achim Frick
Aalen University
Institute of Polymer Science and
Processing (iPSP)
Beethovenstraße 1
73430 Aalen
Germany

Dr. Claudia Stern
INTERCABLE GmbH
Rienzfeldstrasse 21
39031 Bruneck
Italy

Vibunanthan Muralidharan, M.Sc.
VORWERK AUTOTEC GmbH
& Co. KG
Obere Lichtenplatzer Str. 336
42287 Wuppertal
Germany

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Introduction to Plastics

1.1 Plastics

Any synthetic or semi-synthetic organic solid that has been processed from its raw form can be considered a plastic. Arguably, one of the earliest plastics was therefore birch pitch employed by Stone-Age humans to attach flint blades. Since then, the development of improved plastics has seen major technological advances and contributed to the growth of modern prosperity.

Today, the term ‘plastic’ is generally used interchangeably with ‘polymer’ or ‘polymeric material’, signifying a material consisting of macromolecules.

Polymeric materials are a relatively new class of materials, with their first industrial uses beginning around the turn of the twentieth century. Since then, their importance has grown at an unprecedented rate, and they now represent one of the most important classes of engineering materials. For example, the worldwide annual production of steel is approximately 1500 million metric tons compared to approximately 335 million metric tons for plastics. However, polymers tend to be about six times less dense than steel (assuming average densities of about $7.8\,\mathrm{g\,cm^{-3}}$ for steel and $1.2\,\mathrm{g\,cm^{-3}}$ for polymers). This means that the annual production, by volume, of plastics exceeds that of steel, and could be used to cover two football fields over 33.5 km deep (Mt. Everest is 8.8 km high!)

1.1.1 Types of Polymers

All polymers can be classified as one of four major types: thermoplastic, thermoplastic elastomer (or thermoplastic rubber), elastomer (or rubber), and thermoset (Table 1.1).

A *thermoplastic* becomes soft upon heating and gradually turns a viscous melt. Upon cooling, the melt once again solidifies. This process is therefore reversible, and can be used to readily process and recycle thermoplastics.

Thermoplastic elastomers are structurally similar to thermoplastics, and both consist of macromolecules that have not been cross-linked. However, they differ in their mechanical properties at room temperature: thermoplastic elastomers are extremely flexible and elastic, being able to spontaneously resume its original shape after deformation.

An *elastomer* (or rubber) has mechanical properties similar to that of a thermoplastic elastomer at room temperature. However, elastomers differ in their

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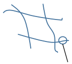
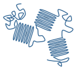
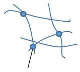
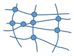
Table 1.1 Classification of polymeric materials.

Characteristics	**Polymeric materials**				
	Thermoplastics		Thermoplastic Elastomers	Elastomers	Thermosets
Molecular	Not cross-linked  Amorphous 	Semi-crystalline 	Not cross-linked 	Cross-linked (weakly) 	Cross-linked (strongly) 
Mechanical	Brittle to tough, hard		Rubber-like, soft	Rubber-like, soft	Brittle, hard
Thermal	Meltable	Meltable (Crystalline melting temperature)	Meltable (Partially crystalline melting temperature)	Not meltable	
Chemical / Physical	Soluble			Insoluble Swellable	Hardly swellable

structure, because their macromolecules have been loosely cross-linked into a three-dimensional network by a vulcanization reaction. Once vulcanized, an elastomer cannot be molten.

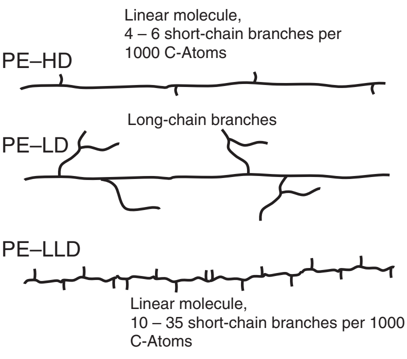
A *thermoset* consists of a three-dimensional network of tightly cross-linked polymeric macromolecules. These materials are relatively rigid, have mechanical properties that are stable over a wide temperature range, do not melt, and are resistant to swelling when exposed to chemical environments.

The primary structural difference between elastomers and thermosets is the degree of cross-linking. The polymeric network of an elastomer is only loosely cross-linked, so that it is highly elastic at temperatures above the glass transition temperature. In contrast, thermosets have a highly cross-linked structure that typically results in a rigid, stiff material. Other elastomers and thermoplastics are manufactured from polymers that are only subsequently cross-linked by a chemical reaction such as vulcanization or curing.

Thermoplastics consist of unconnected linear molecular chains with varied degrees of branching (Figure 1.1). Because these macromolecules are not cross-linked, they can be readily melt processed and therefore easily reused and recycled. Consequently, thermoplastics embody the technically and economically most important class of polymers, and are the primary focus of this discussion.

The material properties of a thermoplastic with a given chemical composition are controlled primarily by the polymer chain length. The average molecular weight and its distribution are commonly used as proxies for chain length, which may be difficult to measure directly. The presence, length, and density of branches also significantly influence the material properties.

A cross-linked polymer, such as a thermoset, consists essentially of a single, large molecule that extends across the entire material. The concept of molecular



Crystallinity (%)	Crystallite melt temperature (°C)	Solidification temperature (°C)	Density (g cm^{-3})
70–75	125–135	115–120	0.93–0.97
40–55	100–110	80–95	0.915–0.935
55–65	120–130	105–115	0.92–0.94

Figure 1.1 Polyethylene (PE) as an example of linear and branched chain molecules.

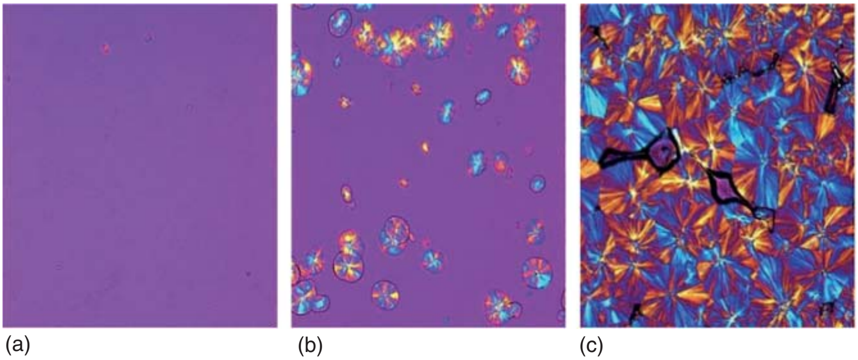


Figure 1.2 Crystallization of isotactic polypropylene (iPP) under isothermal conditions at 135 °C; viewed with a hot-stage microscope. (a) Start of crystallization, (b) after 4 minutes, (c) after 10 minutes.

weight is therefore irrelevant. In this case, the density of cross-links controls the material properties.

Thermoplastics can be further classified on the basis of the molecular organization (Table 1.1) either as amorphous or semi-crystalline.

Amorphous means the polymer chains are randomly oriented and lack order. This means that the mechanical properties are influenced by the density of loops and bends, as well as the temperature-dependent chain mobility, or ease with which chains can move: below the glass transition temperature, T_g, the chains are largely 'frozen in place' and cannot easily move; this results in a brittle material. Around T_g, the chains begin to 'defrost' and relax. Above T_g, the chains are mobile and can rearrange to accommodate mechanical deformation; the material can now be stretched, i.e. deform plastically, as well as creep.

Semi-crystalline thermoplastics consist of polymer chains that are partially ordered. Upon cooling from the melt, the chains will locally align themselves with each other, forming small crystalline regions. These local crystal phases embedded in an otherwise amorphous matrix can reinforce or strengthen the polymer. This crystallization process (Figure 1.2) is controlled by the homonucleation and heteronucleation characteristics of a particular polymer as well as the solidification conditions (such as cooling rate, temperature or pressure gradients, etc.); the resulting distribution, size, and number of crystalline regions influence the material properties, which are therefore a consequence of thermodynamic and kinetic factors. For example, the tool temperature is a key parameter for an injection moulding process. In practice, cooling rates are rarely uniform, often exceeding $1000\,\mathrm{K\,min^{-1}}$, and are accompanied by significant pressure gradients. This means that a manufactured part will usually have non-uniform crystallinity, and therefore non-uniform material properties.

Semi-crystalline polymers generally have higher ductility compared to brittle, amorphous polymers. This means that semi-crystalline polymers usually have improved toughness, resistance to crazing and stress cracking, and are less susceptible to chemical or environmental attack.

The polymeric chains of thermoplastic elastomers consist of stiff and flexible segments. The overall hardness and strength of such a material is largely controlled by the ratio of stiff segments to flexible segments. The structure of thermoplastic elastomers is therefore analogous to a semi-crystalline thermoplastic, where the flexible segments correspond to the amorphous matrix and the stiff segments correspond to the embedded crystalline phases. These materials therefore contain regions of local order that can be formed and manipulated by heat treating (tempering).

1.2 Structure and Behaviour of Plastics

Plastics are polymeric materials and therefore consist of macromolecular chains that are assembled from many identical repeat units (monomer units, MUs) or monomers (Figure 1.3).

Polymeric macromolecules can be synthesized with one of three different types of chemical reactions:

- Polymerization
- Polycondensation
- Polyaddition.

The principle of polymerization can be illustrated by reviewing the formation of the polyvinyl chloride (PVC) polymer from the unsaturated vinyl chloride monomer (Figure 1.4). Unsaturated vinyl chloride monomers are radicalized in an initiation reaction by adding energy. The resulting radicals are highly reactive and will bind to each other, forming the polymer chain of the macromolecule.

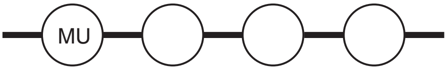


Figure 1.3 Polymers consist of chains assembled from monomeric repeat units (MUs).

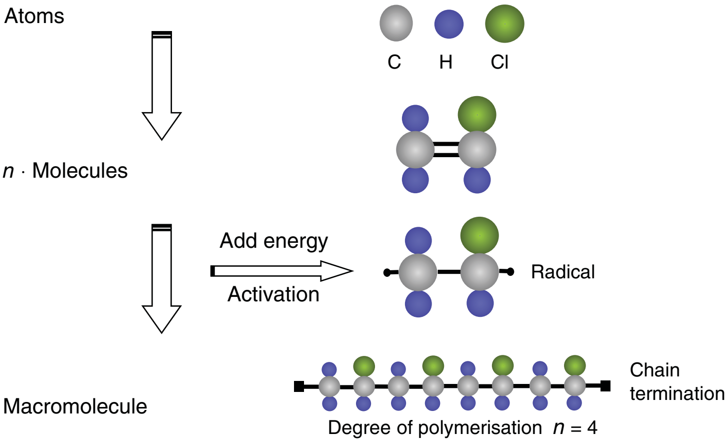


Figure 1.4 Synthesis of polyvinyl chloride (PVC) by radical chain polymerization.

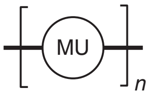


Figure 1.5 Structure of a homopolymer based on a monomer repeat unit (MU).

When the desired chain length is reached, a chain termination reaction passivates the polymer and the reaction ceases. The synthesis of PVC is now complete.

If a polymer consists of n identical monomer repeat units, as shown in Figure 1.5, it is called a homopolymer.

The degree of polymerization, n, refers to the number of monomer repeat units that form the macromolecule. It therefore correlates with the chain length, which in turn correlates with the molecular weight M.

The molecular weight of a macromolecule corresponds to the molecular weight of the monomer multiplied by the degree of polymerization (Eq. (1.1)).

$$M_{\text{polymer}} = n \cdot M_{\text{monomer}} \tag{1.1}$$

Using the example of polyethylene (PE), the molecular weight of the corresponding monomer ethylene is $28\,\text{g mol}^{-1}$. This is obtained by summing the masses of the two carbon atoms ($\text{C} = 12\,\text{g mol}^{-1}$) with the masses of the four hydrogen atoms ($\text{H} = 1\,\text{g mol}^{-1}$) that constitute the monomer (Figure 1.6).

For example, if an injection mouldable PE contains an average molecular weight of $280\,000\,\text{g mol}^{-1}$, then the mean chain length is 10 000 monomer repeat units.

Ethylene is a gas at room temperature and pressure. However, polymerization into PE yields a material with fundamentally different properties. The resulting material can be liquid or solid at room temperature and pressure, depending on the degree of polymerization (see Table 1.2).

Melt processing of the thermoplastic PE is only feasible up to a molecular weight of about $500\,000\,\text{g mol}^{-1}$. Larger molecular weights translate into very long chains with limited mobility that results in excessive viscosity; such a material can no longer be melt processed and instead requires sintering. The melt viscosity η is related to the average molecular weight $\overline{M}$ (Eq. (1.2)).

$$\eta = k \cdot \overline{M^{\alpha}} \tag{1.2}$$

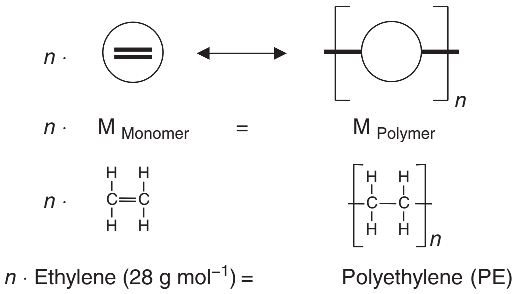


Figure 1.6 Structure of the polymer polyethylene (PE).

Table 1.2 The properties of polyethylene (PE) depend on the degree of polymerization and the molecular weight.

Degree of polymerization n (–)	Molecular weight M (g mol^{-1})	Strength σ_B (MPa)	Density ρ (g cm^{-3})	Physical state at room temperature and ambient pressure
2	56	—	—	Gas
<8	70–240	—	0.63–0.78	Liquid
<50	250–1 400	2	0.87–0.93	Solid
<350	1 400–10 000	3–10	0.92–0.96	Solid
<23 000	10^4–$6.5 \cdot 10^6$	25–40	0.93–0.96	Solid

It denotes:

k and α	material-specific constants

1.2.1 Influence of Molecular Weight on Material Properties

PE has a wide range of applications, depending on the molecular weight: these include lubricants, waxes, injection moulded structures, and sintered components. This range is testament to the importance of molecular weight in determining the material properties.

High strength and toughness are a result of a large molecular weight. This means that if the molecular weight is reduced, then the original material properties are lost (Figure 1.7). A reduction in molecular weight can occur either during processing or due to degradation (i.e. ageing or weathering).

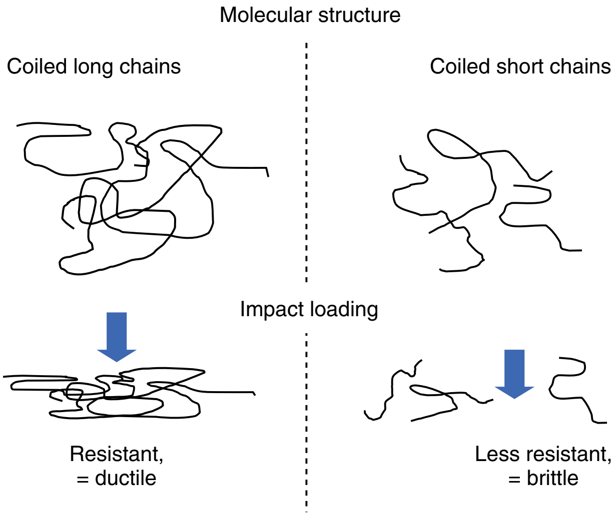


Figure 1.7 Influence of chain length on the material properties.

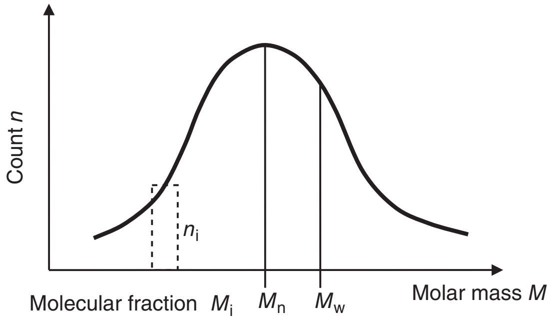


Figure 1.8 Molecular weight distribution.

Generally speaking, a polymer used for structural applications needs to have a molecular weight of at least 10^4 g mol^{-1}. These large molecules consist of sufficiently long, well-intertwined chains that act similar to a cross-link (without requiring a chemical bond). The entropic elasticity of these materials is a direct result of this intertwined nature.

Typical engineering polymers have molecular weights of about $5 \cdot 10^4$ to $5 \cdot 10^5$ g mol^{-1}. Assuming a macromolecule has a diameter of about 1 cm, each molecule would then be between 3 and 300 m long! However, in practice it is rare to find such a stretched molecule – typically, each molecule is twisted and intertwined with its neighbours. The viscosity of a polymer melt is therefore directly related to the chain length.

Short-chain polymers have a low melt viscosity and are therefore easily processed. However, this very property also means they are not tough, but are weak and susceptible to creep.

The random statistical nature of chemical reactions occurring during polymer synthesis means that each molecule will have a different chain length. A polymeric material will therefore contain macromolecules with a distribution of molecular weights (Figure 1.8).

Figure 1.8 defines n_i as the number of molecules of a particular molecular fraction M_i with a given molecular weight.

The average or mean M_n of the distribution is therefore given by Eq. (1.3):

$$M_\mathrm{n} = \frac{\sum n_\mathrm{i} \cdot M_\mathrm{i}}{\sum n_\mathrm{i}} \tag{1.3}$$

If the distribution of molecular weights is symmetric, then M_n also represents the mode, or most commonly occurring chain length.

The weighted average M_w (Eq. (1.4)) is always greater than the mean M_n, if there is a distribution of molecular weights. In this case,

$$M_\mathrm{w} = \frac{\sum m_\mathrm{i} \cdot M_\mathrm{i}}{\sum m_\mathrm{i}} \tag{1.4}$$

where $m_\mathrm{i} = n_\mathrm{i} \cdot M_\mathrm{i}$. We can now define a polydispersity index (PI) for a polymer that characterizes the non-uniformity of the chain length (Eq. (1.5)):

$$\mathrm{PI} = \frac{M_\mathrm{w}}{M_\mathrm{n}} \tag{1.5}$$

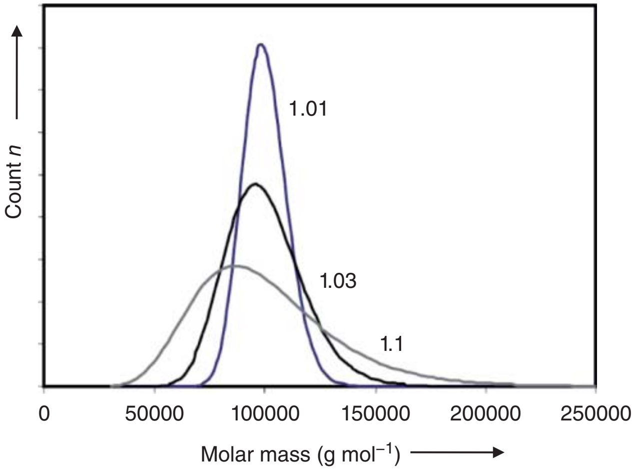


Figure 1.9 Effect of polydispersion index (PI) on the molecular weight distribution. Source: Data from Dealy and Larson (2006).

In practice, polymers often exhibit a PI significantly larger than 1. This suggests a wide distribution of molecular weights.

Figure 1.9 illustrates the effect of the PI (PI = 1.01, 1.03, and 1.10) on the molecular weight distribution, assuming an average molecular weight of 100 000 g mol^{-1}. In typical engineering applications, the PI is usually much greater than 1. This results in an even broader distribution of molecular weights with very small and very large molecules coexisting in the same material.

The molecular weight distribution is controlled in the manufacturing process during the synthesis; the choice of catalyst is particularly important. For example, a metallocene catalyst generally leads to a much narrower molecular weight distribution in polyolefin than a classic Ziegler–Natta catalyst; see Figure 1.10a.

Polymers with a narrow molecular weight distribution have a higher melt viscosity and are therefore commonly used in extrusion processes. Polymers with a wide molecular weight distribution have a lower melt viscosity, due to the existence of a greater number of small molecules. This makes them desirable for injection moulding processes.

The distribution of molecular weights also results in a thermoplastic melt that has non-Newtonian behaviour: the melt viscosity decreases with applied shear velocity (Figure 1.10b), a phenomenon known as shear thinning. This means that a mould is easier to fill when the injection is fast. However, this same property can also lead to defects, such as flash lines in a viscous thermoplastic.

1.2.1.1 Homopolymers and Copolymers

One can differentiate between homopolymers and copolymers on the basis of the number of different constituent monomers or repeat units (Figure 1.11). A homopolymer consists of a single type of monomer or repeat unit. In contrast, a copolymer consists of two or more different types of monomers that together form a polymer chain.

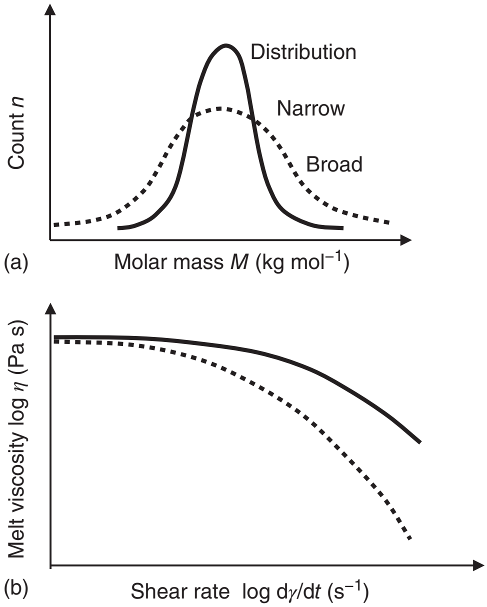


Figure 1.10 (a) Molar mass (molecular weight) distribution and (b) resulting melt viscosity.

For example, pure polystyrene (PS) is a homopolymer. Styrene butadiene (SB) is a copolymer consisting of two different types of monomers, styrene and butadiene. This modification makes SB particularly tough: SB is about three times tougher than PS while maintaining a similar stiffness. However, this comes at the cost of a lower maximum service temperature.

A further modification is acrylonitrile butadiene styrene (ABS), consisting of three different types of monomers. It has a high maximum service temperature similar to that of PS and is about 30% tougher than SB. However, the stiffness of ABS is much lower, with a 50% lower modulus of elasticity than that of PS.

Copolymers are formed by polymerizing various different monomers. The resulting structure can be random, alternating block, or grafted, depending on how the monomers connect with each other; see Figure 1.11.

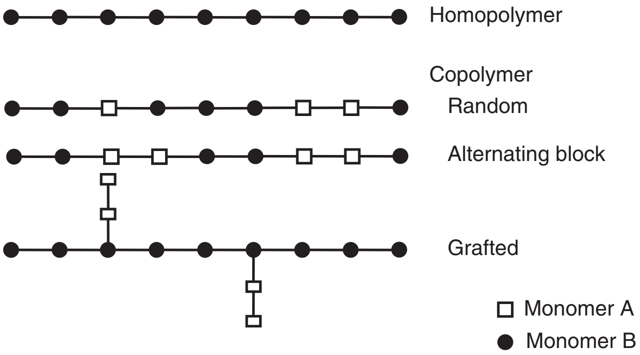


Figure 1.11 Structure of macromolecules.

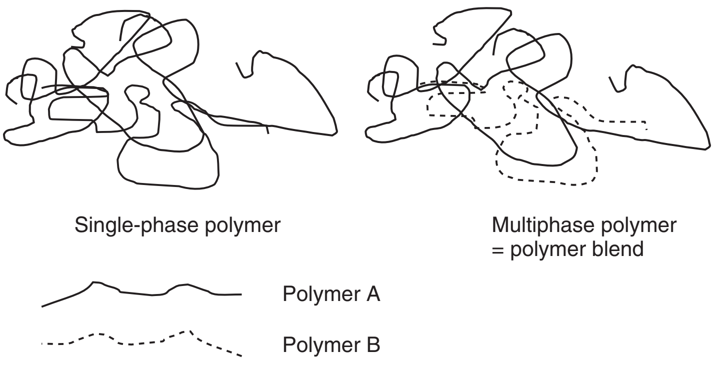


Figure 1.12 Single- and multiphase polymer systems.

1.2.1.2 Polymer Blends

Mixing various polymers to manufacture polymer blends is usually more efficient than developing new chemistries. Compounded blends can be readily found in the market place. The concept is similar to that of a composite material, in that the resulting blend can combine the beneficial properties of the constituent polymers while minimizing the individual disadvantages (Figure 1.12).

For example, although ABS is inexpensive and tough, it has a relatively low maximum service temperature due to its poor thermal stability. By mixing ABS with polycarbonate (PC), the resulting ABS–PC blend can achieve a good thermal stability similar to that of PC at a price comparable to that of pure ABS.

Multiphase systems are characterized by a second discontinuous phase (polymer B) that is dispersed throughout the continuous (polymer A) to form the polymer blend.

The *tacticity* of a polymer refers to the steric order of the monomer units, i.e. how the functional side groups are oriented along the chain. For example, polypropylene (PP) has methyl ($-CH_3$) side groups, while PS has benzene ring side groups. Isotactic polymers have all the side groups arranged regularly on a single side, while the side groups of a syndiotactic polymer alternate (Figure 1.13). The side groups in an atactic polymer are attached randomly.

These stereoregular polymers are synthesized using a stereospecific polymerization reaction that employs appropriate catalysts, e.g. metallocene catalysts.

Iso- and syndiotactic polymers crystallize, while atactic polymers are generally amorphous (Figure 1.14). This means that a typically atactic PS is amorphous and has a glass transition temperature T_g of about 85 °C: the polymer gradually softens above this temperature. However, if a similar polystyrene is isotactic, it will be partially crystalline. Instead of a glass transition temperature, it will therefore exhibit a crystallite melt temperature of about 230 °C. Only at this temperature will the material begin to melt.

Branching of a polymer that can occur during polymerization will restrict crystallization and increase the free volume of the material; these branches also affect the mechanical properties of the polymer. For example, linear PE is highly crystalline, dense, and stiff. However, heavily branched PE is not crystalline and, due to its large free volume, also much softer.

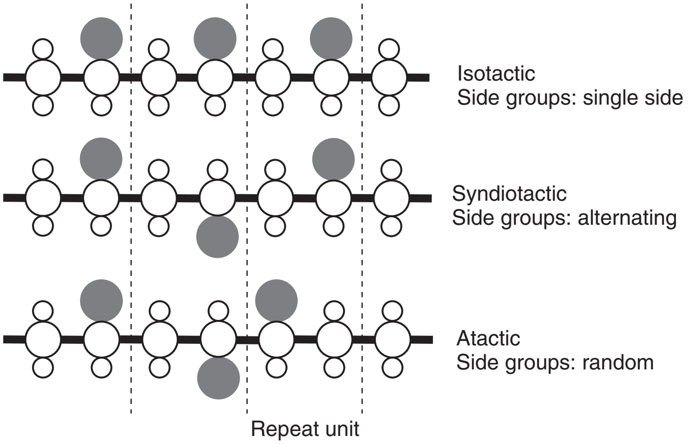


Figure 1.13 Types of steric order or tacticity.

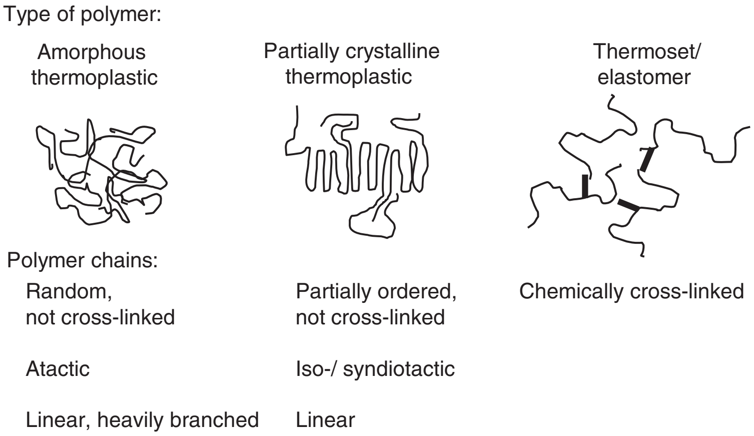


Figure 1.14 Molecular structure of polymers.

1.3 Melting Polymers

Only thermoplastics can be molten, as their polymer chains are not cross-linked. When heating these materials, the polymer chains gain additional mobility due to their increased thermal energy and the material expands. This results in an increase of the free volume, a reduction in density, and a weakening of intermolecular bonds (Figure 1.15).

Upon exceeding the glass transition temperature T_g of an amorphous thermoplastic, the material gradually softens due to the exceedingly mobile polymer chains until the material is liquid. At this point, the polymer chains are free to move and rearrange, and intermolecular bonds are very week. The glass transition temperature corresponds to a kink in the specific volume curve. An amorphous polymer does not have a defined melting point temperature.

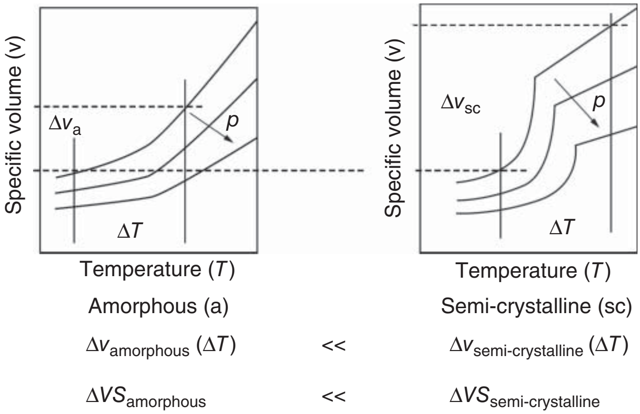


Figure 1.15 Specific volume as a function of temperature and pressure for various thermoplastics (where ΔVS denotes the processing shrinkage).

In contrast, a polymer that is partially crystalline has a defined melting point that corresponds to the temperature at which crystallites melt. At low temperatures, the crystallites consist of regions of lamellar, tightly packed, polymer chains. Upon heating, the free volume in these crystallites expands due to the increasingly mobile polymer chains until the crystallites dissolve completely and the polymer is entirely amorphous; the temperature at which this happens is the melting point. When observed with a hot-stage microscope, the polymer changes appearance from opaque, while partially crystalline, to transparent, once amorphous.

Figure 1.15 illustrates the effect of temperature and pressure on the specific volume. Because these parameters have a greater effect on partially crystalline polymers, one can conclude that these materials are susceptible to greater mould shrinkage when compared to purely amorphous polymers.

1.3.1 Flow Properties of Polymer Melts

Extrusion and injection moulding processes utilize thermoplastic melts. The melt viscosity is therefore a critical materials parameter that determines the processability and limits the mould geometry. Viscosity can be thought of as a material's resistance to flow under a constant load.

Typical processing equipment will shear the melt. Figure 1.16 shows a schematic representation of a viscous melt confined between two stiff boundary plates. The upper boundary plate is pushed to the right, while the lower boundary plate remains stationary. This motion leads to a shear-induced flow with a shear velocity $\dot{\gamma}$ (Eq. (1.6)).

$$\dot{\gamma} = \frac{\mathrm{d}v}{\mathrm{d}y} = \frac{v_{\mathrm{plate}}}{H} \tag{1.6}$$

The shear stress τ between layers in the melt is given by Eq. (1.7):

$$\tau = \frac{F}{A} \tag{1.7}$$

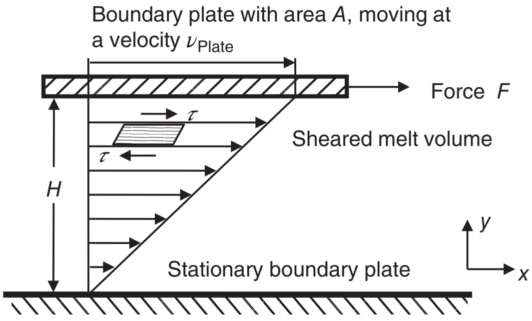


Figure 1.16 Lamellar shear flow.

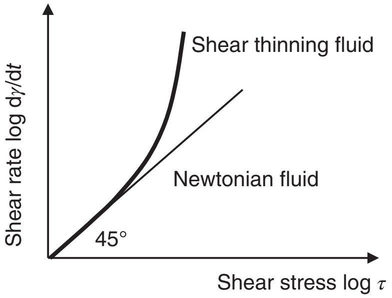


Figure 1.17 Shear rate as a function of shear stress for different fluids.

A Newtonian fluid is the simplest special case, in which the shear stress τ is proportional to the shear velocity $\dot{\gamma}$, i.e.

$$\tau = \eta \cdot \dot{\gamma} \tag{1.8}$$

It denotes:

η	dynamic viscosity of the fluid (Pa s)

The proportionality factor that represents the dynamic viscosity of the fluid (typical units include Pa s or Poise) is often simply referred to as 'viscosity'.

Newtonian fluids have a constant dynamic viscosity η. For example, water has a dynamic viscosity of about 10^{-3} Pa s.

However, polymer melts are typically non-Newtonian: their dynamic viscosity is not constant. Polymers are said to exhibit shear thinning, where their shear velocity increases disproportionately with shear stress, as shown in Figure 1.17.

$$\tau = \eta(\dot{\gamma}) \cdot \dot{\gamma} \tag{1.9}$$

$$\eta(\dot{\gamma}) = \frac{\tau}{\dot{\gamma}} \neq \text{constant} \tag{1.10}$$

Figure 1.18 shows the viscosity η of a polymer melt as a function of shear velocity $\dot{\gamma}$ on a log–log plot.

For low shear velocities, a polymer melt initially behaves Newtonian, with a constant viscosity known as the zero viscosity η_0. However, the viscosity drops upon increasing the shear velocity, an effect referred to as shear thinning. This is