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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 g cm^{-3} for steel and 1.2 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

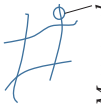


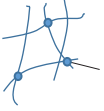

All polymers can be classified as one of four major types: thermoplastic, thermoplastic elastomer (or thermoplastic rubber), elastomer (or rubber), and thermoset (Table 1.1).

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

Table 1.1 Classification of polymeric materials.

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

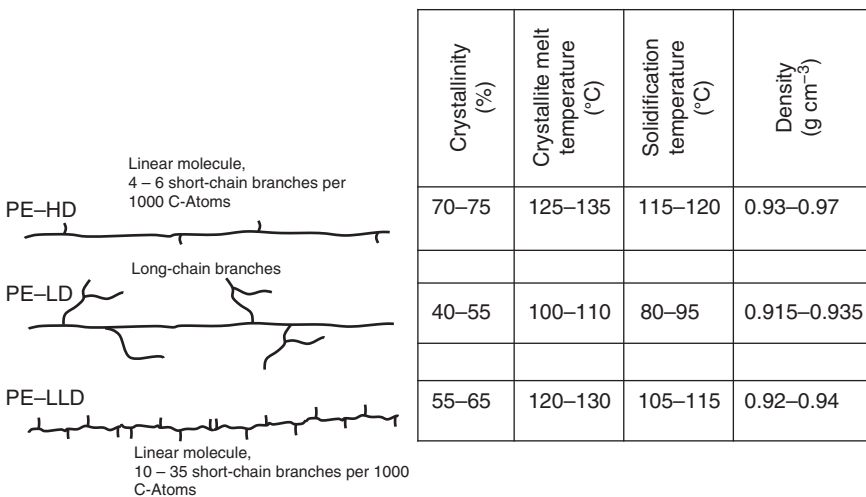


Figure 1.1 Polyethylene (PE) as an example of linear and branched chain molecules.

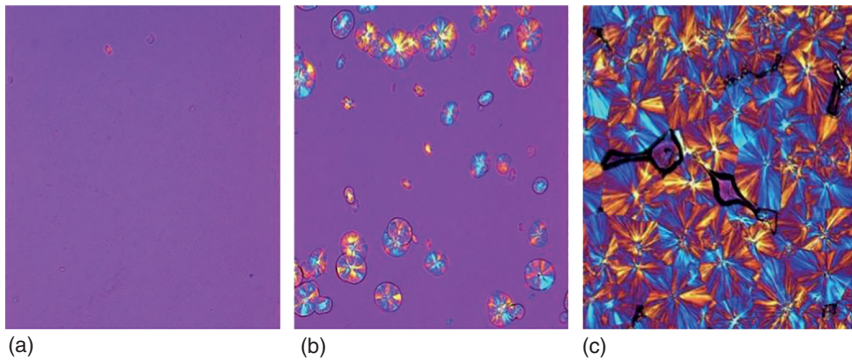


Figure 1.2 Crystallization of isotactic polypropylene (iPP) under isothermal conditions at 135 °C; viewed with a hot-stage microscope. (a) Start of crystallization, (b) after 4 minutes, (c) after 10 minutes.

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 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).

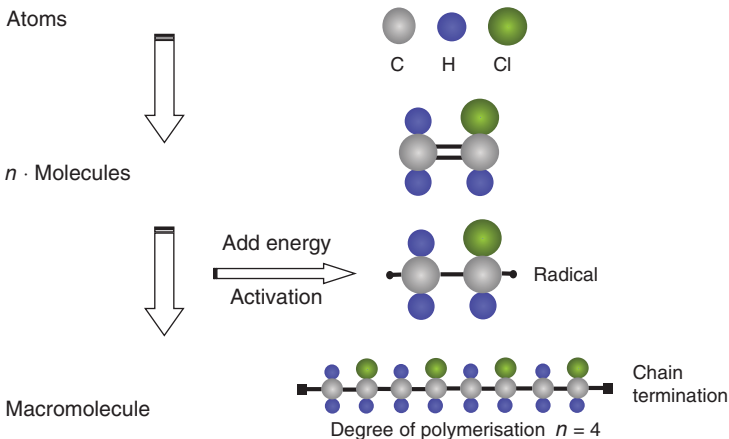
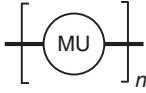


Figure 1.4 Synthesis of polyvinyl chloride (PVC) by radical chain polymerization.

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)).

$$M_{\text{polymer}} = n \cdot M_{\text{monomer}} \quad (1.1)$$

Using the example of polyethylene (PE), the molecular weight of the corresponding monomer ethylene is 28 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 \bar{M} (Eq. (1.2)).

$$\eta = k \cdot \bar{M}^\alpha \quad (1.2)$$

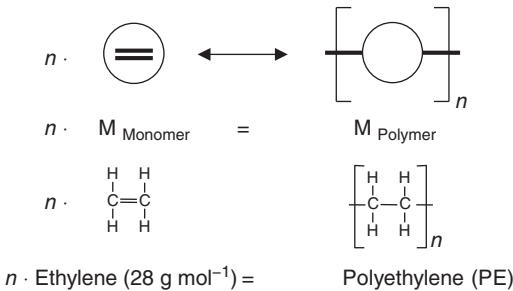


Figure 1.6 Structure of the polymer polyethylene (PE).

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
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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).

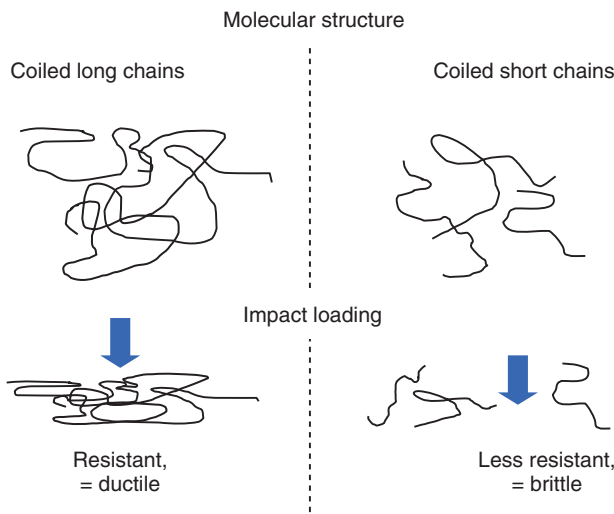


Figure 1.7 Influence of chain length on the material properties.

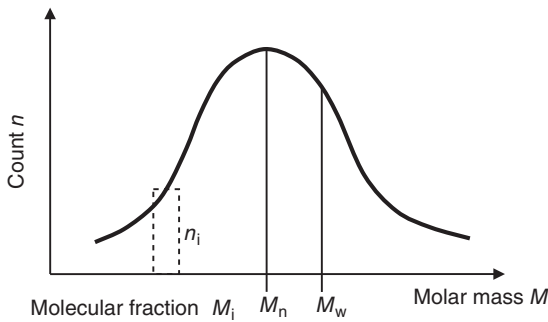


Figure 1.8 Molecular weight distribution.

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 $5 \cdot 10^5 \text{ g mol}^{-1}$. 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):

$$M_n = \frac{\sum n_i \cdot M_i}{\sum n_i} \quad (1.3)$$

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,

$$M_w = \frac{\sum m_i \cdot M_i}{\sum m_i} \quad (1.4)$$

where $m_i = n_i \cdot M_i$. We can now define a polydispersity index (PI) for a polymer that characterizes the non-uniformity of the chain length (Eq. (1.5)):

$$\text{PI} = \frac{M_w}{M_n} \quad (1.5)$$

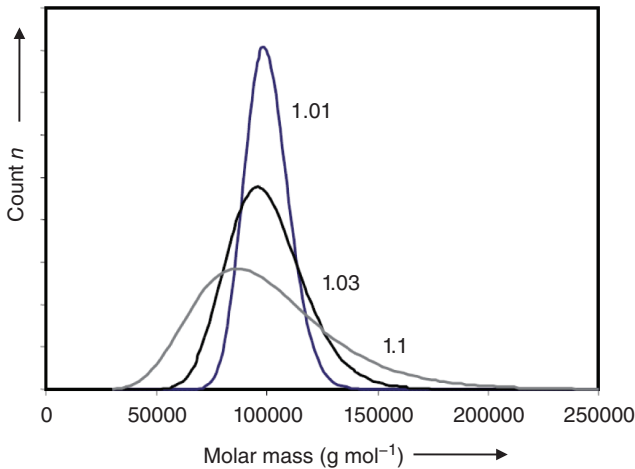


Figure 1.9 Effect of polydispersity index (PI) on the molecular weight distribution. Source: Data from Dealy and Larson (2006).

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 $100\,000\text{ g mol}^{-1}$. 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.

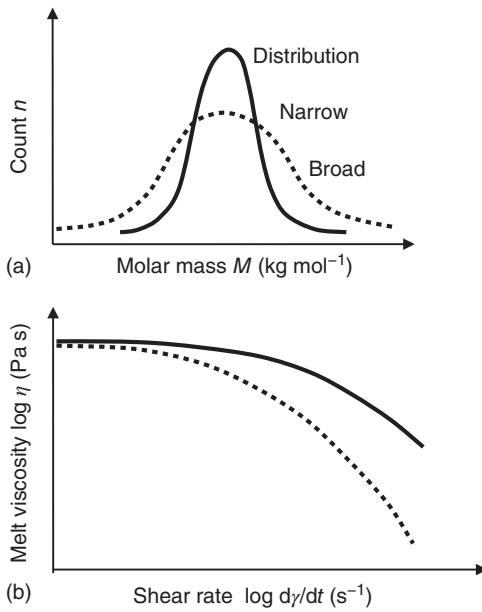


Figure 1.10 (a) Molar mass (molecular weight) distribution and (b) resulting melt viscosity.

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.

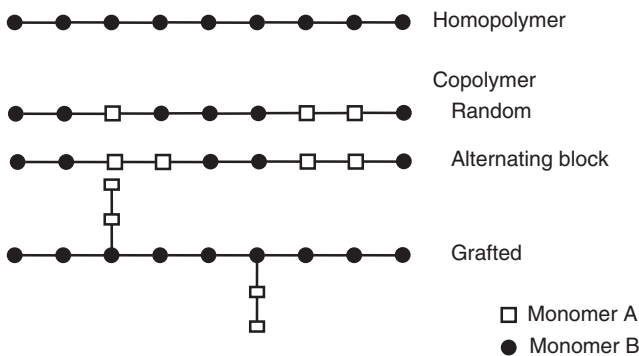


Figure 1.11 Structure of macromolecules.

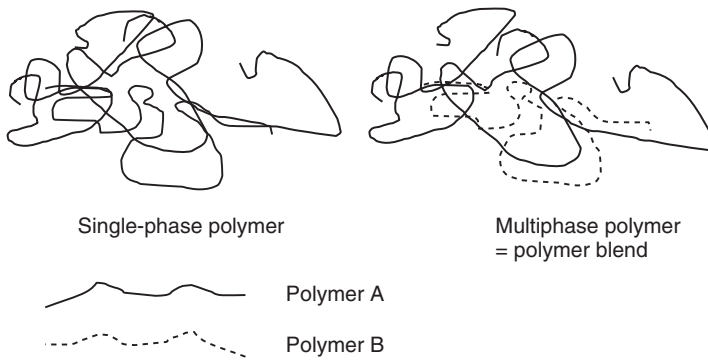


Figure 1.12 Single- and multiphase polymer systems.

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 ($-\text{CH}_3$) 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.

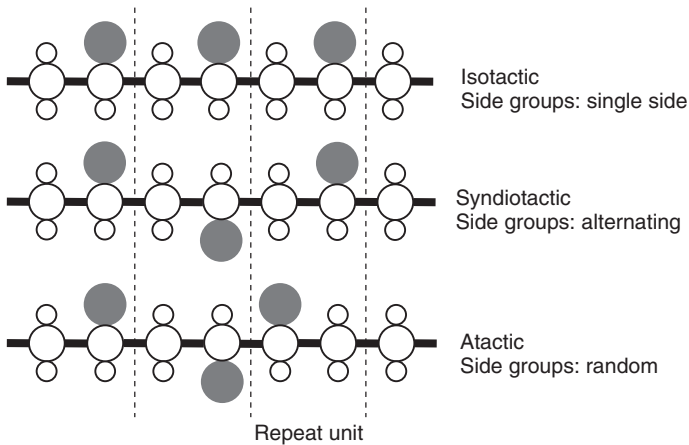


Figure 1.13 Types of steric order or tacticity.

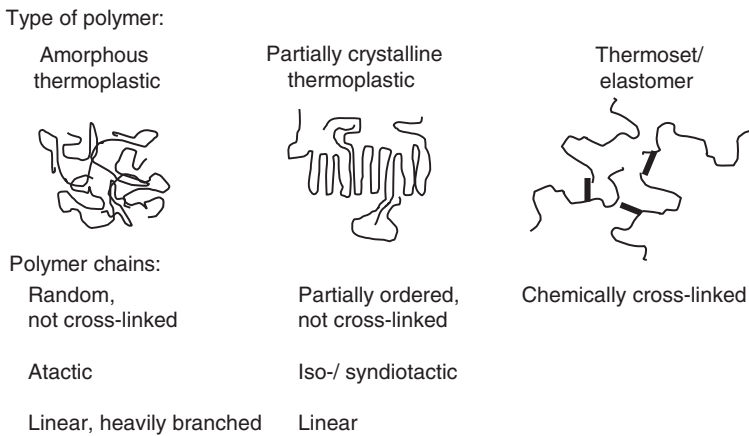


Figure 1.14 Molecular structure of polymers.

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 weak. The glass transition temperature corresponds to a kink in the specific volume curve. An amorphous polymer does not have a defined melting point temperature.

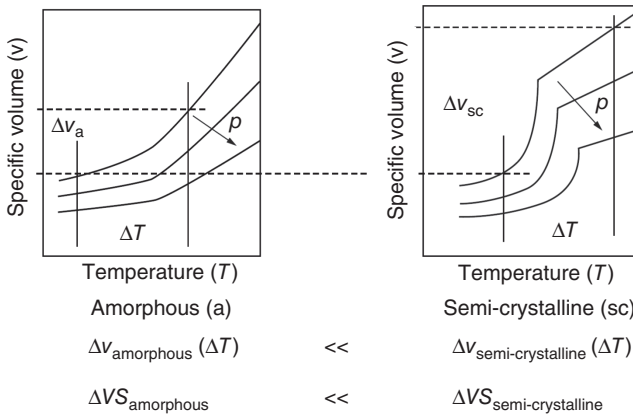


Figure 1.15 Specific volume as a function of temperature and pressure for various thermoplastics (where ΔVS denotes the processing shrinkage).

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)).

$$\dot{\gamma} = \frac{dv}{dy} = \frac{v_{\text{plate}}}{H} \quad (1.6)$$

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

$$\tau = \frac{F}{A} \quad (1.7)$$

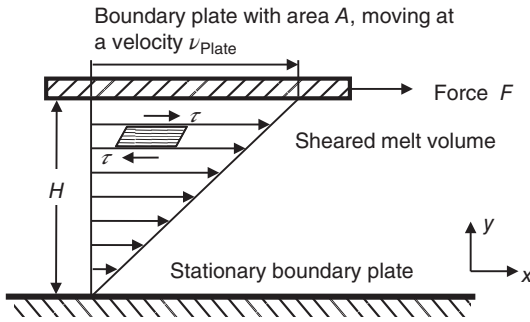


Figure 1.16 Lamellar shear flow.

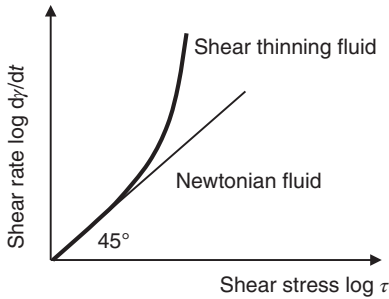


Figure 1.17 Shear rate as a function of shear stress for different fluids.

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)
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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.

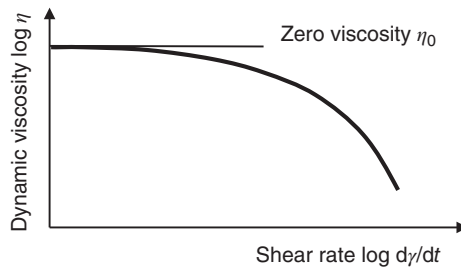
$$\tau = \eta(\dot{\gamma}) \cdot \dot{\gamma} \tag{1.9}$$

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

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

Figure 1.18 Viscosity of shear thinning polymer melt as a function of shear rate.



because it becomes progressively easier for the polymer chains to slip past each other.

1.4 Mechanical Behaviour of Polymers

Polymeric materials are held together by a combination of the strong covalent primary intramolecular bonds within a polymer chain and the weaker secondary intermolecular bonds between different chains. The nature of these secondary intermolecular bonds depends on the chemical structure of the polymer, and can include (in increasing strength) van der Waals forces, dipole–dipole interactions, and hydrogen bonds. Because each type of intermolecular bond has a different strength, polymers exhibit a wide range of mechanical properties. In addition to the nature of the intermolecular bonds, the geometry of the macromolecule is particularly important for plastic deformation, because here the various polymer chains must slide past each other.

Due to the physical nature of the secondary intermolecular bonds, they are necessarily weaker than the primary intramolecular chemical bonds that exist within a macromolecule. Moderately elevated temperatures near room temperature can therefore be sufficient to break some of the secondary bonds without affecting the chemical make-up of the material. The mechanical behaviour of polymers is therefore greatly temperature (and time) dependent.

1.4.1 Relaxation Phenomena

Relaxation processes in polymers or the concept of creep can most easily be described in the case of an amorphous polymer. Amorphous polymers consist of randomly oriented macromolecular polymer chains. These polymer chains are intertwined and interact with each other through intermolecular physical bonds.

At very low temperatures ($T \ll T_g$), where T_g is the glass transition temperature, the polymer chains are largely frozen in place and can therefore not move relative to each other. This means that mechanical stresses can only be accommodated by stretching the strong intramolecular bonds. The material is therefore not only stiff but also brittle (Figure 1.19), and deformation is elastic. Exceeding the strength of the intermolecular bonds will result in a brittle fracture.

The mechanical behaviour becomes more complicated when temperatures approach and exceed the glass transition temperature T_g . The polymer chains become more mobile: individual segments and entire chains can easily twist

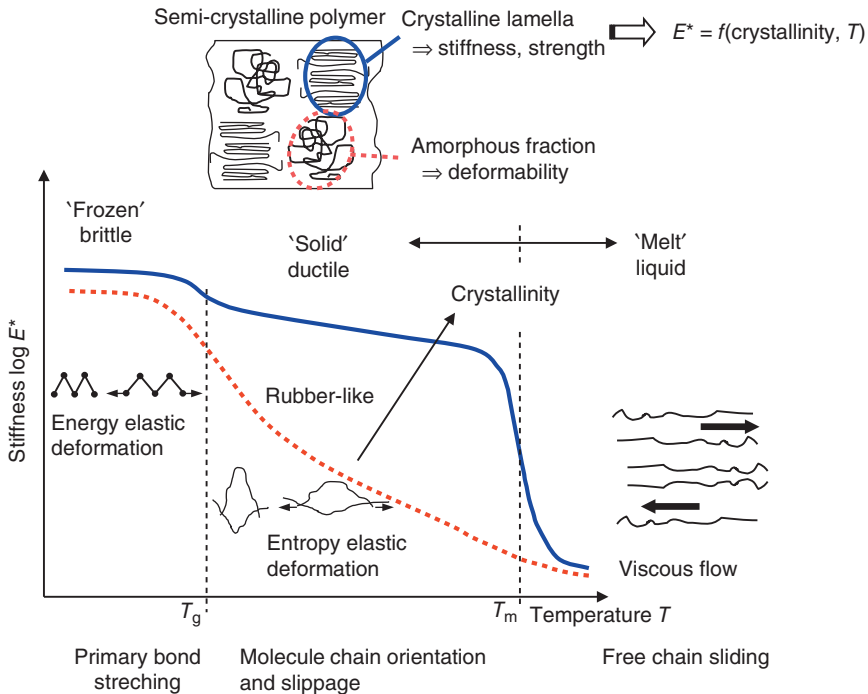


Figure 1.19 Temperature-dependent deformation behaviour of thermoplastics.

and rearrange and it is a thermally activated process. Such a relaxation process can relieve an applied mechanical stress, resulting in plastic deformation (Figure 1.19).

The stiffness E^* of a polymer is a complex number consisting of a storage and loss modulus. Although the stiffness generally decreases with increasing temperature, amorphous and partially crystalline polymers behave differently.

Amorphous and partially crystalline polymers exhibit a glass transition temperature T_g , at which the material begins to soften. However, an amorphous polymer does not have a melting point T_m , which identifies the temperature at which a partially crystalline polymer becomes a viscous melt. Instead, an amorphous polymer gradually changes from a solid that undergoes elastic and plastic deformation to a viscous melt that flows. This means that amorphous plastics are generally limited to an operating or service temperature below T_g .

An amorphous polymer that has only a glass transition temperature (primary transition) will be brittle throughout its service temperature range as the polymer chains are 'frozen'. No mechanical relaxation processes, such as plastic deformation, can occur. Polystyrene (PS) is a good example: it is brittle at any temperature below its primary glass transition at about 90°C (Figure 1.20).

In addition to the primary glass transition, other amorphous plastics like polycarbonate (PC) exhibit a secondary transition (Figure 1.20). In the case of PC, this secondary transition at about -40°C gives the polymer chains enough mobility to partly relieve applied mechanical stress without converting into a

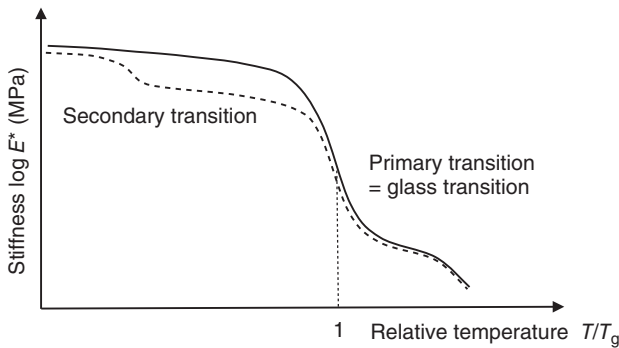


Figure 1.20 Amorphous polymer with and without secondary transition.

viscous melt. PC is therefore an extremely tough plastic between -40°C and its primary transition at about 140°C .

Because partially crystalline polymers contain some amorphous regions, Figure 1.20 also explains why partially crystalline polymers have plastic ductility. The stiff crystallites are embedded in an amorphous polymer matrix. Below the glass transition temperature, all polymer chains in the amorphous matrix are frozen in place and the material behaves in a brittle manner. Upon reaching the glass transition temperature, the amorphous matrix softens, enhancing the ductility (and therefore toughness) of the composite material that still contains stiff crystallites. The mechanical behaviour of a partially crystalline polymer above T_g is therefore a function of the crystallinity, or the volume fraction, of crystallites. The material also has a melting point, which corresponds to the temperature at which the crystallites melt and represents the service temperature ceiling.

Real polymers typically have numerous relaxation mechanisms that manifest themselves at different temperatures. These mechanisms depend on the chemical structure, tacticity, and molecular weight distribution of the material.

1.4.2 Glass Transition Temperature

The physical properties of the crystalline and amorphous regions of a polymer are different. The primary glass transition temperature only affects the amorphous regions of a polymer.

Figure 1.21 shows how the specific volume $v = 1/\rho$ of an amorphous polymer is affected by temperature.

For relatively low temperatures, the specific volume increases with temperature. This is because as the molecules become more energetic, their thermal vibrations increase, and the material expands (thermal expansion).

Upon reaching the glass transition temperature T_g , the specific volume curve exhibits a kink. At this point, the secondary intermolecular bonds between molecules begin to break down and the polymer chains become increasingly mobile. The additional thermal energy allows the molecules to rearrange without any externally applied mechanical stress. These fluctuations form a free volume

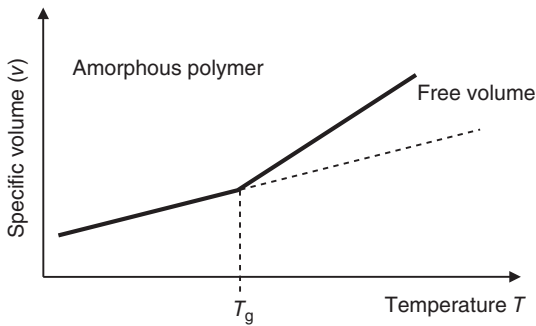


Figure 1.21 Specific volume as a function of temperature for an amorphous polymer.

that increases the thermal expansion of the material. Further heating will increase the ease with which molecules can slide past each other, and result in a viscous melt.

1.4.3 Melting

All thermoplastics can be melted due to the absence of cross-links. Since a softened amorphous thermoplastic transforms gradually into a viscous melt upon heating, it does not exhibit a melting point temperature. This contrasts with a partially crystalline thermoplastic, which has a melting point corresponding to the temperature at which the tightly packed crystalline lamellae melt (crystallite melting temperature). However, because different crystallites melt at slightly different temperatures based on the crystallite size distribution, the melting 'point' is diffuse and can span several degrees; it must be determined experimentally.

Many partially crystalline polymers follow a phenomenological relationship between the glass transition temperature T_g and the crystallite melt temperature T_m (Eq. (1.11)):

$$T_g \approx 0.6 \cdot T_m \quad (1.11)$$

The glass transition temperature and the crystallite melt temperature are controlled by the molecular weight, which in turn also dictates the viscosity of the melt and the crystallinity of the corresponding solid (Figure 1.22).

Low-molecular-weight polymers tend to have a low viscosity melt; increasing the molecular weight results in an increase in the viscosity.

Extremely high-molecular-weight polymers practically cannot be melted and can therefore not be melt processed or injection moulded: these materials must be sintered. One common example is ultrahigh-molecular-weight polyethylene (PE-UHMW) with a molar mass of at least $1\,000\,000\text{ g mol}^{-1}$.

The covalent network of a large, cross-linked polymer results in a stiff material that is thermally stable and cannot be melted. Instead, such a material decomposes upon reaching the upper limit of the service temperature range.

1.4.4 Solidification

Solidification of a molten polymer is thermodynamically the reverse of melting a solid. Crystallizing a polymer requires a certain undercooling so that

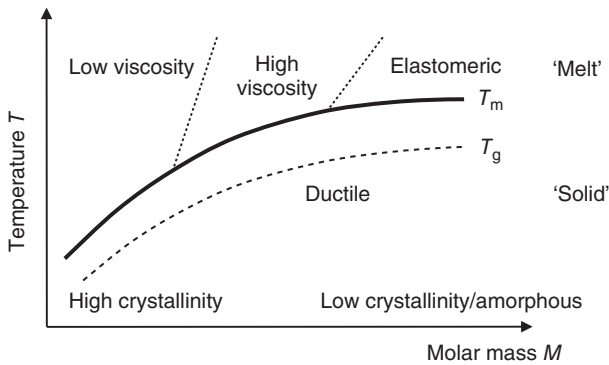


Figure 1.22 Effect of molar mass and respective chain length on the physical behaviour (schematic).

crystallization or nucleation sites can form. These sites act as ‘seeds’ around which, given the necessary thermodynamic conditions, crystals or spherulites can grow. These spherulites grow until they impinge on each other, at which point the entire material has solidified (Figure 1.23).

If the crystallization conditions are isotropic, crystallites will grow uniformly in all three dimensions; the result is a spherical crystallite or ‘spherulite’ (Figure 1.24).

Crystallization is an exothermal process, i.e. heat is released. The macromolecules rearrange from a disordered melt into an ordered solid: this increase in order corresponds to a decrease in entropy. The macromolecules fold into lamellae that form crystalline regions. If the solidification conditions are isotropic, these regions are spherically symmetrical spherulites (3D symmetry); alternatively, shear-induced crystallization conditions lead to ‘shish-kebab-like’ oriented crystallinity (2D symmetry) (Figure 1.25).

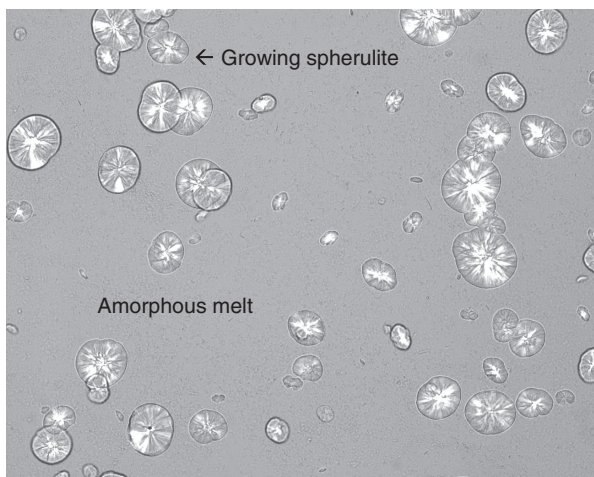


Figure 1.23 Isothermal crystallization of polypropylene at 135 °C after four minutes.

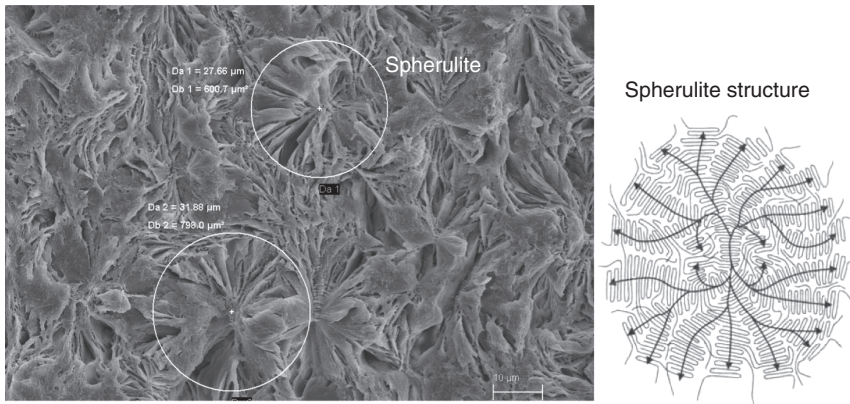


Figure 1.24 Scanning electron microscope (SEM) image showing the spherulitic structure of copolymeric polyacetal (POM); inset shows a schematic representation of a spherulite.

The rate of crystallization is constant at a given temperature (isothermal crystallization), and can therefore be experimentally determined by measuring the diameter of the spherulites; this is achieved by observing the crystallization process using a hot-stage optical microscope.

The rate of crystallization ν (in units of $\mu\text{m min}^{-1}$) is given by the following empirical equation:

$$\log \nu = 10.7 - 2.3 \cdot \frac{T_m}{T} \left(\frac{T_m}{T_m - T_g} + \frac{50}{T_m - T} \right) \quad (1.12)$$

It denotes:

T	temperature (K)
ν	crystallization speed ($\mu\text{m min}^{-1}$)

When $T = 0$ or $T = T_m$, $\nu = 0$, and no crystallization takes place. However, the maximum rate of crystallization, ν_C , occurs at a crystallization temperature $T = T_C$ that lies between T_g and T_m . This crystallization temperature can be approximated as (Eq. (1.13)):

$$T_c \approx \frac{T_g + T_m}{2} \quad (1.13)$$

For example, we can estimate T_C for isotactic PP as 80°C , which represents a highly undercooled PP melt. This contrasts with an experimentally determined crystallization temperature of about 105°C obtained with a cooling rate of 20 K min^{-1} .

If crystallization occurs between T_C and T_m , there is a risk that crystals remelt; this risk is greatest close to T_m . The remaining crystallites then grow at their expense, resulting in a solid that consists of relatively few, large remaining crystallites. This well-ordered morphology is brittle. In order to reduce a polymer's brittleness, nucleation agents or additives are often added during processing; these

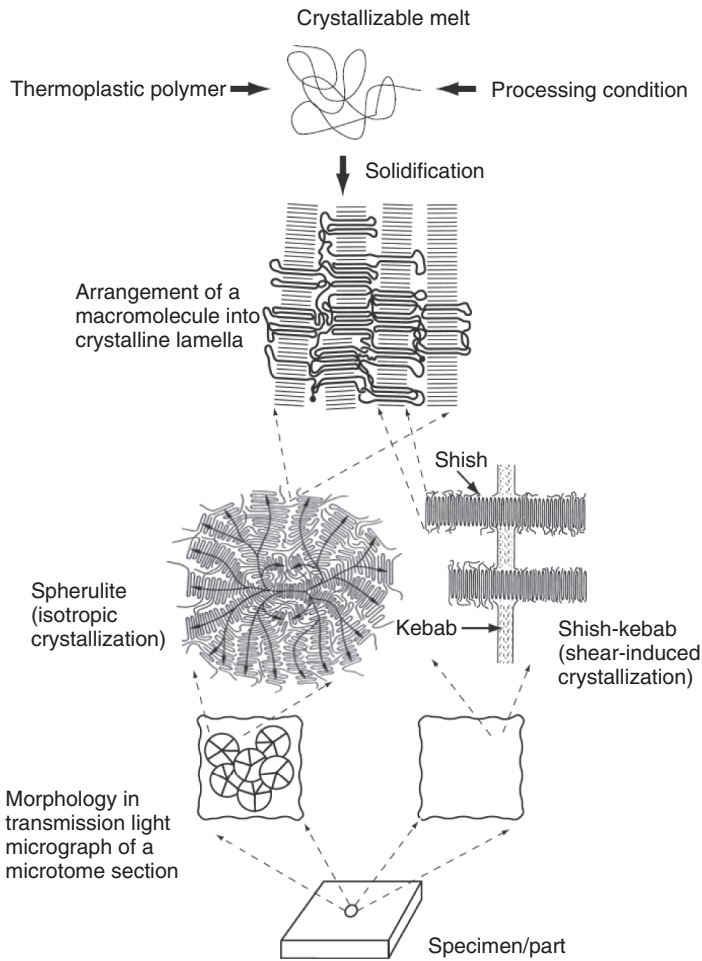


Figure 1.25 Solidification of a crystallizable polymer and the resulting microstructures.

result in a tough material with many small crystallites. Any necessary tempering should occur close to T_C .

Whether a particular polymer can crystallize depends largely on the molecular structure and its symmetry. For example, linear PE or polyacetal (POM) is easier to crystallize than PS. The large benzene ring side groups of the polystyrene prevent a dense packing of the molecular chains (due to steric hindrance) and is therefore very difficult to crystallize (Figure 1.26).

PS can only be crystallized if the particular grade has high stereoregularity, i.e. it is highly isotactic or syndiotactic. This necessary high degree of stereoregularity has only recently been made possible thanks to the advent of metallocene catalysts used during polymer synthesis (Figure 1.27).

A syndiotactic polymer chain allows neighbouring molecules to fit together like a zipper, resulting in a dense structure with strong intermolecular bonding: crystalline lamellae will form.

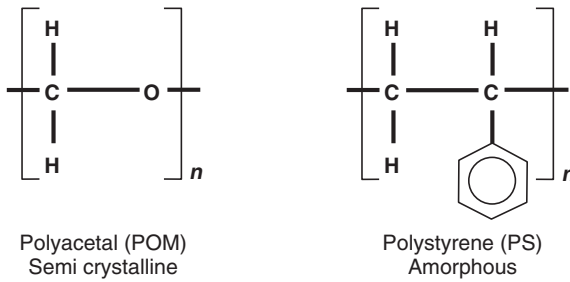


Figure 1.26 Comparing the structural formulae of polyacetal and polystyrene.

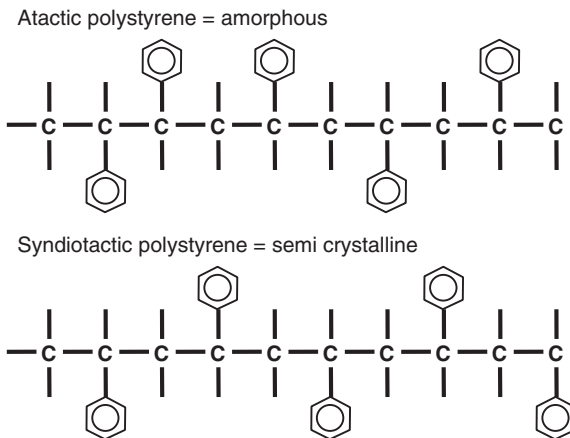


Figure 1.27 Atactic and syndiotactic polystyrene (PS) – chain build-up (schematic).

Due to steric hindrance, the distance between atactic polymer chains is necessarily much larger and the intermolecular interactions therefore much weaker. Atactic PS can therefore not crystallize.

1.4.5 Time-Dependent Deformation

The mechanical deformation of polymers is time dependent. Although this time dependence is observable at room temperature, it becomes more pronounced at higher temperatures.

A constant mechanical stress σ_0 instantaneously applied on a polymer at time t_0 will result in a time-dependent strain $\varepsilon(t)$ (Figure 1.28): the strain will instantaneously jump to a value ε_0 and then gradually increase with time.

Removing the applied stress at time t_1 will cause the strain to instantaneously relax by an amount ε_0 and then gradually diminish further according to an exponential decay function. We can define the retardation time τ_{ret} as the time necessary to decrease the strain by $1/e$.

In this example, there is no permanent deformation and the strain returns to zero. Such behaviour is observed in highly cross-linked elastomers, which exhibit time-dependent elastic deformation that is fully recoverable. This compares to thermoplastic plastics, which will not fully recover and instead deform permanently.

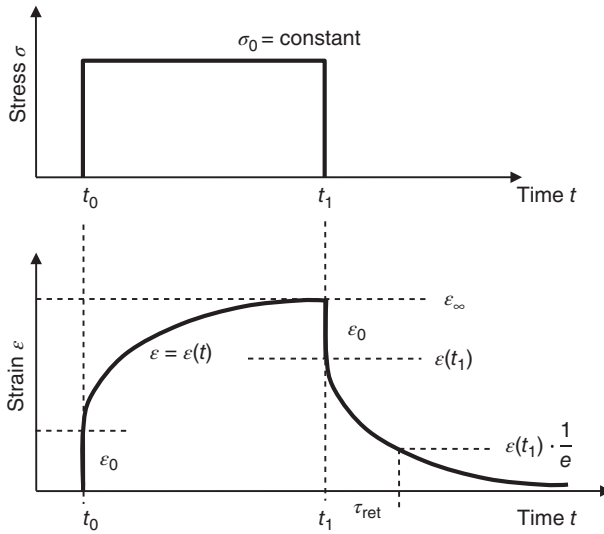
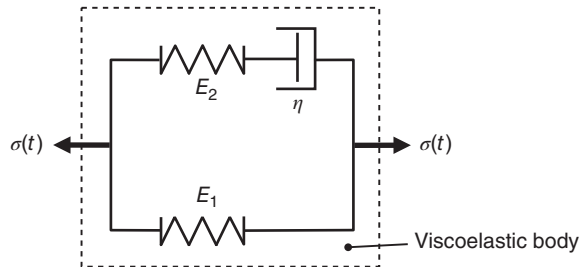


Figure 1.28 Time-dependent deformation of a polymer upon sudden mechanical loading and load recovery.

Figure 1.29 Model of a viscoelastic material according to Poynting–Thomson.



We can model such time-dependent deformation using a combination of two springs with elastic constants E_1 and E_2 and a dashpot with viscosity η (Figure 1.29).

This model predicts two constraints:

- (a) Short-term load applied rapidly ($\Delta t \rightarrow 0$) or at low temperature ($T \ll T_g$):
 → *Polymer is stiff*,
 Because the viscosity of the dashpot $\eta \rightarrow \infty$ so that the resulting elastic modulus of the material $E_{\text{total}}(0) = E_1 + E_2$.
- (b) Long-term load applied slowly ($\Delta t \rightarrow \infty$) or at high temperature ($T \gg T_g$):
 → *Polymer is compliant*
 Because the viscosity of the dashpot $\eta \rightarrow 0$ so that the resulting elastic modulus of the material is only $E_{\text{total}}(\infty) = E_1$.

This time-dependent mechanical behaviour of polymers therefore includes relaxation and retardation mechanisms in the material.

The stress $\sigma(t)$ in a polymer under constant strain follows a time-dependent Hooke's law:

$$\sigma(t) = \epsilon_0 \cdot E(t) \tag{1.14}$$

The stress decreases by a stress relaxation amount $\Delta\sigma = \sigma(0) - \sigma(\infty)$ so that, for a viscoelastic material:

$$\sigma(0) = \epsilon_0 \cdot (E_1 + E_2) \tag{a}$$

$$\sigma(\infty) = \epsilon_0 \cdot E_1 \tag{b}$$

For example, this stress relaxation must be considered when laminating polymer composites, because the joint pressure decreases with time.

Alternatively, one can express the strain $\epsilon(t)$ under constant load that also follows a time-dependent Hooke's law:

$$\epsilon(t) = \frac{\sigma_0}{E(t)} \tag{1.15}$$

The strain increases by a retardation or creep amount $\Delta\epsilon = \epsilon(0) - \epsilon(\infty)$, where

$$\epsilon(0) = \frac{\sigma_0}{E_1 + E_2} \tag{a}$$

$$\epsilon(\infty) = \frac{\sigma_0}{E_1} \tag{b}$$

For example, this creep must be considered in plastic components that are statically loaded, as they will gradually deform. Figure 1.30 summarizes the time-dependent relaxation and creep behaviour in polymers.

The time-dependent modulus of elasticity under constant load is known as the creep modulus E_c , defined as (Eq. (1.16)):

$$E_c(t) = \frac{\sigma}{\epsilon(t)} \tag{1.16}$$

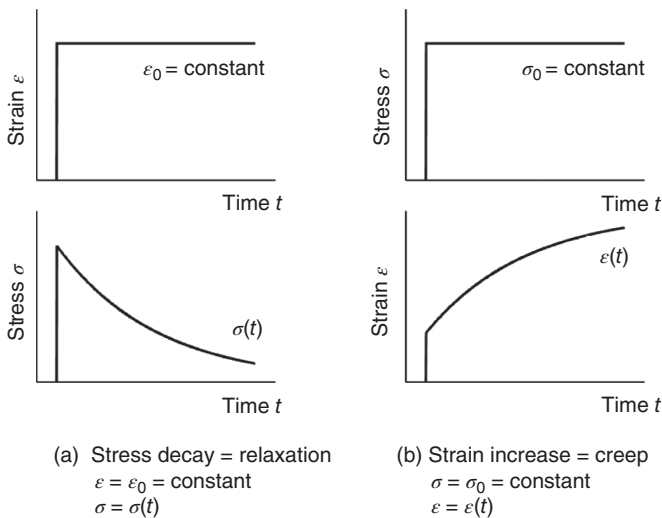


Figure 1.30 (a) Relaxation and (b) creep in polymers.

Similarly, the time-dependent modulus of elasticity under constant strain is known as the relaxation modulus E_r , defined as (Eq. (1.17)):

$$E_r(t) = \frac{\sigma(t)}{\epsilon} \quad (1.17)$$

This time-dependent mechanical deformation behaviour has important practical consequences. Polymers used in extended constant load applications may creep such that the resulting deformation exceeds the design specifications and renders the plastic component unserviceable. Similarly, constant strain applications can result in stress relaxation (e.g. loss of prestresses) that can also result in inadequate long-term material performance.

Isochronous stress–strain curves can be used to describe the time-dependent behaviour of polymeric materials. Such graphs illustrate the relationship between stress and strain for different loading times, t , usually measured in hours. These relationships are phenomenologically determined using relaxation and creep experiments at constant temperature T . Figure 1.31 shows isochronous stress–strain relationships for a particular polymer at temperature T_1 and T_2 , where T_2 is larger than T_1 .

When a polymeric sample is subjected to a constant stress σ_0 at a temperature T_1 (= creep experiment at $T = T_1$), the resulting strain at an initial time t_1 is $\epsilon(t_1)_{T_1}$. If the stress is maintained for a time $\Delta t = t_3 - t_1$, the strain will increase from $\epsilon(t_1)_{T_1}$ to $\epsilon(t_3)_{T_1}$; this is creep.

Alternatively, if the same sample had instead been subjected to a higher temperature T_2 , the same stress σ_0 would have resulted in a larger strain $\epsilon(t_1)_{T_2}$ at initial time t_1 . This larger strain at higher temperature is due to the reduced stiffness of the material, which in turn increases the creep rate.

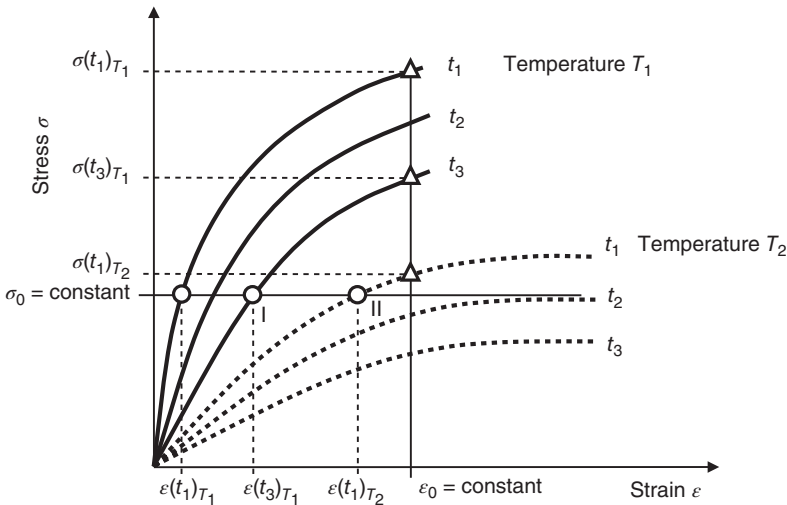


Figure 1.31 Isochronous stress–strain curves for various times t and temperatures T_1 and T_2 ($T_1 < T_2$).

At point I, the average strain rate is given by

$$\dot{\epsilon}_I = \frac{\Delta\epsilon_I}{\Delta t} \quad (1.18)$$

At elevated temperature, the average strain rate at point II increases to

$$\dot{\epsilon}_{II} = \frac{\Delta\epsilon_{II}}{\Delta t} \quad (1.19)$$

We find that under constant load,

$$\dot{\epsilon}_{II} > \dot{\epsilon}_I \quad \text{and} \quad T_2 > T_1$$

A higher temperature therefore leads to a higher strain rate. In this case, the strain rate is so high that an additional time $\Delta t = t_3 - t_1$ would cause the material to deform beyond the limit shown in the graph.

The same Figure 1.31 can also be used to illustrate the stress relaxation behaviour of a polymeric material: if a sample at temperature T_1 is subjected to a constant strain ϵ_0 , then the stress at initial time t_1 is $\sigma(t_1)$. Maintaining the constant strain for a time $\Delta t = t_3 - t_1$ causes the stress to reduce by $\Delta\sigma$ to $\sigma(t_3)$; this is stress relaxation.

Increasing the temperature from T_1 to T_2 will accelerate the stress relaxation and lower the stress further.

1.4.6 Time Dependence and Thermal Activation

The time-dependent deformation behaviour in polymers is the result of thermally activated relaxation processes. The probability P for such a relaxation process can be approximated by an exponential relationship:

$$P \sim \exp\left(\frac{-Q}{k \cdot T}\right) \quad (1.20)$$

where Q is the activation energy barrier for the relaxation process, k is Boltzmann's constant, and T is the temperature in Kelvin. A polymer chain segment must overcome the energy barrier Q before it can move past its neighbour, thereby exchanging places and deforming the material.

In the case of a viscoelastic deformation under constant load σ_0 , dominated by a single relaxation process with activation energy Q , the strain rate $\dot{\epsilon} = d\epsilon/dt$ is therefore given by

$$\dot{\epsilon} = A \cdot \exp\left(\frac{-Q}{k \cdot T}\right) \quad (1.21)$$

This expression corresponds to the Arrhenius equation for chemical reaction kinetics. For example, increasing the temperature by 10 K approximately doubles the reaction rate, so that

$$v_{T_2} = 2 \cdot v_{T_1} \quad \text{for} \quad \Delta T = T_2 - T_1 = 10 \text{ K} \quad (1.22)$$

Since the strain rates are different, the same final strain ϵ for two identical samples at different temperatures, T_1 and T_2 , will be obtained at different times, t_1

and t_2 , respectively, such that

$$t_1 \cdot \dot{\epsilon}_1 = t_2 \cdot \dot{\epsilon}_2 \quad (1.23)$$

So we find that

$$\frac{t_1}{t_2} = \exp\left(\frac{-Q}{k \cdot T} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right) \quad (1.24)$$

However, at temperatures near the glass transition temperature T_g and above, this expression no longer applies. This is because at such elevated temperatures, deformation is dominated by the slippage of molecular chains past each other, and the previously described relaxation processes become negligible. In that case,

$$\frac{t_1}{t_2} = \exp\left(\frac{\ln 10 \cdot C_1 \cdot (T_2 - T_1)}{C_2 + (T_2 - T_1)}\right) \quad (1.25)$$

For $T_1 = T_g$, one can assume the constants for all amorphous polymers as approximately

$$C_1 = 17.5 \text{ K}$$

$$C_2 = 52 \text{ K}$$

This expression is known as the empirical Williams–Landel–Ferry (WLF) equation.

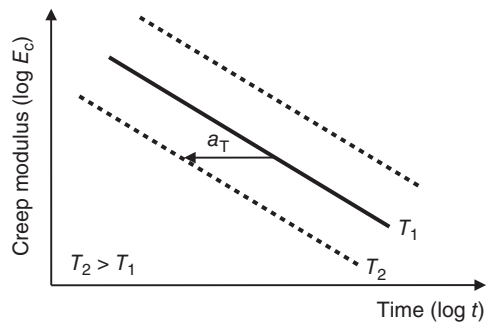
A second way of representing viscoelastic deformation is by plotting the creep modulus as a function of time (in hours) for a temperature T_1 (Figure 1.32). Increasing the temperature to T_2 will cause the curve to shift horizontally by an amount

$$a_T = \log \frac{t_1}{t_2} = \log(t_1/\text{hours}) - \log(t_2/\text{hours}) \quad (1.26)$$

This time–temperature superposition principle allows us to derive master curves for a reference temperature over an experimentally impractical time or frequency range. It becomes possible to predict behaviour in the kilohertz range (very short time) as well as extremely long-term behaviour (over months or years) without having to actually perform experiments at those timescales.

For example, a mechanical spectrometer can be used to determine the complex elastic stiffness modulus E^* of a polymer over a narrow frequency range of four orders of magnitude $\Delta f = f_2 - f_1$. In this case, the modulus can be determined

Figure 1.32 Time–temperature superposition principle of the creep modulus.



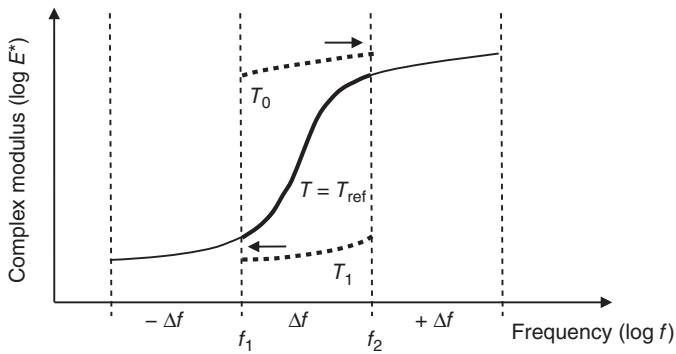


Figure 1.33 Determining a master curve using the time–temperature superposition principle.

at three different temperatures, T_0 , T , and T_1 , inside this frequency range (Figure 1.33). The time–temperature superposition principle can then be used to shift the low-temperature curve T_0 toward the high-frequency range and the high-temperature curve T_1 toward the low-frequency range. In this way, a master curve at reference temperature $T = T_{\text{ref}}$ can be obtained for a much wider frequency range of $\Delta f \pm \Delta f$, spanning 12 orders of magnitude. Direct experimental measurement over such a wide frequency (or time) range would be extremely impractical.

1.5 Uniaxial Stress–Strain Behaviour

Each plastic has a different mechanical behaviour that is time and temperature dependent. However, for illustrative purposes, we discuss the rapid loading of an amorphous polymer. At a temperature $T \ll T_g$, the intermolecular bonds are so strong and the specific volume so small that molecular chains cannot slide past each other. A mechanical load will elastically stretch the chains and no plastic deformation takes place. If the load is increased further, exceeding the strength of the material, brittle fracture takes place as the macromolecular chains break (Figures 1.34 and 1.35).

However, at temperatures near the glass transition temperature, e.g. $T \approx 0.8 T_g$, the polymer is softened and the molecular chains are somewhat mobile. This increased mobility allows the material to undergo limited plastic deformation.

Figure 1.35 shows the engineering stress–strain behaviour of a ductile amorphous polymer under uniaxial load. The initial load causes the sample to elongate elastically. However, upon exceeding the yield stress σ_y , necking begins as the molecular chains begin to reorient, slide past each other, and the sample deforms plastically. The neck is a local region of reduced cross-sectional area. The engineering stress, defined as the load per original cross-sectional area, drops; the true stress, defined as the load per actual cross-sectional area, remains at least constant or increases with increased necking.

As the sample is elongated, the molecular chains are stretched and oriented in parallel, which causes the material to stiffen. This explains the increasing slope of

Figure 1.34 Strength properties of an amorphous polymer (e.g. PS) at low temperature ($T < T_g$) and near the glass transition temperature T_g ($T \approx 0.8 T_g$).

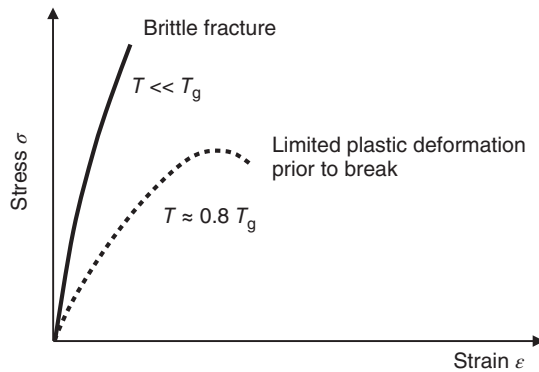
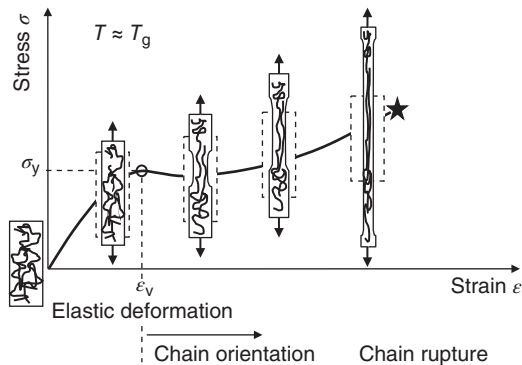


Figure 1.35 Mechanical behaviour of a ductile, amorphous polymer (e.g. PC) under uniaxial tension.



the engineering stress–strain graph. Further loading of these highly oriented and stretched molecular chains causes them to break and the sample to fail.

Figure 1.36 shows the true stress–strain behaviour of a partially crystalline polymer under a quasi-static uniaxial tension load. Each curve differs in the molecular weight M of the samples, where $M_I \ll M_{II}$, so that the crystalline lamellae are also different in size.

During initial loading, the amorphous regions of the partially crystalline polymer are stretched and plastically deformed. If the polymer has a low-molecular weight M_I and correspondingly short chains, then minor stretching is sufficient to break the chains and form voids. These voids grow in size and number and the polymer is crazed. Further loading causes the voids to coalesce and the material to tear.

However, a larger molecular weight M_{II} implies longer polymer chains with more entangled amorphous regions and larger crystalline lamellae. In this case, chains can be partially pulled out of the crystalline lamellae, improving the toughness and increasing the plastic deformation that can be accommodated in the material.

1.5.1 Elastic Properties

Each plastic has different and unique temperature-dependent stiffness properties (Figure 1.37). Nevertheless, it is still possible to describe general trends.

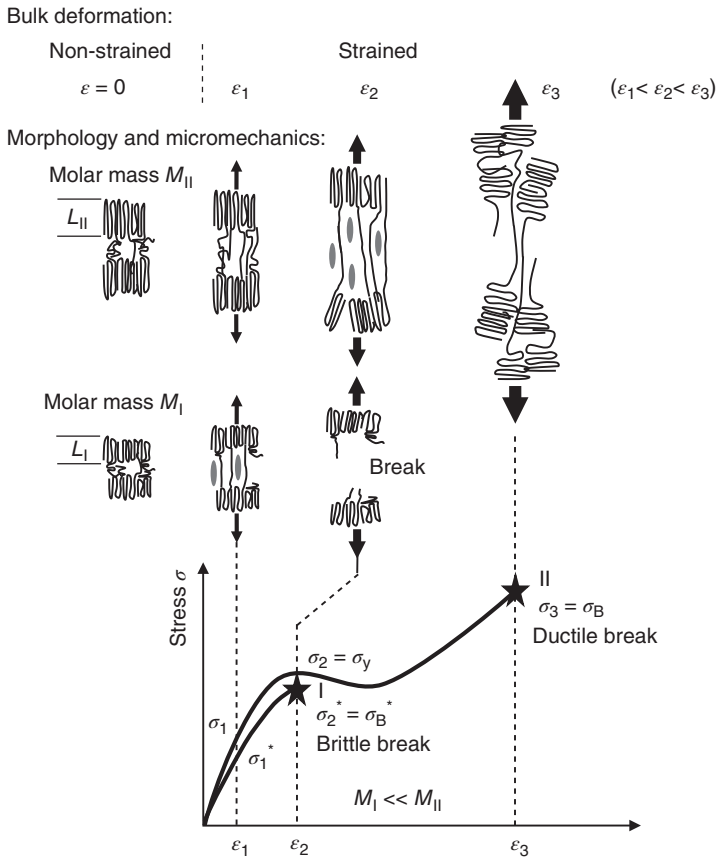


Figure 1.36 Mechanical behaviour of partially crystalline polymers under uniaxial tension; effect of molecular mass on the large strain deformation behaviour (schematic).

All polymeric materials are brittle at low temperatures, since their molecular chains are essentially ‘frozen’ in place and have limited mobility. Upon reaching the glass transition temperature, T_g , the materials soften and become less stiff; thermoplastics enter a viscous melt. For amorphous polymers, this transition is gradual; while for partially crystalline polymers, the more clearly defined melting point coincides with the melting of the last crystallite. Above the glass transition temperature, stiff crystallites (phase c) are embedded in a compliant amorphous matrix (amorphous phase a (Figure 1.37)). The crystallites ultimately melt upon reaching the melting point. While molten, all thermoplastics are viscous liquids due to relatively mobile molecular chains.

This behaviour contrasts with that of cross-linked polymers, such as thermosets and elastomers. These materials cannot be melted, because the chemical bonds forming their cross-linked networks are too strong. Further heating will eventually break these bonds, but at this point, the material is degraded and irreversibly damaged: they decompose.

Elastomers are both amorphous and cross-linked. Other than their high-temperature decomposition in lieu of melting, they behave similar to amorphous thermoplastics. In addition, elastomers typically have a lower glass transition temperature, well below room temperature. In the ‘frozen’ energy elastic region, both types of polymers have a shear modulus G on the order of about 1000 MPa. However, upon reaching the glass transition temperature, this value drops to about 10 MPa. The stiffness of unreinforced amorphous polymers drops by about 10 orders of magnitude between the energy elastic and entropy elastic phases. This explains why elastomers are limited to a service temperature above that of the glass transition temperature, because otherwise they lose their ‘rubbery’ property. In addition, amorphous polymers used for structural applications are limited to service temperatures below T_g , for otherwise they lose their stiffness.

The modulus of elasticity E can be calculated using a Poisson’s ratio ν , of about 0.5 for elastomers and about 0.35 for other polymers, and the following expression:

$$\frac{E}{G} = 2 \cdot (1 + \nu) \tag{1.27}$$

It denotes:

G	shear modulus (MPa)
-----	---------------------

This expression yields an elastic modulus of about 3000 MPa for a typical polymer under the glass transition temperature, consistent with practical observations.

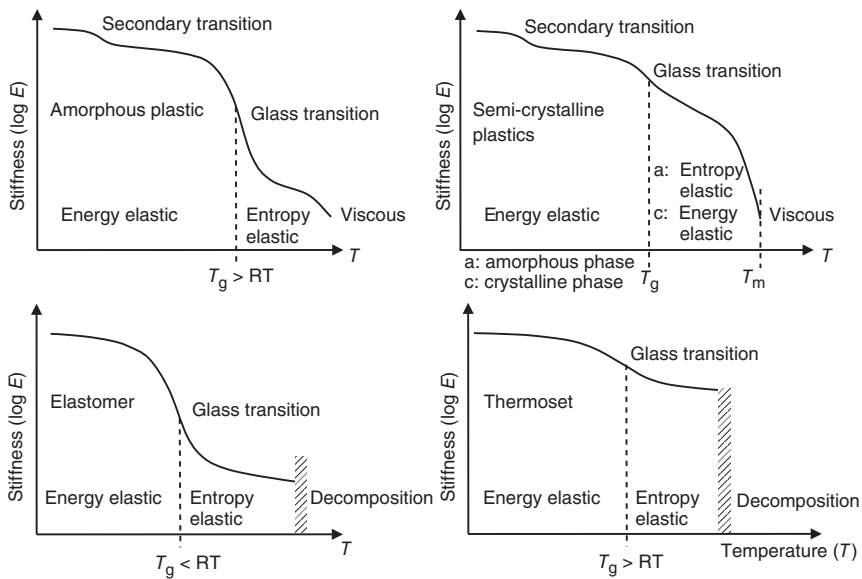


Figure 1.37 Change of stiffness E as a function of temperature T for various types of polymers.

The elastic behaviour of partially crystalline polymers can be understood by modelling these materials as two-phase composites: a matrix of amorphous polymer in which a reinforcing crystalline phase is embedded. The stiffness of this composite is dominated by the properties of the amorphous matrix at temperatures below the glass transition temperature. At higher temperatures, this amorphous matrix loses its stiffness and becomes soft; the mechanical properties are now dominated by the crystallites. These crystallites stiffen and strengthen the composite material so that a partially crystalline polymer can be used as tough, structural material above the glass transition temperature, in stark contrast to purely amorphous polymers.

1.5.2 Effects on Stiffness

The mechanical properties of partially crystalline polymers are largely controlled by the relative amount of the crystalline phase. This amount of crystallinity is in turn partially controlled by the tacticity (i.e. arrangements of side groups) of the molecular chains.

Highly ordered isotactic or syndiotactic polymer chains are easier to crystallize than disordered atactic polymer chains. Table 1.3 illustrates the effect of tacticity on the crystallinity and resulting physical properties of PP.

In addition to the tacticity, the crystallinity is also controlled by the degree of chain branching. An increase in the number and size of polymer chain branches will increase the free volume of the material and thereby impede crystallization.

1.5.3 Effects on Ductility

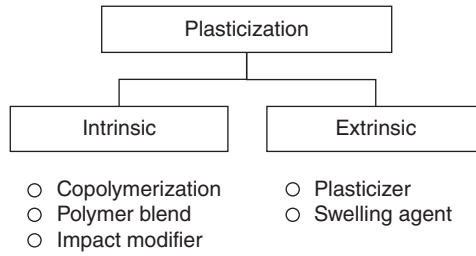
Ductility is a measure of how easily a material can be deformed. For example, amorphous polymers used at temperatures below their glass transition temperature, T_g , tend to be brittle and exhibit low ductility; partially crystalline polymers above their T_g tend to be tough due to their high ductility.

Table 1.3 Effect of tacticity on the physical properties of polypropylene (PP).

Property	Unit	PP type			
		PP-a-LM	PP-a-HM	PP-s-(Me)	PP-i-(Me)
Density	g cm^{-3}	0.836	0.855	0.9	0.903
Melt flow rate	g 10 min^{-1}	670	0.1	3	1.8
Crystallinity	%	Low	Amorphous	30–40	40–60
Melting temperature	$^{\circ}\text{C}$	—	—	168	163
Elastic modulus	MPa	10	5	61	1000–1700
Strength	MPa	1	2	2,4	20–35
Strain at break	%	110	2000		100–300

a, atactic; s, syndiotactic; i, isotactic; (Me), metallocene-catalyzed; LM, low molecular weight; HM, high molecular weight.

Figure 1.38 Plasticization methods.



Plasticization or softening of the polymeric material (Figure 1.38) can be employed to increase the ductility; however, this occurs at the cost of stiffness, which decreases with increasing ductility. Plasticization can occur by intrinsic and extrinsic methods: intrinsic methods are stable and due to a change in the polymer itself, while extrinsic methods are due to the addition of a potentially unstable chemical additive (e.g. plasticizer). Such additives have been known to migrate or diffuse, resulting in deterioration of material properties and possible environmental contamination effects.

All plasticization methods work by lowering the effective glass transition temperature. For example, intrinsic plasticization can be achieved by copolymerizing various comonomers. The type of copolymer synthesized (e.g. random or grafted) will dictate the behaviour of the elastic modulus (Figure 1.39).

Extrinsic plasticization involves the intentional addition of plasticizing agents. One common example includes PVC plasticized with the additive dioctylphthalate (DOP), where the stiffness of the material can be controlled by varying the amount of DOP (Figures 1.40 and 1.41).

The plasticizer is a low-molecular-weight swelling agent that migrates through the polymer, widening the spaces between chains (Figure 1.41). Addition of the swelling agent will increase the volume and mass of the polymer by amounts ΔV and Δm , respectively. This weakens the intermolecular bonds, increases the

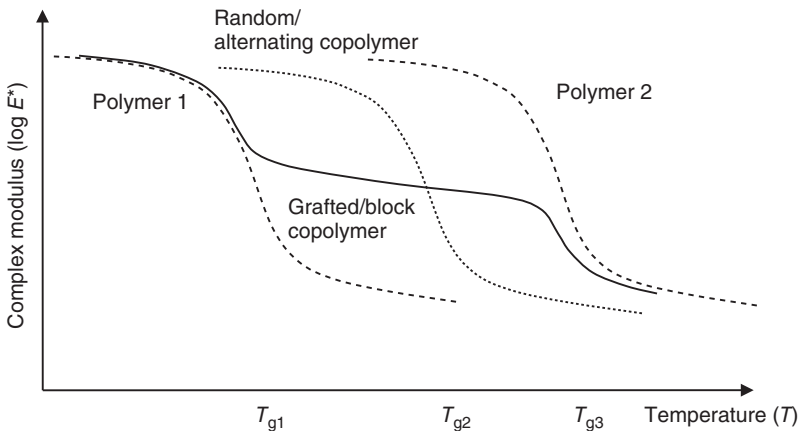


Figure 1.39 Temperature dependence of elastic modulus (complex modulus) for various homopolymers and copolymers (schematic).

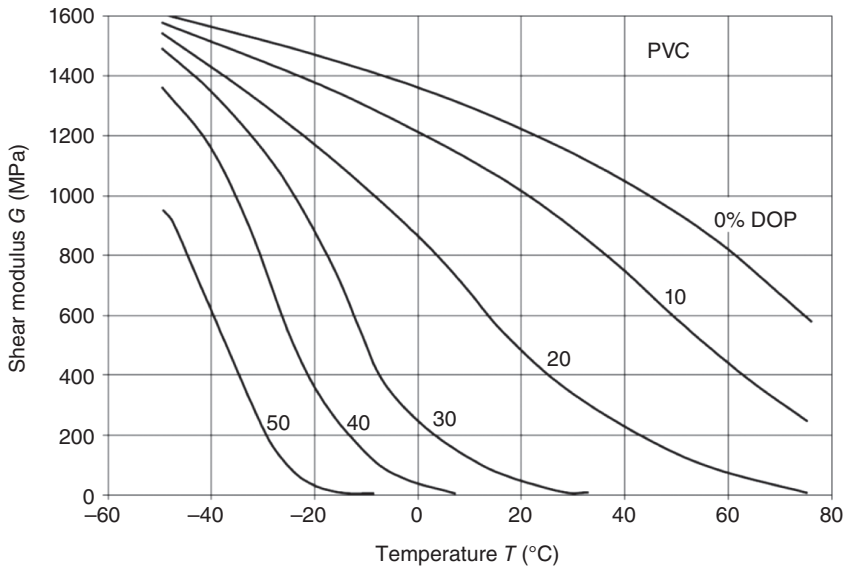


Figure 1.40 Shear modulus as a function of temperature for PVC with various amounts of DOP plasticizer additive (Baur et al. 2007).

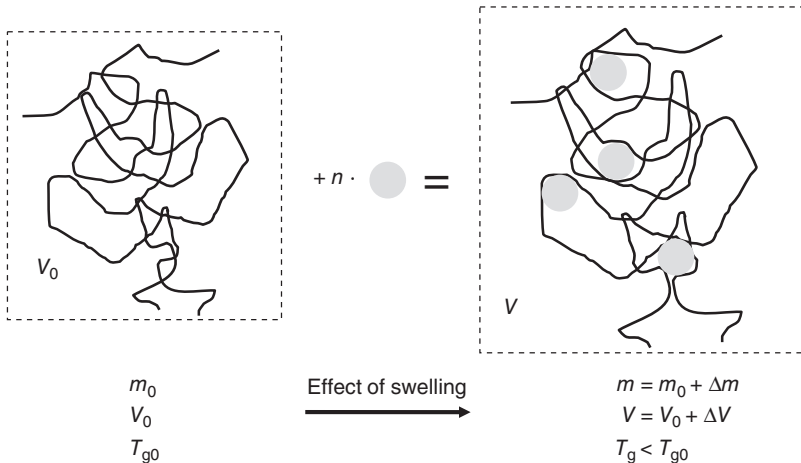


Figure 1.41 Extrinsic plasticization of a polymer using a swelling agent.

mobility of the molecular chains, and thus increases the flexibility of the material; this results in a lower glass transition temperature.

Because the plasticizer is not chemically bonded to the polymer, it is free to migrate during extended service. Loss of the plasticizer leads to an eventual embrittlement of the material.

Plasticization can also occur due to unintended contamination. For example, a polymeric O-ring or seal may inadvertently swell when exposed to lubricants such as grease or oil. Such contaminants may result in increased mass and

volume, accompanied by decreased hardness, stiffness, and strength; these changes may render the polymer unserviceable and lead to failure of the plastic component.

1.5.4 Effect of Time and Temperature on Mechanical Properties

The mechanical properties of polymeric materials are greatly affected by temperature and time. An increase in temperature will increase the ductility but decrease the strength and stiffness of the polymer. A similar result can also be achieved at a given temperature by increasing the loading time (i.e. decreasing the loading rate).

Time and temperature can therefore be considered comparable in terms of their effect on mechanical properties: low temperatures or high loading rates lead to brittle behaviour, while high temperature or low loading rates lead to ductile behaviour (Figure 1.42).

1.5.5 Fatigue Behaviour

Fatigue occurs when a material is structurally damaged due to continual dynamic or cyclic stress (e.g. vibrations). This stress, necessary to cause fatigue damage, is often much lower than the yield stress. Fatigue can occur by mechanical or thermal mechanisms, depending on various factors:

- Stress level
- Exposure time (number of cycles)
- Stress cycle frequency
- Temperature of the surroundings
- Part geometry and heat transfer (convection/conduction).

Thermal fatigue will cause a thermoplastic material to fail due to viscoelastic flow, and a thermoset to fail due to thermal decomposition. The origin of thermal fatigue is extended self-heating of the part due to cyclical mechanical loading, if

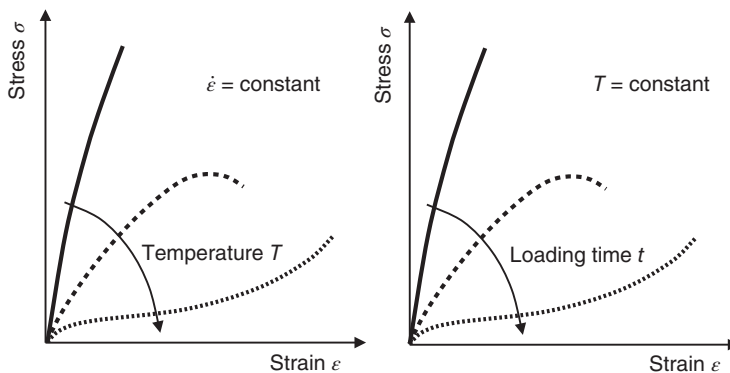


Figure 1.42 Effect of temperature and time on the mechanical properties of polymeric materials.

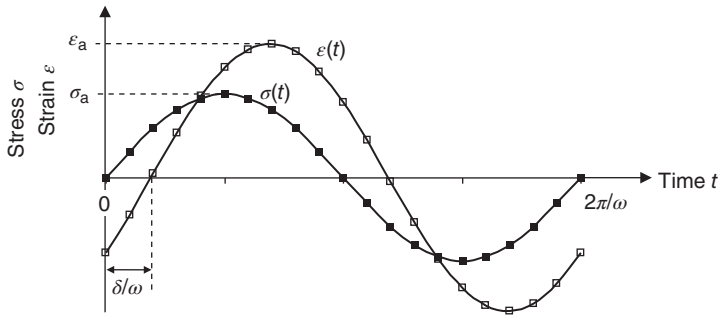


Figure 1.43 Cyclically imposed mechanical stress and the resulting strain in a viscoelastic material.

the heat is not removed by conduction or convection. Any viscoelastic material will dampen a dynamic load (Figure 1.43); this dampening occurs due to a dissipative loss, in which mechanical energy is converted into thermal energy, and is expressed as hysteresis in a stress–strain curve (Figure 1.44).

The area of the hysteresis A (Eq. (1.28)) describes the work W dissipated over a unit volume due to cyclic loading; this loss is the result of a phase shift δ between the load $\sigma(t) = \sigma_0 \cdot \sin(\omega t)$ and the resulting deformation $\varepsilon(t) = \varepsilon_0 \cdot \sin(\omega t - \delta)$.

$$A_{\text{hysteresis}} = W_{\text{dissipative}} = \sigma_0 \cdot \sin \delta \cdot \varepsilon_0 \cdot \pi \tag{1.28}$$

A purely elastic material deforms instantaneously upon loading, such that the phase shift $\delta = 0$ and there is no hysteresis, no loss, and therefore no self-heating. We find that hysteresis loss and self-heating only occur in viscoelastic materials under a cyclically applied mechanical load.

A thermally induced failure is most likely when the material is exposed to a stress-controlled cyclical load (Figure 1.44). A strain-limited cyclical load is less damaging, as the resulting stress is able to relax over time.

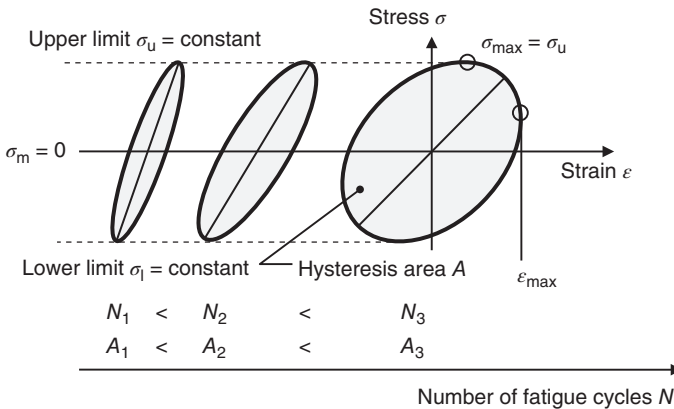


Figure 1.44 Development of hysteresis due to a stress-controlled cyclical load applied on a viscoelastic polymer.

Table 1.4 Estimating the endurance limit of polymers using the tensile strength σ_B .

Type of polymers	Endurance limit
Semi-crystalline	$0.3-0.4 \cdot \sigma_B$
Amorphous	$0.2-0.3 \cdot \sigma_B$

Increasing the number of cycles increases the dissipative loss and hysteresis of the polymer. Since this loss is a conversion of mechanical into thermal energy, the polymer gradually heats up. The progressive rise in temperature will cause the viscoelastic material to soften, which in turn further increases the mechanical loss. This positive feedback ultimately leads to the self-destruction of the material due to overheating, a process termed thermal fatigue.

This contrasts with mechanical fatigue, where cyclic loading leads to craze formation. These crazes represent microscopic areas of localized mechanical deformation, which gradually grow in size and form microcracks upon continual loading. These microcracks continue to grow in size and number until they ultimately cause the entire sample to fracture; this process is termed mechanical fatigue.

The endurance limit is the stress, below which a fatigue failure never occurs, regardless of the number of loading cycles. Such a limit is known for many metals, but unfortunately can only be estimated for polymers. However, the fatigue behaviour of partially crystalline polymers tends to be better than that of amorphous polymers (Table 1.4).

1.6 Resins

Pure polymers are rarely employed directly and are more commonly found as resins (moulding compounds). A resin is a melt processable polymeric material that is typically delivered by a raw material supplier as small pellets or granules and is ready to be processed into the final form. These pellets or granules are approximately uniform in size and usually either cylindrical or lens shaped.

The pellets or granules themselves are typically fabricated by the raw material manufacturer from polymer powder; a typical powder obtained directly from polymer synthesis might have an average particle size of about 200 μm . This raw polymer powder is pure and lacks additives or modifying agents. The raw material manufacturer combines this pure polymer powder with the necessary additives, pigments, fillers, reinforcing agents, etc. to produce the desired resin (Figure 1.45). Such a process ensures the homogeneous raw material with a uniform dispersion of additives.

The composition of the polymeric material can be customized to the desired application. It is therefore possible to tailor the material properties, such as colour or thermomechanical behaviour, using specific additives or agents. Possible examples include thermal stabilizers, pigments, dyes, release agents, lubricants, nucleation agents, and flame retardant additives. Fillers or reinforcements can be used to increase the hardness, stiffness, or structural strength of the raw material.

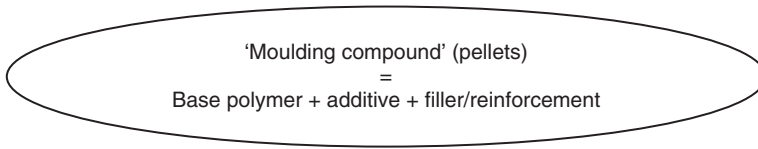


Figure 1.45 Composition of a resin (moulding compound).

This adaptability makes plastics particularly interesting engineering materials. For example, although there are about 100 different base polymers, the international raw material market offers over 5000 different types of resins: polymer science offers functional materials that can be designed to order.

However, such variability also has drawbacks. For example, the plastics industry has no standardized ‘polymer grades’ analogous to the normative ‘steel grades’ found in metallurgy. The closest thing to standardization involves materials testing of polymers, such as the CAMPUS database. This means that the formulation of resins is usually unknown to the purchaser and typically varies between suppliers; nominally identical resins from different manufacturers are therefore not necessarily interchangeable.

Practically speaking, it is only possible to identify a particular resin by the specific nomenclature of the relevant raw material manufacturer (e.g. see Table 1.5).

This raw material manufacturer-specific nomenclature means that the full identification must be used. For example, ULTRAMID A3WG6 and ULTRAMID A3EG6 both have similar names and contain reinforced polyamide (PA66-GF30), but they have very different material properties and are therefore suitable for different service applications.

In addition, the user can supplement the resin with further additives. Examples include pigments or dyes to achieve the desired colour of the final product, or an additional nucleation agent to increase the solidification rate of the moulded component and thereby reduce the cycle time. Various additives will normally be combined into a single compatible master batch, which is then mixed into the resin at the necessary concentration to achieve the desired material properties. The final material must then be identified using both the resin and the master batch including its concentration.

Table 1.6 gives an example of the information necessary to describe the blackening of an otherwise uncoloured POM resin. The colouring agent is added as a dry mix into the pellet feed of the machine. One drawback of such a final customization is that there exists the potential for a non-uniform dispersion of the additive, resulting in an inhomogeneous manufactured part.

Table 1.5 Description of a typical colour pigmented PA66 resin.

Resin	Polymer
ULTRAMID A3WG6 black 168 ^{a)}	PA66-GF30, thermally stabilized, black pigments (colour formulation 168 BASF)

a) Raw material manufacturer: BASF AG.

Table 1.6 Example of information required when using a master batch to modify a POM resin.

Resin	Master batch	Polymeric compound
HOSTAFORM C9021 ^{a)}	1.5 wt% UN MB 101 ^{b)}	POM-copolymer (MFR: 9 g/ 10 min) + 1.5 wt% masterbatch, colour: black, type: 101

a) Raw material manufacturer: Celanese GmbH.

b) Manufacturer of Colour Masterbatch: Color-Service GmbH & Co. KG.

1.7 Material Selection

The common thermoplastics can be separated into three groups, depending on their relative engineering performance (Figure 1.46).

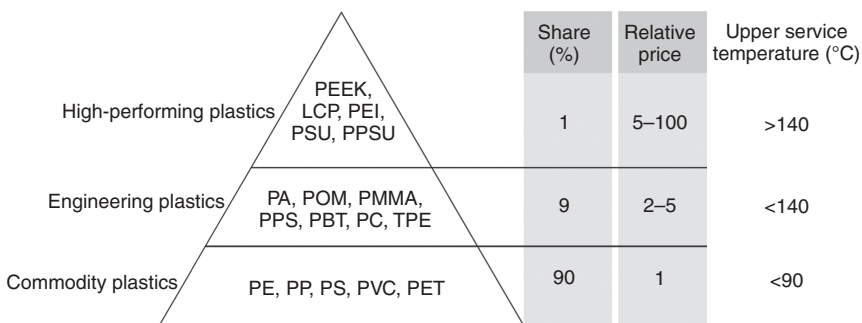
As shown in Figure 1.46, the majority of applications use commodity plastics: they are inexpensive but are limited in their thermal stability and strength. Engineering plastics are used for stressed structural components, because these materials present a good compromise between improved properties and price.

Although the high-tech engineering plastics have the best material properties and are highly temperature resistant, they are expensive and therefore their use is only justified in the most demanding applications. However, because of the ease and speed at which highly complex multifunctional engineering components can be injection moulded, even an expensive high-tech plastic may be very cost-effective.

1.7.1 Quality Considerations

The appropriate plastic for a demanded application is selected taking into account its performances and its respective processability, and the processing considerations.

For example, the viscosity and shear velocity of the melt are critical parameters when melt processing a linear polymer. In addition, thermoplastics often exhibit shear thinning, i.e. the viscosity decreases disproportionately with increasing shear velocity. These rheological properties of the melt dictate the achievable

**Figure 1.46** Material selection for thermoplastics.

flow length to wall thickness ratio; this ratio controls how easily a given mould can be filled. Long-chain polymers with their high molecular weight have good mechanical strength; they also have high melt viscosity, meaning that it is relatively difficult to fill a mould.

A given polymer material will normally have various similar types available, each with a different flow behaviour to accommodate diverse processing parameters. The final material choice therefore requires a compromise between desired material properties and processing limitations. If processing limitations were not an issue, only extremely viscous, high-molecular-weight polymers would be employed. These materials have superior mechanical toughness, improved creep resistance, and better recyclability.

When designing an injection moulded part, the engineer must take into account both processing and material performance factors. Material performance goes beyond material selection to include quality control, which in turn requires independent materials testing and evaluation. Many plastic processors rely on the raw material manufacturers' quality certifications, although they rarely disclose adequate data on tolerances and permissible variations. If the material quality is incorrectly assumed to be certified and adequate, a root cause analysis of possible processing difficulties may be skewed. Any attempt at process optimization will then be in vain because the underlying cause of the process difficulty was mistakenly ruled out (e.g. inconsistent average molecular weight can lead to variability in the melt viscosity, or the unpredictable crystallization behaviour of crystallisable polymers can lead to under-fill).

When communicating with raw material manufacturers, it is not enough to merely indicate the trade name of the resin one wishes to discuss: in addition, designating the lot number is necessary. This enables the raw material manufacturer to uniquely identify the material, including additives and internal quality control tolerances. Nominally identical resins with different lot numbers represent different batches that may have been manufactured according to different quality control criteria. This means that a resin user or processor must understand, and, if necessary, limit compositional tolerances when producing a high-precision part. An effective quality management system will therefore document the complete raw material specification including lot and master batch identification.

1.8 Processing of Polymers

Polymeric materials are processed into finished and semi-finished parts by compression moulding (pressing), transfer compression moulding, injection moulding, or extrusion. In each case, the material input is a polymeric or elastomeric resin. Thermosets use a resin that can chemically react during thermal or mechanical processing of the melt to form a cross-linked network. Elastomers use similarly reactive resins that require a vulcanization step after being moulded into the desired geometry. This contrasts with thermoplastics, which generally do not react during processing (a rare exception is if a reactive blowing agent is included).

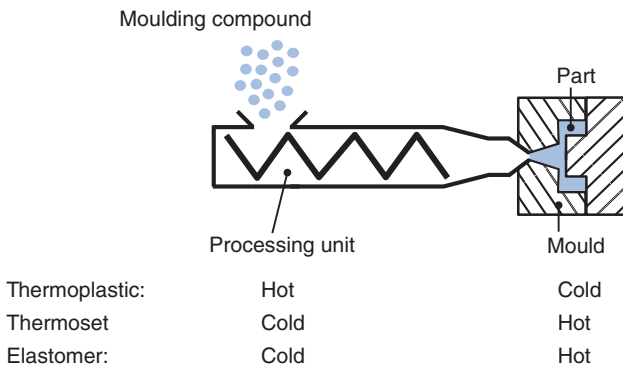


Figure 1.47 Processing temperatures for various types of polymeric materials.

The most important practical difference in processing these diverse materials lies in the required temperature control of the mould and processing equipment such as reciprocating screw and barrel (Figure 1.47).

Thermoplastics are typically processed at temperatures above 200 °C so that they melt; the melt is then injected into the relatively cold mould where the polymer solidifies in the desired geometry. This steep temperature gradient ensures quick solidification, so that cycle times of as low as five seconds can be achieved.

Chemically reactive resins (thermosets and elastomers) must undergo a non-reversible chemical reaction before attaining the desired material properties. As with any resin, moderate heating is necessary to cause the resin to flow. However, the processing temperature must be kept low enough to prevent a premature reaction or cross-linking before the final geometry is achieved. This is the reason why cross-linkable polymers typically require processing equipment to be kept at a relatively low temperature (about 80 °C) and the mould to be at a high temperature of around 200 °C. This high mould temperature corresponds to the cross-linking or vulcanization temperature of the reactive polymer. A certain dwell time inside the high-temperature mould is required so that these chemical reactions can come to completion. This results in relatively long cycle times on the order of minutes and is the primary drawback of thermosets and elastomers compared to thermoplastics.

One approach to improving this long cycle time of thermosets and elastomers is to shorten the dwell time so that the moulded component is only partially cross-linked. Such a partial cross-linking is enough to maintain the geometric integrity of the part during demoulding, but is not yet sufficient for service. After demoulding, the component is placed in a tempering oven so that the reaction can come to completion. Omission of the tempering step will lead to quality issues, including inadequate strength and viscous creep.

1.8.1 Preconditioning

Polymers typically do not require preconditioning prior to processing. However, one exception is made for hygroscopic materials, which can absorb moisture from the environment during storage or transit. Such materials include

polyamide, polyester, polyurethane, and polycarbonate; they require desiccation prior to processing. Otherwise, hydrolytically induced deterioration, or hydrolysis, can occur: the water or steam present in the melt will cut and shorten the polymer chains, thereby resulting in a brittle, low-molecular-weight material with inferior mechanical properties.

When considering a preconditioning step prior to processing, it is important to evaluate potentially negative effects on the polymer. For example, a chemically reactive resin, such as an elastomer, can unintentionally cross-link due to inappropriate preconditioning, storage, or transport; this renders it unworkable. Such resins can therefore only be stored for a limited amount of time, preferably under refrigeration to reduce the rate of chemical reactions.

Quality control systems must therefore incorporate safeguards to prevent improper preconditioning, storage, transport, or handling, of susceptible raw materials.

1.8.2 Production Processes

In practice, plastics can be processed using all basic manufacturing technologies. All polymeric materials can be moulded and machined. However, only thermoplastics can be recast or the semi-finished product mechanically reworked into the final shape; this is because thermoplastics can be softened by gentle heating. Melt processing and reworking are the two most important types of processing methods for polymeric materials.

Melt processing can be defined as the fabrication of a solid body from a formless substance. For a polymer, the formless substance is the resin; the resin is melted and injected into the mould cavity or extruded prior to solidifying in the desired geometry. In this way, the shape of the product is created at the same time as the material is formed. This means that the manufacturing process controls the microstructure of the polymer, and consequently dictates mould shrinkage, geometric integrity, and other material properties.

Reworking can be defined as the forming of the final solid shape from another solid body by plastic deformation. In this case, the final product is plastically fashioned from the semi-finished form using mechanical or thermal means. The ease with which a semi-finished product can be reworked depends on the fabrication process and the material.

For example, thermoplastics, i.e. non-cross-linked polymers, can be both melt processed and reworked. For example, they can be melted at higher temperatures, and then extruded, blow moulded, or injection moulded. Alternatively, they can be reworked using thermoforming where the solid is softened at moderate temperatures. Thermosets and elastomers are preferentially processed using pressing, transfer moulding, and injection moulding methods.

Both the part geometry and the polymeric material itself are produced during the melt processing steps. This means that the material quality of the finished part does not necessarily coincide with the quality of the original resin, as the polymer could have been affected by conditioning and processing parameters.

The ultimate dimensions of an injection moulded part are typically smaller than the dimensions of the mould, due to mould shrinkage. Mould shrinkage is

affected by the type of polymer (amorphous or partially crystalline), type and quantity of fillers or additives, and processing conditions. These parameters also affect the nucleation rate of a partially crystalline polymer, which can lead to inconsistent part sizing if not properly controlled.

Practically all plastics can be machined. However, some materials, including elastomers or any polymeric sheet, do not have adequate geometric stability or stiffness to be machined at room temperature. A workaround can usually be achieved by cooling the material to a low enough temperature so that an adequate stiffness is obtained – in this case, it is important to take into account thermal expansion coefficients when determining manufacturing tolerances.

An additional potential complication that can arise when machining a polymeric material is that friction can lead to localized heating. Such heating can result in an altered microstructure or even thermally induced degradation of the polymer. It is unadvisable to use conventional cooling fluids or machining lubricants in an attempt to reduce heating, because incompatible substances can lead to environmental stress cracking. Therefore, cooling with air is recommended if the machining operation is expected to cause excessive heating.

1.8.3 Effects on Quality

When manufacturing a finished product out of polymeric materials, one important consideration is product quality and consistency; a comprehensive approach to quality control is essential.

The ultimate quality of a plastic component is determined in total by suitable part geometry and mould design, appropriate polymeric material selection, and optimized processing (Figure 1.48).

The design of an injection moulded component affects the design of the mould, which affects the processability and, in turn, the feasibility of manufacturing a given part geometry. In addition, the type of polymeric material selected will affect the mould design, because mould shrinkage must be taken into account when producing a precision part. The mould temperature and injection pressure profile during melt processing will also affect mould shrinkage; this means that the mould might have to be modified to accommodate necessarily processing conditions to achieve the desired geometric dimensions.

There are therefore multiple factors that affect the geometry and material properties of a plastic component, including part design, material selection, mould design, and various processing parameters.

Figure 1.49 illustrates the complex relationship of these factors in forming a desirable plastic component. The geometric shape and material microstructure

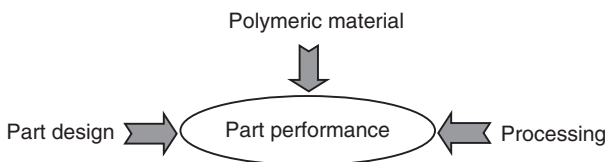


Figure 1.48 Factors influencing the achievable properties of plastic products.

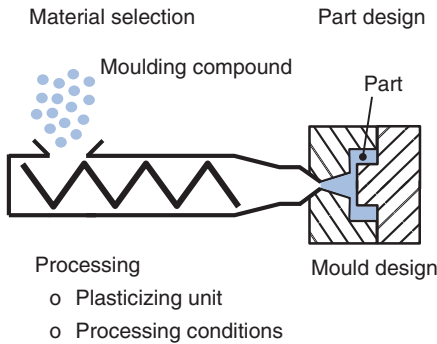


Figure 1.49 Factors influencing the quality of injection moulded thermoplastic parts.

of the part are formed simultaneously during the injection moulding process. Evaluating or controlling the quality of the finished product, therefore, requires the engineer to acknowledge and understand all these interrelated factors, within a holistic approach.

Any effective quality control system will require an adequate evaluation and understanding of the properties of the polymeric resin as well as the processing conditions of the melt; both factors interact to determine the material properties of the final component. For example, a resin might not meet the design specifications, or else even if it meets the specifications, it might be damaged due to poor manufacturing conditions: the material properties of an otherwise high-quality resin can be impaired by unsuitable processing conditions: processing conditions are known to affect the anisotropy, internal stress, and microstructure of plastic components.

An optimized microstructure is particularly important for partially crystalline polymers. In these cases, the material properties are a combination of microscopic and macroscopic structural features. The type and size of crystalline lamellae in a partially crystalline polymer (microscopic morphology) interacts with the thermodynamically controlled superstructure (macroscopic morphology) to determine the material behaviour of the plastic component. These morphologies form during cooling of the polymer from the melt to the mould ejection temperature.

The mechanical properties of the material are dictated by the morphology, which in turn also influences the mould shrinkage. This means that mechanical behaviour and mould reproducibility are related. An attempt at unilaterally optimizing manufacturing tolerances is consequently misguided, and will likely lead to quality problems.

For all polymeric materials, a complete understanding of the relationship between processing parameters and the resulting morphology of a manufactured component are therefore critical for thorough quality control.