

Figure 3.14 Schematic of the molecular structure of polyethylene with different densities

■ 3.5 Arrangement of Polymer Molecules

As mentioned in Chapter 1, polymeric materials can be divided into two general categories: thermoplastics and thermosets. Thermoplastics are materials that have the ability to remelt after they have solidified, and thermosets are those that solidify via a chemical reaction that causes polymer molecules to cross-link. These cross-linked materials cannot be remelted after solidification.

As thermoplastic polymers solidify, they take on two different types of structure: amorphous or semi-crystalline. Amorphous polymers are those where the molecules solidify in a random arrangement, whereas some of the molecules in semi-crystalline polymers align with their neighbors, forming regions with a three-dimensional order. In semi-crystalline polymers, the molecules that do not align into crystals remain amorphous structures.

3.5.1 Thermoplastic Polymers

The formation of macromolecules from monomers occurs if there are unsaturated carbon atoms (carbon atoms connected with double bonds), or if there are monomers with reactive end-groups. The double bond, say in an ethylene monomer, is split, which frees two valences per monomer and leads to the formation of a macromolecule such as polyethylene. This process is often referred to as polymerization. Similarly, monomers (R) that possess two reactive end-groups (bifunctional) can react with other monomers (R') that also have two other reactive end-groups that can react with each other, also leading to the formation of a polymer chain. A list of typical reactive end-groups is given in Table 3.2.

Table 3.2 List of Selected Reactive End-Groups

Hydrogen in aromatic monomers	-H
Hydroxyl group in alcohols	-OH
Aldehyde group as in formaldehyde	$\begin{array}{c} \text{H} \\ \\ -\text{C} \\ \\ \text{O} \end{array}$
Carboxyl group in organic acids	$\begin{array}{c} \text{OH} \\ \\ -\text{C} \\ \\ \text{O} \end{array}$
Isocyanate group in isocyanates	-N=C=O
Epoxy group in polyepoxys	$\begin{array}{c} \text{CH} \quad \text{CH}_2 \\ \diagdown \quad / \\ \text{O} \end{array}$
Amido groups in amides and polyamides	-CO-NH ₂
Amino groups in amines	-NH ₂

3.5.2 Amorphous Thermoplastics

Amorphous thermoplastics, with their randomly arranged molecular structure, are analogous to a bowl of spaghetti. Due to their random structure, the characteristic size of the largest ordered region is on the order of a carbon-carbon bond. This dimension is much smaller than the wavelength of visible light and so generally amorphous thermoplastics are transparent.

Figure 3.15 [4] shows the shear modulus⁵, G' , versus temperature for polystyrene, one of the most common amorphous thermoplastics. The figure shows two general

⁵ The dynamic shear modulus, G' , is obtained using the dynamic mechanical properties test described in Chapter 9.

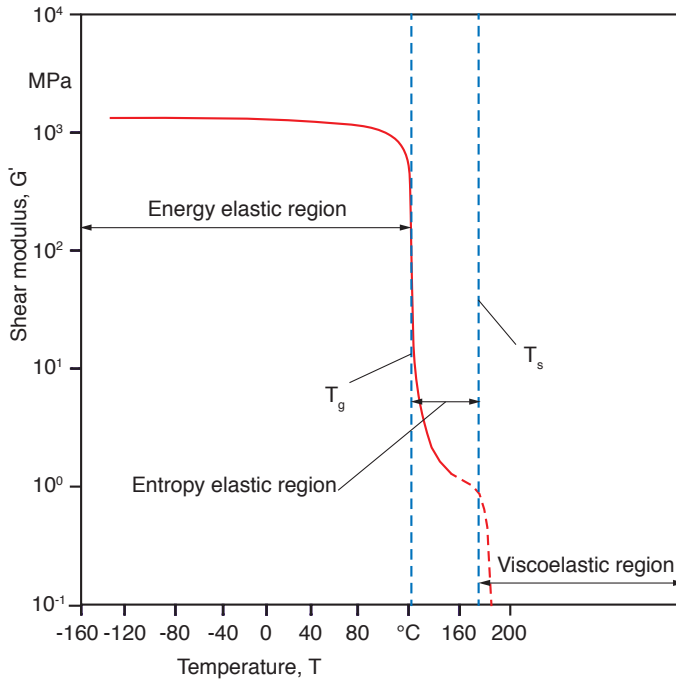


Figure 3.15 Shear modulus of polystyrene as a function of temperature

regions: one where the modulus appears fairly constant⁶, and one where the modulus drops significantly with increasing temperature. With decreasing temperatures, the material enters the glassy region where the slope of the modulus approaches zero. At high temperatures the modulus is negligible and the material is soft enough to flow. Although there is not a clear transition between “solid” and “liquid”, the temperature that divides the two states in an amorphous thermoplastic is referred to as the *glass transition temperature*, T_g . For the polystyrene in Fig. 3.15 the glass transition temperature is approximately 110 °C. At temperatures below the glass transition temperature the material behaves like a viscoelastic solid, the area in the curve denoted as *energy elastic region*. Once the material is above the glass transition temperature, it enters the so-called *entropy elastic region*. At this point the material can be more easily deformed, such as is done during the thermoforming process. However, in order for the material to flow, its temperature must be above a softening temperature, T_s , at which point it behaves like a viscoelastic fluid. The softening temperature defines the point where the viscous forces during deformation (loss) exceed the elastic forces during deformation (storage), and for amorphous thermoplastics it typically ranges about 50 K

⁶ When plotting G' versus temperature on a linear scale, a steady decrease of the modulus is observed.

above the glass transition temperature. Storage and loss moduli are discussed in more detail in Chapter 10.

It should be mentioned here that the curve shown in Fig. 3.15 was measured at a constant frequency. If the frequency of the test is increased – reducing the time scale – the curve is shifted to the right, because higher temperatures are required to achieve movement of the molecules at the new frequency. Figure 3.16 [5] demonstrates this concept by displaying the elastic modulus as a function of temperature for polyvinyl chloride at various test frequencies. The relation between time scale and temperature, also known as the *time-temperature superposition principle*, is discussed in detail Chapter 9. A similar effect as observed with time scale and temperature can be seen when the molecular weight of the material is increased. The longer molecules have more difficulty sliding past each other, thus requiring higher temperatures to achieve “flow.”

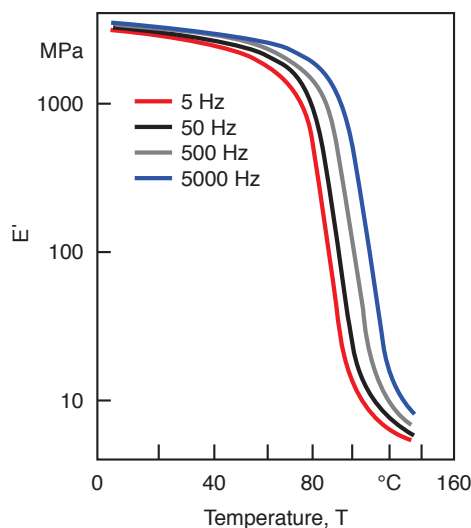


Figure 3.16 Modulus of polyvinyl chloride as a function of temperature at various test frequencies

3.5.3 Semi-Crystalline Thermoplastics

Semi-crystalline thermoplastic polymers show more order than amorphous thermoplastics. The molecules arrange in an ordered crystalline form as shown for polypropylene in Fig. 3.17. The crystalline structure shown in the photograph is composed of *spherulites*, which are formed by *lamellar crystals*. The formation of spherulites during solidification of semi-crystalline thermoplastics is covered in Chapter 8. The schematic in Fig. 3.18 shows the general structure and hierarchical arrangement in semi-crystalline materials, using polyethylene as an example. The spherulitic structure is the largest domain with a specific order and has a characteristic size of 50 to 500 μm . Some of the polypropylene spherulites in the

micrograph presented in Fig. 3.17 are about 150 μm in diameter. The size of spherulites is much larger than the wavelength of visible light, making semi-crystalline materials translucent and not transparent.

However, the crystalline regions are very small with molecular chains comprised of both crystalline and amorphous regions. The degree of crystallinity in a typical thermoplastic will vary from grade to grade. For example, in polyethylene the degree of crystallinity depends on the branching and the cooling rate. A low density polyethylene (LDPE) with its long branches (Fig. 3.14) can only crystallize to approximate 40 – 50%, whereas a high density polyethylene (HDPE) crystallizes to up to 80%. The density and strength of semi-crystalline thermoplastics increase with the degree of crystallinity, as demonstrated in Table 3.3 [6], which compares low and high density polyethylene. Figure 3.19 shows the different properties and molecular structure that may arise in polyethylene plotted as a function of degree of crystallinity and molecular weight.

Table 3.3 Influence of Crystallinity on Properties for Low and High Density Polyethylene

Property	Low density	High density
Density (g/cm^3)	0.91 – 0.925	0.941 – 0.965
% crystallinity	42 – 53	64 – 80
Melting temperature ($^{\circ}\text{C}$)	110 – 120	130 – 136
Tensile modulus (MPa)	17 – 26	41 – 124
Tensile strength (MPa)	4.1 – 16	21 – 38

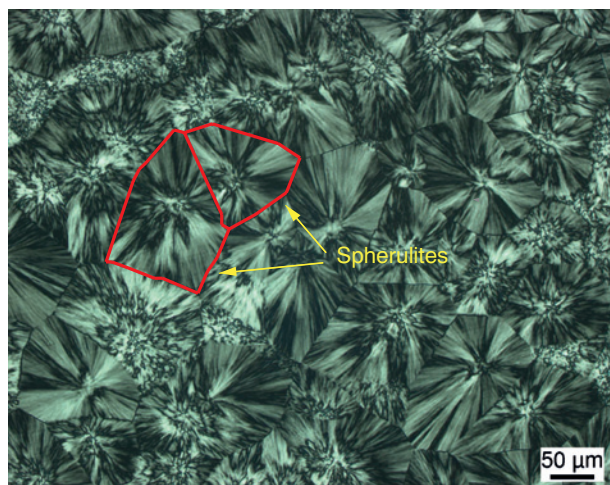


Figure 3.17 Micrograph of the spherulitic crystalline structure in a polypropylene polymer (Courtesy of the Institute of Plastics Technology, LKT, University of Erlangen-Nuremberg)

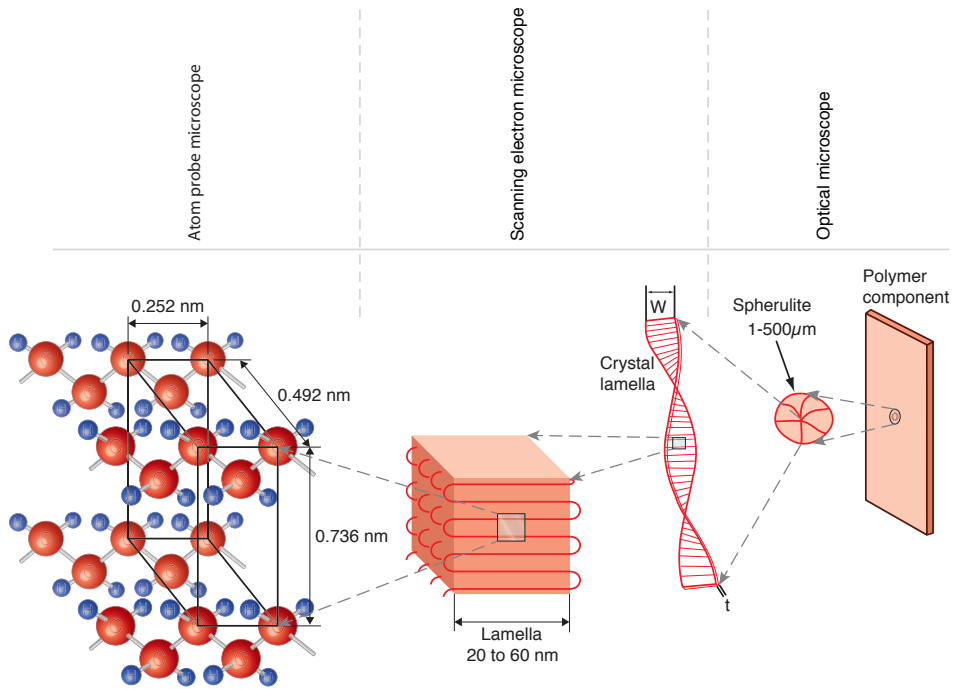


Figure 3.18 Schematic representation of the general molecular structure and arrangement of typical semi-crystalline materials

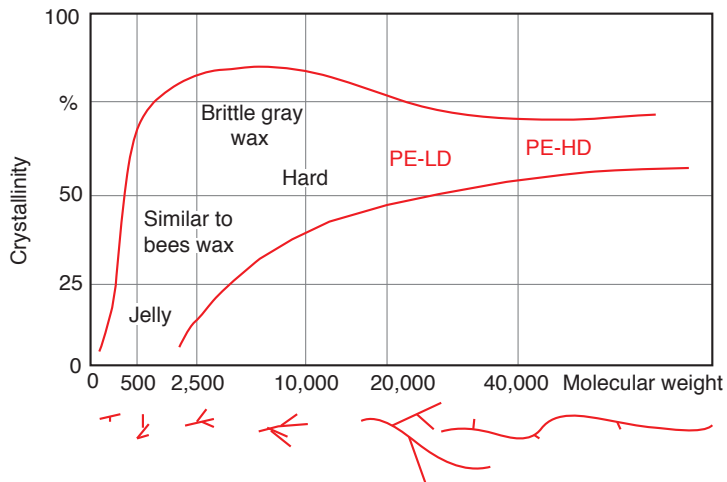


Figure 3.19 Influence of degree of crystallinity and molecular weight on different properties of polyethylene

Figure 3.20 [4] shows the dynamic shear modulus versus temperature for a high density polyethylene, the most common semi-crystalline thermoplastic. Again, this curve presents data measured at one test frequency. The figure clearly shows two distinct transitions: one at about $-110\text{ }^{\circ}\text{C}$, the *glass transition temperature*, and another near $140\text{ }^{\circ}\text{C}$, the *melting temperature*. Above the melting temperature, the shear modulus is negligible and the material will flow. Crystalline arrangement begins to develop as the temperature decreases below the melting point. Between the melting and glass transition temperatures, the material behaves like a leathery solid. As the temperature decreases below the glass transition temperature, the amorphous regions within the semi-crystalline structure solidify, forming a glassy, stiff, and in some cases brittle polymer.

To summarize, Table 3.4 presents the basic structure of several amorphous and semi-crystalline thermoplastics with their melting and/or glass transition temperatures.

Furthermore, Fig. 3.21 [7] summarizes the property behavior of amorphous, crystalline, and semi-crystalline materials using schematic diagrams of material properties plotted as functions of temperature.

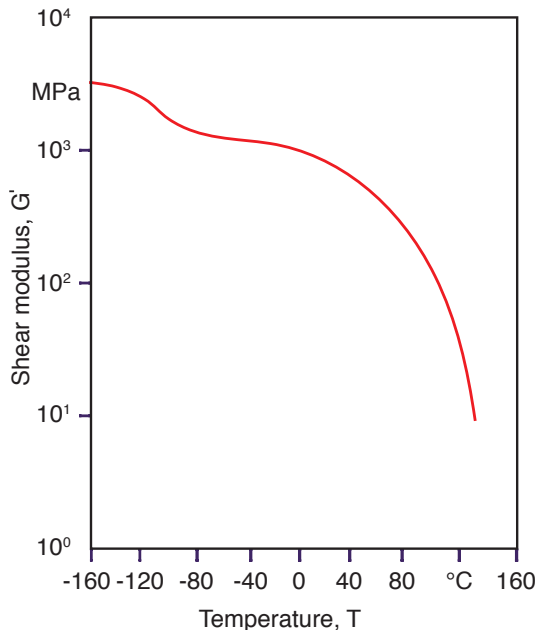


Figure 3.20 Shear modulus of a high density polyethylene as a function of temperature

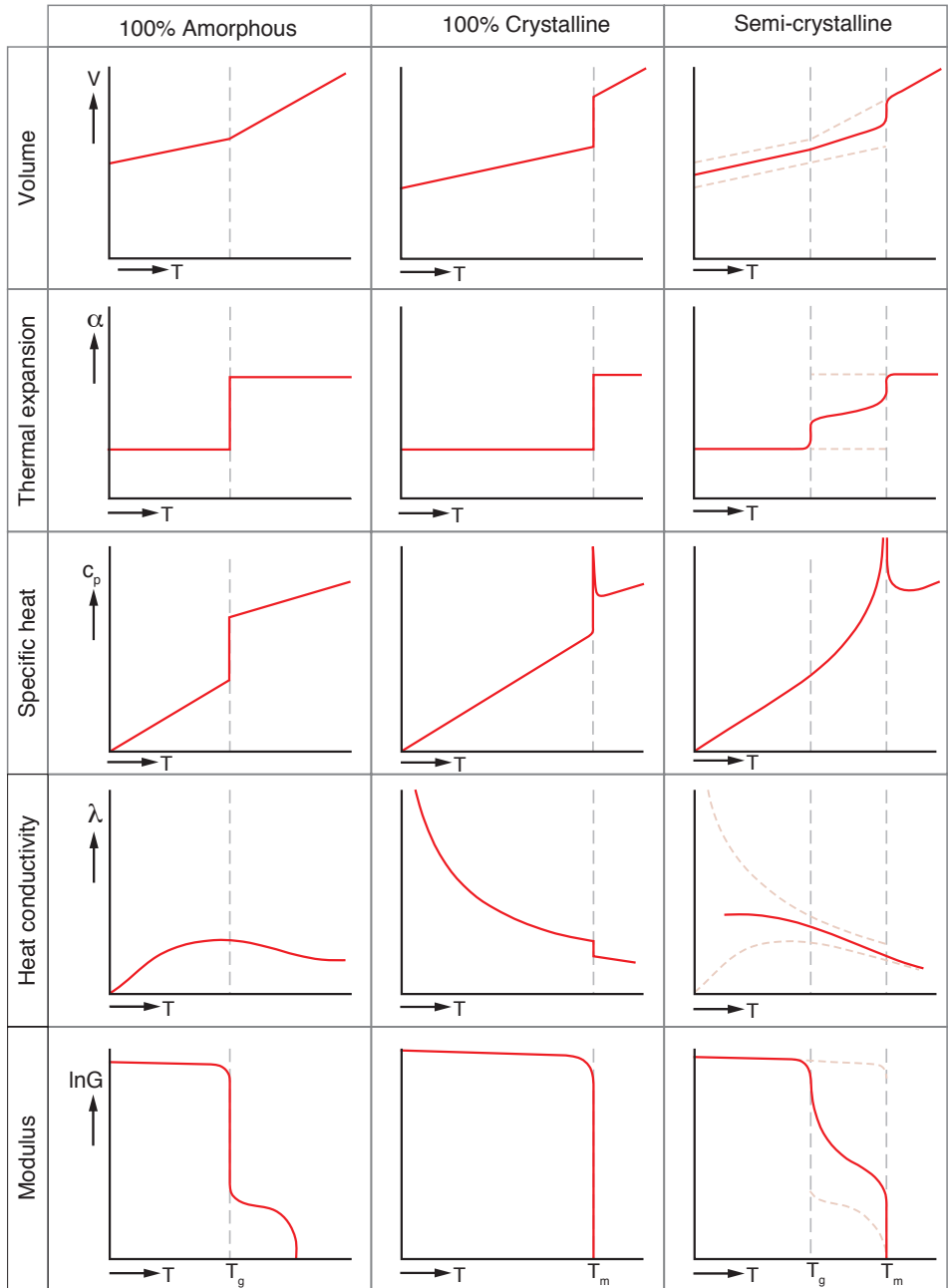


Figure 3.21 Schematic of the behavior of some polymer properties as a function of temperature for different thermoplastics

Table 3.4 Structural Units for Selected Polymers (*continued*)

Structural unit	Polymers	
$\begin{array}{c} \text{—O—CH—} \\ \\ \text{CH}_3 \end{array}$	Polyacetaldehyde	$T_g = -30\text{ }^\circ\text{C}$ $T_m = 165\text{ }^\circ\text{C}$
$\text{—O—CH}_2\text{—}$	Polyformaldehyde (polyacetal, polyoxymethylene)	$T_g = -85\text{ }^\circ\text{C}$ $T_m \approx 190\text{ }^\circ\text{C}$
$\begin{array}{c} \text{—O—CH—CH}_2\text{—} \\ \\ \text{CH}_3 \end{array}$	Isotactic polypropyleneoxide	$T_g = -75\text{ }^\circ\text{C}$ $T_m = 75\text{ }^\circ\text{C}$
$\begin{array}{c} \text{—O—CH}_2\text{—C—CH}_2\text{—} \\ \quad \\ \text{CH}_2\text{—Cl} \quad \text{CH}_2\text{—Cl} \end{array}$	Poly-[2.2-bis-(chloromethyl)- trimethylene-oxide]	$T_g = 5\text{ }^\circ\text{C}$ $T_m = 181\text{ }^\circ\text{C}$
$\begin{array}{c} \text{—CH}_2\text{—C—} \\ \quad \\ \text{CH}_3 \quad \text{CO}_2\text{—CH}_3 \end{array}$	Isotactic polymethylmeth- acrylate	$T_g = 50\text{ }^\circ\text{C}$ $T_m = 160\text{ }^\circ\text{C}$
$\begin{array}{c} \text{Cl} \quad \text{F} \\ \quad \\ \text{—C—C—} \\ \quad \\ \text{F} \quad \text{F} \end{array}$	Polychlorotrifluoroethylene	$T_g = 45\text{ }^\circ\text{C}$ $T_m = 220\text{ }^\circ\text{C}$
$\text{—CF}_2\text{—CF}_2\text{—}$	Polytetrafluoroethylene	$T_{g1} = -113\text{ }^\circ\text{C}$ $T_{g2} = 127\text{ }^\circ\text{C}$ $T_m = 330\text{ }^\circ\text{C}$

Table 3.4 Structural Units for Selected Polymers (*continued*)

Structural unit	Polymers	
$\begin{array}{c} \text{Cl} \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{Cl} \end{array}$	Polyvinylidenechloride	$T_g = -19\text{ }^\circ\text{C}$ $T_m = 190\text{ }^\circ\text{C}$
$\begin{array}{c} \text{F} \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{F} \end{array}$	Polyvinylidene fluoride	$T_g = -45\text{ }^\circ\text{C}$ $T_m = 171\text{ }^\circ\text{C}$
$\begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{Cl} \end{array}$	Polyvinylchloride (PVC) - amorphous	$T_g = 80\text{ }^\circ\text{C}$ $T_m = -$
$\begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{Cl} \end{array}$	Polyvinylchloride (PVC) - crystalline	$T_g = 80\text{ }^\circ\text{C}$ $T_m = 212\text{ }^\circ\text{C}$
$\begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{F} \end{array}$	Polyvinyl fluoride (PVF)	$T_g = -20\text{ }^\circ\text{C}$ $T_m = 200\text{ }^\circ\text{C}$
$-\text{CO}_2-\text{C}_6\text{H}_4-\text{CO}_2-\text{CH}_2-\text{CH}_2-\text{O}-$	Polyethyleneterephthalate (PET) (linear polyester)	$T_g = 69\text{ }^\circ\text{C}$ $T_m = 245\text{ }^\circ\text{C}$
$-\text{CO}-[\text{CH}_2]_{14}-\text{CO}-\text{NH}-[\text{CH}_2]_{26}-\text{NH}-$	Polyamide 66	$T_g = 57\text{ }^\circ\text{C}$ $T_m = 265\text{ }^\circ\text{C}$

Table 3.4 Structural Units for Selected Polymers (*continued*)

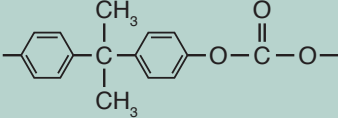
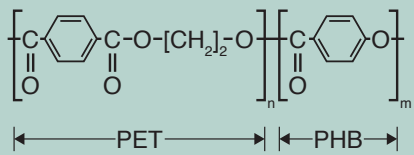
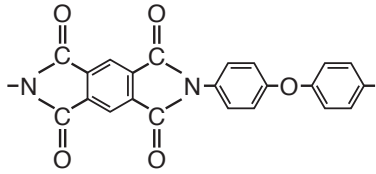
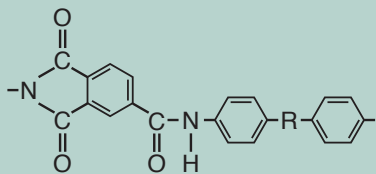
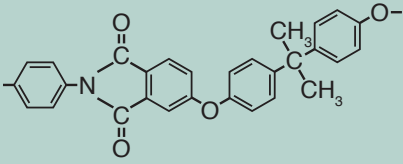
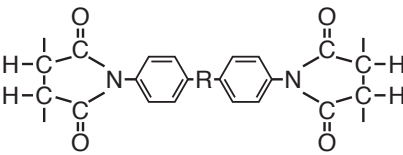
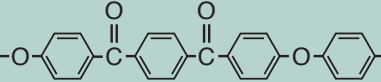
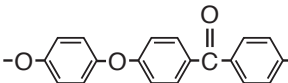
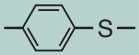
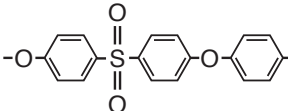
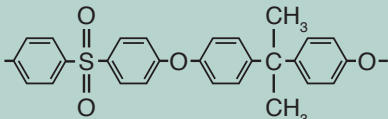
Structural unit	Polymers	
$-\text{CO}-[\text{CH}_2]_8-\text{CO}-\text{NH}-[\text{CH}_2]_6-\text{NH}-$	Polyamide 610	$T_g = 57\text{ }^\circ\text{C}$ $T_m = 265\text{ }^\circ\text{C}$
$-\text{CO}-[\text{CH}_2]_5-\text{NH}-$	Polycaprolactam, Polyamide 6	$T_g = 75\text{ }^\circ\text{C}$ $T_m = 233\text{ }^\circ\text{C}$
	Polycarbonate (PC)	$T_g = 149\text{ }^\circ\text{C}$ $T_m = 267\text{ }^\circ\text{C}$
$-\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2-$	Poly-(p-xylylene) (Parylene R)	$T_g = -$ $T_m = 400\text{ }^\circ\text{C}$
	Polyethyleneterephthalate / p-Hydroxybenzoate- copolymers LC-PET, polymers with flexible chains	$T_g = 75\text{ }^\circ\text{C}$ $T_m = 280\text{ }^\circ\text{C}$
	Polyimide (PI)	T_g : up to $400\text{ }^\circ\text{C}$
	Polyamidimide (PAI)	$T_g \approx 260\text{ }^\circ\text{C}$

Table 3.4 Structural Units for Selected Polymers (*continued*)

Structural unit	Polymers	
	Polyetherimide (PEI)	$T_g \approx 215\text{ }^\circ\text{C}$
	Polybismaleinimide (PBI)	$T_g \approx 250\text{ }^\circ\text{C}$
	Polyoxybenzoate (POB)	$T_g \approx 290\text{ }^\circ\text{C}$
	Polyetherketone (PEEK)	$T_g = 145\text{ }^\circ\text{C}$ $T_m = 335\text{ }^\circ\text{C}$
	Polyphenylene-sulfide (PPS)	$T_g \approx 230\text{ }^\circ\text{C}$
	Polyethersulfone (PES)	$T_g = 85\text{ }^\circ\text{C}$ $T_m = 280\text{ }^\circ\text{C}$
	Polysulfone (PSU)	$T_g \approx 180\text{ }^\circ\text{C}$

3.5.4 Thermosets and Cross-Linked Elastomers

Thermosets, and some elastomers, are polymeric materials that have the ability to crosslink. The crosslinking causes the material to become heat resistant after it has solidified. A more in-depth explanation of the chemical crosslinking reaction that occurs during solidification is given in Chapter 8.

The crosslinking usually is a result of the presence of double bonds that break, allowing the molecules to link with their neighbors. One of the oldest thermosetting polymers is phenol-formaldehyde, or phenolic. Figure 3.22 shows the chemical symbol representation of the reaction, and Fig. 3.23 shows a schematic of the reaction. The phenol molecules react with formaldehyde molecules to create a three-dimensional crosslinked network that is stiff and strong. The by-product of this chemical reaction is water.

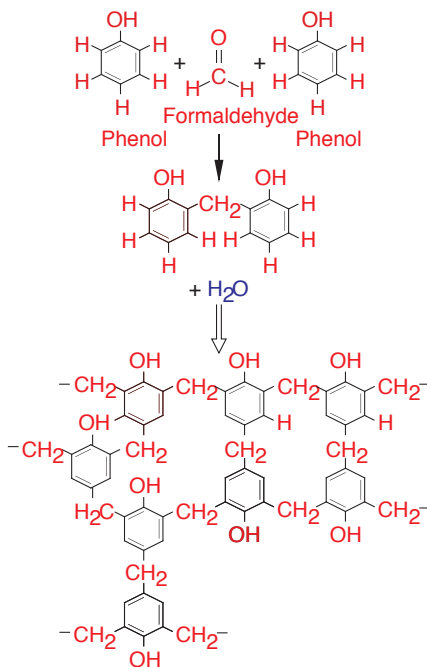


Figure 3.22 Symbolic representation of the condensation polymerization of phenol-formaldehyde resins

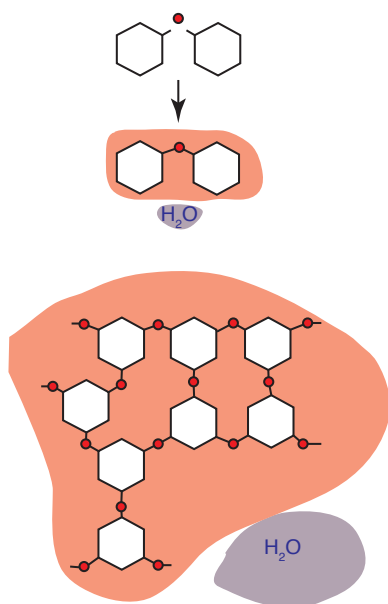


Figure 3.23 Schematic representation of the condensation polymerization of phenol-formaldehyde resins

■ 3.6 Copolymers and Polymer Blends

Copolymers are polymeric materials with two or more monomer types in the same chain. A copolymer that is composed of two monomer types is referred to as a *bipolymer*, and one that is formed by three different monomer groups is called a *terpolymer*. Depending on how the different monomers are arranged in the polymer chain, one distinguishes between *random*, *alternating*, *block*, or *graft* copolymers. The four types of copolymers are schematically represented in Fig. 3.24.

A common example of a copolymer is ethylene-propylene. Although both monomers would result in semi-crystalline polymers when polymerized individually, the melting temperature disappears in the *randomly* distributed copolymer with ratios between 35/65 and 65/35, resulting in an elastomeric material, as shown in Fig. 3.25. In fact, EPDM⁷ rubbers are continuously gaining acceptance in industry because of their resistance to weathering. On the other hand, the ethylene-propylene *block* copolymer maintains a melting temperature for all ethylene/propylene ratios, as shown in Fig. 3.26.

Another widely used copolymer is high impact polystyrene (PS-HI), which is formed by grafting polystyrene to polybutadiene. Again, when styrene and buta-

⁷ The D in EP(D)M stands for the added unsaturated diene component which results in a crosslinked elastomer.

diene are randomly copolymerized, the resulting material is an elastomer called styrene-butadiene-rubber (SBR). Another classic example of copolymerization is the terpolymer acrylonitrile-butadiene-styrene (ABS).

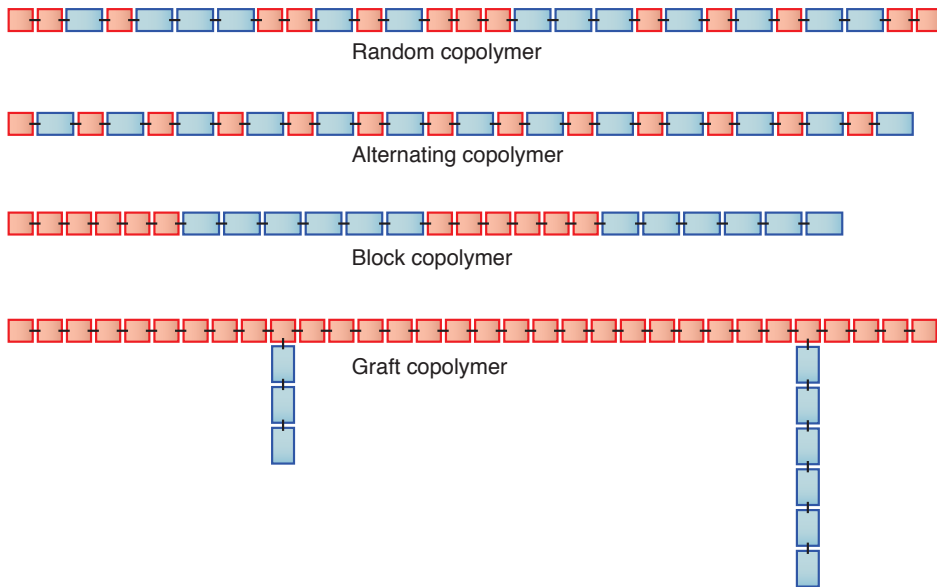


Figure 3.24 Schematic representation of different copolymers

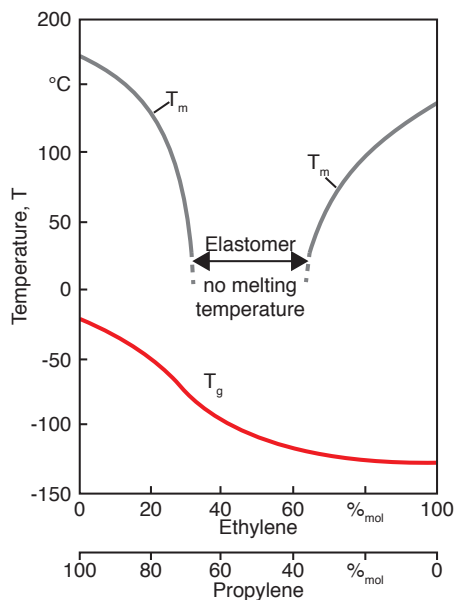


Figure 3.25 Melting and glass transition temperature for random ethylene-propylene copolymers

Polymer blends belong to another family of polymeric materials that are made by mixing or blending two or more polymers to enhance the physical properties of each individual component. Common polymer blends include PP-PC, PVC-ABS, and PE-PTFE.

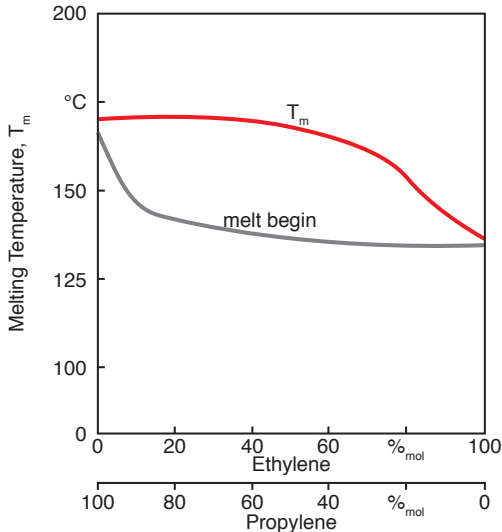


Figure 3.26 Melting temperature for ethylene-propylene block copolymers

■ 3.7 Polymer Additives

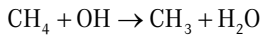
There are many polymer additives that are mixed into a polymer to improve the mechanical, optical, electrical, and acoustic – to name a few – performance of a component.

3.7.1 Flame Retardants

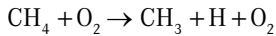
Since polymers are organic materials, most of them are flammable. The flammability of polymers has always been a serious technical problem. A parameter that can be used to assess the flammability of polymers is the *limiting oxygen index* (LOI), also known as the *critical oxygen index* (COI). This value defines the minimum volume percent of oxygen concentration, mixed with nitrogen, needed to support combustion of the polymer under the test conditions specified by ASTM D 2863. Since air contains 21% oxygen by volume, only those polymers with an LOI greater than 0.21 are considered self-extinguishing. In practice, an LOI value higher than 0.27 is recommended as the limiting self-extinguishing threshold. Table 3.5 presents LOI values for selected polymers.

It is impossible to make a polymer completely inflammable. However, some additives containing halogens, such as bromine, chlorine, or phosphorous, reduce the possibility of either starting combustion within a polymer component or, once ignited, reduce the rate of flame spread. When rating the performance of flame retardants, bromine is more effective than chlorine.

In the *radical trap* theory of flame retardancy it is believed that bromine or phosphorous containing additives compete in the reaction of a combustion process. To illustrate this we examine two examples of typical combustion reactions. These are:



and



where OH and H are active chain carriers. With the presence of HBr the following reaction can take place

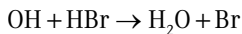


Table 3.5 LOI Values for Selected Polymers

Polymer	LOI
Polyformaldehyde	0.15
Polyethylene oxide	0.15
Polymethyl methacrylate	0.17
Polyacrylonitrile	0.18
Polyethylene	0.18
Polypropylene	0.18
Polyisoprene	0.185
Polybutadiene	0.185
Polystyrene	0.185
Cellulose	0.19
Polyethylene terephthalate	0.21
Polyvinyl alcohol	0.22
Polyamide 66	0.23
Epoxy	0.23
Polycarbonate	0.27
Aramid fibers	0.285
Polyphenylene oxide	0.29
Polysulfone	0.30
Phenolic resins	0.35

Table 3.5 LOI Values for Selected Polymers (*continued*)

Polymer	LOI
Polychloroprene	0.40
Polyvinyl chloride	0.42
Polyvinylidene fluoride	0.44
Polyvinylidene chloride	0.60
Carbon	0.60
Polytetrafluoroethylene	0.95

where the active chain carrier was replaced by the less active Br radical, helping with flame extinguishment. Similarly, with the presence of Br the following reaction can take place

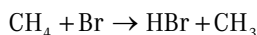


Table 3.6 [8] lists selected polymers and commonly used flame retardants.

Table 3.6 Selected Polymers with Typical Commercial Flame Retardants

Polymer	Flame retardants
Acrylonitrile butadiene styrene	Octabromodiphenyl oxide
High impact polystyrene	Decabromodiphenyl oxide
Polyamide	Dechlorane plus
Polycarbonate	Tetrabromobisphenol A carbonate oligomer
Polyethylene	Chlorinated paraffin
Polypropylene	Dechlorane plus
Polystyrene	Pentabromocyclododecane
Polyvinyl chloride	Phosphate ester

3.7.2 Stabilizers

The combination of heat and oxygen will bring about thermal degradation in a polymer. Heat or energy will produce free radicals that will react with oxygen to form carbonyl compounds, which give rise to yellow or brown discolorations in the final product.

Thermal degradation can be slowed by adding stabilizers such as antioxidants or peroxide decomposers. These additives do not eliminate thermal degradation, but they slow down the reaction process. Once the stabilizer has been consumed by the reaction with the free radicals, the protection of the polymer against thermal degradation ends. The time period over which the stabilizer renders protection

against thermal degradation is called *induction time*. A test used to measure thermal stability of a polymer is the *Oxidative Induction Time* (OIT) by differential scanning calorimetry (DSC). The OIT test is defined as the time it takes for a polymer sample to thermally degrade in an oxygen environment at a set temperature above the polymer's transition temperature. The transitions must occur in a nitrogen environment. The standard test is described by ASTM D 3895. Another test used to measure the thermal stability of a polymer and its additives is the thermal gravimetric analysis (TGA) discussed in Chapter 4.

Polyvinyl chloride is probably the polymer most vulnerable to thermal degradation. In polyvinyl chloride, scission of the C-Cl bond occurs at the weakest point of the molecule. The chlorine radicals will react with their nearest CH group, forming HCl and creating new weak C-Cl bonds. A stabilizer must therefore neutralize HCl and stop the auto-catalytic reaction, as well as prevent corrosion of the processing equipment.

3.7.3 Antistatic Agents

Since polymers have such low electric conductivity, they can build-up electric charges quite easily. The amount of charge build-up is controlled by the rate at which the charge is generated compared to the charge decay. The rate of charge generation at the surface of the component can be reduced by reducing the intimacy of contact, whereas the rate of charge decay is increased through surface conductivity. Hence, a good antistatic agent should be an ionizable additive that allows charge migration to the surface, at the same time as creating bridges to the atmosphere through moisture in the surroundings. Typical antistatic agents are nitrogen compounds, such as long chain amines and amides, polyhydric alcohols, among others.

3.7.4 Fillers

Fillers can be divided into two categories: those that reinforce the polymer and improve its mechanical performance and those that are used to take up space and so reduce the amount of actual resin to produce a part – sometimes referred to as *extenders*. A third, less common, category of filled polymers are those where fillers are dispersed into the polymer to improve its electric conductivity.

Polymers that contain fillers that improve their mechanical performance are often referred to as *composites*. Composites can be divided into two further categories: composites with *high performance* reinforcements, and composites with *low performance* reinforcements. In high performance composites the reinforcement is

placed inside the polymer in such a way that optimal mechanical behavior is achieved, such as unidirectional glass fibers in an epoxy resin. High performance composites usually have 50–80% reinforcement by volume and the composites are usually laminates, tubular shapes containing braided reinforcements, etc. In low performance composites the reinforcement is small enough that it can be dispersed well into the matrix, allowing to process these materials the same way their unreinforced counterparts are processed. The most common filler used to reinforce polymeric materials is glass fiber. However, wood fiber, which is commonly used as an extender, also increases the stiffness and mechanical performance of some thermoplastics. To improve the bonding between the polymer matrix and the reinforcing agent, *coupling agents*, such as *silanes* and *titanates* are often added. Polymer composites and their performance are discussed in more detail in Chapters 8 and 9.

Extenders, used to reduce the cost of the component, often come in the form of particulate fillers. The most common particulate fillers are calcium carbonate, silica flour, clay, and wood flour or fiber. As mentioned earlier, some fillers also slightly reinforce the polymer matrix, such as clay, silica flour, and wood fiber. It should be pointed out that polymers with extenders often have significantly lower toughness than the unfilled resin. This concept is covered in more detail in Chapter 10.

3.7.5 Blowing Agents

The task of blowing or foaming agents is to produce cellular polymers, also referred to as expanded plastics. The cells can be completely enclosed (closed cell) or they can be interconnected (open cell). Polymer foams are produced with densities ranging from 1.6 kg/m³ to 960 kg/m³. There are many reasons for using polymer foams, such as their high strength/weight ratio, excellent insulating and acoustic properties, and high energy and vibration absorbing properties.

Polymer foams can be made by mechanically whipping gases into the polymer, or by either chemical or physical means. Some of the most commonly used foaming methods are [9]:

- Thermal decomposition of chemical blowing agents, which generates nitrogen and/or carbon monoxide and dioxide. An example of such a foaming agent is *azodicarbonamide*, which is the most widely used commercial polyolefin foaming agent.
- Heat induced volatilization of low-boiling liquids such as pentane and heptane in the production of polystyrene foams, and methylene chloride when producing flexible polyvinyl chloride and polyurethane foams.

- Volatilization by the exothermic reaction of gases produced during polymerization. This is common in the reaction of isocyanate with water to produce carbon dioxide.
- Expansion of the gas dissolved in a polymer upon reduction of the processing pressure.

The basic steps of the foaming process are nucleation of the cells, expansion or growth of the cells, and stabilization of the cells. The nucleation of a cell occurs when, at a given temperature and pressure, the solubility of a gas is reduced, leading to saturation, expelling the excess gas to form a bubble. Nucleating agents are used for initial formation of the bubbles. The bubble reaches an equilibrium shape when the pressure inside the bubble balances with the surface tension surrounding the cell.

Examples

1. What is the maximum possible separation between the ends of a high density polyethylene molecule with an average molecular weight of 100,000.

Our first task is to estimate the number of repeat units, n , in the polyethylene chain. Each repeat unit has 2 carbon and 4 hydrogen atoms. The molecular weight of carbon is 12 and that of hydrogen 1. Hence,

$$\text{MW/repeat unit} = 2(12) + 4(1) = 28.$$

The number of repeat units is computed as

$$n = \text{MW}/(\text{MW/repeat unit}) = 100,000/28 = 3,571 \text{ units.}$$

Using the diagram presented in Fig. 3.27, we can now estimate the length of the fully extended molecule using

$$l = 0.252 \text{ nm}(3571) = 890 \text{ nm} = 0.89 \mu\text{m}$$

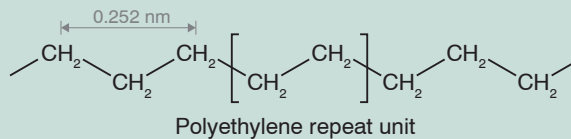


Figure 3.27 Schematic diagram of a polyethylene molecule

As we know, even high density polyethylene molecules are branched and therefore our result is an overprediction.

Problems

1. Estimate the degree of polymerization of a polyethylene with an average molecular weight of 150,000. The molecular weight of an ethylene monomer is 28.
2. What is the maximum possible separation between the ends of a polystyrene molecule with a molecular weight of 160,000?
3. To enhance processability of a polymer, why would you want to decrease its molecular weight?
4. Why would an uncrosslinked polybutadiene flow at room temperature?
5. What role does the cooling rate play in the morphological structure of semi-crystalline polymers?
6. Explain how crosslinking between the molecules affect the molecular mobility and elasticity of elastomers.
7. Increasing the molecular weight of a polymer increases its strength and stiffness, as well as its viscosity. Is too high of a viscosity a limiting factor when increasing the strength by increasing the molecular weight? Why?
8. Given two polyethylene grades, one for extrusion and one for injection molding, which one should have the higher molecular weight? Why?
9. A fractional analysis of a commercial polypropylene sample has a distribution of chain lengths from which the following data is obtained:

Table 3.7 Chain Length Distribution of a Commercial Polypropylene

Degree of Polymerization	Mole fraction
200	0.08
400	0.12
600	0.15
900	0.34
1500	0.16
2000	0.15

What is the number-average molecular weight? What is the weight average molecular weight and what is the polydispersity index of the sample? Derive the equations that can also represent these molecular weights using the mole fraction (x_i) and weight fraction (w_i) of polymers with similar molecular weight.

10. Which broad class of thermoplastic polymers densifies the least during cooling and solidification from a melt state into a solid state? Why?
11. What class of polymers would you probably use to manufacture frying pan handles? Even though most polymers could not actually be used for this particular application, what single property do all polymers exhibit that would be considered advantageous in this particular application.

12. In terms of recycling, which material is easier to handle, thermosets or thermoplastics? Why?
13. Polymers are considered flammable materials. How can flammability of a polymer be reduced? Can the flammability of a polymer be measured?
14. What type of general polymerization technique is used to make PA, PE, PET, POM, PP, PS, and PVC?
15. Given a typical polymer, is the polydispersity index greater than one, smaller than one, or equal to one?
16. For a low \bar{M}_w polymer with a PI close to 1, name typical properties that go with this trend.

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4

Thermal Properties of Polymers

The heat flow through a material can be defined by Fourier's law of heat conduction. Fourier's law can be expressed as¹

$$q_x = -k_x \frac{\partial T}{\partial x} \quad (4.1)$$

where q_x is the energy transport per unit area in the x direction, k_x the thermal conductivity and $\frac{\partial T}{\partial x}$ is the temperature gradient. At the onset of heating the polymer responds solely as a heat sink, and the amount of energy per unit volume, Q , stored in the material before reaching steady state conditions can be approximated by

$$Q = \rho C_p \Delta T \quad (4.2)$$

where ρ is the density of the material, C_p the specific heat, and ΔT the change in temperature.

Using the notation found in Fig. 4.1 and balancing the heat flow through the element via conduction, including the transient, convective, and viscous heating effects, the energy balance can be written as

$$\rho C_p \frac{\partial T}{\partial t} + \rho C_p \underline{\mathbf{v}} \cdot \nabla T = (\nabla \cdot \underline{\mathbf{k}} \cdot \nabla T) + \mu (\underline{\dot{\gamma}} : \underline{\dot{\gamma}}) + \rho \dot{Q} \quad (4.3)$$

where on the left are the transient and convective terms, and on the right the conductive term, viscous heating, and an arbitrary heat generation term. The full form of the energy equation is found along with the continuity equation and momentum balance in Tables IV and V of the appendix of this book.

The material properties found in Eqs. 4.1–4.3 are often written as one single property, namely the thermal diffusivity, α , which for an isotropic material is defined by

$$\alpha = \frac{k}{\rho C_p} \quad (4.4)$$

¹ For more detailed information on transport phenomena the reader can refer to: Bird, R. B., Stewart, W. E. and Lightfoot, E. N., *Transport Phenomena*, John Wiley & Sons, (1960).

Typical values of thermal properties for selected polymers are shown in Table 4.1 [1]. For comparison, the properties for stainless steel are also shown at the end of the list.

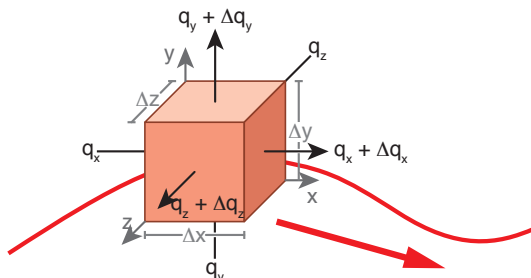


Figure 4.1 Heat flow through a differential material element

Table 4.1 Thermal Properties for Selected Polymeric Materials

Polymer	Specific gravity	Specific heat (kJ/kg°C)	Thermal conductivity (W/m/K)	Coeff. of therm. exp. (μm/m/K)	Thermal diffusivity (m ² /s)×10 ⁻⁷	Max temperature (°C)
ABS	1.04	1.47	0.3	90	1.7	70
Acetal (homo-pol.)	1.42	1.47	0.2	80	0.7	85
Acetal (co-pol.)	1.41	1.47	0.2	95	0.72	90
Acrylic	1.18	1.47	0.2	70	1.09	50
Cellulose acetate	1.28	1.50	0.15	100	1.04	60
Epoxy	1.90	–	0.23	70	–	130
Mod. PPO	1.06	–	0.22	60	–	120
PA 66	1.14	1.67	0.24	90	1.01	90
PA 66 +30% GF	1.38	1.26	0.52	30	1.33	100
PET	1.37	1.05	0.24	90	–	110
PET +30% GF	1.63	–	–	40	–	150
Phenolic	1.40	1.30	0.35	22	1.92	185
PC	1.15	1.26	0.2	65	1.47	125
u-Polyester	1.20	1.20	0.2	100	–	–
PP	0.905	1.93	0.24	100	0.65	100
PS	1.05	1.34	0.15	80	0.6	50
LDPE	0.92	2.30	0.33	200	1.17	50
HDPE	0.95	2.30	0.63	120	1.57	55
PTFE	2.10	1.00	0.25	140	0.7	50
u-PVC	1.40	1.00	0.16	70	1.16	50
p-PVC	1.30	1.67	0.14	140	0.7	50
SAN	1.08	1.38	0.17	70	0.81	60
PS-foam	0.032	–	0.032	–	–	–
Steel	7.854	0.434	60.00	–	14.1	800

It should be pointed out that the material properties of polymers are not constant and may vary with temperature, pressure or phase changes. This chapter will discuss each of these properties individually and present examples of some of the most widely used polymers and measurement techniques. For a more in-depth study of thermal properties of polymers the reader is encouraged to consult the literature [2–4].

■ 4.1 Material Properties

4.1.1 Thermal Conductivity

When analyzing thermal processes, thermal conductivity, k , is the most commonly used property that helps quantify the transport of heat through a material. By definition, energy is transported proportionally to the speed of sound. Accordingly, thermal conductivity follows the relation

$$k \approx C_p \rho u l \quad (4.5)$$

where u is the speed of sound and l the molecular separation. Amorphous polymers show an increase in thermal conductivity with increasing temperature, up to their glass transition temperature, T_g . Above T_g , the thermal conductivity decreases with increasing temperature. Figure 4.2 [3] presents the thermal conductivity, below the glass transition temperature, for various amorphous thermoplastics as a function of temperature.

Due to the increase in density upon solidification of semi-crystalline thermoplastics, the thermal conductivity is higher in the solid state than in the melt. In the melt state, however, the thermal conductivity of semi-crystalline polymers reduces to that of amorphous polymers, as can be seen in Fig. 4.3 [5]. Furthermore, it is not surprising that the thermal conductivity of melts increases with hydrostatic pressure. This effect is clearly shown in Fig. 4.4 [6]. As long as thermosets are unfilled, their thermal conductivity is very similar to that of amorphous thermoplastics.

Anisotropy in thermoplastic polymers also significantly influences their thermal conductivity. Highly drawn semi-crystalline polymer specimens may have a much higher thermal conductivity as a result of the orientation of the polymer chains in the direction of the draw. For amorphous polymers, the thermal conductivity in the direction of the draw can increase by a factor of two. Figure 4.5 [3] presents the thermal conductivity in the directions parallel and perpendicular to the draw direction for high density polyethylene, polypropylene, and polymethyl methacrylate.

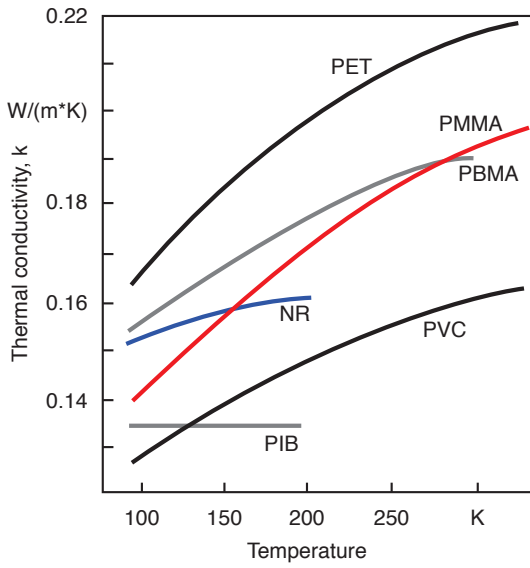


Figure 4.2 Thermal conductivity of various materials

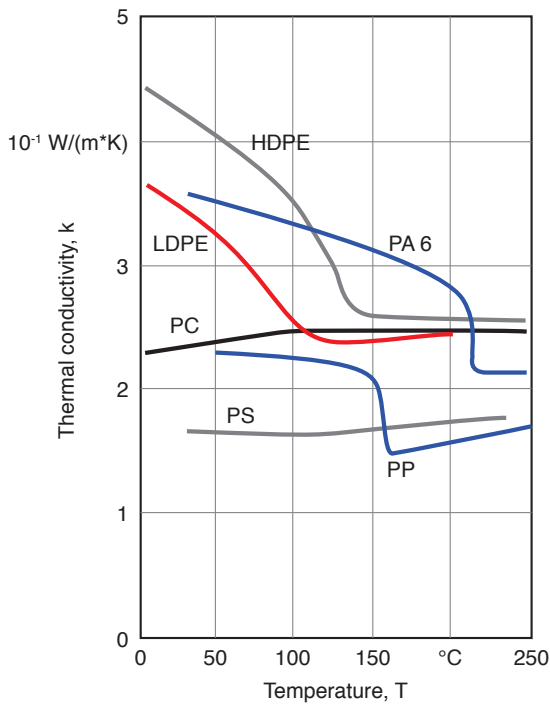


Figure 4.3 Thermal conductivity of various thermoplastics

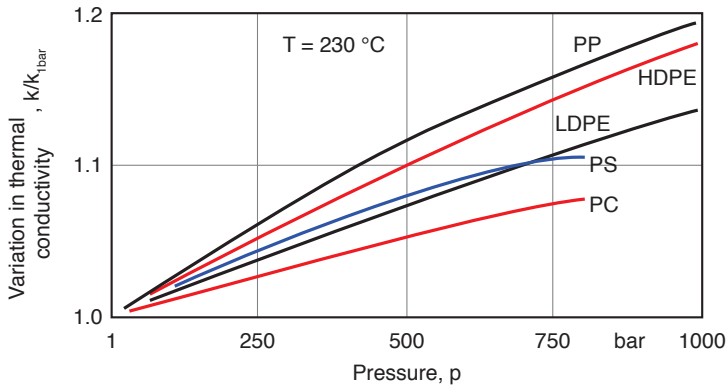


Figure 4.4 Influence of pressure on thermal conductivity of various thermoplastics

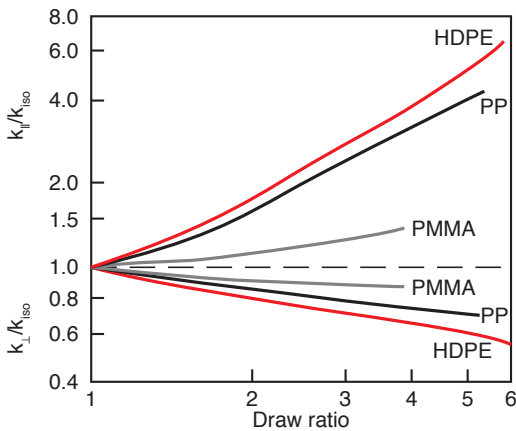


Figure 4.5 Thermal conductivity as a function of draw ratio in the directions perpendicular and parallel to the draw direction for various oriented thermoplastics

A simple relation exists between anisotropic and the isotropic thermal conductivity [7]; it can be written as

$$\frac{1}{k_{\parallel}} + \frac{2}{k_{\perp}} = \frac{3}{k} \quad (4.6)$$

where the subscripts \parallel and \perp represent the directions parallel and perpendicular to the draw direction, respectively.

The higher thermal conductivity of inorganic fillers increases the thermal conductivity of filled polymers. Nevertheless, a sharp decrease in thermal conductivity around the melting temperature of crystalline polymers can still be seen with filled materials. The effect of fillers on thermal conductivity of various thermoplastics is shown in Figs. 4.6 to 4.9. Figure 4.6 [8] shows the effect of fiber orientation as well as the effect of quartz powder on the thermal conductivity of low density polyethylene. Figures 4.7 to 4.9 show the effect of various volume fractions of glass fiber in polyamide 6, polycarbonate, and ABS, respectively. Figure 4.10 demonstrates

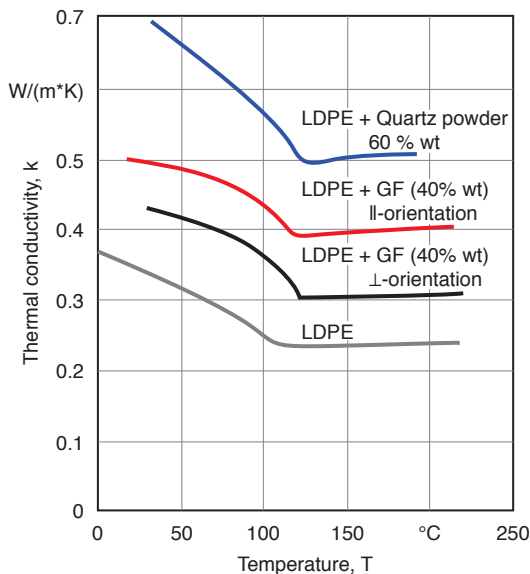


Figure 4.6 Influence of filler on the thermal conductivity of LDPE

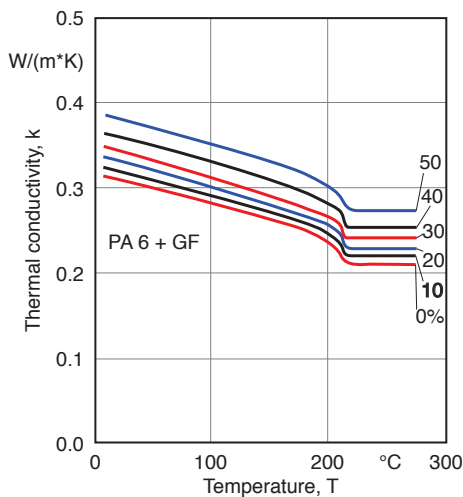


Figure 4.7 Influence of glass fiber on the thermal conductivity of polyamide 6 (Courtesy of Bayer AG, Germany)

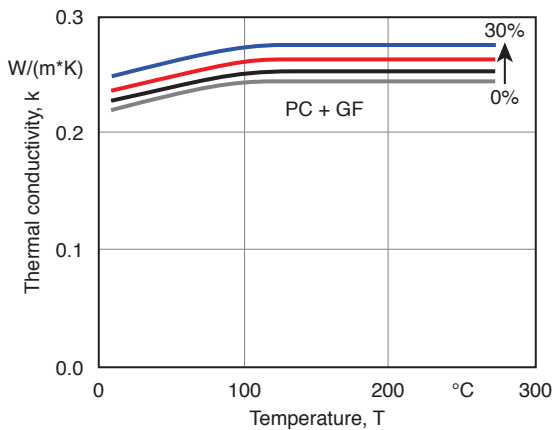


Figure 4.8 Influence of glass fiber on the thermal conductivity of polycarbonate (Courtesy of Bayer AG, Germany)

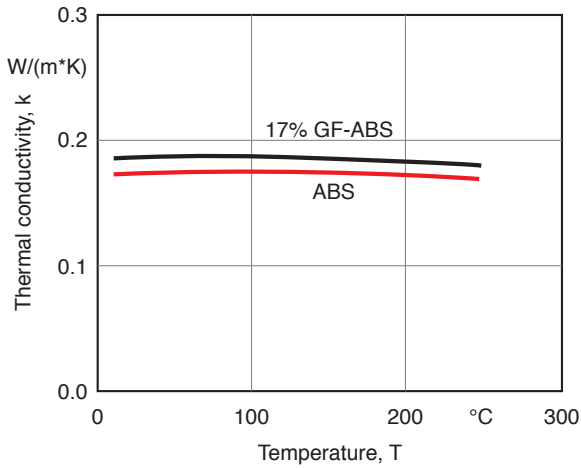


Figure 4.9 Influence of glass fiber on the thermal conductivity of ABS (Courtesy of Bayer AG, Germany)

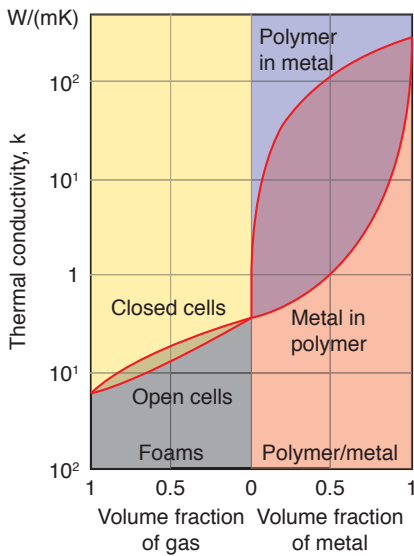


Figure 4.10 Thermal conductivity of plastics filled with glass or metal

the influence of gas content on thermal conductivity of expanded or foamed polymers, and the influence of mineral content on thermal conductivity of filled polymers. There are various models available to compute the thermal conductivity of foamed or filled plastics [7, 9, 10]. A rule of mixtures, suggested by Knappe [7], commonly used to compute thermal conductivity of composite materials is written as

$$k_c = \frac{2k_m + k_f - 2\phi_f(k_m - k_f)}{2k_m + k_f + \phi_f(k_m - k_f)} k_m \quad (4.7)$$

where, ϕ_f is the volume fraction of filler, and k_m , k_f and k_c are the thermal conductivity of the matrix, filler and composite, respectively. Figure 4.11 compares Eq. 4.7

with experimental data [11] for an epoxy filled with copper particles of various diameters. The figure also compares the data to the classic model given by Maxwell [9], which is written as

$$k_c = \left(1 + 3\phi_f \left(\frac{k_f / k_m - 1}{k_f / k_m + 2} \right) \right) k_m \quad (4.8)$$

In addition, a model derived by Meredith and Tobias [10] applies to a cubic array of spheres inside a matrix. Consequently, it cannot be used for volumetric concentration above 52% because the spheres will touch at that point. However, their model predicts the thermal conductivity very well up to 40% by volume of particle concentration.

When mixing several materials the following variation of Knappe's model applies

$$k_c = \frac{1 - \sum_{i=1}^n 2\phi_i \frac{k_m - k_i}{2k_m + k_i}}{1 - \sum_{i=1}^n \phi_i \frac{k_m - k_i}{2k_m - k_i}} k_m \quad (4.9)$$

where k_i is the thermal conductivity of the filler and ϕ_i its volume fraction. This relation is useful for glass fiber reinforced composites (FRC) with glass concentrations up to 50% by volume. This is also valid for FRC with unidirectional reinforcement. However, one must differentiate between the direction longitudinal to the fibers and that transverse to them. For high fiber content one can approximate the thermal conductivity of the composite by the thermal conductivity of the fiber.

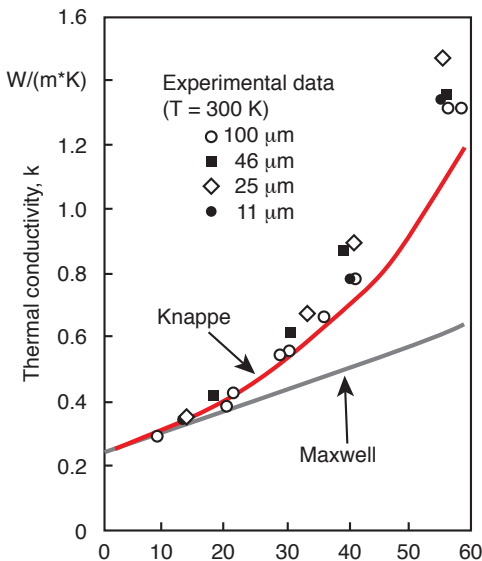


Figure 4.11 Thermal conductivity versus volume concentration of metallic particles of an epoxy resin. Solid lines represent predictions using Maxwell and Knappe models

Thermal conductivity can be measured using the standard tests ASTM C177 and DIN 52612. A new method is currently being balloted, ASTM D20.30, which is preferred by most people today.

4.1.2 Specific Heat

The specific heat, C , represents the energy required to change the temperature of a unit mass of material by one degree. It can be measured at either constant pressure, C_p , or constant volume, C_v . Since the specific heat at constant pressure includes the effect of volumetric change, it is higher than the specific heat at constant volume. However, the volume changes of a polymer with changing temperatures have a negligible effect on the specific heat. Hence, one can usually assume that the specific heat at constant volume or constant pressure is the same. It is usually true that specific heat only changes modestly in the range of practical processing and design temperatures of polymers. However, semi-crystalline thermoplastics display a discontinuity in their specific heat at the melting point of the crystallites. This jump or discontinuity in specific heat includes the heat that is required to melt the crystallites which is usually called the *heat of fusion*. Hence, specific heat is dependent on the degree of crystallinity. Values of heat of fusion for typical semi-crystalline polymers are shown in Table 4.2.

Table 4.2² Heat of Fusion of Various Thermoplastic Polymers

Polymer	λ (kJ / kg)	T_m (°C)
Polyethylene	268–300	141
Polypropylene	209–259	183
Polyvinyl chloride	181	285
Polybutadiene	170–187	148
Polyamide 6	193–208	223
Polyamide 66	205	265

The chemical reaction that takes place during solidification of thermosets also leads to considerable thermal effects. In a hardened state, their thermal data are similar to those of amorphous thermoplastics. Figure 4.12 shows the specific heat graphs for the three polymer categories.

For filled polymer systems with inorganic and powdery fillers a rule of mixtures³ can be written as

² The values for heat of fusion were computed using data taken from: van Krevelen, D. W., and Hoftyzer, P. J., *Properties of Polymers*, Elsevier Scientific Publishing Company, Amsterdam, (1976).

³ Valid up to 65% filler content by volume.

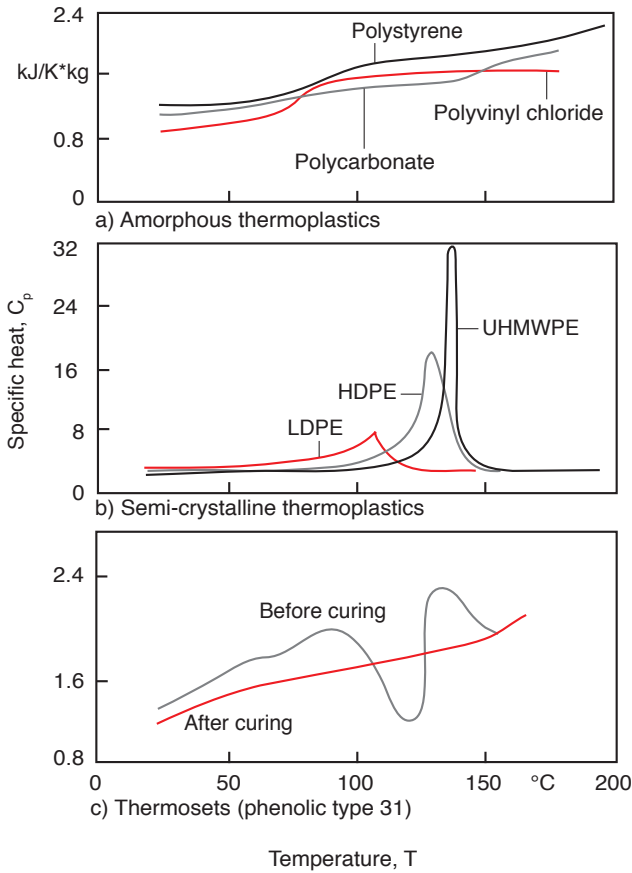


Figure 4.12 Specific heat curves for selected polymers of the three general polymer categories

$$C_p(T) = (1 - \psi_f)C_{PM}(T) + \psi_f C_{pf}(T) \quad (4.10)$$

where ψ_f represents the weight fraction of the filler and C_{PM} and C_{pf} the specific heat of the polymer matrix and the filler, respectively. As an example for the application of Eq. 4.10, Fig. 4.13 shows a specific heat curve of an unfilled polycarbonate and its corresponding computed specific heat curves for 10%, 20%, and 30% glass fiber content. In most cases, temperature dependence of C_p of inorganic fillers is minimal and need not be taken into consideration.

The specific heat of copolymers can be calculated using the mole fraction of the polymer components.

$$C_{p_{\text{copolymer}}} = \sigma_1 C_{p1} + \sigma_2 C_{p2} \quad (4.11)$$

where σ_1 and σ_2 are the mole fractions of the comonomer components and C_{p1} and C_{p2} the corresponding specific heat values.

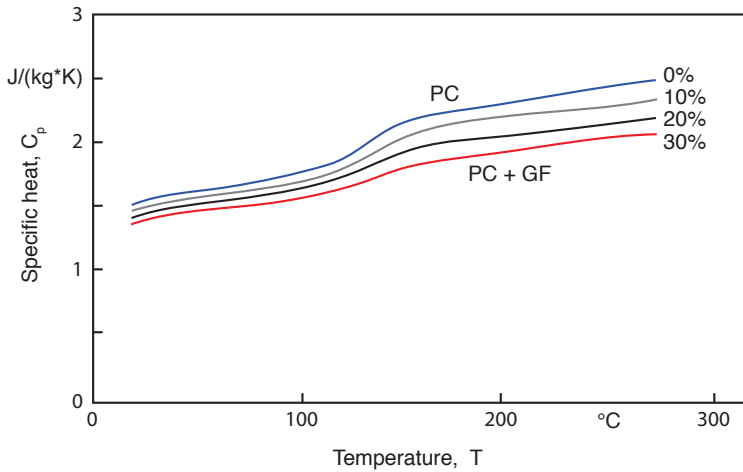


Figure 4.13 Generated specific heat curves for a filled and unfilled polycarbonate (Courtesy of Bayer AG, Germany)

4.1.3 Density

The density or its reciprocal, the specific volume, is a commonly used property for polymeric materials. The specific volume is often plotted as a function of pressure and temperature in what is known as a p-v-T diagram. Using polycarbonate as an example, a typical p-v-T diagram for an unfilled and a filled amorphous polymer is shown, in Figs. 4.14 to 4.16. The two slopes in the curves represent the specific volume of the melt and of the glassy amorphous polycarbonate, separated by the glass transition temperature. Figure 4.17 presents the p-v-T diagram for polyamide 66 as an example of a typical semi-crystalline polymer. Figure 4.18 shows the p-v-T

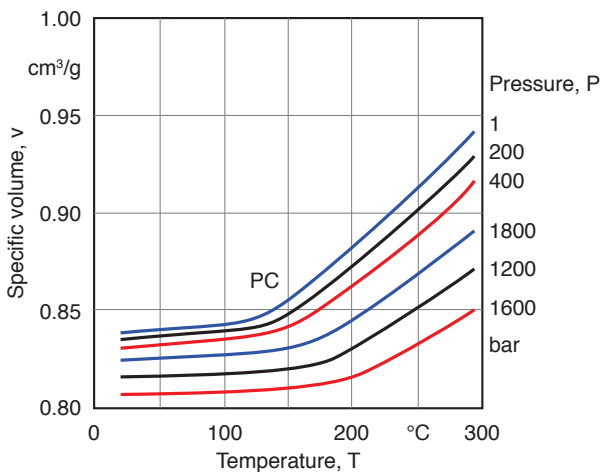


Figure 4.14 p-v-T diagram for a polycarbonate (Courtesy of Bayer AG, Germany)

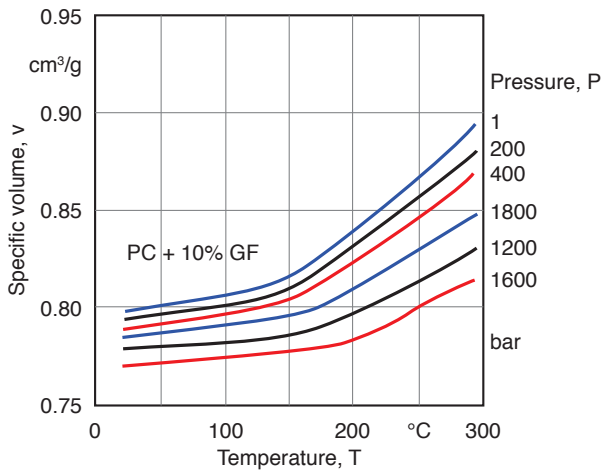


Figure 4.15 p-v-T diagram for a polycarbonate filled with 10% glass fiber (Courtesy of Bayer AG, Germany)

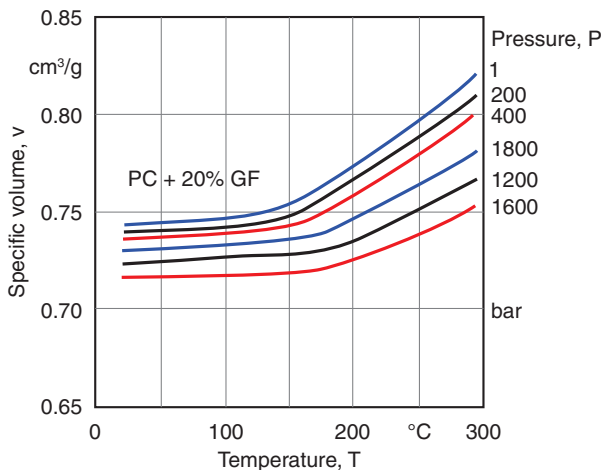


Figure 4.16 p-v-T diagram for a polycarbonate filled with 20% glass fiber (Courtesy of Bayer AG, Germany)

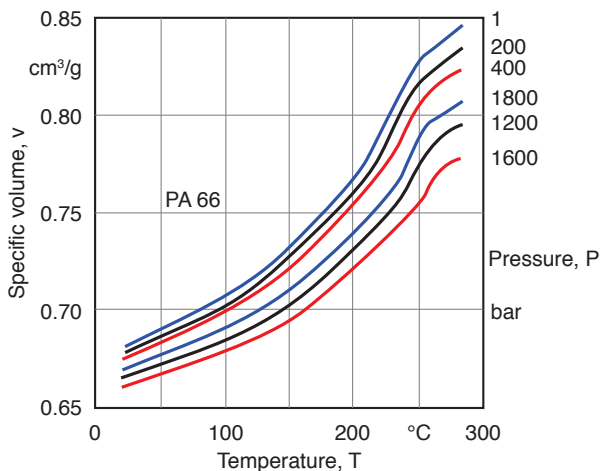


Figure 4.17 p-v-T diagram for a polyamide 66 (Courtesy of Bayer AG, Germany)

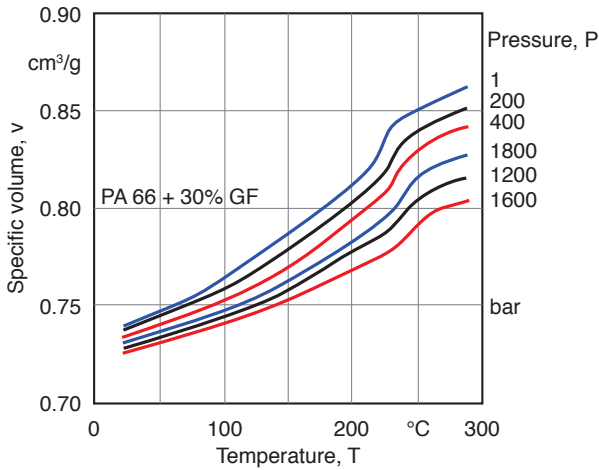


Figure 4.18 p-v-T diagram for a polyamide 66 filled with 30% glass fiber (Courtesy of Bayer AG, Germany)

diagram for polyamide 66 filled with 30% glass fiber. The curves clearly show the melting temperature (i. e., $T_m \approx 250$ °C for the unfilled PA 66 cooled at 1 bar, which marks the beginning of crystallization as the material cools). It should also come as no surprise that the glass transition temperatures are the same for the filled and unfilled materials.

When carrying out die flow calculations, the temperature dependence of the specific volume must often be dealt with analytically. At constant pressures, the density of pure polymers can be approximated by

$$\rho(T) = \rho_0 \frac{1}{1 + \alpha_t (T - T_0)} \quad (4.12)$$

where ρ_0 is the density at reference temperature T_0 , and α_t is the linear coefficient of thermal expansion.

For amorphous polymers, Eq. 4.12 is valid only for the linear segments (i. e., below or above T_g), and for semi-crystalline polymers it is only valid for temperatures above T_m .

The density of polymers filled with inorganic materials can be computed at any temperature using the following rule of mixtures

$$\rho_c(T) = \frac{\rho_m(T) \rho_f}{\psi \rho_m(T) + (1 - \psi) \rho_f} \quad (4.13)$$

where ρ_c , ρ_m and ρ_f are the densities of the composite, the polymer and the filler, respectively, and ψ is the weight fraction of the filler.

4.1.4 Thermal Diffusivity

Thermal diffusivity, defined in Eq. 4.4, is the material property that governs the process of thermal diffusion over time. The thermal diffusivity in amorphous thermoplastics decreases with temperature. A small jump is observed around the glass transition temperature due to the decrease in heat capacity at T_g . Figure 4.19 [3] presents the thermal diffusivity for selected amorphous thermoplastics.

With increasing temperature, a decrease in thermal diffusivity, is also observed in semi-crystalline thermoplastics. These materials show a minimum at the melting

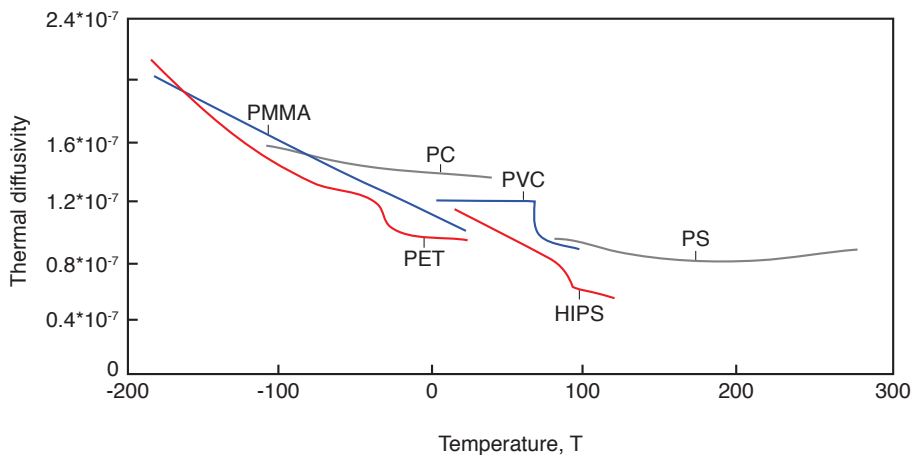


Figure 4.19 Thermal diffusivity as a function of temperature T for various amorphous thermoplastics

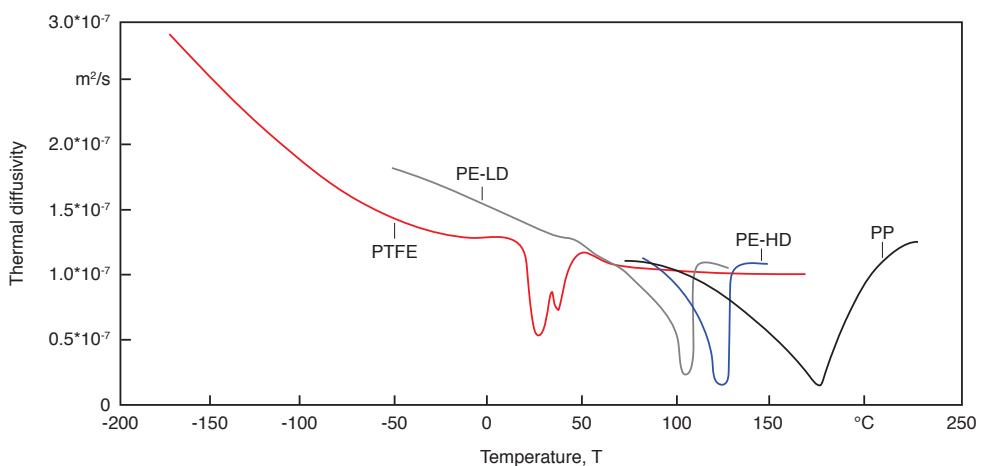


Figure 4.20 Thermal diffusivity as a function of temperature for various semi-crystalline thermoplastics

temperature as demonstrated in Fig. 4.20 [3] for a selected number of semi-crystalline thermoplastics. It has also been observed that the thermal diffusivity increases with increasing degree of crystallinity and that it depends on the rate of crystalline growth, hence, on the cooling speed.

4.1.5 Linear Coefficient of Thermal Expansion

The linear coefficient of thermal expansion is related to volume changes that occur in a polymer due to temperature variations; it is well represented in the p-v-T diagram. For many materials, thermal expansion is related to the melting temperature of that material, clearly demonstrated for a number of important materials in Fig. 4.21. Although the linear coefficient of thermal expansion varies with temperature, it can be considered constant within typical design and processing conditions. It is especially high for polyolefins, for which it ranges from $1.5 \times 10^{-4}/\text{K}$ to $2 \times 10^{-4}/\text{K}$; however, fibers and other fillers significantly reduce thermal expansion. A rule of mixtures is sufficient to calculate the thermal expansion coefficient of polymers that are filled with powdery and small particles as well as with short fibers. For this case, the rule of mixtures is written as

$$\alpha_c = \alpha_p(1 - \phi_f) + \alpha_f \phi_f \quad (4.14)$$

where ϕ_f is the volume fraction of the filler, and α_c , α_p and α_f are coefficients for the composite, the polymer, and the filler, respectively. In case of continuous fiber

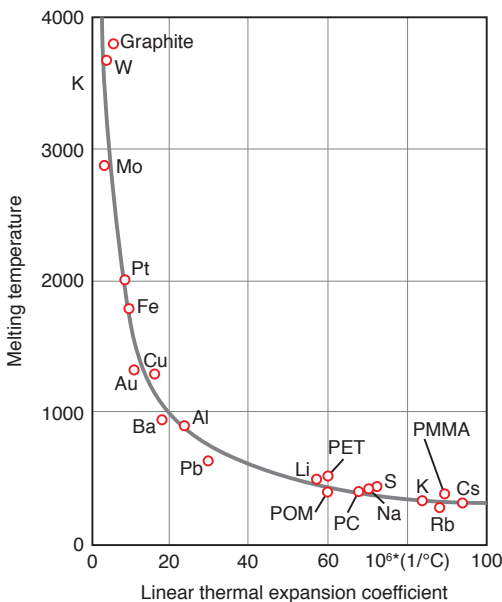


Figure 4.21 Relation between thermal expansion of some metals and plastics at 2°C and their respective melting temperatures

reinforcement, the rule of mixtures presented in Eq. 4.14 applies for the coefficient perpendicular to the reinforcing fibers. Parallel to the fiber direction, however, the thermal expansion of the fibers determines the linear coefficient of thermal expansion of the composite. Extensive calculations are necessary to determine coefficients in layered laminated composites.

4.1.6 Thermal Penetration

In addition to thermal diffusivity, the thermal penetration number is of considerable practical interest. It is given by

$$b = \sqrt{kC_p\rho} \quad (4.15)$$

If the thermal penetration number is known, the contact temperature T_C , which results when two bodies A and B that are at different temperatures touch, can easily be computed using

$$T_C = \frac{b_A T_A + b_B T_B}{b_A + b_B} \quad (4.16)$$

where T_A and T_B are the temperatures of the touching bodies and b_A and b_B are the thermal penetrations for both materials. The contact temperature is very important for many objects in daily use (e. g., from the handles of heated objects or drinking cups made of plastic, to the heat insulation of space crafts). It is also very important for the calculation of temperatures in tools and molds during polymer processing. The constants used to compute temperature dependent thermal penetration numbers for common thermoplastics are given in Table 4.3 [12].

Table 4.3 Thermal Penetration of Some Plastics

Plastic	Coefficients to calculate thermal penetration $b = a_a T + b_b$ ($W/s^{1/2}/m^2K$)	
	a_a	b_b
HDPE	1.41	441.7
LDPE	0.0836	615.1
PMMA	0.891	286.4
POM	0.674	699.6
PP	0.846	366.8
PS	0.909	188.9
PVC	0.649	257.8

4.1.7 Glass Transition Temperature

The glass transition temperature, T_g , is closely related to the secondary forces. Typical values for the glass transition temperature of common thermoplastics are listed in Chapter 3. If a polymer is mixed with a solvent, the glass transition temperature can be lowered and we can compute it with the following rule of mixtures⁴

$$T_{gM} = \frac{\phi_p \alpha_{ip} T_{gp} - (1 - \phi_p) T_{gs}}{\alpha_{ip} \phi_p + (1 - \phi_p) \alpha_{is}} \quad (4.17)$$

where α_{ip} and α_{is} are the linear coefficients of thermal expansion for the polymer and the solvent, respectively; T_{gM} , T_{gp} and T_{gs} are the glass transition temperatures of the mixture, the polymer, and the solvent, respectively; and ϕ_p is the volume fraction of polymer in the mixture. Stabilizers, plasticizers, and similar auxiliary processing agents work the same way. Usually, the rule of thumb applies that 1% by volume of plasticizer reduces the glass transition temperature by 2 K.

When mixing two incompatible polymers, two glass transition temperatures result, which are visible when measuring the elastic or loss modulus of the polymer blend.

4.1.8 Melting Temperature

The melting temperature, T_m , is the highest temperature at which crystalline structures can exist. Above this temperature the polymer can be considered a viscous or viscoelastic liquid, depending on the molecular weight of the polymer and the time scale associated with its deformation. An interesting observation to be noted is the relation between the melting and the glass transition temperatures. This relation can be written as

$$\frac{T_g}{T_m} \approx \frac{2}{3} \quad (4.18)$$

where the temperatures are expressed in degrees Kelvin.

■ 4.2 Measuring Thermal Data

Thanks to modern analytical instruments it is possible to measure thermal data with a high degree of accuracy. These data provide good insight into chemical and manufacturing processes. Accurate thermal data or properties are necessary for

⁴ This rule of mixtures only applies for compatible or miscible materials.

everyday calculations and computer simulations of thermal processes. Such analyses are used to design polymer processing installations and to determine and optimize processing conditions.

Over the last twenty years several physical thermal measuring devices have been developed to determine thermal data necessary to analyze processing and polymer component behavior.

4.2.1 Differential Thermal Analysis (DTA)

Differential thermal analysis tests are used to examine transitions and reactions that occur on the order between seconds and minutes, and involve a measurable energy differential of less than 0.04 J/g. Usually, measuring is done dynamically (i. e., with linear temperature variations in time). However, in some cases isothermal measurements are also done. DTA is mainly used to determine the transition temperatures. The principle is shown schematically in Fig. 4.22. Here, the sample, S , and an inert substance, I , are placed in an oven that has the ability to raise its temperature linearly. Two thermocouples that monitor the samples are connected opposite to one another such that no voltage is measured as long as S and I are at the same temperature:

$$\Delta T = T_s - T_I = 0 \quad (4.19)$$

However, if a transition or a reaction occurs in the sample at a temperature T_c , then heat is consumed or released, in which case $\Delta T \neq 0$. This thermal disturbance in time can be recorded and used to interpret possible information about the reaction temperature, T_c , the heat of transition or reaction, ΔH , or simply about the existence of a transition or reaction.

Figure 4.23 presents the temperature history in a sample with an endothermic melting point (i. e., such as the one that occurs during melting of semi-crystalline

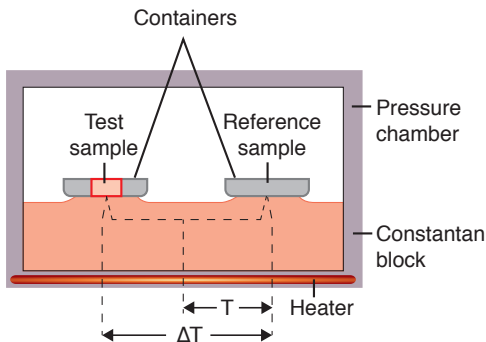


Figure 4.22 Schematic of a differential thermal analysis test

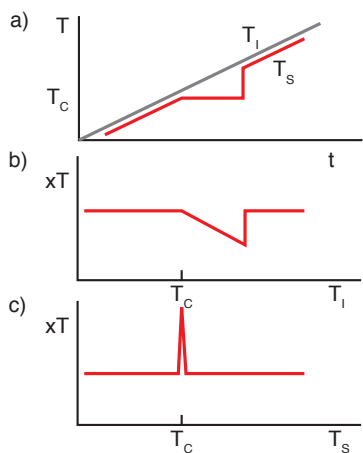


Figure 4.23 Temperature and temperature differences measured during melting of a semi-crystalline polymer sample

polymers). The figure also shows the functions $\Delta T(T_i)$ and $\Delta T(T_s)$ which result from such a test. A comparison between Figs. 4.23 (b) and (c) demonstrates that it is very important to record the sample temperature, T_s , to determine a transition temperature such as the melting or glass transition temperature.

4.2.2 Differential Scanning Calorimeter (DSC)

With the help of differential scanning calorimetry it is possible to determine thermal transitions of polymers in a range of temperatures between -180 and $+600$ °C. Other than in a DTA cell, in the DSC device thermocouples are not placed directly inside the sample or the reference substance. Instead, they are embedded in the specimen holder or stage on which the sample and reference pans are placed; the thermocouples make contact with the containers from the outside. A schematic diagram of a differential scanning calorimeter is very similar to the one shown in Fig. 4.22. Materials that do not show or undergo transition or react in the measuring range (e.g., air, glass powder, etc.) are placed inside the reference container. For standardization purposes typically materials whose properties are exactly known, such as mercury, tin, or zinc are used. In contrast to the DTA test, where samples larger than 10 g are needed, the DSC test requires samples that are in the mg range (< 10 mg). Although DSC tests are less sensitive than the DTA tests, they are the most widely used tests for thermal analysis. In fact, DTA tests are rarely used in the polymer industry.

Figure 4.24 [4] shows a typical DSC curve measured using a partly crystalline polymer sample. In the figure, the area enclosed between the trend line (bold) and the base line is a direct measurement for the amount of heat, ΔH , needed for transition. In this case, the transition is melting and the area corresponds to the *heat of fusion*.

The degree of crystallinity, χ , is determined from the ratio of the heat of fusion of a polymer sample, ΔH_{sc} , and the enthalpy of fusion of a 100% crystalline sample ΔH_c .

$$\chi = \frac{\Delta H_{sc}}{\Delta H_c} \quad (4.20)$$

In a DSC analysis of a semi-crystalline polymer, a jump in the specific heat curve, as shown in Fig. 4.24, becomes visible; a phenomenon that can easily be traced with a DSC. The glass transition temperature, T_g , is determined at the inflection point of the specific heat curve. The release of residual stresses as a material's temperature is raised above the glass transition temperature is often observed in a DSC analysis.

Specific heat, C_p , is one of the many material properties that can be measured using DSC. During a DSC temperature sweep, the sample pan and the reference pan are maintained at the same temperature. This allows the measurement of the differential energy required to maintain identical temperatures. The sample with the higher heat capacity will absorb a larger amount of heat, which is proportional to the difference between the heat capacity of the measuring sample and the reference sample.

It is also possible to determine the purity of a polymer sample when additional peaks or curve shifts are detected in a DSC measurement.

Thermal degradation is generally accompanied by an exothermic reaction that may result from oxidation. Such a reaction can easily be detected in a DSC output. By further warming of the test sample, crosslinking may take place and, finally, chain breakage, as shown in Fig. 4.24.

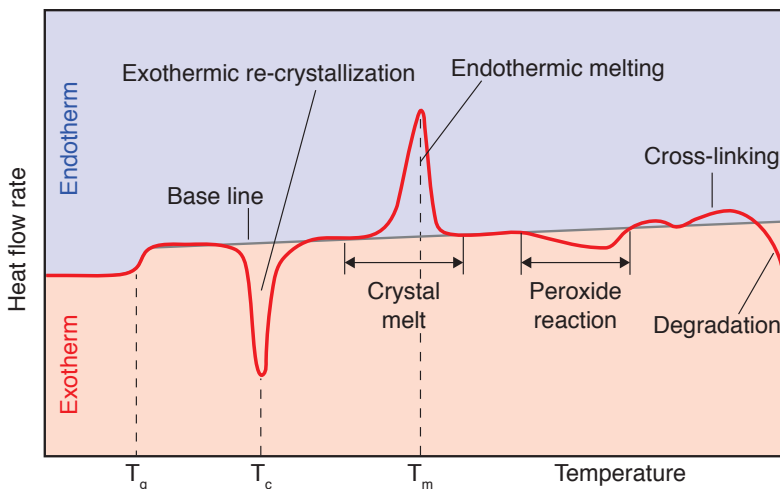


Figure 4.24 Typical DSC heat flow for a semi-crystalline polymer

An important aspect in DSC data interpretation is the finite heat flow resistance between the sample pan and the furnace surface. Studies by Janeschitz-Kriegl, Eder and co-workers [13, 14] have demonstrated that the heat transfer coefficient between the sample pan and furnace is of finite value, and cannot be disregarded when interpreting the data. In fact, with materials that have a low thermal conductivity, such as polymers, the finite heat transfer coefficient will significantly influence the temperature profiles of the samples.

4.2.3 Thermomechanical Analysis (TMA)

Thermomechanical analysis (TMA) measures shape stability of a material at elevated temperatures by physically penetrating it with a metal rod. A schematic diagram of TMA equipment is shown in Fig. 4.25. During TMA, the test specimen's temperature is raised at a constant rate, the sample is placed inside the measuring device, and a rod with a specified weight is placed on top of it. To allow for measurements at low temperatures, the sample, oven, and rod can be cooled with liquid nitrogen. TMA also allows the measurement of Vicat temperatures described in Chapter 9.

Most instruments are so precise that they can be used to measure the melting temperature of the material and, by using linear dilatometry to measure the thermal expansion coefficients. The thermal expansion coefficient can be measured using

$$\alpha_t = \frac{1}{L_0} \frac{\Delta L}{\Delta T} \quad (4.21)$$

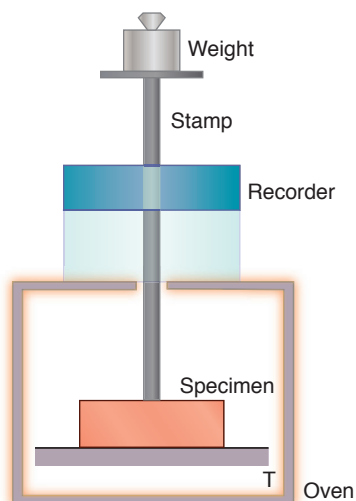


Figure 4.25 Schematic diagram of the thermomechanical analysis (TMA) device

where L_0 is the initial dimension of the test specimen, ΔL the change in size and ΔT the temperature difference. For isotropic materials a common relation between the linear and the volumetric thermal expansion coefficient can be used:

$$\gamma = 3\alpha_t \quad (4.22)$$

4.2.4 Thermogravimetry (TGA)

A thermogravimetric analyzer can measure weight changes of less than $10 \mu\text{g}$ as a function of temperature and time. This measurement technique, typically used to measure thermal stability, works on the principle of a beam balance. The testing chamber can be heated (up to approximately 1200°C) and rinsed with gases (inert or reactive). Measurements are performed on isothermal reactions or at temperature sweeps of less than 100 K/min . The maximum sample weight used during thermogravimetric analyses is 500 mg . Thermogravimetry is often used to identify the components in a blend or a compound based on the thermal stability of each component. Figure 4.26 shows results from a TGA analysis of a PVC fabric. The figure clearly shows the transitions at which the various components of the compound decompose. The percent of the original sample weight is recorded along with the change of the weight with respect to temperature. Five transitions representing (1) the decomposition of volatile components, (2) decomposition of the DOP plasticizer, (3) formation of HCl, (4) carbon-carbon scission, and (5) the forming of CO_2 , are clearly visible.

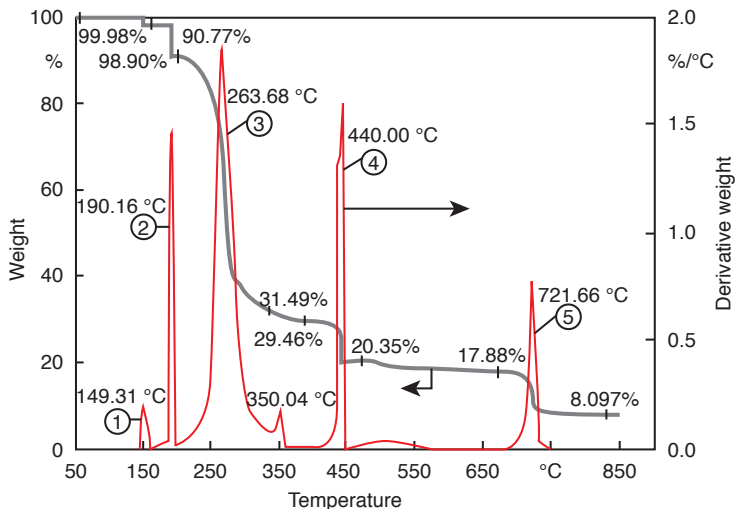


Figure 4.26 TGA analysis of a PVC fabric; (1) volatiles: humidity, monomers, solvents etc., (2) DOP plasticizer, (3) HCl formation, (4) carbon-carbon scission, and (5) CO_2 formation (Courtesy of the ICIPC, Medellín, Colombia)

4.2.5 Density Measurements

One simple form of calculating the density of a polymer sample is to first weigh the sample immersed in water. Assuming the density of water to be 1.0 g/cm^3 we can use the relation

$$\rho = \frac{m}{(m - m_i) \left(1 \text{ cm}^3/\text{g}\right)} \quad (4.23)$$

where m is mass of the specimen, m_i is the mass of the immersed specimen and $(m - m_i)$ is the mass of the displaced body of water.

Some common ways of determining density of polymeric materials are described by the test methods defined by ASTM D792, ISO 1183, and DIN 53 479 standards. Another common way of measuring density is the “through flow density meter”. Here, the density of water is changed to that of the polymer by adding ethanol until the plastic shavings are suspended in the solution. The density of the solution is then measured in a device that pumps the liquid through a U-pipe, where it is measured using ultrasound techniques. A density gradient technique is described by the standard ASTM D1505 test method.

Examples

1. A differential scanning calorimetry (DSC) test was performed on a 25 mg polyethylene terephthalate (PET) sample taken from the screw-top of a soda bottle. The test was performed using a heating rate of 5 K/min (5 K rise every minute). The DSC output is presented in Fig. 4.27.

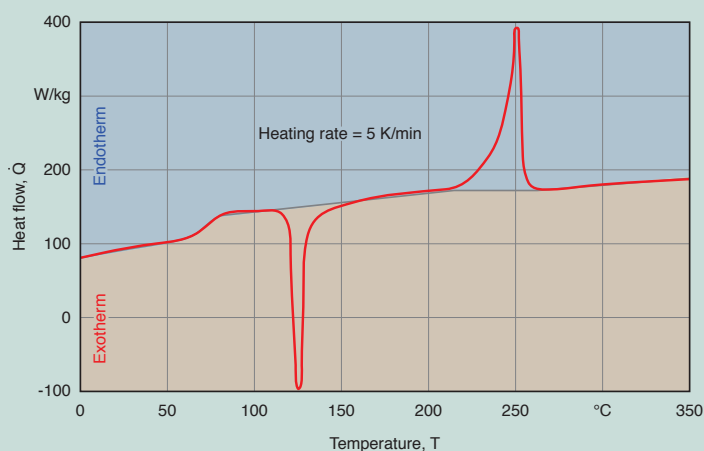


Figure 4.27 DSC scan of a PET bottle screw-top sample

Using the curve, estimate the glass transition temperature, T_g , the melting temperature, T_m , the crystallization temperature, T_c , and the heat of fusion, λ , for this specific PET sample during the temperature ramp-up.

If the heat of fusion for a hypothetically 100% crystalline PET sample is 137 kJ/kg [15], what was the degree of crystallinity in the PET bottle screw-top?

From the curve presented in Fig. 4.27 we can deduce that the glass transition temperature is approx. 72 °C, the crystallization temperature approx. 125 °C, and the melting temperature approx. 250 °C. Note that in all three cases there is range of temperatures at which each transition occurs. To compute the heat of fusion during the ramp-up we need to find the area between \dot{Q} and the base-line for the endothermic deviation around the melting point, between 210 and 260 °C. To do this, we must first transform the temperature scale to time by dividing it by the heating rate as

$$t = \frac{T}{5 \text{ K/min}} \frac{60 \text{ s}}{1 \text{ min}}$$

Hence, 50 °C becomes 600 s, 100 °C becomes 1200 s, etc. The integral equals 37.8 kJ/kg, which represents the heat of fusion of the sample during the temperature ramp-up. However, one must consider that this melting energy includes the extra crystallization that occurs between 108 and 155 °C. The exothermic energy is computed by integrating the curve between those two temperatures in a transformed time scale. The integral equals 22.9 kJ/kg. We can also find the area under the curve by transforming the heat flow, \dot{Q} , to heat capacity, C_p , and integrating using the temperature scale instead of a time scale. Heat capacity can be computed using

$$C_p = \frac{\dot{Q}}{5 \text{ K/min}} \frac{60 \text{ s}}{\text{min}}$$

The degree of crystallinity of the initial PET bottle screw-top can now easily be computed using

$$\chi = \frac{37.8 \text{ kJ/kg} - 22.9 \text{ kJ/kg}}{137 \text{ kJ/kg}} = 0.109 \text{ or } 10.9\%$$

Problems

1. Does the coefficient of linear expansion of a polymer increase or decrease after the addition of glass fibers?
2. Plot T_g versus T_m for several polymers. What trend or relation do you observe?
3. In a soda bottle, how does the degree of crystallinity in the screw-top region compare to the degree of crystallinity in the wall? Explain.
4. A 5 K/min heating and 5 K/min cooling differential scanning calorimetry (DSC) test (Fig. 4.28) was performed on a 10.8 mg sample of PE-LD. What is the specific heat of the PE-LD just after melting during heating

and just before crystallization during cooling? What is the degree of crystallinity of the initial and the final samples?

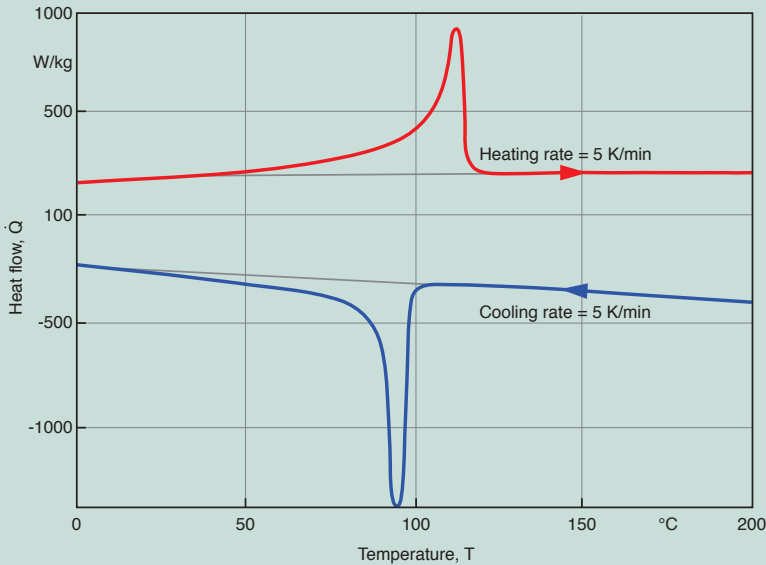


Figure 4.28 Heating and cooling DSC scans of a PE-LD sample

5. A differential scanning calorimetry (DSC) test was performed on an 11.4 mg polyethylene terephthalate (PET) sample using the standard ASTM D 3417 test method. The ASTM test calls for a temperature heating rate of 20 °C/min (20 °C rise every minute). The DSC output is presented below⁵.

Using the curve in Fig. 4.29, estimate the glass transition temperature, T_g , the melting temperature, T_m , the crystallization temperature, T_c and the heat of fusion, λ , for this specific PET sample during the temperature ramp-up. Note that the heat flow scale has already been transformed to heat capacity. How do T_g and T_m compare to the “book values”?

If the heat of fusion for a hypothetically 100% crystalline PET is 137 kJ/kg, what was the degree of crystallinity of the original PET sample?

In the graph of Fig. 4.29 sketch a hypothetical DSC output for the original PET sample with a temperature heating rate that is too fast to allow any additional crystallization during heating.

6. A typical injection pack/hold pressure during injection molding of polyamide 66 components is 1000 bar and the injection temperature is 280 °C. The gate freezes shut when the average temperature inside the mold reaches 225 °C.

Draw the process on the p-v-T diagram given in Fig. 4.17.

⁵ Courtesy of ICIPC, Medellín, Colombia.

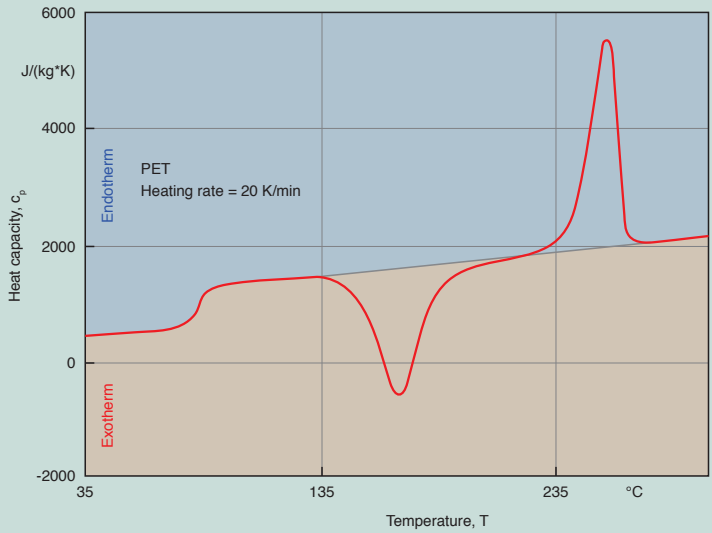


Figure 4.29 DSC scan of a PET sample

What volume shrinkage should be taken into account when designing the mold? Note that the shrinkage is mostly taken up by a thickness reduction.

7. Isothermal differential scanning calorimetry (DSC) tests were performed on three unsaturated polyester (UPE) samples at three different temperatures (100 °C, 110 °C, and 120 °C). The output for the three DSC tests is presented in the Fig. 4.30. On the graph, label which curve is associated with which test temperature. From the curves in Fig. 4.30 estimate the total heat of reaction, Q_T .

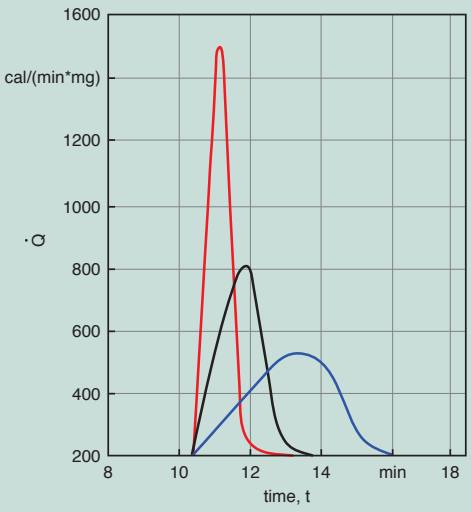


Figure 4.30 Isothermal DSC measurements of UPE samples (Courtesy of Gen-Corp Research, Akron, OH)

8. A differential scanning calorimetry (DSC) test (Fig. 4.31) was performed on an 18.3 mg sample of polystyrene. What is the glass transition temperature of the sample? Determine the specific heat of this PS just before the glass transition temperature has been reached. What is C_p just beyond T_g ? Why is the heat higher as the temperature increases?

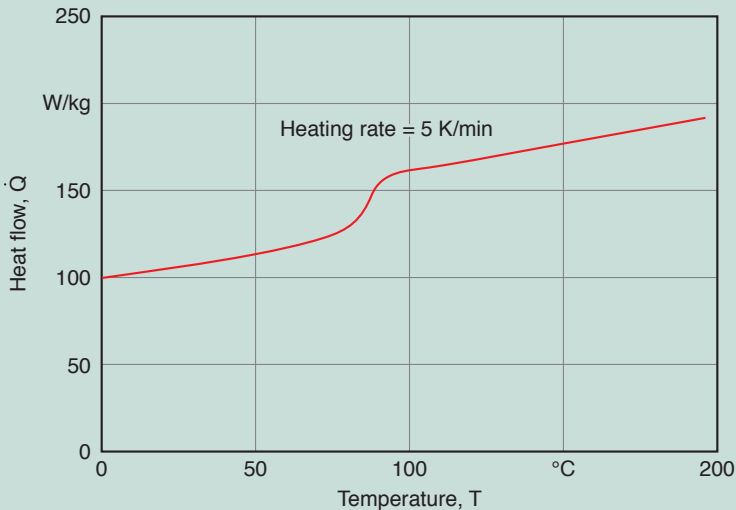


Figure 4.31 DSC scan of a PS sample

9. Sketch the p-v-T diagrams for a semi-crystalline polymer with a high and a low cooling rate.
10. A polystyrene sample is split in two and the glass transition temperature for each half is measured using DSC in two different laboratories. They reported the values for this property to be 96 °C and 106 °C, respectively. Suggest 3 possible explanations for this difference.

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5

Rheology of Polymer Melts

■ 5.1 Introduction

Rheology is the field of science that studies fluid behavior during flow-induced deformation. Of the variety of materials that rheologists study, polymers have been found to be the most interesting and complex. Polymer melts are shear-thinning, viscoelastic, and their flow properties are temperature dependent. Viscosity is the most widely used material parameter when determining the behavior of polymers during processing. Because the majority of polymer processes are shear rate dominated, the viscosity of the melt is commonly measured using shear deformation measurement devices. However, some polymer processes, such as blow molding, thermoforming, and fiber spinning, are dominated by either elongational deformation or by a combination of shear and elongational deformation. In addition, some polymer melts exhibit significant elastic effects during deformation. This chapter will concentrate on shear deformation models but, for completeness, elongational flows, concentrated suspensions, and viscoelastic fluids will also be covered. Modeling and simulation of polymer flows will be briefly discussed. For further reading on rheology of polymer melts, the reader should consult the literature [1–6]. For more detail on polymer flow and processing simulation the literature [7, 8] should also be reviewed.

5.1.1 Continuum Mechanics

When analyzing the flow or deformation of polymers during processing, a balance of energy, mass, and forces must be preserved.

Using the notation found in Fig. 5.1 and performing a mass balance on the differential element, for an incompressible liquid¹ one can write

¹ It is clear that a polymer melt is not incompressible. However, assuming incompressibility simplifies the analysis significantly without losing accuracy in flow predictions.

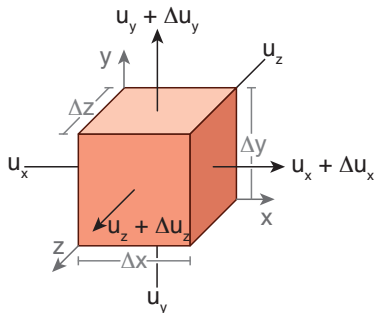


Figure 5.1 Differential element used for mass balance

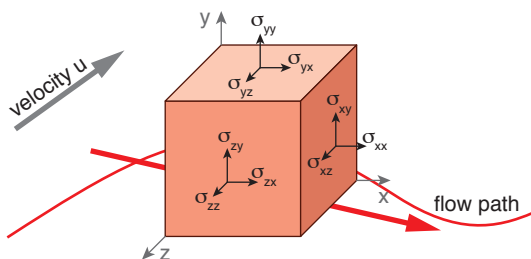


Figure 5.2 Differential element used for force balance

$$\nabla \cdot \underline{\mathbf{u}} = 0 \quad (5.1)$$

where Eq. 5.1 represents the divergence of the velocity vector and is presented in Appendix A in expanded form for various coordinate systems.

Using a similar differential element that is moving with the fluid, as shown in Fig. 5.2, a force balance results in

$$\rho \frac{D\underline{\mathbf{u}}}{Dt} = [\nabla \cdot \underline{\underline{\sigma}}] + \rho \underline{\underline{\mathbf{g}}} \quad (5.2)$$

where the term on the left side represents the inertia of the polymer melt, the first term on the right is the divergence of the stress tensor and represents viscous and elastic forces, and the second term on the right represents the gravitational effects. The operator D/Dt is the *substantial* or *material derivative* defined by

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + \underline{\mathbf{u}} \cdot \nabla \quad (5.3)$$

which represents a convective or embedded frame of reference that moves with a material particle.

The stress $\underline{\underline{\sigma}}$, sometimes referred to as the *total stress*, can be split into *hydrostatic pressure*, $\underline{\underline{\sigma}}_H$, and *deviatoric stress*, $\underline{\underline{\tau}}$. The hydrostatic pressure is a stress vector that acts only in the normal direction to the surfaces and can be represented by $-p\underline{\underline{\delta}}$, where p is the pressure and $\underline{\underline{\delta}}$ is a unit tensor. The momentum balance can now be written as