Chapter 15 Characteristics, Applications, and Processing of Polymers

Photograph of several billiard balls that are made of phenol-formaldehyde (Bakelite). The Materials of Importance piece that follows Section 15.15 discusses the invention of phenol-formaldehyde and its replacement of ivory for billiard balls. (Photography by S. Tanner.)

WHY STUDY *the Characteristics, Applications, and Processing of Polymers?*

There are several reasons why an engineer should know something about the characteristics, applications, and processing of polymeric materials. Polymers are used in a wide variety of applications from construction materials to microelectronics processing. Thus, most engineers will be required to work with polymers at some point in their careers. Understanding the mechanisms by which polymers elastically and plastically deform allows one to alter and control their moduli of elasticity and strengths (Sections 15.7 and 15.8). Also, additives may be incorporated into polymeric materials to modify a host of properties, including strength, abrasion resistance, toughness, thermal stability, stiffness, deteriorability, color, and flammability resistance (Section 15.21).

Learning Objectives

After careful study of this chapter you should be able to do the following:

1. Make schematic plots of the three characteristic stress–strain behaviors observed for polymeric materials.
2. Describe/sketch the various stages in the elastic and plastic deformations of a semicrystalline (spherulitic) polymer.
3. Discuss the influence of the following factors on polymer tensile modulus and/or strength: (a) molecular weight, (b) degree of crystallinity, (c) predeformation, and (d) heat treating of undeformed materials.
4. Describe the molecular mechanism by which elastomeric polymers deform elastically.
5. List four characteristics or structural components of a polymer that affect both its melting and glass-transition temperatures.
6. Cite the seven different polymer application types and, for each, note its general characteristics.
7. Briefly describe addition and condensation polymerization mechanisms.
8. Name the five types of polymer additives and, for each, indicate how it modifies the properties.
9. Name and briefly describe five fabrication techniques used for plastic polymers.

15.1 INTRODUCTION

This chapter discusses some of the characteristics important to polymeric materials and, in addition, the various types and processing techniques.

Mechanical Behavior of Polymers

15.2 STRESS–STRAIN BEHAVIOR

The mechanical properties of polymers are specified with many of the same parameters that are used for metals—that is, modulus of elasticity, and yield and tensile strengths. For many polymeric materials, the simple stress–strain test is employed for the characterization of some of these mechanical parameters.[1] The mechanical characteristics of polymers, for the most part, are highly sensitive to the rate of deformation (strain rate), the temperature, and the chemical nature of the environment (the presence of water, oxygen, organic solvents, etc.). Some modifications of the testing techniques and specimen configurations used for metals (Chapter 6) are necessary with polymers, especially for the highly elastic materials, such as rubbers.

Polymers

elastomer

Three typically different types of stress–strain behavior are found for polymeric materials, as represented in Figure 15.1. Curve *A* illustrates the stress–strain character for a brittle polymer, inasmuch as it fractures while deforming elastically. The behavior for a plastic material, curve *B*, is similar to that for many metallic materials; the initial deformation is elastic, which is followed by yielding and a region of plastic deformation. Finally, the deformation displayed by curve *C* is totally elastic; this rubber-like elasticity (large recoverable strains produced at low stress levels) is displayed by a class of polymers termed the **elastomers.**

Modulus of elasticity (termed *tensile modulus* or sometimes just *modulus* for polymers) and ductility in percent elongation are determined for polymers in the

---

[1] ASTM Standard D 638, "Standard Test Method for Tensile Properties of Plastics."

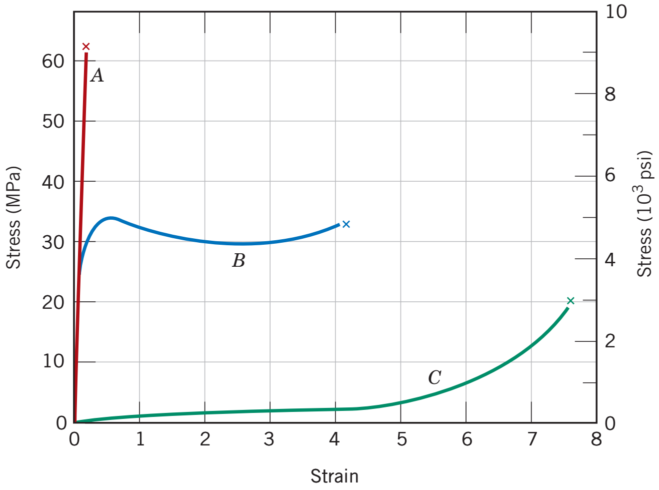


Figure 15.1 The stress–strain behavior for brittle (curve *A*), plastic (curve *B*), and highly elastic (elastomeric) (curve *C*) polymers.

same manner as for metals (Section 6.6). For plastic polymers (curve *B*, Figure 15.1), the yield point is taken as a maximum on the curve, which occurs just beyond the termination of the linear-elastic region (Figure 15.2). The stress at this maximum is the yield strength (σ_y). Furthermore, tensile strength (*TS*) corresponds to the stress at which fracture occurs (Figure 15.2); *TS* may be greater than or less than σ_y. Strength, for these plastic polymers, is normally taken as tensile strength. Table 15.1 gives these mechanical properties for several polymeric materials; more comprehensive lists are provided in Tables B.2, B.3, and B.4, Appendix B.

Polymers are, in many respects, mechanically dissimilar to metals (Figures 1.4, 1.5, and 1.6). For example, the modulus for highly elastic polymeric materials may be as low as 7 MPa (10^3 psi), but may run as high as 4 GPa (0.6×10^6 psi) for some of the very stiff polymers; modulus values for metals are much larger and range between 48 and 410 GPa (7×10^6 to 60×10^6 psi). Maximum tensile strengths for polymers are about 100 MPa (15,000 psi)—for some metal alloys 4100 MPa (600,000 psi). And, whereas metals rarely elongate plastically to more than 100%, some highly elastic polymers may experience elongations to greater than 1000%.

In addition, the mechanical characteristics of polymers are much more sensitive to temperature changes near room temperature. Consider the stress–strain behavior for poly(methyl methacrylate) (Plexiglas) at several temperatures between 4 and

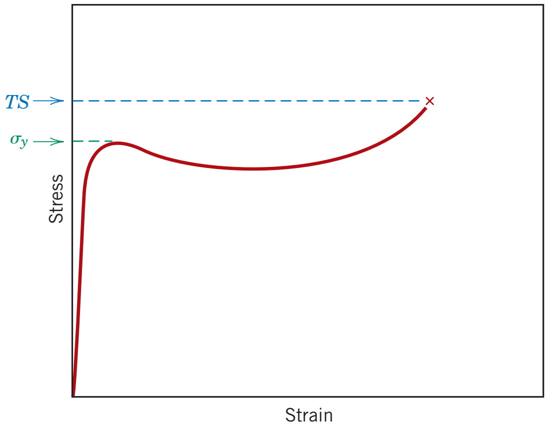


Figure 15.2 Schematic stress–strain curve for a plastic polymer showing how yield and tensile strengths are determined.

Table 15.1 Room-Temperature Mechanical Characteristics of Some of the More Common Polymers

Material	*Specific Gravity*	*Tensile Modulus [GPa (ksi)]*	*Tensile Strength [MPa (ksi)]*	*Yield Strength [MPa (ksi)]*	*Elongation at Break (%)*
Polyethylene (low density)	0.917–0.932	0.17–0.28 (25–41)	8.3–31.4 (1.2–4.55)	9.0–14.5 (1.3–2.1)	100–650
Polyethylene (high density)	0.952–0.965	1.06–1.09 (155–158)	22.1–31.0 (3.2–4.5)	26.2–33.1 (3.8–4.8)	10–1200
Poly(vinyl chloride)	1.30–1.58	2.4–4.1 (350–600)	40.7–51.7 (5.9–7.5)	40.7–44.8 (5.9–6.5)	40–80
Polytetrafluoroethylene	2.14–2.20	0.40–0.55 (58–80)	20.7–34.5 (3.0–5.0)	—	200–400
Polypropylene	0.90–0.91	1.14–1.55 (165–225)	31–41.4 (4.5–6.0)	31.0–37.2 (4.5–5.4)	100–600
Polystyrene	1.04–1.05	2.28–3.28 (330–475)	35.9–51.7 (5.2–7.5)	—	1.2–2.5
Poly(methyl methacrylate)	1.17–1.20	2.24–3.24 (325–470)	48.3–72.4 (7.0–10.5)	53.8–73.1 (7.8–10.6)	2.0–5.5
Phenol-formaldehyde	1.24–1.32	2.76–4.83 (400–700)	34.5–62.1 (5.0–9.0)	—	1.5–2.0
Nylon 6,6	1.13–1.15	1.58–3.80 (230–550)	75.9–94.5 (11.0–13.7)	44.8–82.8 (6.5–12)	15–300
Polyester (PET)	1.29–1.40	2.8–4.1 (400–600)	48.3–72.4 (7.0–10.5)	59.3 (8.6)	30–300
Polycarbonate	1.20	2.38 (345)	62.8–72.4 (9.1–10.5)	62.1 (9.0)	110–150

Source: *Modern Plastics Encyclopedia '96*. Copyright 1995, The McGraw-Hill Companies. Reprinted with permission.

60°C (40 and 140°F) (Figure 15.3). It should be noted that increasing the temperature produces (1) a decrease in elastic modulus, (2) a reduction in tensile strength, and (3) an enhancement of ductility—at 4°C (40°F) the material is totally brittle, while there is considerable plastic deformation at both 50 and 60°C (122 and 140°F).

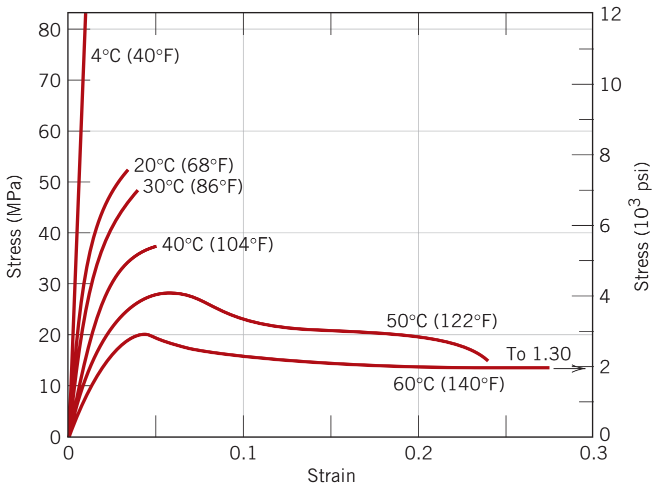


Figure 15.3 The influence of temperature on the stress–strain characteristics of poly(methyl methacrylate). (From T. S. Carswell and H. K. Nason, "Effect of Environmental Conditions on the Mechanical Properties of Organic Plastics," *Symposium on Plastics,* American Society for Testing and Materials, Philadelphia, 1944. Copyright, ASTM, 1916 Race Street, Philadelphia, PA 19103. Reprinted with permission.)

The influence of strain rate on the mechanical behavior may also be important. In general, decreasing the rate of deformation has the same influence on the stress–strain characteristics as increasing the temperature; that is, the material becomes softer and more ductile.

15.3 MACROSCOPIC DEFORMATION

Polymers

Some aspects of the macroscopic deformation of semicrystalline polymers deserve our attention. The tensile stress–strain curve for a semicrystalline material, which was initially undeformed, is shown in Figure 15.4; also included in the figure are schematic representations of the specimen profiles at various stages of deformation. Both upper and lower yield points are evident on the curve, which are followed by a near horizontal region. At the upper yield point, a small neck forms within the gauge section of the specimen. Within this neck, the chains become oriented (i.e., chain axes become aligned parallel to the elongation direction, a condition that is represented schematically in Figure 15.13*d*), which leads to localized strengthening. Consequently, there is a resistance to continued deformation at this point, and specimen elongation proceeds by the propagation of this neck region along the gauge length; the chain orientation phenomenon (Figure 15.13*d*) accompanies this neck extension. This tensile behavior may be contrasted to that found for ductile metals (Section 6.6), wherein once a neck has formed, all subsequent deformation is confined to within the neck region.

Concept Check 15.1

When citing the ductility as percent elongation for semicrystalline polymers, it is not necessary to specify the specimen gauge length, as is the case with metals. Why is this so?

[*The answer may be found at www.wiley.com/college/callister (Student Companion Site).*]

15.4 VISCOELASTIC DEFORMATION

viscoelasticity

An amorphous polymer may behave like a glass at low temperatures, a rubbery solid at intermediate temperatures [above the glass transition temperature (Section 15.12)], and a viscous liquid as the temperature is further raised. For relatively small deformations, the mechanical behavior at low temperatures may be elastic; that is, in conformity to Hooke's law, $\sigma = E\epsilon$. At the highest temperatures, viscous or liquid-like behavior prevails. For intermediate temperatures the polymer is a rubbery solid that exhibits the combined mechanical characteristics of these two extremes; the condition is termed **viscoelasticity.**

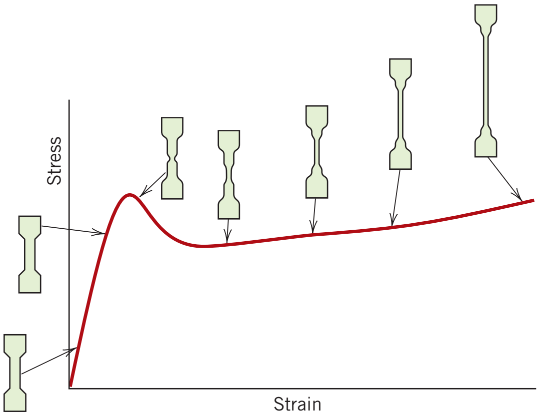


Figure 15.4 Schematic tensile stress–strain curve for a semicrystalline polymer. Specimen contours at several stages of deformation are included. (From Jerold M. Schultz, *Polymer Materials Science,* copyright © 1974, p. 488. Reprinted by permission of Prentice Hall, Inc., Englewood Cliffs, NJ.)

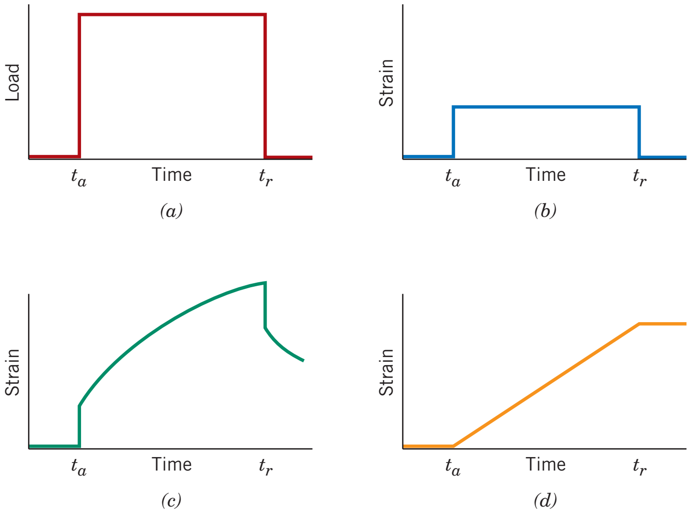


Figure 15.5 (*a*) Load versus time, where load is applied instantaneously at time t_a and released at t_r. For the load–time cycle in (*a*), the strain-versus-time responses are for totally elastic (*b*), viscoelastic (*c*), and viscous (*d*) behaviors.

Elastic deformation is instantaneous, which means that total deformation (or strain) occurs the instant the stress is applied or released (i.e., the strain is independent of time). In addition, upon release of the external stress, the deformation is totally recovered—the specimen assumes its original dimensions. This behavior is represented in Figure 15.5*b* as strain versus time for the instantaneous load–time curve, shown in Figure 15.5*a*.

By way of contrast, for totally viscous behavior, deformation or strain is not instantaneous; that is, in response to an applied stress, deformation is delayed or dependent on time. Also, this deformation is not reversible or completely recovered after the stress is released. This phenomenon is demonstrated in Figure 15.5*d*.

For the intermediate viscoelastic behavior, the imposition of a stress in the manner of Figure 15.5*a* results in an instantaneous elastic strain, which is followed by a viscous, time-dependent strain, a form of anelasticity (Section 6.4); this behavior is illustrated in Figure 15.5*c*.

A familiar example of these viscoelastic extremes is found in a silicone polymer that is sold as a novelty and known by some as "silly putty." When rolled into a ball and dropped onto a horizontal surface, it bounces elastically—the rate of deformation during the bounce is very rapid. On the other hand, if pulled in tension with a gradually increasing applied stress, the material elongates or flows like a highly viscous liquid. For this and other viscoelastic materials, the rate of strain determines whether the deformation is elastic or viscous.

Viscoelastic Relaxation Modulus

The viscoelastic behavior of polymeric materials is dependent on both time and temperature; several experimental techniques may be used to measure and quantify this behavior. *Stress relaxation* measurements represent one possibility. With these tests, a specimen is initially strained rapidly in tension to a predetermined and relatively low strain level. The stress necessary to maintain this strain is measured as a function of time, while temperature is held constant. Stress is found to decrease with time due to molecular relaxation processes that take place within the polymer. We may define a **relaxation modulus** $E_r(t)$, a time-dependent elastic modulus for viscoelastic polymers, as

$$E_r(t) = \frac{\sigma(t)}{\epsilon_0} \tag{15.1}$$

relaxation modulus

Relaxation modulus—ratio of time-dependent stress and constant strain value

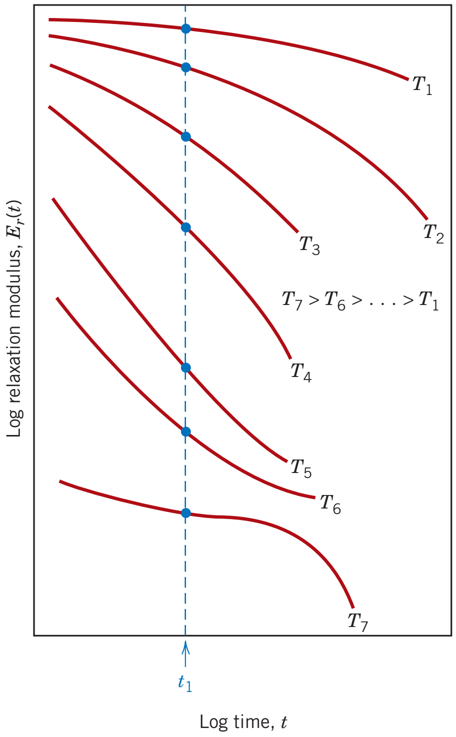


Figure 15.6 Schematic plot of logarithm of relaxation modulus versus logarithm of time for a viscoelastic polymer; isothermal curves are generated at temperatures T_1 through T_7. The temperature dependence of the relaxation modulus is represented as log $E_r(t_1)$ versus temperature.

where $\sigma(t)$ is the measured time-dependent stress and ϵ_0 is the strain level, which is maintained constant.

Furthermore, the magnitude of the relaxation modulus is a function of temperature; and to more fully characterize the viscoelastic behavior of a polymer, isothermal stress relaxation measurements must be conducted over a range of temperatures. Figure 15.6 is a schematic log $E_r(t)$-versus-log time plot for a polymer that exhibits viscoelastic behavior. Curves generated at a variety of temperatures are included. Key features of this plot are that (1) the magnitude of $E_r(t)$ decreases with time (corresponding to the decay of stress, Equation 15.1), and (2) the curves are displaced to lower $E_r(t)$ levels with increasing temperature.

To represent the influence of temperature, data points are taken at a specific time from the log $E_r(t)$-versus-log time plot—for example, t_1 in Figure 15.6—and then cross-plotted as log $E_r(t_1)$ versus temperature. Figure 15.7 is such a plot for an amorphous (atactic) polystyrene; in this case, t_1 was arbitrarily taken 10 s after the load application. Several distinct regions may be noted on the curve shown in this figure. At the lowest temperatures, in the glassy region, the material is rigid and brittle, and the value of $E_r(10)$ is that of the elastic modulus, which initially is virtually independent of temperature. Over this temperature range, the strain–time characteristics are as represented in Figure 15.5*b*. On a molecular level, the long molecular chains are essentially frozen in position at these temperatures.

As the temperature is increased, $E_r(10)$ drops abruptly by about a factor of 10^3 within a 20°C (35°F) temperature span; this is sometimes called the leathery, or glass transition region, and the glass transition temperature (T_g, Section 15.13) lies near the upper temperature extremity; for polystyrene (Figure 15.7), $T_g = 100°\text{C}$ (212°F). Within this temperature region, a polymer specimen will be leathery; that is, deformation will be time dependent and not totally recoverable on release of an applied load, characteristics that are depicted in Figure 15.5*c*.

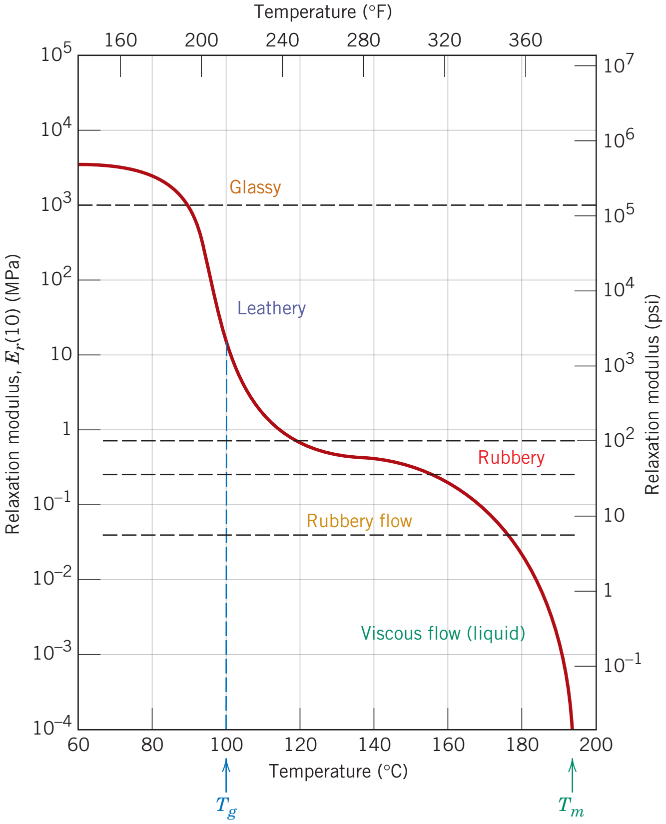


Figure 15.7 Logarithm of the relaxation modulus versus temperature for amorphous polystyrene, showing the five different regions of viscoelastic behavior. (From A. V. Tobolsky, *Properties and Structures of Polymers.* Copyright © 1960 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

Within the rubbery plateau temperature region (Figure 15.7), the material deforms in a rubbery manner; here, both elastic and viscous components are present, and deformation is easy to produce because the relaxation modulus is relatively low.

The final two high-temperature regions are rubbery flow and viscous flow. Upon heating through these temperatures, the material experiences a gradual transition to a soft rubbery state, and finally to a viscous liquid. In the rubbery flow region, the polymer is a very viscous liquid that exhibits both elastic and viscous flow components. Within the viscous flow region, the modulus decreases dramatically with increasing temperature; again, the strain–time behavior is as represented in Figure 15.5*d*. From a molecular standpoint, chain motion intensifies so greatly that for viscous flow, the chain segments experience vibration and rotational motion largely independent of one another. At these temperatures, any deformation is entirely viscous and essentially no elastic behavior occurs.

Normally, the deformation behavior of a viscous polymer is specified in terms of viscosity, a measure of a material's resistance to flow by shear forces. Viscosity is discussed for the inorganic glasses in Section 12.10.

The rate of stress application also influences the viscoelastic characteristics. Increasing the loading rate has the same influence as lowering temperature.

The log $E_r(10)$-versus-temperature behavior for polystyrene materials having several molecular configurations is plotted in Figure 15.8. The curve for the amorphous material (curve *C*) is the same as in Figure 15.7. For a lightly crosslinked atactic polystyrene (curve *B*), the rubbery region forms a plateau that extends to the temperature at which the polymer decomposes; this material will not experience melting. For increased crosslinking, the magnitude of the plateau $E_r(10)$ value will

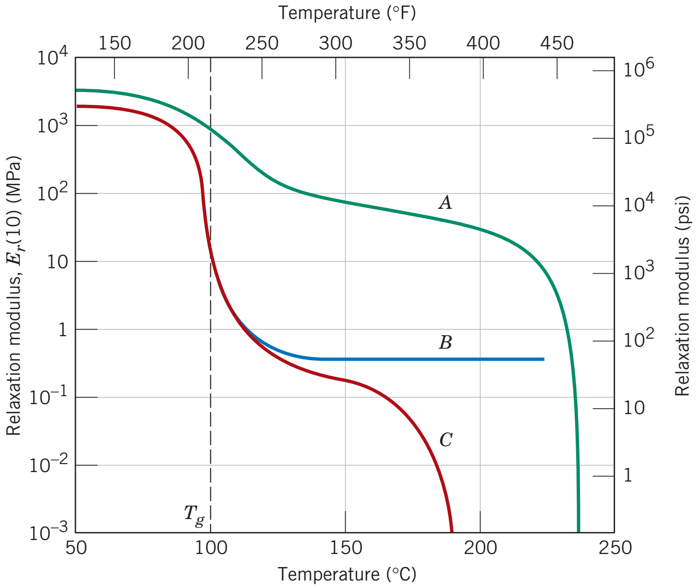


Figure 15.8 Logarithm of the relaxation modulus versus temperature for crystalline isotactic (curve *A*), lightly crosslinked atactic (curve *B*), and amorphous (curve *C*) polystyrene. (From A. V. Tobolsky, *Properties and Structures of Polymers.* Copyright © 1960 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

also increase. Rubber or elastomeric materials display this type of behavior and are ordinarily used at temperatures within this plateau range.

Also shown in Figure 15.8 is the temperature dependence for an almost totally crystalline isotactic polystyrene (curve *A*). The decrease in $E_r(10)$ at T_g is much less pronounced than the other polystyrene materials since only a small volume fraction of this material is amorphous and experiences the glass transition. Furthermore, the relaxation modulus is maintained at a relatively high value with increasing temperature until its melting temperature T_m is approached. From Figure 15.8, the melting temperature of this isotactic polystyrene is about 240°C (460°F).

Viscoelastic Creep

Many polymeric materials are susceptible to time-dependent deformation when the stress level is maintained constant; such deformation is termed *viscoelastic creep.* This type of deformation may be significant even at room temperature and under modest stresses that lie below the yield strength of the material. For example, automobile tires may develop flat spots on their contact surfaces when the automobile is parked for prolonged time periods. Creep tests on polymers are conducted in the same manner as for metals (Chapter 8); that is, a stress (normally tensile) is applied instantaneously and is maintained at a constant level while strain is measured as a function of time. Furthermore, the tests are performed under isothermal conditions. Creep results are represented as a time-dependent *creep modulus* $E_c(t)$, defined by[2]

$$E_c(t) = \frac{\sigma_0}{\epsilon(t)} \tag{15.2}$$

wherein σ_0 is the constant applied stress and $\epsilon(t)$ is the time-dependent strain. The creep modulus is also temperature sensitive and diminishes with increasing temperature.

---

[2] *Creep compliance,* $J_c(t)$, the reciprocal of the creep modulus, is also sometimes used in this context.

With regard to the influence of molecular structure on the creep characteristics, as a general rule the susceptibility to creep decreases [i.e., $E_c(t)$ increases] as the degree of crystallinity increases.

Concept Check 15.2

An amorphous polystyrene that is deformed at 120°C will exhibit which of the behaviors shown in Figure 15.5?

[*The answer may be found at* www.wiley.com/college/callister *(Student Companion Site).*]

15.5 FRACTURE OF POLYMERS

The fracture strengths of polymeric materials are low relative to those of metals and ceramics. As a general rule, the mode of fracture in thermosetting polymers (heavily crosslinked networks) is brittle. In simple terms, during the fracture process, cracks form at regions where there is a localized stress concentration (i.e., scratches, notches, and sharp flaws). As with metals (Section 8.5), the stress is amplified at the tips of these cracks leading to crack propagation and fracture. Covalent bonds in the network or crosslinked structure are severed during fracture.

For thermoplastic polymers, both ductile and brittle modes are possible, and many of these materials are capable of experiencing a ductile-to-brittle transition. Factors that favor brittle fracture are a reduction in temperature, an increase in strain rate, the presence of a sharp notch, increased specimen thickness, and any modification of the polymer structure that raises the glass transition temperature (T_g) (see Section 15.14). Glassy thermoplastics are brittle below their glass transition temperatures. However, as the temperature is raised, they become ductile in the vicinity of their T_gs and experience plastic yielding prior to fracture. This behavior is demonstrated by the stress–strain characteristics of poly(methyl methacrylate) in Figure 15.3. At 4°C, PMMA is totally brittle, whereas at 60°C it becomes extremely ductile.

One phenomenon that frequently precedes fracture in some thermoplastic polymers is *crazing*. Associated with crazes are regions of very localized plastic deformation, which lead to the formation of small and interconnected microvoids (Figure 15.9*a*).

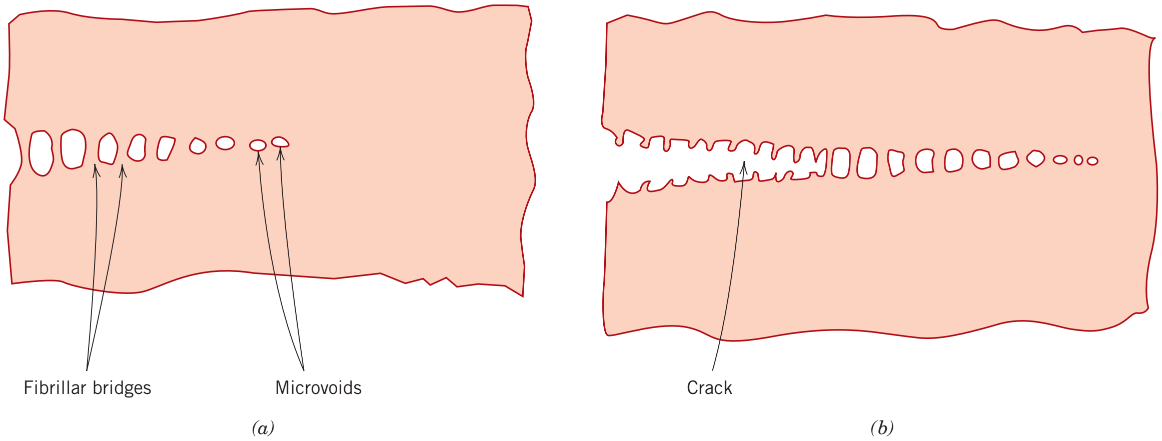


Figure 15.9 Schematic drawings of (*a*) a craze showing microvoids and fibrillar bridges, and (*b*) a craze followed by a crack. (From J. W. S. Hearle, *Polymers and Their Properties,* Vol. 1, *Fundamentals of Structure and Mechanics,* Ellis Horwood, Ltd., Chichester, West Sussex, England, 1982.)

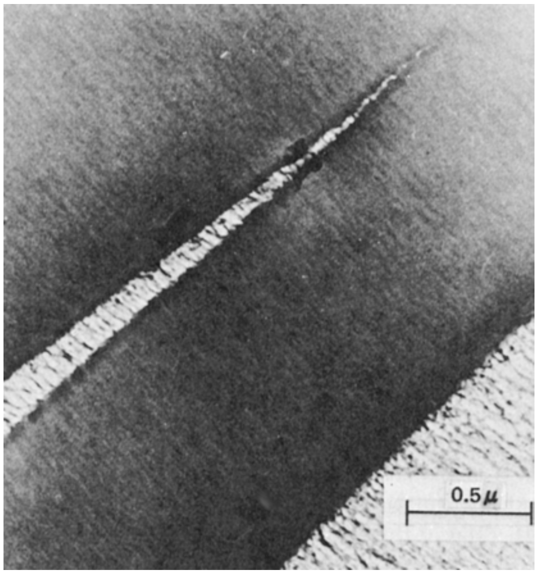


Figure 15.10 Photomicrograph of a craze in poly(phenylene oxide). (From R. P. Kambour and R. E. Robertson, "The Mechanical Properties of Plastics," in *Polymer Science, A Materials Science Handbook,* A. D. Jenkins, Editor. Reprinted with permission of Elsevier Science Publishers.)

Fibrillar bridges form between these microvoids wherein molecular chains become oriented as in Figure 15.13*d*. If the applied tensile load is sufficient, these bridges elongate and break, causing the microvoids to grow and coalesce. As the microvoids coalesce, cracks begin to form, as demonstrated in Figure 15.9*b*. A craze is different from a crack in that it can support a load across its face. Furthermore, this process of craze growth prior to cracking absorbs fracture energy and effectively increases the fracture toughness of the polymer. In glassy polymers, the cracks propagate with little craze formation resulting in low fracture toughnesses. Crazes form at highly stressed regions associated with scratches, flaws, and molecular inhomogeneities; in addition, they propagate perpendicular to the applied tensile stress, and typically are 5 μm or less thick. Figure 15.10 is a photomicrograph in which a craze is shown.

Principles of fracture mechanics developed in Section 8.5 also apply to brittle and quasi-brittle polymers; the susceptibility of these materials to fracture when a crack is present may be expressed in terms of the plane strain fracture toughness. The magnitude of K_{Ic} will depend on characteristics of the polymer (i.e., molecular weight, percent crystallinity, etc.) as well as temperature, strain rate, and the external environment. Representative values of K_{Ic} for several polymers are included in Table 8.1 and Table B.5, Appendix B.

15.6 MISCELLANEOUS MECHANICAL CHARACTERISTICS

Impact Strength

The degree of resistance of a polymeric material to impact loading may be of concern in some applications. Izod or Charpy tests are ordinarily used to assess impact strength (Section 8.6). As with metals, polymers may exhibit ductile or brittle fracture under impact loading conditions, depending on the temperature, specimen size, strain rate, and mode of loading, as discussed in the preceding section. Both semicrystalline and amorphous polymers are brittle at low temperatures, and both have relatively low impact strengths. However, they experience a ductile-to-brittle transition over a relatively narrow temperature range, similar to that shown for

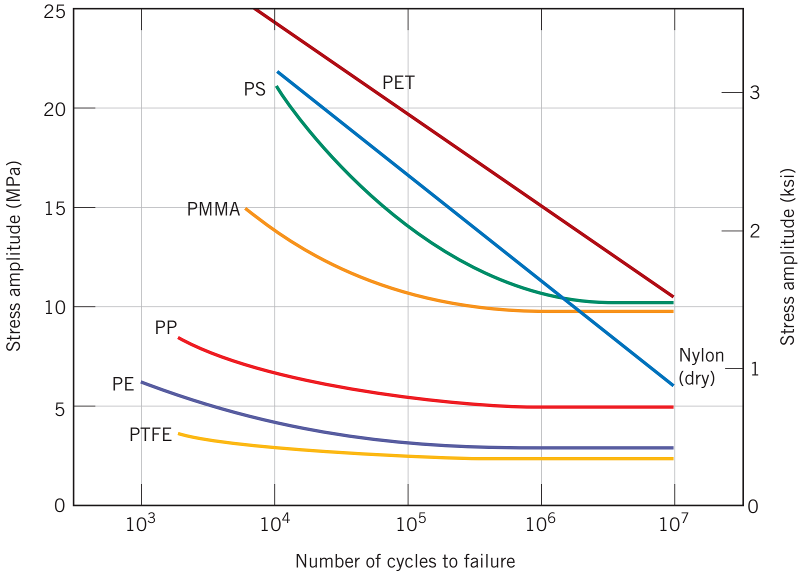


Figure 15.11 Fatigue curves (stress amplitude versus the number of cycles to failure) for poly(ethylene terephthalate) (PET), nylon, polystyrene (PS), poly(methyl methacrylate) (PMMA), polypropylene (PP), polyethylene (PE), and polytetrafluoroethylene (PTFE). The testing frequency was 30 Hz. (From M. N. Riddell, "A Guide to Better Testing of Plastics," *Plast. Eng.,* Vol. 30, No. 4, p. 78, 1974.)

a steel in Figure 8.13. Of course, impact strength undergoes a gradual decrease at still higher temperatures as the polymer begins to soften. Ordinarily, the two impact characteristics most sought after are a high impact strength at the ambient temperature and a ductile-to-brittle transition temperature that lies below room temperature.

Fatigue

Polymers may experience fatigue failure under conditions of cyclic loading. As with metals, fatigue occurs at stress levels that are low relative to the yield strength. Fatigue testing in polymers has not been nearly as extensive as with metals; however, fatigue data are plotted in the same manner for both types of material, and the resulting curves have the same general shape. Fatigue curves for several common polymers are shown in Figure 15.11, as stress versus the number of cycles to failure (on a logarithmic scale). Some polymers have a fatigue limit (a stress level at which the stress at failure becomes independent of the number of cycles); others do not appear to have such a limit. As would be expected, fatigue strengths and fatigue limits for polymeric materials are much lower than for metals.

The fatigue behavior of polymers is much more sensitive to loading frequency than for metals. Cycling polymers at high frequencies and/or relatively large stresses can cause localized heating; consequently, failure may be due to a softening of the material rather than as a result of typical fatigue processes.

Tear Strength and Hardness

Other mechanical properties that are sometimes influential in the suitability of a polymer for some particular application include tear resistance and hardness. The ability to resist tearing is an important property of some plastics, especially those used for thin films in packaging. *Tear strength,* the mechanical parameter that is measured, is the energy required to tear apart a cut specimen that has a standard geometry. The magnitude of tensile and tear strengths are related.

As with metals, hardness represents a material's resistance to scratching, penetration, marring, and so on. Polymers are softer than metals and ceramics, and most hardness tests are conducted by penetration techniques similar to those described for metals in Section 6.10. Rockwell tests are frequently used for polymers.[3] Other indentation techniques employed are the Durometer and Barcol.[4]

Mechanisms of Deformation and for Strengthening of Polymers

An understanding of deformation mechanisms of polymers is important in order for us to be able to manage the mechanical characteristics of these materials. In this regard, deformation models for two different types of polymers—semicrystalline and elastomeric—deserve our attention. The stiffness and strength of semicrystalline materials are often important considerations; elastic and plastic deformation mechanisms are treated in the succeeding section, whereas methods used to stiffen and strengthen these materials are discussed in Section 15.8. On the other hand, elastomers are utilized on the basis of their unusual elastic properties; the deformation mechanism of elastomers is also treated.

15.7 DEFORMATION OF SEMICRYSTALLINE POLYMERS

Many semicrystalline polymers in bulk form will have the spherulitic structure described in Section 14.12. By way of review, let us repeat here that each spherulite consists of numerous chain-folded ribbons, or lamellae, that radiate outward from the center. Separating these lamellae are areas of amorphous material (Figure 14.13); adjacent lamellae are connected by tie chains that pass through these amorphous regions.

Mechanism of Elastic Deformation

As with other material types, elastic deformation of polymers occurs at relatively low stress levels on the stress-strain curve (Figure 15.1). The onset of elastic deformation for semicrystalline polymers results from chain molecules in amorphous regions elongating in the direction of the applied tensile stress. This process is represented schematically for two adjacent chain-folded lamellae and the interlamellar amorphous material as Stage 1 in Figure 15.12. Continued deformation in the second stage occurs by changes in both amorphous and lamellar crystalline regions. Amorphous chains continue to align and become elongated; in addition, there is bending and stretching of the strong chain covalent bonds within the lamellar crystallites. This leads to a slight, reversible increase in the lamellar crystallite thickness as indicated by Δt in Figure 15.12*c*.

Inasmuch as semicrystalline polymers are composed of both crystalline and amorphous regions, they may, in a sense, be considered composite materials. As such, the elastic modulus may be taken as some combination of the moduli of crystalline and amorphous phases.

Mechanism of Plastic Deformation

The transition from elastic to plastic deformation occurs in Stage 3 of Figure 15.13. (Note that Figure 15.12*c* is identical to Figure 15.13*a*.) During Stage 3, adjacent

---

[3] ASTM Standard D 785, "Rockwell Hardness of Plastics and Electrical Insulating Materials."

[4] ASTM Standard D 2240, "Standard Test Method for Rubber Property—Durometer Hardness;" and ASTM Standard D 2583, "Standard Test Method for Indentation of Rigid Plastics by Means of a Barcol Impressor."

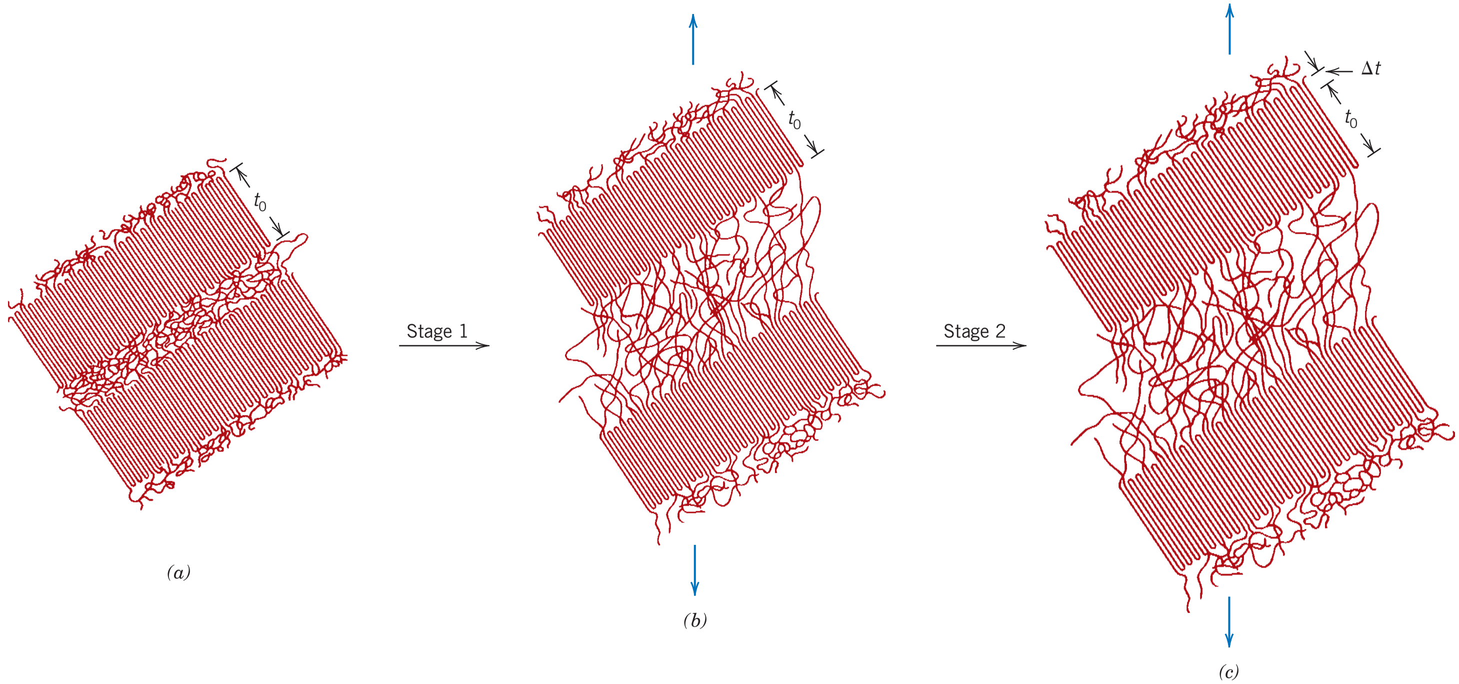


Figure 15.12 Stages in the elastic deformation of a semicrystalline polymer. (*a*) Two adjacent chain-folded lamellae and interlamellar amorphous material before deformation. (*b*) Elongation of amorphous tie chains during the first stage of deformation. (*c*) Increase in lamellar crystallite thickness (which is reversible) due to bending and stretching of chains in crystallite regions. (From Schultz, Jerold M., *Polymer Materials Science,* 1st edition, © 1974, pp. 500, 501. Adapted by permission of Pearson Education, Inc., Upper Saddle River, NJ.)

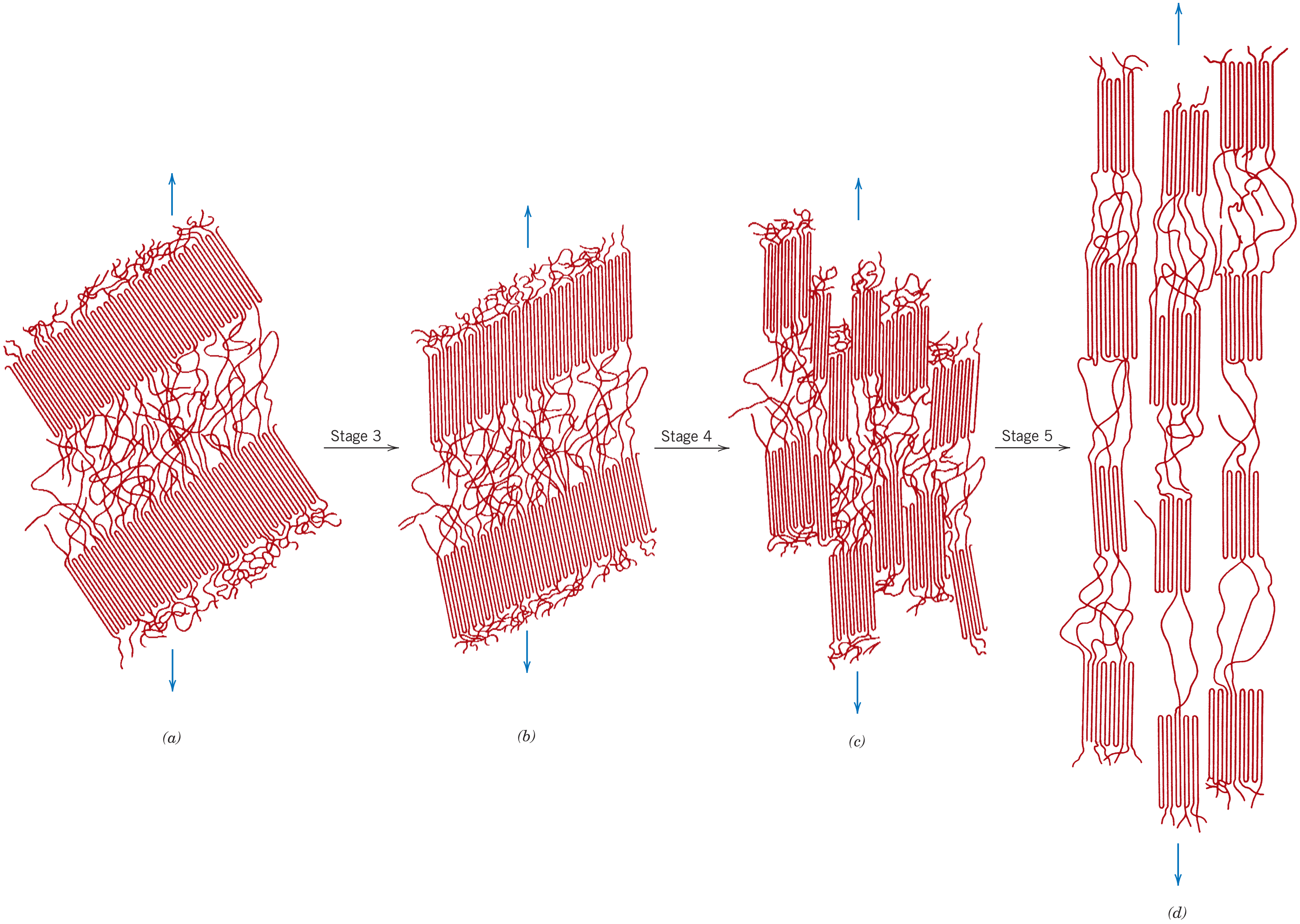


Figure 15.13 Stages in the plastic deformation of a semicrystalline polymer. (*a*) Two adjacent chain-folded lamellae and interlamellar amorphous material after elastic deformation (also shown as Figure 15.12*c*). (*b*) Tilting of lamellar chain folds. (*c*) Separation of crystalline block segments. (*d*) Orientation of block segments and tie chains with the tensile axis in the final plastic deformation stage. (From Schultz, Jerold M., *Polymer Materials Science,* 1st edition, © 1974, pp. 500, 501. Adapted by permission of Pearson Education, Inc., Upper Saddle River, NJ.)

chains in the lamellae slide past one another (Figure 15.13*b*); this results in tilting of the lamellae so that the chain folds become more aligned with the tensile axis. Any chain displacement is resisted by relatively weak secondary or van der Waals bonds.

Crystalline block segments separate from the lamellae, in Stage 4 (Figure 15.13*c*), with the segments attached to one another by tie chains. In the final stage, Stage 5, the blocks and tie chains become oriented in the direction of the tensile axis (Figure 15.13*d*). Thus, appreciable tensile deformation of semicrystalline polymers produces a highly oriented structure. This process of orientation is referred to as **drawing,** and is commonly used to improve the mechanical properties of polymer fibers and films (this is discussed in more detail in Section 15.24).

drawing

During deformation the spherulites experience shape changes for moderate levels of elongation. However, for large deformations, the spherulitic structure is virtually destroyed. Also, to a degree, the processes represented in Figure 15.13 are reversible. That is, if deformation is terminated at some arbitrary stage, and the specimen is heated to an elevated temperature near its melting point (i.e., is annealed), the material will recrystallize to again form a spherulitic structure. Furthermore, the specimen will tend to shrink back, in part, to the dimensions it had prior to deformation. The extent of this shape and structural recovery will depend on the annealing temperature and also the degree of elongation.

15.8 FACTORS THAT INFLUENCE THE MECHANICAL PROPERTIES OF SEMICRYSTALLINE POLYMERS

A number of factors influence the mechanical characteristics of polymeric materials. For example, we have already discussed the effects of temperature and strain rate on stress–strain behavior (Section 15.2, Figure 15.3). Again, increasing the temperature or diminishing the strain rate leads to a decrease in the tensile modulus, a reduction in tensile strength, and an enhancement of ductility.

In addition, several structural/processing factors have decided influences on the mechanical behavior (i.e., strength and modulus) of polymeric materials. An increase in strength results whenever any restraint is imposed on the process illustrated in Figure 15.13; for example, extensive chain entanglements or a significant degree of intermolecular bonding inhibit relative chain motions. It should be noted that even though secondary intermolecular (e.g., van der Waals) bonds are much weaker than the primary covalent ones, significant intermolecular forces result from the formation of large numbers of van der Waals interchain bonds. Furthermore, the modulus rises as both the secondary bond strength and chain alignment increase. As a result, polymers with polar groups will have stronger secondary bonds and a larger elastic modulus. We now discuss how several structural/processing factors [viz. molecular weight, degree of crystallinity, predeformation (drawing), and heat treating] affect the mechanical behavior of polymers.

Molecular Weight

The magnitude of the tensile modulus does not seem to be directly influenced by molecular weight. On the other hand, for many polymers it has been observed that tensile strength increases with increasing molecular weight. Mathematically, *TS* is a function of the number-average molecular weight according to

For some polymers, dependence of tensile strength on number-average molecular weight

$$TS = TS_\infty - \frac{A}{\overline{M}_n} \tag{15.3}$$

where TS_∞ is the tensile strength at infinite molecular weight and A is a constant. The behavior described by this equation is explained by increased chain entanglements with rising $\overline{M}_n$.

Degree of Crystallinity

For a specific polymer, the degree of crystallinity can have a rather significant influence on the mechanical properties, since it affects the extent of the intermolecular secondary bonding. For crystalline regions in which molecular chains are closely packed in an ordered and parallel arrangement, extensive secondary bonding ordinarily exists between adjacent chain segments. This secondary bonding is much less prevalent in amorphous regions, by virtue of the chain misalignment. As a consequence, for semicrystalline polymers, tensile modulus increases significantly with degree of crystallinity. For example, for polyethylene, the modulus increases approximately an order of magnitude as the crystallinity fraction is raised from 0.3 to 0.6.

Furthermore, increasing the crystallinity of a polymer generally enhances its strength; in addition, the material tends to become more brittle. The influence of chain chemistry and structure (branching, stereoisomerism, etc.) on degree of crystallinity was discussed in Chapter 14.

The effects of both percent crystallinity and molecular weight on the physical state of polyethylene are represented in Figure 15.14.

Predeformation by Drawing

On a commercial basis, one of the most important techniques used to improve mechanical strength and tensile modulus is to permanently deform the polymer in tension. This procedure is sometimes termed *drawing,* and corresponds to the neck extension process illustrated schematically in Figure 15.4. In terms of property alterations, drawing is the polymer analog of strain hardening in metals. It is an important stiffening and strengthening technique that is employed in the production of fibers and films. During drawing the molecular chains slip past one another and become highly oriented; for semicrystalline materials the chains assume conformations similar to that represented schematically in Figure 15.13*d*.

Degrees of strengthening and stiffening will depend on the extent of deformation (or extension) of the material. Furthermore, the properties of drawn polymers are highly anisotropic. For those materials drawn in uniaxial tension, tensile modulus and strength values are significantly greater in the direction of deformation than in other directions. Tensile modulus in the direction of drawing may be enhanced by up to approximately a factor of three relative to the undrawn material. At an angle

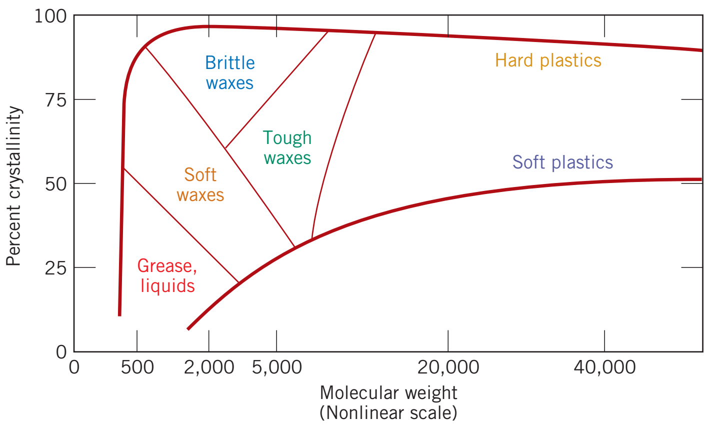


Figure 15.14 The influence of degree of crystallinity and molecular weight on the physical characteristics of polyethylene. (From R. B. Richards, "Polyethylene—Structure, Crystallinity and Properties," *J. Appl. Chem.*, **1,** 370, 1951.)

of 45° from the tensile axis the modulus is a minimum; at this orientation the modulus has a value on the order of one-fifth that of the undrawn polymer.

Tensile strength parallel to the direction of orientation may be improved by a factor of at least two to five relative to that of the unoriented material. On the other hand, perpendicular to the alignment direction, tensile strength is reduced by on the order of one-third to one-half.

For an amorphous polymer that is drawn at an elevated temperature, the oriented molecular structure is retained only when the material is quickly cooled to the ambient; this procedure gives rise to the strengthening and stiffening effects described in the previous paragraph. On the other hand, if, after stretching, the polymer is held at the temperature of drawing, molecular chains relax and assume random conformations characteristic of the predeformed state; as a consequence, drawing will have no effect on the mechanical characteristics of the material.

Heat Treating

Heat treating (or annealing) of semicrystalline polymers can lead to an increase in the percent crystallinity, and crystallite size and perfection, as well as modifications of the spherulite structure. For undrawn materials that are subjected to constant-time heat treatments, increasing the annealing temperature leads to the following: (1) an increase in tensile modulus, (2) an increase in yield strength, and (3) a reduction in ductility. Note that these annealing effects are opposite to those typically observed for metallic materials (Section 7.12)—i.e., weakening, softening, and enhanced ductility.

For some polymer fibers that have been drawn, the influence of annealing on the tensile modulus is contrary to that for undrawn materials—that is, modulus decreases with increased annealing temperature due to a loss of chain orientation and strain-induced crystallinity.

✓ Concept Check 15.3

For the following pair of polymers, do the following: (1) state whether or not it is possible to decide if one polymer has a higher tensile modulus than the other; (2) if this is possible, note which has the higher tensile modulus and then cite the reason(s) for your choice; and (3) if it is not possible to decide, then state why not.

- Syndiotactic polystyrene having a number-average molecular weight of 400,000 g/mol
- Isotactic polystyrene having a number-average molecular weight of 650,000 g/mol.

[*The answer may be found at www.wiley.com/college/callister (Student Companion Site).*]

✓ Concept Check 15.4

For the following pair of polymers, do the following: (1) state whether or not it is possible to decide if one polymer has a higher tensile strength than the other; (2) if this is possible, note which has the higher tensile strength and then cite the reason(s) for your choice; and (3) if it is not possible to decide, then state why not.

- Syndiotactic polystyrene having a number-average molecular weight of 600,000 g/mol
- Isotactic polystyrene having a number-average molecular weight of 500,000 g/mol.

[*The answer may be found at www.wiley.com/college/callister (Student Companion Site).*]

MATERIALS OF IMPORTANCE

Shrink-Wrap Polymer Films

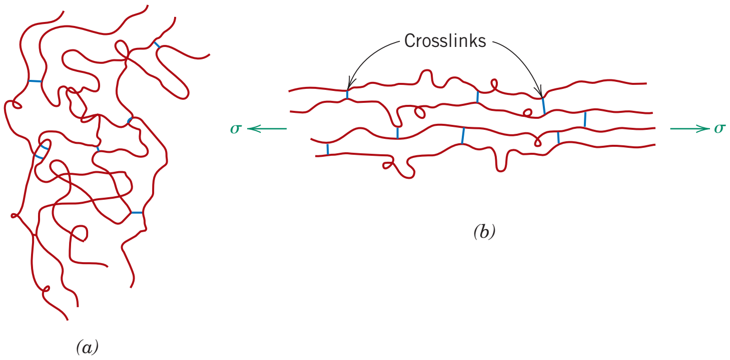
An interesting application of heat treatment in polymers is the shrink-wrap used in packaging. Shrink-wrap is a polymer film, usually made of poly(vinyl chloride), polyethylene, or polyolefin (a multilayer sheet with alternating layers of polyethylene and polypropylene). It is initially plastically deformed (cold drawn) by about 20-300% to provide a prestretched (aligned) film. The film is wrapped around an object to be packaged and sealed at the edges. When heated to about 100 to 150°C, this prestretched material shrinks to recover 80-90% of its initial deformation, which gives a tightly stretched, wrinkle-free, transparent polymer film. For example, CDs and many other objects that you purchase are packaged in shrink-wrap.

Photograph showing (from top to bottom) an electrical connection, a piece of as-received polymer shrink-tubing, and the constricted tubing around the junction—application of heat to the tubing caused its diameter to shrink. (Photography by S. Tanner.)

15.9 DEFORMATION OF ELASTOMERS

One of the fascinating properties of the elastomeric materials is their rubber-like elasticity. That is, they have the ability to be deformed to quite large deformations, and then elastically spring back to their original form. This results from crosslinks in the polymer that provide a force to restore the chains to their undeformed conformations. Elastomeric behavior was probably first observed in natural rubber; however, the past few years have brought about the synthesis of a large number of elastomers with a wide variety of properties. Typical stress–strain characteristics of elastomeric materials are displayed in Figure 15.1, curve *C*. Their moduli of elasticity are quite small and, furthermore, vary with strain since the stress–strain curve is nonlinear.

In an unstressed state, an elastomer will be amorphous and composed of crosslinked molecular chains that are highly twisted, kinked, and coiled. Elastic deformation, upon application of a tensile load, is simply the partial uncoiling, untwisting, and straightening, and the resultant elongation of the chains in the stress direction, a phenomenon represented in Figure 15.15. Upon release of the stress,



(*a*)

(*b*)

Figure 15.15 Schematic representation of crosslinked polymer chain molecules (*a*) in an unstressed state and (*b*) during elastic deformation in response to an applied tensile stress. (Adapted from Z. D. Jastrzebski, *The Nature and Properties of Engineering Materials,* 3rd edition. Copyright © 1987 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

the chains spring back to their prestressed conformations, and the macroscopic piece returns to its original shape.

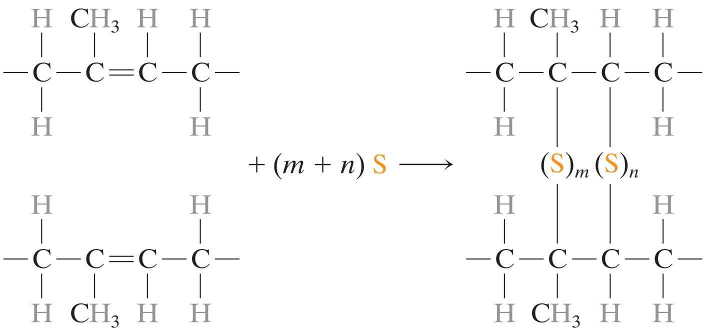
Part of the driving force for elastic deformation is a thermodynamic parameter called *entropy,* which is a measure of the degree of disorder within a system; entropy increases with increasing disorder. As an elastomer is stretched and the chains straighten and become more aligned, the system becomes more ordered. From this state, the entropy increases if the chains return to their original kinked and coiled contours. Two intriguing phenomena result from this entropic effect. First, when stretched, an elastomer experiences a rise in temperature; second, the modulus of elasticity increases with increasing temperature, which is opposite to the behavior found in other materials (see Figure 6.8).

Several criteria must be met for a polymer to be elastomeric: (1) It must not easily crystallize; elastomeric materials are amorphous, having molecular chains that are naturally coiled and kinked in the unstressed state. (2) Chain bond rotations must be relatively free for the coiled chains to readily respond to an applied force. (3) For elastomers to experience relatively large elastic deformations, the onset of plastic deformation must be delayed. Restricting the motions of chains past one another by crosslinking accomplishes this objective. The crosslinks act as anchor points between the chains and prevent chain slippage from occurring; the role of crosslinks in the deformation process is illustrated in Figure 15.15. Crosslinking in many elastomers is carried out in a process called vulcanization, to be discussed below. (4) Finally, the elastomer must be above its glass transition temperature (Section 15.13). The lowest temperature at which rubber-like behavior persists for many of the common elastomers is between −50 and −90°C (−60 and −130°F). Below its glass transition temperature, an elastomer becomes brittle such that its stress–strain behavior resembles curve *A* in Figure 15.1.

Vulcanization

vulcanization

The crosslinking process in elastomers is called **vulcanization,** which is achieved by a nonreversible chemical reaction, ordinarily carried out at an elevated temperature. In most vulcanizing reactions, sulfur compounds are added to the heated elastomer; chains of sulfur atoms bond with adjacent polymer backbone chains and crosslink them, which is accomplished according to the following reaction:



(15.4)

in which the two crosslinks shown consist of *m* and *n* sulfur atoms. Crosslink main chain sites are carbon atoms that were doubly bonded before vulcanization but, after vulcanization, have become singly bonded.

Unvulcanized rubber, which contains very few crosslinks, is soft and tacky and has poor resistance to abrasion. Modulus of elasticity, tensile strength, and resistance to degradation by oxidation are all enhanced by vulcanization. The magnitude of the modulus of elasticity is directly proportional to the density of the

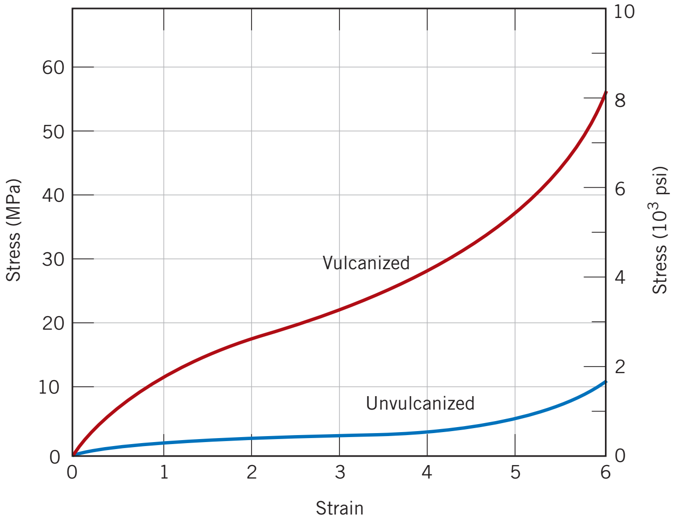


Figure 15.16 Stress–strain curves to 600% elongation for unvulcanized and vulcanized natural rubber.

Polymers: Rubber

crosslinks. Stress–strain curves for vulcanized and unvulcanized natural rubber are presented in Figure 15.16. To produce a rubber that is capable of large extensions without rupture of the primary chain bonds, there must be relatively few crosslinks, and these must be widely separated. Useful rubbers result when about 1 to 5 parts (by weight) of sulfur are added to 100 parts of rubber. This corresponds to about one crosslink for every 10 to 20 repeat units. Increasing the sulfur content further hardens the rubber and also reduces its extensibility. Also, since they are crosslinked, elastomeric materials are thermosetting in nature.

Concept Check 15.5

For the following pair of polymers, plot and label schematic stress–strain curves on the same graph.

- Poly(styrene-butadiene) random copolymer having a number-average molecular weight of 100,000 g/mol and 10% of the available sites crosslinked and tested at 20°C
- Poly(styrene-butadiene) random copolymer having a number-average molecular weight of 120,000 g/mol and 15% of the available sites crosslinked and tested at −85°C. *Hint:* poly(styrene-butadiene) copolymers may exhibit elastomeric behavior.

[*The answer may be found at www.wiley.com/college/callister (Student Companion Site).*]

Concept Check 15.6

In terms of molecular structure, explain why phenol-formaldehyde (Bakelite) will not be an elastomer. (The molecular structure for phenol-formaldehyde is presented in Table 14.3.)

[*The answer may be found at www.wiley.com/college/callister (Student Companion Site).*]

Crystallization, Melting, and Glass Transition Phenomena in Polymers

Three phenomena that are important with respect to the design and processing of polymeric materials are crystallization, melting, and the glass transition. Crystallization is the process by which, upon cooling, an ordered (i.e., crystalline) solid phase is produced from a liquid melt having a highly random molecular structure. The melting transformation is the reverse process that occurs when a polymer is heated. The glass-transition phenomenon occurs with amorphous or noncrystallizable polymers that, when cooled from a liquid melt, become rigid solids yet retain the disordered molecular structure that is characteristic of the liquid state. Of course, alterations of physical and mechanical properties attend crystallization, melting, and the glass transition. Furthermore, for semicrystalline polymers, crystalline regions will experience melting (and crystallization), while noncrystalline areas pass through the glass transition.

15.10 CRYSTALLIZATION

An understanding of the mechanism and kinetics of polymer crystallization is important because the degree of crystallinity influences the mechanical and thermal properties of these materials. The crystallization of a molten polymer occurs by nucleation and growth processes, topics discussed in the context of phase transformations for metals in Section 10.3. For polymers, upon cooling through the melting temperature, nuclei form wherein small regions of the tangled and random molecules become ordered and aligned in the manner of chain-folded layers, Figure 14.12. At temperatures in excess of the melting temperature, these nuclei are unstable due to the thermal atomic vibrations that tend to disrupt the ordered molecular arrangements. Subsequent to nucleation and during the crystallization growth stage, nuclei grow by the continued ordering and alignment of additional molecular chain segments; that is, the chain-folded layers remain the same thickness, but increase in lateral dimensions, or for spherulitic structures (Figure 14.13) there is an increase in spherulite radius.

The time dependence of crystallization is the same as for many solid-state transformations—Figure 10.10; that is, a sigmoidal-shaped curve results when fraction transformation (i.e., fraction crystallized) is plotted versus the logarithm of time (at constant temperature). Such a plot is presented in Figure 15.17 for the crystallization of polypropylene at three temperatures. Mathematically, fraction crystallized y is a function of time t according to the Avrami equation, Equation 10.17, as

$$y = 1 - \exp(-kt^n) \qquad (10.17)$$

where k and n are time-independent constants, whose values depend on the crystallizing system. Normally, the extent of crystallization is measured by specimen volume changes since there will be a difference in volume for liquid and crystallized phases. Rate of crystallization may be specified in the same manner as for the transformations discussed in Section 10.3, and according to Equation 10.18; that is, rate is equal to the reciprocal of time required for crystallization to proceed to 50% completion. This rate is dependent on crystallization temperature (Figure 15.17) and also on the molecular weight of the polymer; rate decreases with increasing molecular weight.

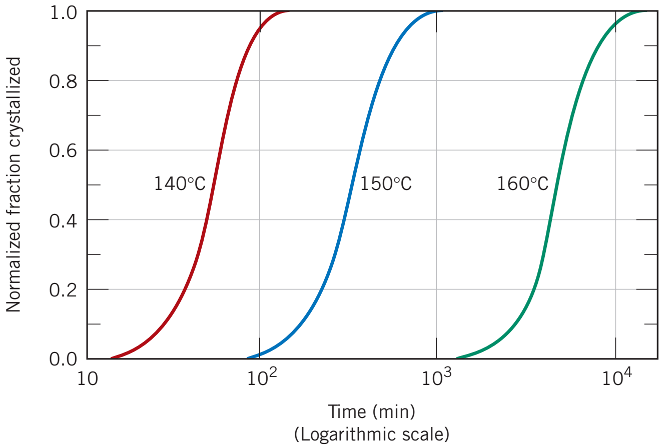


Figure 15.17 Plot of normalized fraction crystallized versus the logarithm of time for polypropylene at constant temperatures of 140°C, 150°C, and 160°C. (Adapted from P. Parrini and G. Corrieri, *Makromol. Chem.*, **62,** 83, 1963. Reprinted by permission of Hüthig & Wepf Publishers, Zug, Switzerland.)

For polypropylene (as well as any polymer), the attainment of 100% crystallinity is not possible. Therefore, in Figure 15.17, the vertical axis is scaled as "normalized fraction crystallized." A value of 1.0 for this parameter corresponds to the highest level of crystallization that is achieved during the tests, which, in reality, is less than complete crystallization.

15.11 MELTING

melting temperature

The melting of a polymer crystal corresponds to the transformation of a solid material, having an ordered structure of aligned molecular chains, to a viscous liquid in which the structure is highly random. This phenomenon occurs, upon heating, at the **melting temperature,** T_m. There are several features distinctive to the melting of polymers that are not normally observed with metals and ceramics; these are consequences of the polymer molecular structures and lamellar crystalline morphology. First of all, melting of polymers takes place over a range of temperatures; this phenomenon is discussed in more detail below. In addition, the melting behavior depends on the history of the specimen, in particular the temperature at which it crystallized. The thickness of chain-folded lamellae will depend on crystallization temperature; the thicker the lamellae, the higher the melting temperature. Impurities in the polymer and imperfections in the crystals also decrease the melting temperature. Finally, the apparent melting behavior is a function of the rate of heating; increasing this rate results in an elevation of the melting temperature.

As a previous section notes, polymeric materials are responsive to heat treatments that produce structural and property alterations. An increase in lamellar thickness may be induced by annealing just below the melting temperature. Annealing also raises the melting temperature by decreasing the vacancies and other imperfections in polymer crystals and increasing crystallite thickness.

15.12 THE GLASS TRANSITION

The glass transition occurs in amorphous (or glassy) and semicrystalline polymers, and is due to a reduction in motion of large segments of molecular chains with decreasing temperature. Upon cooling, the glass transition corresponds to the gradual transformation from a liquid to a rubbery material, and finally, to a rigid solid.

glass transition temperature

The temperature at which the polymer experiences the transition from rubbery to rigid states is termed the **glass transition temperature,** T_g. Of course, this sequence of events occurs in the reverse order when a rigid glass at a temperature below T_g is heated. In addition, abrupt changes in other physical properties accompany this glass transition: for example, stiffness (Figure 15.7), heat capacity, and coefficient of thermal expansion.

15.13 MELTING AND GLASS TRANSITION TEMPERATURES

Melting and glass transition temperatures are important parameters relative to in-service applications of polymers. They define, respectively, the upper and lower temperature limits for numerous applications, especially for semicrystalline polymers. The glass transition temperature may also define the upper use temperature for glassy amorphous materials. Furthermore, T_m and T_g also influence the fabrication and processing procedures for polymers and polymer-matrix composites. These issues are discussed in succeeding sections of this chapter.

The temperatures at which melting and/or the glass transition occur for a polymer are determined in the same manner as for ceramic materials—from a plot of specific volume (the reciprocal of density) versus temperature. Figure 15.18 is such a plot, where curves *A* and *C*, for amorphous and crystalline polymers, respectively, have the same configurations as their ceramic counterparts (Figure 13.6).[5] For the crystalline material, there is a discontinuous change in specific volume at the melting temperature T_m. The curve for the totally amorphous material is continuous but experiences a slight decrease in slope at the glass transition temperature, T_g. The behavior is intermediate between these extremes for a semicrystalline polymer (curve *B*) in that both melting and glass transition phenomena are observed; T_m and T_g are properties of the respective crystalline and amorphous phases in this

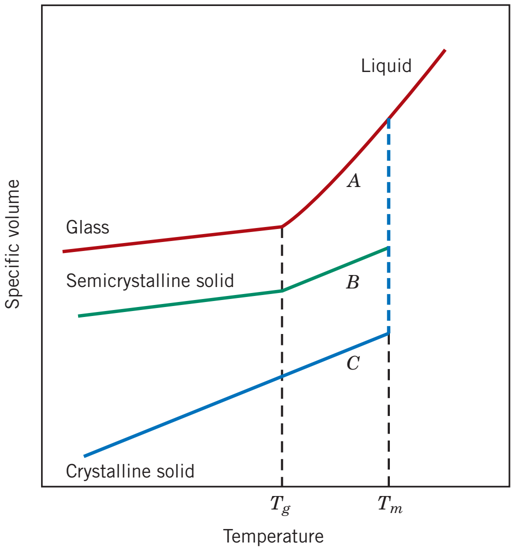


Figure 15.18 Specific volume versus temperature, upon cooling from the liquid melt, for totally amorphous (curve *A*), semicrystalline (curve *B*), and crystalline (curve *C*) polymers.

---

[5] It should be noted that no engineering polymer is 100% crystalline; curve *C* is included in Figure 15.18 to illustrate the extreme behavior that would be displayed by a totally crystalline material.

Table 15.2 **Melting and Glass Transition Temperatures for Some of the More Common Polymeric Materials**

Material	*Glass Transition Temperature* [°*C* (°*F*)]	*Melting Temperature* [°*C* (°*F*)]
Polyethylene (low density)	−110 (−165)	115 (240)
Polytetrafluoroethylene	−97 (−140)	327 (620)
Polyethylene (high density)	−90 (−130)	137 (279)
Polypropylene	−18 (0)	175 (347)
Nylon 6,6	57 (135)	265 (510)
Polyester (PET)	69 (155)	265 (510)
Poly(vinyl chloride)	87 (190)	212 (415)
Polystyrene	100 (212)	240 (465)
Polycarbonate	150 (300)	265 (510)

semicrystalline material. As discussed above, the behaviors represented in Figure 15.18 will depend on the rate of cooling or heating. Representative melting and glass transition temperatures of a number of polymers are contained in Table 15.2 and Appendix E.

15.14 FACTORS THAT INFLUENCE MELTING AND GLASS TRANSITION TEMPERATURES

Melting Temperature

During melting of a polymer there will be a rearrangement of the molecules in the transformation from ordered to disordered molecular states. Molecular chemistry and structure will influence the ability of the polymer chain molecules to make these rearrangements and, therefore, will also affect the melting temperature.

Chain stiffness, which is controlled by the ease of rotation about the chemical bonds along the chain, has a pronounced effect. The presence of double bonds and aromatic groups in the polymer backbone lowers chain flexibility and causes an increase in T_m. Furthermore, the size and type of side groups influence chain rotational freedom and flexibility; bulky or large side groups tend to restrict molecular rotation and raise T_m. For example, polypropylene has a higher melting temperature than polyethylene (175°C versus 115°C, Table 15.2); the CH_3 methyl side group for polypropylene is larger than the H atom found on polyethylene. The presence of polar groups (viz. Cl, OH, and CN), even though not excessively large, leads to significant intermolecular bonding forces and relatively high T_ms. This may be verified by comparing the melting temperatures of polypropylene (175°C) and poly(vinyl chloride) (212°C).

The melting temperature of a polymer will also depend on molecular weight. At relatively low molecular weights, increasing $\overline{M}$ (or chain length) raises T_m (Figure 15.19). Furthermore, the melting of a polymer takes place over a range of temperatures, and, thus, there will be a range of T_ms, rather than a single melting temperature. This is because every polymer will be composed of molecules having a variety of molecular weights (Section 14.5), and because T_m depends on molecular weight. For most polymers, this melting temperature range will normally be on the order of several degrees Celsius. Those melting temperatures cited in Table 15.2 and Appendix E are near the high ends of these ranges.

Degree of branching will also affect the melting temperature of a polymer. The introduction of side branches introduces defects into the crystalline material and

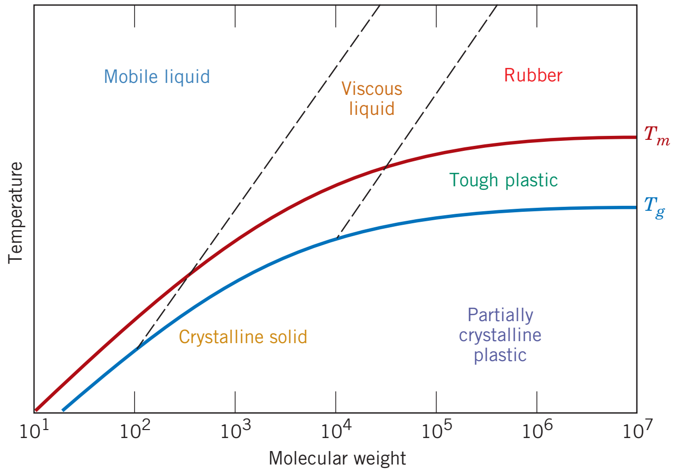


Figure 15.19 Dependence of polymer properties as well as melting and glass transition temperatures on molecular weight. (From F. W. Billmeyer, Jr., *Textbook of Polymer Science,* 3rd edition. Copyright © 1984 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

lowers the melting temperature. High-density polyethylene, being a predominately linear polymer, has a higher melting temperature (137°C, Table 15.2) than low-density polyethylene (115°C) which has some branching.

Glass Transition Temperature

Upon heating through the glass transition temperature, the amorphous solid polymer transforms from a rigid to a rubbery state. Correspondingly, the molecules that are virtually frozen in position below T_g begin to experience rotational and translational motions above T_g. Thus, the value of the glass transition temperature will depend on molecular characteristics that affect chain stiffness; most of these factors and their influences are the same as for the melting temperature, as discussed above. Again, chain flexibility is diminished and T_g is increased by the presence of the following:

1. Bulky side groups; from Table 15.2, the respective values for polypropylene and polystyrene are −18°C and 100°C.
2. Polar groups; for example, the T_g values for poly(vinyl chloride) and polypropylene are 87°C and −18°C, respectively.
3. Double bonds and aromatic groups in the backbone, which tend to stiffen the polymer chain.

Increasing the molecular weight also tends to raise the glass transition temperature, as noted in Figure 15.19. A small amount of branching will tend to lower T_g; on the other hand, a high density of branches reduces chain mobility, and elevates the glass transition temperature. Some amorphous polymers are crosslinked, which has been observed to elevate T_g; crosslinks restrict molecular motion. With a high density of crosslinks, molecular motion is virtually disallowed; long-range molecular motion is prevented, to the degree that these polymers do not experience a glass transition or its accompanying softening.

From the preceding discussion it is evident that essentially the same molecular characteristics raise and lower both melting and glass transition temperatures. Normally the value of T_g lies somewhere between 0.5 and $0.8T_m$ (in Kelvin). Consequently, for a homopolymer, it is not possible to independently vary both T_m and T_g. A greater degree of control over these two parameters is possible by the synthesis and utilization of copolymeric materials.

Concept Check 15.7

For each of the following two polymers, plot and label a schematic specific volume-versus-temperature curve (include both curves on the same graph):

- Spherulitic polypropylene, of 25% crystallinity, and having a weight-average molecular weight of 75,000 g/mol
- Spherulitic polystyrene, of 25% crystallinity, and having a weight-average molecular weight of 100,000 g/mol.

[*The answer may be found at* www.wiley.com/college/callister *(Student Companion Site)*.]

Concept Check 15.8

For the two polymers described below, do the following: (1) state whether or not it is possible to determine whether one polymer has a higher melting temperature than the other; (2) if it is possible, note which has the higher melting temperature and then cite reason(s) for your choice; and (3) if it is not possible to decide, then state why not.

- Isotactic polystyrene that has a density of 1.12 g/cm^3 and a weight-average molecular weight of 150,000 g/mol
- Syndiotactic polystyrene that has a density of 1.10 g/cm^3 and a weight-average molecular weight of 125,000 g/mol.

[*The answer may be found at* www.wiley.com/college/callister *(Student Companion Site)*.]

Polymer Types

There are many different polymeric materials that are familiar to us and find a wide variety of applications; in fact, one way of classifying them is according to their end-use. Within this scheme the various polymer types include plastics, elastomers (or rubbers), fibers, coatings, adhesives, foams, and films. Depending on its properties, a particular polymer may be used in two or more of these application categories. For example, a plastic, if crosslinked and utilized above its glass transition temperature, may make a satisfactory elastomer. Or a fiber material may be used as a plastic if it is not drawn into filaments. This portion of the chapter includes a brief discussion of each of these types of polymer.

15.15 PLASTICS

plastic

Possibly the largest number of different polymeric materials come under the plastic classification. **Plastics** are materials that have some structural rigidity under load, and are used in general-purpose applications. Polyethylene, polypropylene, poly(vinyl chloride), polystyrene, and the fluorocarbons, epoxies, phenolics, and polyesters may all be classified as plastics. They have a wide variety of combinations of properties. Some plastics are very rigid and brittle (Figure 15.1, curve *A*). Others are flexible, exhibiting both elastic and plastic deformations when stressed, and sometimes experiencing considerable deformation before fracture (Figure 15.1, curve *B*).

Polymers falling within this classification may have any degree of crystallinity, and all molecular structures and configurations (linear, branched, isotactic, etc.) are possible. Plastic materials may be either thermoplastic or thermosetting; in fact, this is the manner in which they are usually subclassified. However, to be considered plastics, linear or branched polymers must be used below their glass transition temperatures (if amorphous) or below their melting temperatures (if semicrystalline), or must be crosslinked enough to maintain their shape. The trade names, characteristics, and typical applications for a number of plastics are given in Table 15.3.

Several plastics exhibit especially outstanding properties. For applications in which optical transparency is critical, polystyrene and poly(methyl methacrylate) are especially well suited; however, it is imperative that the material be highly amorphous or, if semicrystalline, have very small crystallites. The fluorocarbons have a low coefficient of friction and are extremely resistant to attack by a host of chemicals, even at relatively high temperatures. They are utilized as coatings on nonstick cookware, in bearings and bushings, and for high-temperature electronic components.

Table 15.3 Trade Names, Characteristics, and Typical Applications for a Number of Plastic Materials

Material Type	*Trade Names*	*Major Application Characteristics*	*Typical Applications*
		Thermoplastics	
Acrylonitrile-butadiene-styrene (ABS)	Abson Cycolac Kralastic Lustran Novodur Tybrene	Outstanding strength and toughness, resistant to heat distortion; good electrical properties; flammable and soluble in some organic solvents	Refrigerator linings, lawn and garden equipment, toys, highway safety devices
Acrylics [poly(methyl methacrylate)]	Acrylite Diakon Lucite Plexiglas	Outstanding light transmission and resistance to weathering; only fair mechanical properties	Lenses, transparent aircraft enclosures, drafting equipment, outdoor signs
Fluorocarbons (PTFE or TFE)	Teflon Fluon Halar Hostaflon TF Neoflon	Chemically inert in almost all environments, excellent electrical properties; low coefficient of friction; may be used to 260°C (500°F); relatively weak and poor cold-flow properties	Anticorrosive seals, chemical pipes and valves, bearings, antiadhesive coatings, high-temperature electronic parts
Polyamides (nylons)	Nylon Baylon Durethan Herox Nomex Ultramid Zytel	Good mechanical strength, abrasion resistance, and toughness; low coefficient of friction; absorbs water and some other liquids	Bearings, gears, cams, bushings, handles, and jacketing for wires and cables
Polycarbonates	Calibre Iupilon Lexan Makrolon Merlon	Dimensionally stable; low water absorption; transparent; very good impact resistance and ductility; chemical resistance not outstanding	Safety helmets, lenses, light globes, base for photographic film
Polyethylene	Alathon Alkathene Fortiflex Hi-fax Petrothene Rigidex Rotothene Zendel	Chemically resistant and electrically insulating; tough and relatively low coefficient of friction; low strength and poor resistance to weathering	Flexible bottles, toys, tumblers, battery parts, ice trays, film wrapping materials

Table 15.3 ***(Continued)***

Material Type	*Trade Names*	*Major Application Characteristics*	*Typical Applications*
Polypropylene	Herculon Meraklon Moplen Poly-pro Pro-fax Propak Propathene	Resistant to heat distortion; excellent electrical properties and fatigue strength; chemically inert; relatively inexpensive; poor resistance to UV light	Sterilizable bottles, packaging film, TV cabinets, luggage
Polystyrene	Carinex Dylene Hostyren Lustrex Styron Vestyron	Excellent electrical properties and optical clarity; good thermal and dimensional stability; relatively inexpensive	Wall tile, battery cases, toys, indoor lighting panels, appliance housings
Vinyls	Darvic Exon Geon Pliovic Saran Tygon Vista	Good low-cost, general-purpose materials; ordinarily rigid, but may be made flexible with plasticizers; often copolymerized; susceptible to heat distortion	Floor coverings, pipe, electrical wire insulation, garden hose, phonograph records
Polyester (PET or PETE)	Celanar Dacron Eastapak Hylar Melinex Mylar Petra	One of the toughest of plastic films; excellent fatigue and tear strength, and resistance to humidity, acids, greases, oils, and solvents	Magnetic recording tapes, clothing, automotive tire cords, beverage containers
		Thermosetting Polymers	
Epoxies	Araldite Epikote Epon Epi-rez Lekutherm Lytex	Excellent combination of mechanical properties and corrosion resistance; dimensionally stable; good adhesion; relatively inexpensive; good electrical properties	Electrical moldings, sinks, adhesives, protective coatings, used with fiberglass laminates
Phenolics	Bakelite Amberol Arofene Durite Resinox	Excellent thermal stability to over 150°C (300°F); may be compounded with a large number of resins, fillers, etc.; inexpensive	Motor housings, telephones, auto distributors, electrical fixtures
Polyesters	Aropol Baygal Derakane Laminac Selectron	Excellent electrical properties and low cost; can be formulated for room- or high-temperature use; often fiber reinforced	Helmets, fiberglass boats, auto body components, chairs, fans

Source: Adapted from C. A. Harper (Editor), *Handbook of Plastics and Elastomers.* Copyright © 1975 by McGraw-Hill Book Company. Reproduced with permission.

MATERIAL OF IMPORTANCE

Phenolic Billiard Balls

Up until about 1912 virtually all billiard balls were made of ivory that came only from the tusks of elephants. For a ball to roll true, it needed to be fashioned from high-quality ivory that came from the center of flaw-free tusks—on the order of one tusk in fifty had the requisite consistency of density. At this time, ivory was becoming scarce and expensive as more and more elephants were being killed (and billiards was becoming popular). Also, there was then (and still is) a serious concern about reductions in elephant populations (and their ultimate extinction) due to ivory hunters, and some countries had imposed (and still impose) severe restrictions on the importation of ivory and ivory products.

Consequently, substitutes for ivory were sought for billiard balls. For example, one early alternative was a pressed mixture of wood pulp and bone dust; this material proved quite unsatisfactory. The most suitable replacement (which is still being used for billiard balls today) is one of the first man-made polymers—phenol-formaldehyde, sometimes also called "phenolic".

The invention of this material is one of the important and interesting events in the annals of man-made polymers. The discoverer of the process for synthesizing phenol-formaldehyde was Leo Baekeland. As a young and very bright Ph.D. chemist, he immigrated from Belgium to the United States in the early 1900s. Shortly after his arrival, he began research into creating a synthetic shellac, to replace the natural material, which was relatively expensive to manufacture; shellac was (and is still) used as a lacquer, a wood preservative, and as an electrical insulator in the then-emerging electrical industry. His efforts eventually led to the discovery that a suitable substitute could be synthesized by reacting phenol [or carbolic acid (C_6H_5OH), a white crystalline material] with formaldehyde ($HCHO$, a colorless and poisonous gas) under controlled conditions of heat and pressure. The product of this reaction was a liquid that subsequently hardened into a transparent and amber-colored solid. Baekeland named his new material "Bakelite"; today we use the generic names "phenol-formaldehyde" or just "phenolic". Shortly after its discovery, Bakelite was found to be the ideal synthetic material for billiard balls (per the chapter-opening photograph for this chapter).

Phenol-formaldehyde is a thermosetting polymer, and has a number of desirable properties: for a polymer it is very heat resistant and hard, is less brittle than many of the ceramic materials, is very stable and unreactive with most common solutions and solvents, and doesn't easily chip, fade, or discolor. Furthermore, it is a relatively inexpensive material, and modern phenolics can be produced having a large variety of colors. The elastic characteristics of this polymer are very similar to those of ivory, and when phenolic billiard balls collide, they make the same clicking sound as ivory balls. Other uses of this important polymeric material are found in Table 15.3.

15.16 ELASTOMERS

The characteristics of and deformation mechanism for elastomers were treated previously (Section 15.9). The present discussion, therefore, focuses on the types of elastomeric materials.

Table 15.4 lists properties and applications of common elastomers; these properties are typical and, of course, depend on the degree of vulcanization and on whether any reinforcement is used. Natural rubber is still utilized to a large degree because it has an outstanding combination of desirable properties. However, the most important synthetic elastomer is SBR, which is used predominantly in automobile tires, reinforced with carbon black. NBR, which is highly resistant to degradation and swelling, is another common synthetic elastomer.

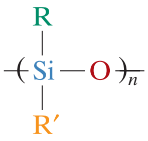
Table 15.4 Tabulation of Important Characteristics and Typical Applications for Five Commercial Elastomers

Chemical Type	*Trade (Common) Names*	*Elongation (%)*	*Useful Temperature Range [°C (°F)]*	*Major Application Characteristics*	*Typical Applications*
Natural polyisoprene	Natural rubber (NR)	500–760	−60 to 120 (−75 to 250)	Excellent physical properties; good resistance to cutting, gouging, and abrasion; low heat, ozone, and oil resistance; good electrical properties	Pneumatic tires and tubes; heels and soles; gaskets
Styrene-butadiene copolymer	GRS, Buna S (SBR)	450–500	−60 to 120 (−75 to 250)	Good physical properties; excellent abrasion resistance; not oil, ozone, or weather resistant; electrical properties good, but not outstanding	Same as natural rubber
Acrylonitrile-butadiene copolymer	Buna A, Nitrile (NBR)	400–600	−50 to 150 (−60 to 300)	Excellent resistance to vegetable, animal, and petroleum oils; poor low-temperature properties; electrical properties not outstanding	Gasoline, chemical, and oil hose; seals and O-rings; heels and soles
Chloroprene	Neoprene (CR)	100–800	−50 to 105 (−60 to 225)	Excellent ozone, heat, and weathering resistance; good oil resistance; excellent flame resistance; not as good in electrical applications as natural rubber	Wire and cable; chem. tank linings; belts, hoses, seals, and gaskets
Polysiloxane	Silicone (VMQ)	100–800	−115 to 315 (−175 to 600)	Excellent resistance to high and low temperatures; low strength; excellent electrical properties	High- and low-temperature insulation; seals, diaphragms; tubing for food and medical uses

Sources: Adapted from C. A. Harper (Editor), *Handbook of Plastics and Elastomers.* Copyright © 1975 by McGraw-Hill Book Company, reproduced with permission; and Materials Engineering's *Materials Selector,* copyright Penton/IPC.

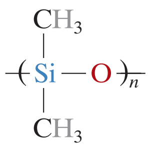
For many applications (e.g., automobile tires), the mechanical properties of even vulcanized rubbers are not satisfactory in terms of tensile strength, abrasion and tear resistance, and stiffness. These characteristics may be further improved by additives such as carbon black (Section 16.2).

Finally, some mention should be made of the silicone rubbers. For these materials, the backbone chain is made of alternating silicon and oxygen atoms:



$$-\!\!\left(\begin{matrix}\text{R}\\ |\\ \text{Si}\\ |\\ \text{R}'\end{matrix}-\text{O}\right)_{\!n}\!\!-$$

where R and R′ represent side-bonded atoms such as hydrogen or groups of atoms such as CH_3. For example, polydimethylsiloxane has the repeat unit



$$-\!\left(\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{Si}}-O\right)_{n}\!-$$

Of course, as elastomers, these materials are crosslinked.

The silicone elastomers possess a high degree of flexibility at low temperatures [to −90°C (−130°F)] and yet are stable to temperatures as high as 250°C (480°F). In addition, they are resistant to weathering and lubricating oils, which makes them particularly desirable for applications in automobile engine compartments. Biocompatibility is another of their assets, and, therefore, they are often employed in medical applications such as blood tubing. A further attractive characteristic is that some silicone rubbers vulcanize at room temperature (RTV rubbers).

Concept Check 15.9

During the winter months, the temperature in some parts of Alaska may go as low as −55°C (−65°F). Of the elastomers natural isoprene, styrene-butadiene, acrylonitrile-butadiene, chloroprene, and polysiloxane, which would be suitable for automobile tires under these conditions? Why?

[*The answer may be found at www.wiley.com/college/callister (Student Companion Site).*]

Concept Check 15.10

Silicone polymers may be prepared to exist as liquids at room temperature. Cite differences in molecular structure between them and the silicone elastomers. *Hint:* You may want to consult Sections 14.5 and 15.9.

[*The answer may be found at www.wiley.com/college/callister (Student Companion Site).*]

15.17 FIBERS

fiber

The **fiber** polymers are capable of being drawn into long filaments having at least a 100:1 length-to-diameter ratio. Most commercial fiber polymers are utilized in the textile industry, being woven or knit into cloth or fabric. In addition, the aramid fibers are employed in composite materials, Section 16.8. To be useful as a textile material, a fiber polymer must have a host of rather restrictive physical and chemical properties. While in use, fibers may be subjected to a variety of mechanical deformations—stretching, twisting, shearing, and abrasion. Consequently, they must have a high tensile strength (over a relatively wide temperature range) and a high modulus of elasticity, as well as abrasion resistance. These properties are governed by the chemistry of the polymer chains and also by the fiber drawing process.

The molecular weight of fiber materials should be relatively high or the molten material will be too weak and will break during the drawing process. Also, because the tensile strength increases with degree of crystallinity, the structure and configuration of the chains should allow the production of a highly crystalline polymer. That translates into a requirement for linear and unbranched chains that are symmetrical and have regular repeat units. Polar groups in the polymer also improve the fiber-forming properties by increasing both crystallinity and the intermolecular forces between the chains.

Convenience in washing and maintaining clothing depends primarily on the thermal properties of the fiber polymer, that is, its melting and glass transition temperatures. Furthermore, fiber polymers must exhibit chemical stability to a rather extensive variety of environments, including acids, bases, bleaches, dry cleaning solvents, and sunlight. In addition, they must be relatively nonflammable and amenable to drying.

15.18 MISCELLANEOUS APPLICATIONS

Coatings

Coatings are frequently applied to the surface of materials to serve one or more of the following functions: (1) to protect the item from the environment that may produce corrosive or deteriorative reactions; (2) to improve the item's appearance; and (3) to provide electrical insulation. Many of the ingredients in coating materials are polymers, the majority of which are organic in origin. These organic coatings fall into several different classifications, as follows: paint, varnish, enamel, lacquer, and shellac.

Many common coatings are *latexes*. A latex is a stable suspension of small insoluble polymer particles dispersed in water. These materials have become increasingly popular because they don't contain large quantities of organic solvents that are emitted into the environment—that is, they have low volatile organic compound (VOC) emissions. VOCs react in the atmosphere to produce smog. Large users of coatings such as automobile manufacturers continue to reduce their VOC emissions to comply with environmental regulations.

Adhesives

adhesive

An **adhesive** is a substance used to bond together the surfaces of two solid materials (termed "adherends"). There are two types of bonding mechanisms: mechanical and chemical. For mechanical there is actual penetration of the adhesive into surface pores and crevices. Chemical bonding involves intermolecular forces between the adhesive and adherend, which forces may be covalent and/or van der Waals; degree of van der Waals bonding is enhanced when the adhesive material contains polar groups.

Although natural adhesives (animal glue, casein, starch, and rosin) are still used for many applications, a host of new adhesive materials based on synthetic polymers have been developed; these include polyurethanes, polysiloxanes (silicones), epoxies, polyimides, acrylics, and rubber materials. Adhesives may be used to join a large variety of materials—viz. metals, ceramics, polymers, composites, skin, etc.—and the choice of which adhesive to use will depend on such factors as (1) the materials to be bonded and their porosities; (2) the required adhesive properties (i.e., whether the bond is to be temporary or permanent); (3) maximum/minimum exposure temperatures; and (4) processing conditions.

For all but the pressure-sensitive adhesives (discussed below), the adhesive material is applied as a low-viscosity liquid, so as to cover evenly and completely the adherend surfaces, and allow for maximum bonding interactions. The actual bonding joint forms as the adhesive undergoes a liquid-to-solid transition (or cures), which may be accomplished through either a physical process (e.g., crystallization, solvent evaporation) or a chemical process [e.g., addition polymerization, condensation polymerization (Section 15.20), vulcanization]. Characteristics of a sound joint should include high shear, peel, and fracture strengths.

Adhesive bonding offers some advantages over other joining technologies (e.g., riveting, bolting, and welding) including lighter weight, the ability to join dissimilar materials and thin components, better fatigue resistance, and lower manufacturing costs. Furthermore, it is the technology of choice when exact positioning of components as well as processing speed are essential. The chief drawback of adhesive joints is service temperature limitation; polymers maintain their mechanical integrity only at relatively low temperatures, and strength decreases rapidly with increasing temperature. The maximum temperature possible for continuous use for some of the newly-developed polymers is 300°C. Adhesive joints are found in a large number applications, especially in the aerospace, automotive, and construction industries, in packaging, and some household goods.

A special class of this group of materials is the pressure-sensitive adhesives (or self-adhesive materials), such as those found on self-stick tapes, labels, and postage stamps. These materials are designed to adhere to just about any surface by making contact and with the application of slight pressure. Unlike the adhesives described above, bonding action does not result from a physical transformation or a chemical reaction. Rather, these materials contain polymer tackifying resins; during detachment of the two bonding surfaces, small fibrils form that are attached to the surfaces and tend to hold them together. Polymers used for pressure-sensitive adhesives include the acrylics, styrenic block copolymers (Section 15.19), and natural rubber.

Films

Polymeric materials have found widespread use in the form of thin *films*. Films having thicknesses between 0.025 and 0.125 mm (0.001 and 0.005 in.) are fabricated and used extensively as bags for packaging food products and other merchandise, as textile products, and a host of other uses. Important characteristics of the materials produced and used as films include low density, a high degree of flexibility, high tensile and tear strengths, resistance to attack by moisture and other chemicals, and low permeability to some gases, especially water vapor (Section 14.14). Some of the polymers that meet these criteria and are manufactured in film form are polyethylene, polypropylene, cellophane, and cellulose acetate.

Foams

foam

Foams are plastic materials that contain a relatively high volume percentage of small pores and trapped gas bubbles. Both thermoplastic and thermosetting materials are used as foams; these include polyurethane, rubber, polystyrene, and poly(vinyl chloride). Foams are commonly used as cushions in automobiles and furniture as well as in packaging and thermal insulation. The foaming process is often carried out by incorporating into the batch of material a blowing agent that, upon heating, decomposes with the liberation of a gas. Gas bubbles are generated throughout the now-fluid mass, which remain in the solid upon cooling and give rise to a sponge-like structure. The same effect is produced by dissolving an inert gas into a molten polymer under high pressure. When the pressure is rapidly reduced, the gas comes out of solution and forms bubbles and pores that remain in the solid as it cools.

15.19 ADVANCED POLYMERIC MATERIALS

A number of new polymers having unique and desirable combinations of properties have been developed over the past several years; many have found niches in new technologies and/or have satisfactorily replaced other materials. Some of these include ultrahigh molecular weight polyethylene, liquid crystal polymers, and thermoplastic elastomers. Each of these will now be discussed.

Ultrahigh Molecular Weight Polyethylene

ultrahigh molecular weight polyethylene (UHMWPE)

Ultrahigh molecular weight polyethylene (*UHMWPE*) is a linear polyethylene that has an extremely high molecular weight. Its typical $\overline{M}_w$ is approximately 4×10^6 g/mol, which is an order of magnitude (i.e., factor of ten) greater than that of high-density polyethylene. In fiber form, UHMWPE is highly aligned and has the trade name Spectra$^{\text{TM}}$. Some of the extraordinary characteristics of this material are as follows:

1. An extremely high impact resistance
2. Outstanding resistance to wear and abrasion
3. A very low coefficient of friction
4. A self-lubricating and nonstick surface
5. Very good chemical resistance to normally encountered solvents
6. Excellent low-temperature properties
7. Outstanding sound damping and energy absorption characteristics
8. Electrically insulating and excellent dielectric properties

However, since this material has a relatively low melting temperature, its mechanical properties diminish rapidly with increasing temperature.

This unusual combination of properties leads to numerous and diverse applications for this material, including bullet-proof vests, composite military helmets, fishing line, ski-bottom surfaces, golf ball cores, bowling alley and ice skating rink surfaces, biomedical prostheses (Section 22.12), blood filters, marking pen nibs, bulk material handling equipment (for coal, grain, cement, gravel, etc.), bushings, pump impellers, and valve gaskets.

Liquid Crystal Polymers

liquid crystal polymer

The **liquid crystal polymers** (*LCP*s) are a group of chemically complex and structurally distinct materials that have unique properties and are utilized in diverse applications. Discussion of the chemistry of these materials is beyond the scope of this book. Suffice it to say that LCPs are composed of extended, rod-shaped, and rigid molecules. In terms of molecular arrangement, these materials do not fall within any of conventional liquid, amorphous, crystalline, or semicrystalline classifications, but may be considered as a new state of matter—the liquid crystalline state, being neither crystalline nor liquid. In the melt (or liquid) condition, whereas other polymer molecules are randomly oriented, LCP molecules can become aligned in highly ordered configurations. As solids, this molecular alignment remains, and, in addition, the molecules form in domain structures having characteristic intermolecular spacings. A schematic comparison of liquid crystals, amorphous polymers, and semicrystalline polymers in both melt and solid states is illustrated in Figure 15.20. Furthermore, there are three types of liquid crystals, based on orientation and positional ordering—smectic, nematic, and cholesteric; distinctions among these types are also beyond the scope of this discussion.

The principal use of liquid crystal polymers is in *liquid crystal displays* (*LCD*s) on digital watches, flat-panel computer monitors and televisions, and other digital displays. Here cholesteric types of LCPs are employed which, at room temperature, are fluid liquids, transparent, and optically anisotropic. The displays are composed of two sheets of glass between which is sandwiched the liquid crystal material. The outer face of each glass sheet is coated with a transparent and

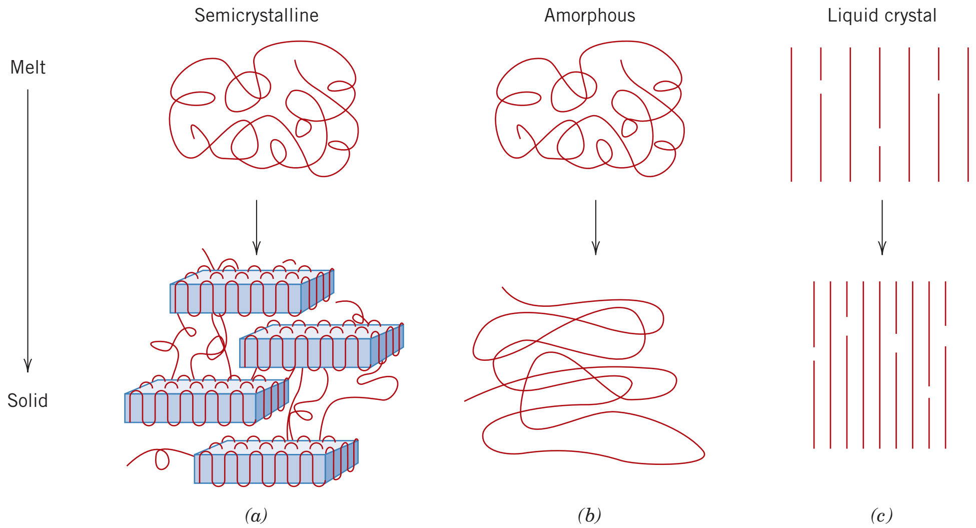


Figure 15.20 Schematic representations of the molecular structures in both melt and solid states for (*a*) semicrystalline, (*b*) amorphous, and (*c*) liquid crystal polymers. (Adapted from G. W. Calundann and M. Jaffe, "Anisotropic Polymers, Their Synthesis and Properties," Chapter VII in *Proceedings of the Robert A. Welch Foundation Conferences on Polymer Research,* 26th Conference, Synthetic Polymers, Nov. 1982.)

electrically conductive film; in addition, the character-forming number/letter elements are etched into this film on the side that is to be viewed. A voltage applied through the conductive films (and thus between these two glass sheets) over one of these character-forming regions causes a disruption of the orientation of the LCP molecules in this region, a darkening of this LCP material, and, in turn, the formation of a visible character.

Some of the nematic type of liquid crystal polymers are rigid solids at room temperature and, on the basis of an outstanding combination of properties and processing characteristics, have found widespread use in a variety of commercial applications. For example, these materials exhibit the following behaviors:

1. Excellent thermal stability; they may be used to temperatures as high as 230°C (450°F).
2. Stiff and strong; their tensile moduli range between 10 and 24 GPa (1.4×10^6 and 3.5×10^6 psi), while tensile strengths are from 125 to 255 MPa (18,000 to 37,000 psi).
3. High impact strengths, which are retained upon cooling to relatively low temperatures.
4. Chemical inertness to a wide variety of acids, solvents, bleaches, etc.
5. Inherent flame resistance and combustion products that are relatively nontoxic.

The thermal stability and chemical inertness of these materials are explained by extremely high intermolecular interactions.

The following may be said about their processing and fabrication characteristics:

1. All conventional processing techniques available for thermoplastic materials may be used.
2. Extremely low shrinkage and warpage take place during molding.

3. Exceptional dimensional repeatability from part to part.
4. Low melt viscosity, which permits molding of thin sections and/or complex shapes.
5. Low heats of fusion; this results in rapid melting and subsequent cooling, which shortens molding cycle times.
6. Anisotropic finished-part properties; molecular orientation effects are produced from melt flow during molding.

These materials are used extensively by the electronics industry (interconnect devices, relay and capacitor housings, brackets, etc.), by the medical equipment industry (in components to be repeatedly sterilized), and in photocopiers and fiber-optic components.

Thermoplastic Elastomers

thermoplastic elastomer

The **thermoplastic elastomers** (*TPE*s or *TE*s) are a type of polymeric material that, at ambient conditions, exhibits elastomeric (or rubbery) behavior, yet is thermoplastic in nature (Section 14.9). By way of contrast, most elastomers heretofore discussed are thermosets, because they are crosslinked during vulcanization. Of the several varieties of TPEs, one of the best known and widely used is a block copolymer consisting of block segments of a hard and rigid thermoplastic (commonly styrene [S]), that alternate with block segments of a soft and flexible elastic material (often butadiene [B] or isoprene [I]). For a common TPE, hard polymerized segments are located at chain ends, whereas each soft central region consists of polymerized butadiene or isoprene units. These TPEs are frequently termed *styrenic block copolymers,* and chain chemistries for the two (S-B-S and S-I-S) types are shown in Figure 15.21

At ambient temperatures, the soft, amorphous, central (butadiene or isoprene) segments impart the rubbery, elastomeric behavior to the material. Furthermore, for temperatures below the T_m of the hard (styrene) component, hard chain-end segments from numerous adjacent chains aggregate together to form rigid crystalline domain regions. These domains are "physical crosslinks" that act as anchor points so as to restrict soft-chain segment motions; they function in much the same way as "chemical crosslinks" for the thermoset elastomers. A schematic illustration for the structure of this TPE type is presented in Figure 15.22.

The tensile modulus of this TPE material is subject to alteration; increasing the number of soft-component blocks per chain will lead to a decrease in modulus and, therefore, a diminishment of stiffness. Furthermore, the useful temperature range lies between T_g of the soft and flexible component and T_m of the hard, rigid one.

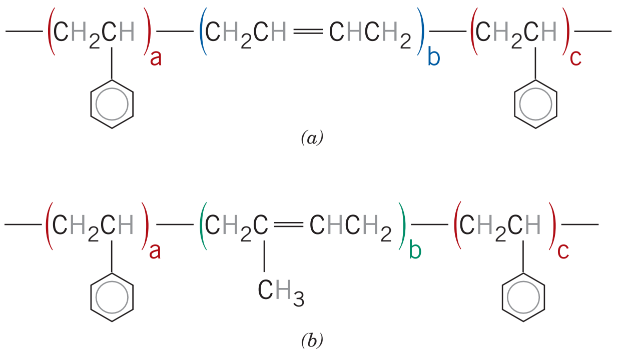


Figure 15.21 Representations of the chain chemistries for (*a*) styrene-butadiene-styrene (S-B-S), and (*b*) styrene-isoprene-styrene (S-I-S) thermoplastic elastomers.

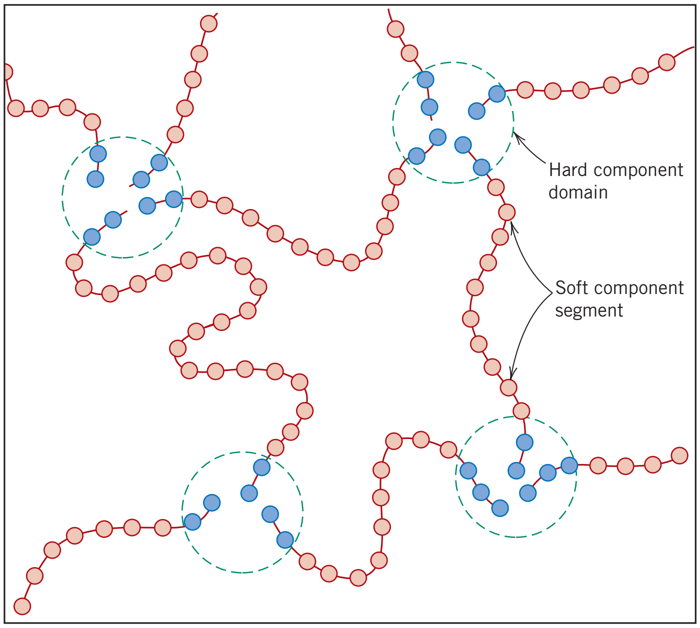


Figure 15.22 Schematic representation of the molecular structure for a thermoplastic elastomer. This structure consists of "soft" (i.e., butadiene or isoprene) repeat unit center-chain segments and "hard" (i.e., styrene) domains (chain ends), which act as physical crosslinks at room temperature. (From *The Science and Engineering of Materials,* fifth edition by ASKELAND/PHULE. © 2006. Reprinted with permission of Nelson, a division of Thomson Learning: www.thomsonrights.com. Fax 800 730-2215.)

For the styrenic block copolymers this range is between about −70°C (−95°F) and 100°C (212°F).

In addition to the styrenic block copolymers, there are other types of TPEs, including thermoplastic olefins, copolyesters, thermoplastic polyurethanes, and elastomeric polyamides.

The chief advantage of the TPEs over the thermoset elastomers is that upon heating above T_m of the hard phase, they melt (i.e., the physical crosslinks disappear), and, therefore, they may be processed by conventional thermoplastic forming techniques [e.g., blow molding, injection molding, etc. (Section 15.22)]; thermoset polymers do not experience melting, and, consequently, forming is normally more difficult. Furthermore, since the melting-solidification process is reversible and repeatable for thermoplastic elastomers, TPE parts may be reformed into other shapes. In other words, they are recyclable; thermoset elastomers are, to a large degree, nonrecyclable. Scrap that is generated during forming procedures may also be recycled, which results in lower production costs than with thermosets. In addition, tighter controls may be maintained on part dimensions for TPEs, and TPEs have lower densities.

In quite a variety of applications, the thermoplastic elastomers have replaced the conventional thermoset elastomers. Typical uses for the TPEs include automotive exterior trim (bumpers, fascia, etc.), automotive underhood components (electrical insulation and connectors, and gaskets), shoe soles and heels, sporting goods (e.g., bladders for footballs and soccer balls), medical barrier films and protective coatings, and as components in sealants, caulking, and adhesives.

Polymer Synthesis and Processing

The large macromolecules of the commercially useful polymers must be synthesized from substances having smaller molecules in a process termed polymerization. Furthermore, the properties of a polymer may be modified and enhanced by the inclusion of additive materials. Finally, a finished piece having a desired shape must be fashioned during a forming operation. This section treats polymerization processes and the various forms of additives, as well as specific forming procedures.

15.20 POLYMERIZATION

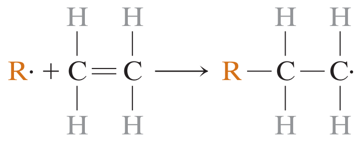
The synthesis of these large molecules (polymers) is termed *polymerization;* it is simply the process by which monomers are linked together to generate long chains composed of repeat units. Most generally, the raw materials for synthetic polymers are derived from coal, natural gas, and petroleum products. The reactions by which polymerization occur are grouped into two general classifications—addition and condensation—according to the reaction mechanism, as discussed below.

Addition Polymerization

addition polymerization

Addition polymerization (sometimes called *chain reaction polymerization*) is a process by which monomer units are attached one at a time in chainlike fashion to form a linear macromolecule. The composition of the resultant product molecule is an exact multiple for that of the original reactant monomer.

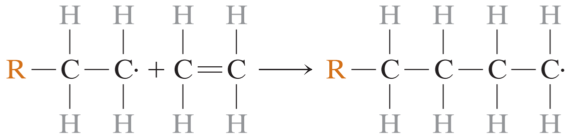
Three distinct stages—initiation, propagation, and termination—are involved in addition polymerization. During the initiation step, an active center capable of propagation is formed by a reaction between an initiator (or catalyst) species and the monomer unit. This process has already been demonstrated for polyethylene (Equation 14.1), which is repeated as follows:



$$\mathrm{R}\cdot + \underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}=\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}} \longrightarrow \mathrm{R}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}\cdot \tag{15.5}$$

Again, R· represents the active initiator, and · is an unpaired electron.

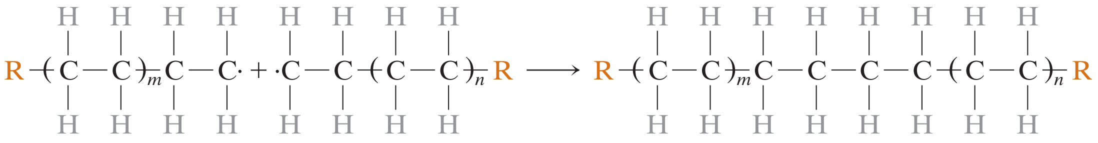
Propagation involves the linear growth of the polymer chain by the sequential addition of monomer units to this active growing chain molecule. This may be represented, again for polyethylene, as follows:



$$\mathrm{R}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}\cdot + \underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}=\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}} \longrightarrow \mathrm{R}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}\cdot \tag{15.6}$$

Chain growth is relatively rapid; the period required to grow a molecule consisting of, say, 1000 repeat units is on the order of 10^{-2} to 10^{-3} s.

Propagation may end or terminate in different ways. First, the active ends of two propagating chains may link together to form one molecule according to the following reaction:[6]

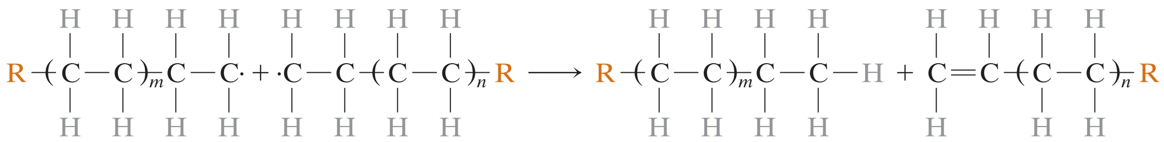


$$\mathrm{R}\left(\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}\right)_m\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}\cdot + \cdot\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}\left(\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}\right)_n\mathrm{R} \longrightarrow \mathrm{R}\left(\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}\right)_m\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}\left(\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}\right)_n\mathrm{R} \tag{15.7}$$

---

[6] This type of termination reaction is referred to as *combination*.

The other termination possibility involves two growing molecules that react to form two "dead chains" as[7]



$$R{-}(\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}})_m{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}\cdot + \cdot\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}(\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}})_n{-}R \longrightarrow R{-}(\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}})_m{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}H + \overset{H}{\underset{H}{C}}{=}\overset{H}{C}{-}(\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}})_n{-}R \qquad (15.8)$$

thus terminating the growth of each chain.

Molecular weight is governed by the relative rates of initiation, propagation, and termination. Ordinarily, they are controlled to ensure the production of a polymer having the desired degree of polymerization.

Addition polymerization is used in the synthesis of polyethylene, polypropylene, poly(vinyl chloride), and polystyrene, as well as many of the copolymers.

Concept Check 15.11

Cite whether the molecular weight of a polymer that is synthesized by addition polymerization is relatively high, medium, or relatively low for the following situations:

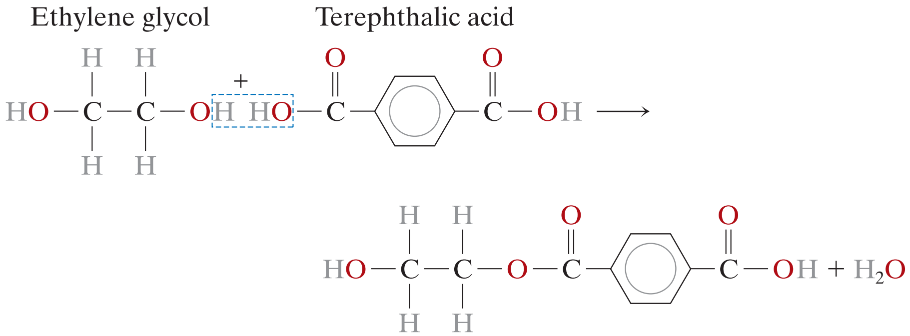
(a) Rapid initiation, slow propagation, and rapid termination.
(b) Slow initiation, rapid propagation, and slow termination.
(c) Rapid initiation, rapid propagation, and slow termination.
(d) Slow initiation, slow propagation, and rapid termination.

[*The answer may be found at www.wiley.com/college/callister (Student Companion Site).*]

Condensation Polymerization

condensation polymerization

Condensation (or *step reaction*) **polymerization** is the formation of polymers by stepwise intermolecular chemical reactions that may involve more than one monomer species. There is usually a small molecular weight byproduct such as water that is eliminated (or condensed). No reactant species has the chemical formula of the repeat unit, and the intermolecular reaction occurs every time a repeat unit is formed. For example, consider the formation of the polyester, poly(ethylene terephthalate) (PET), from the reaction between ethylene glycol and terephthalic acid; the intermolecular reaction is as follows:



(15.9)

---

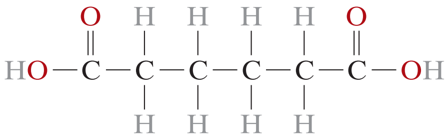
[7] This type of termination reaction is called *disproportionation.*

This stepwise process is successively repeated, producing a linear molecule. The chemistry of the specific reaction is not important but the condensation polymerization mechanism is. Furthermore, reaction times for condensation are generally longer than for addition polymerization.

For the previous condensation reaction, both ethylene glycol and terephthalic acid are bifunctional. However, condensation reactions can include trifunctional or higher functional monomers capable of forming crosslinked and network polymers. The thermosetting polyesters and phenol-formaldehyde, the nylons, and the polycarbonates are produced by condensation polymerization. Some polymers, such as nylon, may be polymerized by either technique.

Concept Check 15.12

Nylon 6,6 may be formed by means of a condensation polymerization reaction in which hexamethylene diamine [NH_2—$(CH_2)_6$—NH_2] and adipic acid react with one another with the formation of water as a byproduct. Write out this reaction in the manner of Equation 15.9. *Note:* the structure for adipic acid is



$$\begin{array}{ccccccccccccccc} & & \mathrm{O} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{O} & & \\ & & \| & & | & & | & & | & & | & & \| & & \\ \mathrm{HO} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{OH} \\ & & & & | & & | & & | & & | & & & & \\ & & & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & & & \end{array}$$

[*The answer may be found at www.wiley.com/college/callister (Student Companion Site).*]

15.21 POLYMER ADDITIVES

Most of the properties of polymers discussed earlier in this chapter are intrinsic ones—that is, characteristic of or fundamental to the specific polymer. Some of these properties are related to and controlled by the molecular structure. Many times, however, it is necessary to modify the mechanical, chemical, and physical properties to a much greater degree than is possible by the simple alteration of this fundamental molecular structure. Foreign substances called *additives* are intentionally introduced to enhance or modify many of these properties, and thus render a polymer more serviceable. Typical additives include filler materials, plasticizers, stabilizers, colorants, and flame retardants.

Fillers

filler

Filler materials are most often added to polymers to improve tensile and compressive strengths, abrasion resistance, toughness, dimensional and thermal stability, and other properties. Materials used as particulate fillers include wood flour (finely powdered sawdust), silica flour and sand, glass, clay, talc, limestone, and even some synthetic polymers. Particle sizes range all the way from 10 nm to macroscopic dimensions. Polymers that contain fillers may also be classified as composite materials, which are discussed in Chapter 16. Often the fillers are inexpensive materials that replace some volume of the more expensive polymer, reducing the cost of the final product.

Plasticizers

plasticizer

The flexibility, ductility, and toughness of polymers may be improved with the aid of additives called **plasticizers.** Their presence also produces reductions in hardness and stiffness. Plasticizers are generally liquids having low vapor pressures and low molecular weights. The small plasticizer molecules occupy positions between the large polymer chains, effectively increasing the interchain distance with a reduction in the secondary intermolecular bonding. Plasticizers are commonly used in polymers that are intrinsically brittle at room temperature, such as poly(vinyl chloride) and some of the acetate copolymers. The plasticizer lowers the glass transition temperature, so that at ambient conditions the polymers may be used in applications requiring some degree of pliability and ductility. These applications include thin sheets or films, tubing, raincoats, and curtains.

Concept Check 15.13

(a) Why must the vapor pressure of a plasticizer be relatively low?

(b) How will the crystallinity of a polymer be affected by the addition of a plasticizer? Why?

(c) How does the addition of a plasticizer influence the tensile strength of a polymer? Why?

[*The answer may be found at www.wiley.com/college/callister (Student Companion Site).*]

Stabilizers

stabilizer

Some polymeric materials, under normal environmental conditions, are subject to rapid deterioration, generally in terms of mechanical integrity. Additives that counteract deteriorative processes are called **stabilizers.**

One common form of deterioration results from exposure to light [in particular ultraviolet (UV) radiation]. Ultraviolet radiation interacts with and causes a severance of some of the covalent bonds along the molecular chains, which may also result in some crosslinking. There are two primary approaches to UV stabilization. The first is to add a UV absorbent material, often as a thin layer at the surface. This essentially acts as a sunscreen and blocks out the UV radiation before it can penetrate into and damage the polymer. The second approach is to add materials that react with the bonds broken by UV radiation before they can participate in other reactions that lead to additional polymer damage.

Another important type of deterioration is oxidation (Section 17.12). It is a consequence of the chemical interaction between oxygen [as either diatomic oxygen (O_2) or ozone (O_3)] and the polymer molecules. Stabilizers that protect against oxidation either consume oxygen before it reaches the polymer, and/or they prevent the occurrence of oxidation reactions that would further damage the material.

Colorants

colorant

Colorants impart a specific color to a polymer; they may be added in the form of dyes or pigments. The molecules in a dye actually dissolve in the polymer. Pigments are filler materials that do not dissolve, but remain as a separate phase; normally they have a small particle size and a refractive index near to that of the parent polymer. Others may impart opacity as well as color to the polymer.

Flame Retardants

The flammability of polymeric materials is a major concern, especially in the manufacture of textiles and children's toys. Most polymers are flammable in their pure form; exceptions include those containing significant contents of chlorine and/or fluorine, such as poly(vinyl chloride) and polytetrafluoroethylene. The flammability

flame retardant

resistance of the remaining combustible polymers may be enhanced by additives called **flame retardants.** These retardants may function by interfering with the combustion process through the gas phase, or by initiating a different combustion reaction that generates less heat, thereby reducing the temperature; this causes a slowing or cessation of burning.

15.22 FORMING TECHNIQUES FOR PLASTICS

Quite a variety of different techniques are employed in the forming of polymeric materials. The method used for a specific polymer depends on several factors: (1) whether the material is thermoplastic or thermosetting; (2) if thermoplastic, the temperature at which it softens; (3) the atmospheric stability of the material being formed; and (4) the geometry and size of the finished product. There are numerous similarities between some of these techniques and those utilized for fabricating metals and ceramics.

Fabrication of polymeric materials normally occurs at elevated temperatures and often by the application of pressure. Thermoplastics are formed above their glass transition temperatures, if amorphous, or above their melting temperatures, if semicrystalline. An applied pressure must be maintained as the piece is cooled so that the formed article will retain its shape. One significant economic benefit of using thermoplastics is that they may be recycled; scrap thermoplastic pieces may be remelted and reformed into new shapes.

Fabrication of thermosetting polymers is ordinarily accomplished in two stages. First comes the preparation of a linear polymer (sometimes called a prepolymer) as a liquid, having a low molecular weight. This material is converted into the final hard and stiff product during the second stage, which is normally carried out in a mold having the desired shape. This second stage, termed "curing," may occur during heating and/or by the addition of catalysts, and often under pressure. During curing, chemical and structural changes occur on a molecular level: a crosslinked or a network structure forms. After curing, thermoset polymers may be removed from a mold while still hot, since they are now dimensionally stable. Thermosets are difficult to recycle, do not melt, are usable at higher temperatures than thermoplastics, and are often more chemically inert.

molding

Molding is the most common method for forming plastic polymers. The several molding techniques used include compression, transfer, blow, injection, and extrusion molding. For each, a finely pelletized or granulized plastic is forced, at an elevated temperature and by pressure, to flow into, fill, and assume the shape of a mold cavity.

Compression and Transfer Molding

For compression molding, the appropriate amounts of thoroughly mixed polymer and necessary additives are placed between male and female mold members, as illustrated in Figure 15.23. Both mold pieces are heated; however, only one is movable. The mold is closed, and heat and pressure are applied, causing the plastic to become viscous and flow to conform to the mold shape. Before molding, raw materials may be mixed and cold pressed into a disc, which is called a preform. Preheating of the preform reduces molding time and pressure, extends the die lifetime, and produces a more uniform finished piece. This molding technique lends itself to the fabrication of both thermoplastic and thermosetting polymers; however, its use with thermoplastics is more time-consuming and expensive than the more commonly used extrusion or injection molding techniques discussed below.

In transfer molding, a variation of compression molding, the solid ingredients are first melted in a heated transfer chamber. As the molten material is injected into the

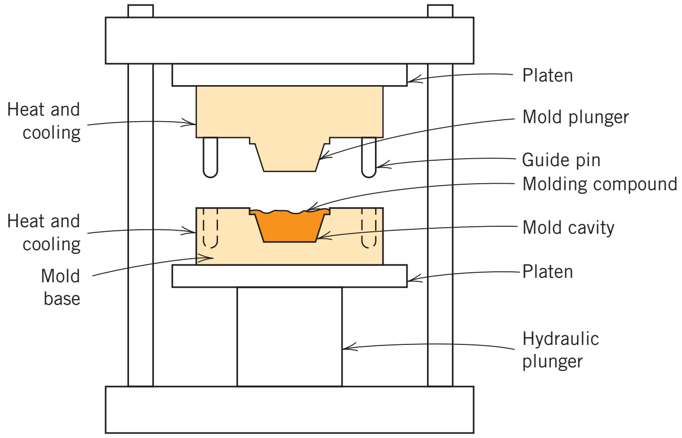


Figure 15.23 Schematic diagram of a compression molding apparatus. (From F. W. Billmeyer, Jr., *Textbook of Polymer Science,* 3rd edition. Copyright © 1984 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

mold chamber, the pressure is distributed more uniformly over all surfaces. This process is used with thermosetting polymers and for pieces having complex geometries.

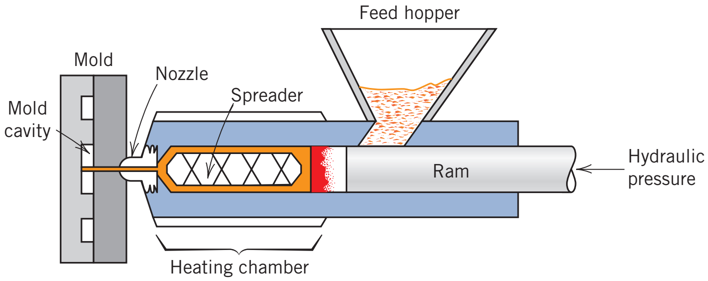
Injection Molding

Injection molding, the polymer analogue of die casting for metals, is the most widely used technique for fabricating thermoplastic materials. A schematic cross section of the apparatus used is illustrated in Figure 15.24. The correct amount of pelletized material is fed from a feed hopper into a cylinder by the motion of a plunger or ram. This charge is pushed forward into a heating chamber where it is forced around a spreader so as to make better contact with the heated wall. As a result, the thermoplastic material melts to form a viscous liquid. Next, the molten plastic is impelled, again by ram motion, through a nozzle into the enclosed mold cavity; pressure is maintained until the molding has solidified. Finally, the mold is opened, the piece is ejected, the mold is closed, and the entire cycle is repeated. Probably the most outstanding feature of this technique is the speed with which pieces may be produced. For thermoplastics, solidification of the injected charge is almost immediate; consequently, cycle times for this process are short (commonly within the range of 10 to 30 s). Thermosetting polymers may also be injection molded; curing takes place while the material is under pressure in a heated mold, which results in longer cycle times than for thermoplastics. This process is sometimes termed reaction injection molding (RIM) and is commonly used for materials such as polyurethane.

Extrusion

The extrusion process is the molding of a viscous thermoplastic under pressure through an open-ended die, similar to the extrusion of metals (Figure 11.8*c*). A mechanical screw or auger propels through a chamber the pelletized material, which

Figure 15.24 Schematic diagram of an injection molding apparatus. (Adapted from F. W. Billmeyer, Jr., *Textbook of Polymer Science,* 2nd edition. Copyright © 1971 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)



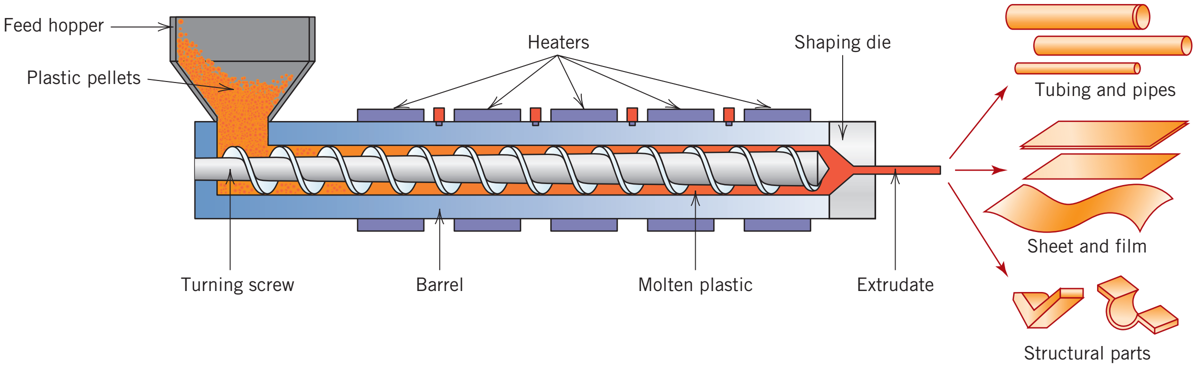


Figure 15.25 Schematic diagram of an extruder. (Reprinted with permission from *Encyclopædia Britannica,* © 1997 by Encyclopædia Britannica, Inc.)

is successively compacted, melted, and formed into a continuous charge of viscous fluid (Figure 15.25). Extrusion takes place as this molten mass is forced through a die orifice. Solidification of the extruded length is expedited by blowers, a water spray, or bath. The technique is especially adapted to producing continuous lengths having constant cross-sectional geometries—for example, rods, tubes, hose channels, sheets, and filaments.

Blow Molding

The blow-molding process for the fabrication of plastic containers is similar to that used for blowing glass bottles, as represented in Figure 13.8. First, a parison, or length of polymer tubing, is extruded. While still in a semimolten state, the parison is placed in a two-piece mold having the desired container configuration. The hollow piece is formed by blowing air or steam under pressure into the parison, forcing the tube walls to conform to the contours of the mold. Of course the temperature and viscosity of the parison must be carefully regulated.

Casting

Like metals, polymeric materials may be cast, as when a molten plastic material is poured into a mold and allowed to solidify. Both thermoplastic and thermosetting plastics may be cast. For thermoplastics, solidification occurs upon cooling from the molten state; however, for thermosets, hardening is a consequence of the actual polymerization or curing process, which is usually carried out at an elevated temperature.

15.23 FABRICATION OF ELASTOMERS

Techniques used in the actual fabrication of rubber parts are essentially the same as those discussed for plastics as described above—that is, compression molding, extrusion, and so on. Furthermore, most rubber materials are vulcanized (Section 15.9) and some are reinforced with carbon black (Section 16.2).

Concept Check 15.14

For a rubber component that, in its final form is to be vulcanized, should vulcanization be carried out prior to or subsequent to the forming operation? Why? *Hint:* you may want to consult Section 15.9.

[*The answer may be found at* www.wiley.com/college/callister *(Student Companion Site).*]

15.24 FABRICATION OF FIBERS AND FILMS

Fibers

spinning

The process by which fibers are formed from bulk polymer material is termed **spinning.** Most often, fibers are spun from the molten state in a process called melt spinning. The material to be spun is first heated until it forms a relatively viscous liquid. Next, it is pumped through a plate called a spinneret, which contains numerous small, typically round holes. As the molten material passes through each of these orifices, a single fiber is formed, which is rapidly solidified by cooling with air blowers or a water bath.

The crystallinity of a spun fiber will depend on its rate of cooling during spinning. The strength of fibers is improved by a postforming process called drawing, as discussed in Section 15.8. Again, drawing is simply the permanent mechanical elongation of a fiber in the direction of its axis. During this process the molecular chains become oriented in the direction of drawing (Figure 15.13*d*), such that the tensile strength, modulus of elasticity, and toughness are improved. The cross section of melt spun, drawn fibers is nearly circular, and the properties are uniform throughout the cross section.

Two other techniques that involve producing fibers from solutions of dissolved polymers are *dry spinning* and *wet spinning*. For dry spinning the polymer is dissolved in a volatile solvent. The polymer-solvent solution is then pumped through a spinneret into a heated zone; here the fibers solidify as the solvent evaporates. In wet spinning, the fibers are formed by passing a polymer-solvent solution through a spinneret directly into a second solvent that causes the polymer fiber to come out of (i.e., precipitate from) the solution. For both of these techniques, a skin first forms on the surface of the fiber. Subsequently, some shrinkage occurs such that the fiber shrivels up (like a raisin); this leads to a very irregular cross-section profile, which causes the fiber to become stiffer (i.e., increases the modulus of elasticity).

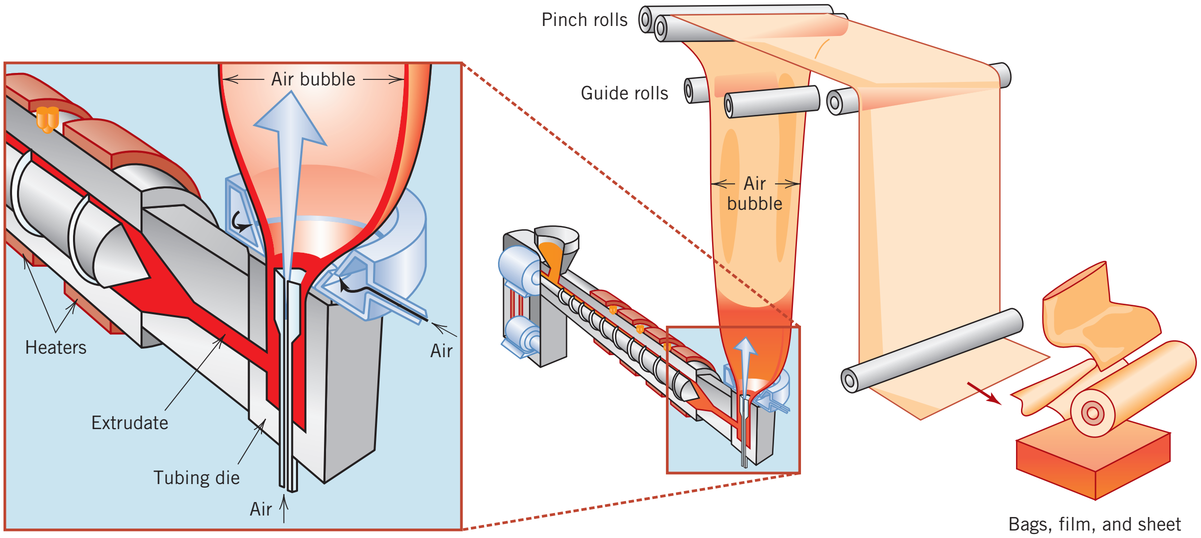


Figure 15.26 Schematic diagram of an apparatus that is used to form thin polymer films. (Reprinted with permission from *Encyclopædia Britannica,* © 1997 by Encyclopædia Britannica, Inc.)

Films

Many films are simply extruded through a thin die slit; this may be followed by a rolling (calendering) or drawing operation that serves to reduce thickness and improve strength. Alternatively, film may be blown: continuous tubing is extruded through an annular die; then, by maintaining a carefully controlled positive gas pressure inside the tube and by drawing the film in the axial direction as it emerges from the die, the material expands around this trapped air bubble like a balloon (Figure 15.26). As a result the wall thickness is continuously reduced to produce a thin cylindrical film which can be sealed at the end to make garbage bags, or which may be cut and laid flat to make a film. This is termed a biaxial drawing process and produces films that are strong in both stretching directions. Some of the newer films are produced by coextrusion; that is, multilayers of more than one polymer type are extruded simultaneously.

SUMMARY

Stress–Strain Behavior

On the basis of stress–strain behavior, polymers fall within three general classifications: brittle, plastic, and highly elastic. These materials are neither as strong nor as stiff as metals, and their mechanical properties are sensitive to changes in temperature and strain rate. However, their high flexibilities, low densities, and resistance to corrosion make them the materials of choice for many applications.

Viscoelastic Deformation

Viscoelastic mechanical behavior, being intermediate between totally elastic and totally viscous, is displayed by a number of polymeric materials. It is characterized by the relaxation modulus, a time-dependent modulus of elasticity. The magnitude of the relaxation modulus is very sensitive to temperature; critical to the in-service temperature range for elastomers is this temperature dependence.

Fracture of Polymers

Fracture strengths of polymeric materials are low relative to metals and ceramics. Both brittle and ductile fracture modes are possible, and some thermoplastic materials experience a ductile-to-brittle transition with a lowering of temperature, an increase in strain rate, and/or an alteration of specimen thickness or geometry. In some thermoplastics, the crack-formation process may be preceded by crazing; crazing can lead to an increase in ductility and toughness of the material.

Deformation of Semicrystalline Polymers

During the elastic deformation of a semicrystalline polymer having a spherulitic structure that is stressed in tension, the molecules in amorphous regions elongate in the stress direction. In addition, molecules in crystallites experience bending and stretching, which causes a slight increase in lamellar thickness.

The mechanism of plastic deformation for spherulitic polymers was also presented. Tensile deformation occurs in several stages as both amorphous tie chains and chain-folded block segments (which separate from the ribbon-like lamellae) become oriented with the tensile axis. Also, during deformation the shapes of spherulites are altered (for moderate deformations); relatively large degrees of deformation lead to a complete destruction of the spherulites to form highly aligned structures. Furthermore, the predeformed spherulitic structure and macroscopic shape may be partially restored by annealing at an elevated temperature below the polymer's melting temperature.

Factors That Influence the Mechanical Properties of Semicrystalline Polymers

The mechanical behavior of a polymer will be influenced by both in-service and structural/processing factors. With regard to the former, increasing the temperature and/or diminishing the strain rate leads to reductions in tensile modulus and tensile strength and an enhancement of ductility. In addition, other factors that affect the mechanical properties include molecular weight, degree of crystallinity, predeformation drawing, and heat treating. The influence of each of these factors was discussed.

Deformation of Elastomers

Large elastic extensions are possible for the elastomeric materials that are amorphous and lightly crosslinked. Deformation corresponds to the unkinking and uncoiling of chains in response to an applied tensile stress. Crosslinking is often achieved during a vulcanization process. Many of the elastomers are copolymers, whereas the silicone elastomers are really inorganic materials.

Crystallization
Melting
The Glass Transition
Melting and Glass Transition Temperatures
Factors That Influence Melting and Glass Transition Temperatures

The molecular mechanics of crystallization, melting, and the glass transition were discussed. The manner in which melting and glass transition temperatures are determined was outlined; these parameters are important relative to the temperature range over which a particular polymer may be utilized and processed. The magnitudes of T_m and T_g increase with increasing chain stiffness; stiffness is enhanced by the presence of chain double bonds and side groups that are either bulky or polar. Molecular weight and degree of branching also affect T_m and T_g.

Plastics

The various types and applications of polymeric materials were also discussed. Plastic materials are perhaps the most widely used group of polymers, which include the following: polyethylene, polypropylene, poly(vinyl chloride), polystyrene, and the fluorocarbons, epoxies, phenolics, and polyesters.

Fibers

Many polymeric materials may be spun into fibers, which are used primarily in textiles. Mechanical, thermal, and chemical characteristics of these materials are especially critical.

Miscellaneous Applications

Other miscellaneous applications that employ polymers include coatings, adhesives, films, and foams.

Advanced Polymeric Materials

Also discussed were three advanced polymeric materials: ultrahigh molecular weight polyethylene, liquid crystal polymers, and thermoplastic elastomers. These materials have unusual properties and are used in a host of high-technology applications.

Polymerization
Polymer Additives

The final sections of this chapter treated synthesis and fabrication techniques for polymeric materials. Synthesis of large molecular weight polymers is attained by polymerization, of which there are two types: addition and condensation. The properties of polymers may be further modified by using additives; these include fillers, plasticizers, stabilizers, colorants, and flame retardants.

Forming Techniques for Plastics

Fabrication of plastic polymers is usually accomplished by shaping the material in molten form at an elevated temperature, using at least one of several different molding techniques—compression, transfer, injection, and blow. Extrusion and casting are also possible.

Fabrication of Fibers and Films

Some fibers are spun from a viscous melt, after which they are plastically elongated during a drawing operation, which improves the mechanical strength. Films are formed by extrusion and blowing, or by calendering.

IMPORTANT TERMS AND CONCEPTS

Addition polymerization
Adhesive
Colorant
Condensation polymerization
Drawing
Elastomer
Fiber
Filler
Flame retardant
Foam
Glass transition temperature
Liquid crystal polymer
Melting temperature
Molding
Plasticizer
Plastic
Relaxation modulus
Spinning
Stabilizer
Thermoplastic elastomer
Ultrahigh molecular weight polyethylene
Viscoelasticity
Vulcanization

REFERENCES

Billmeyer, F. W., Jr., *Textbook of Polymer Science,* 3rd edition, Wiley-Interscience, New York, 1984.

Carraher, C. E., Jr., *Seymour/Carraher's Polymer Chemistry,* 6th edition, Marcel Dekker, New York, 2003.

Engineered Materials Handbook, Vol. 2, *Engineering Plastics,* ASM International, Metals Park, OH, 1988.

Harper, C. A. (Editor), *Handbook of Plastics, Elastomers and Composites,* 3rd edition, McGraw-Hill Professional Book Group, New York, 1996.

Landel, R. F. (Editor), *Mechanical Properties of Polymers and Composites,* 2nd edition, Marcel Dekker, New York, 1994.

McCrum, N. G., C. P. Buckley, and C. B. Bucknall, *Principles of Polymer Engineering,* 2nd edition, Oxford University Press, Oxford, 1997. Chapters 7–8.

Muccio, E. A., *Plastic Part Technology,* ASM International, Materials Park, OH, 1991.

Muccio, E. A., *Plastics Processing Technology,* ASM International, Materials Park, OH, 1994.

Powell, P. C., and A. J. Housz, *Engineering with Polymers,* 2nd edition, Nelson Thornes, Cheltenham, UK, 1998.

Rosen, S. L., *Fundamental Principles of Polymeric Materials,* 2nd edition, Wiley, New York, 1993.

Rudin, A., *The Elements of Polymer Science and Engineering,* 2nd edition, Academic Press, San Diego, 1998.

Strong, A. B., *Plastics: Materials and Processing,* 3rd edition, Prentice Hall PTR, Paramus, IL, 2006.

Tobolsky, A. V., *Properties and Structures of Polymers,* Wiley, New York, 1960. Advanced treatment.

Ward, I. M. and J. Sweeney, *An Introduction to the Mechanical Properties of Solid Polymers,* 2nd edition, John Wiley & Sons, Hoboken, NJ, 2004.

QUESTIONS AND PROBLEMS

Stress–Strain Behavior

15.1 From the stress–strain data for poly(methyl methacrylate) shown in Figure 15.3, determine the modulus of elasticity and tensile strength at room temperature [20°C (68°F)], and compare these values with those given in Table 15.1.

Viscoelastic Deformation

15.2 In your own words, briefly describe the phenomenon of viscoelasticity.

15.3 For some viscoelastic polymers that are subjected to stress relaxation tests, the stress decays with time according to

$$\sigma(t) = \sigma(0)\exp\left(-\frac{t}{\tau}\right) \tag{15.10}$$

where $\sigma(t)$ and $\sigma(0)$ represent the time-dependent and initial (i.e., time = 0) stresses, respectively, and t and τ denote elapsed time and the relaxation time; τ is a time-independent constant characteristic of the material. A specimen of some viscoelastic polymer with the stress relaxation that obeys Equation 15.10 was suddenly pulled in tension to a measured strain of 0.5; the stress necessary to maintain this constant strain was measured as a function of time. Determine $E_r(10)$ for this material if the initial stress level was 3.5 MPa (500 psi), which dropped to 0.5 MPa (70 psi) after 30 s.

15.4 In Figure 15.27, the logarithm of $E_r(t)$ versus the logarithm of time is plotted for PMMA at a variety of temperatures. Make a plot of log $E_r(10)$ versus temperature and then estimate its T_g.

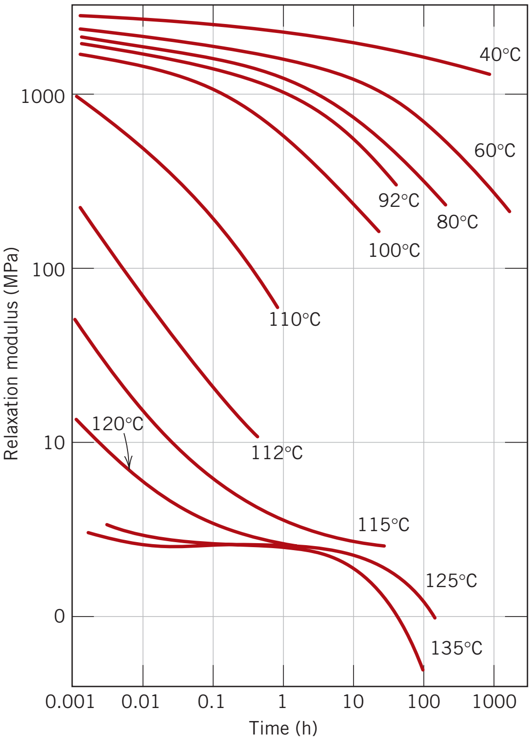


Figure 15.27 Logarithm of relaxation modulus versus logarithm of time for poly(methyl methacrylate) between 40 and 135°C. (From J. R. McLoughlin and A. V. Tobolsky, *J. Colloid Sci.,* **7,** 555, 1952. Reprinted with permission.)

15.5 On the basis of the curves in Figure 15.5, sketch schematic strain–time plots for the following polystyrene materials at the specified temperatures:

(a) Crystalline at 70°C

(b) Amorphous at 180°C

(c) Crosslinked at 180°C

(d) Amorphous at 100°C

15.6 **(a)** Contrast the manner in which stress relaxation and viscoelastic creep tests are conducted.

(b) For each of these tests, cite the experimental parameter of interest and how it is determined.

15.7 Make two schematic plots of the logarithm of relaxation modulus versus temperature for an amorphous polymer (curve *C* in Figure 15.8).

(a) On one of these plots demonstrate how the behavior changes with increasing molecular weight.

(b) On the other plot, indicate the change in behavior with increasing crosslinking.

Fracture of Polymers
Miscellaneous Mechanical Characteristics

15.8 For thermoplastic polymers, cite five factors that favor brittle fracture.

15.9 **(a)** Compare the fatigue limits for PMMA (Figure 15.11) and the steel alloy for which fatigue data are given in Problem 8.20.

(b) Compare the fatigue strengths at 10^6 cycles for nylon 6 (Figure 15.11) and 2014-T6 aluminum (Figure 8.34).

Deformation of Semicrystalline Polymers (Deformation of Elastomers)

15.10 In your own words, describe the mechanisms by which semicrystalline polymers **(a)** elastically deform and **(b)** plastically deform, and **(c)** by which elastomers elastically deform.

Factors That Influence the Mechanical Properties of Semicrystalline Polymers
Deformation of Elastomers

15.11 Briefly explain how each of the following influences the tensile modulus of a semicrystalline polymer and why:

(a) Molecular weight

(b) Degree of crystallinity

(c) Deformation by drawing

(d) Annealing of an undeformed material

(f) Annealing of a drawn material

15.12 Briefly explain how each of the following influences the tensile or yield strength of a semicrystalline polymer and why:

(a) Molecular weight

(b) Degree of crystallinity

(c) Deformation by drawing

(d) Annealing of an undeformed material

15.13 Normal butane and isobutane have boiling temperatures of −0.5 and −12.3°C (31.1 and 9.9°F), respectively. Briefly explain this behavior on the basis of their molecular structures, as presented in Section 14.2.

15.14 The tensile strength and number-average molecular weight for two poly(methyl methacrylate) materials are as follows:

Tensile Strength (MPa)	*Number-Average Molecular Weight (g/mol)*
50	30,000
150	50,000

Estimate the tensile strength at a number-average molecular weight of 40,000 g/mol.

15.15 The tensile strength and number-average molecular weight for two polyethylene materials are as follows:

Tensile Strength (MPa)	*Number-Average Molecular Weight (g/mol)*
90	20,000
180	40,000

Estimate the number-average molecular weight that is required to give a tensile strength of 140 MPa.

15.16 For each of the following pairs of polymers, do the following: (1) state whether or not it is possible to decide whether one polymer has a higher tensile modulus than the other; (2) if this is possible, note which has the higher tensile modulus and then cite the reason(s) for your choice; and (3) if it is not possible to decide, then state why.

(a) Branched and atactic poly(vinyl chloride) with a weight-average molecular weight of 100,000 g/mol; linear and isotactic poly(vinyl chloride) having a weight-average molecular weight of 75,000 g/mol

(b) Random styrene-butadiene copolymer with 5% of possible sites crosslinked; block styrene-butadiene copolymer with 10% of possible sites crosslinked

(c) Branched polyethylene with a number-average molecular weight of 100,000 g/mol; atactic polypropylene with a number-average molecular weight of 150,000 g/mol

15.17 For each of the following pairs of polymers, do the following: (1) state whether or not it is possible to decide whether one polymer has a higher tensile strength than the other; (2) if this is possible, note which has the higher tensile strength and then cite the reason(s) for your choice; and (3) if it is not possible to decide, then state why.

(a) Linear and isotactic poly(vinyl chloride) with a weight-average molecular weight of 100,000 g/mol; branched and atactic poly(vinyl chloride) having a weight-average molecular weight of 75,000 g/mol

(b) Graft acrylonitrile-butadiene copolymer with 10% of possible sites crosslinked; alternating acrylonitrile-butadiene copolymer with 5% of possible sites crosslinked

(c) Network polyester; lightly branched polytetrafluoroethylene

15.18 Would you expect the tensile strength of polychlorotrifluoroethylene to be greater than, the same as, or less than that of a polytetrafluoroethylene specimen having the same molecular weight and degree of crystallinity? Why?

15.19 For each of the following pairs of polymers, plot and label schematic stress–strain curves on the same graph (i.e., make separate plots for parts a, b, and c).

(a) Polyisoprene having a number-average molecular weight of 100,000 g/mol and 10% of available sites crosslinked; polyisoprene having a number-average molecular weight of 100,000 g/mol and 20% of available sites crosslinked

(b) Syndiotactic polypropylene having a weight-average molecular weight of 100,000 g/mol; atactic polypropylene having a weight-average molecular weight of 75,000 g/mol

(c) Branched polyethylene having a number-average molecular weight of 90,000 g/mol; heavily crosslinked polyethylene having a number-average molecular weight of 90,000 g/mol

15.20 List the two molecular characteristics that are essential for elastomers.

15.21 Which of the following would you expect to be elastomers and which thermosetting polymers at room temperature? Justify each choice.

(a) Linear and highly crystalline polyethylene

(b) Phenol-formaldehyde

(c) Heavily crosslinked polyisoprene having a glass-transition temperature of 50°C (122°F)

(d) Lightly crosslinked polyisoprene having a glass-transition temperature of −60°C (−76°F)

(e) Linear and partially amorphous poly(vinyl chloride)

15.22 Fifteen kilogram of polychloroprene is vulcanized with 5.2 kg sulfur. What fraction of the possible crosslink sites is bonded to sulfur crosslinks, assuming that, on the average, 5.5 sulfur atoms participate in each crosslink?

15.23 Compute the weight percent sulfur that must be added to completely crosslink an alternating acrylonitrile-butadiene copolymer, assuming that four sulfur atoms participate in each crosslink.

15.24 The vulcanization of polyisoprene is accomplished with sulfur atoms according to Equation 15.4. If 45.3 wt% sulfur is combined with polyisoprene, how many crosslinks will be associated with each isoprene repeat unit if it is assumed that, on the average, five sulfur atoms participate in each crosslink?

15.25 For the vulcanization of polyisoprene, compute the weight percent of sulfur that must be added to ensure that 10% of possible sites will be crosslinked; assume that, on the average, 3.5 sulfur atoms are associated with each crosslink.

15.26 Demonstrate, in a manner similar to Equation 15.4, how vulcanization may occur in a chloroprene rubber.

Crystallization

15.27 Determine values for the constants n and k (Equation 10.17) for the crystallization of polypropylene (Figure 15.17) at 150°C.

Melting and Glass Transition Temperatures

15.28 Name the following polymer(s) that would be suitable for the fabrication of cups to contain hot coffee: polyethylene, polypropylene, poly(vinyl chloride), PET polyester, and polycarbonate. Why?

15.29 Of those polymers listed in Table 15.2, which polymer(s) would be best suited for use as ice cube trays? Why?

Factors That Influence Melting and Glass Transition Temperatures

15.30 For each of the following pairs of polymers, plot and label schematic specific volume versus temperature curves on the same graph (i.e., make separate plots for parts a, b, and c).

(a) Linear polyethylene with a weight-average molecular weight of 75,000 g/mol; branched polyethylene with a weight-average molecular weight of 50,000 g/mol

(b) Spherulitic poly(vinyl chloride), of 50% crystallinity, and having a degree of polymerization of 5000; spherulitic polypropylene, of 50% crystallinity, and degree of polymerization of 10,000

(c) Totally amorphous polystyrene having a degree of polymerization of 7000; totally amorphous polypropylene having a degree of polymerization of 7000

15.31 For each of the following pairs of polymers, do the following: (1) state whether or not it is possible to determine whether one polymer has a higher melting temperature than the other; (2) if it is possible, note which has the higher melting temperature and then cite reason(s) for your choice; and (3) if it is not possible to decide, then state why.

(a) Branched polyethylene having a number-average molecular weight of 850,000 g/mol; linear polyethylene having a number-average molecular weight of 850,000 g/mol

(b) Polytetrafluoroethylene having a density of 2.14 g/cm^3 and a weight-average molecular weight of 600,000 g/mol; PTFE having a density of 2.20 g/cm^3 and a weight-average molecular weight of 600,000 g/mol

(c) Linear and syndiotactic poly(vinyl chloride) having a number-average molecular weight of 500,000 g/mol; linear polyethylene having a number-average molecular weight of 225,000 g/mol

(d) Linear and syndiotactic polypropylene having a weight-average molecular weight of 500,000 g/mol; linear and atactic polypropylene having a weight-average molecular weight of 750,000 g/mol

15.32 Make a schematic plot showing how the modulus of elasticity of an amorphous polymer depends on the glass transition temperature. Assume that molecular weight is held constant.

Elastomers
Fibers
Miscellaneous Applications

15.33 Briefly explain the difference in molecular chemistry between silicone polymers and other polymeric materials.

15.34 List two important characteristics for polymers that are to be used in fiber applications.

15.35 Cite five important characteristics for polymers that are to be used in thin-film applications.

Polymerization

15.36 Cite the primary differences between addition and condensation polymerization techniques.

15.37 **(a)** How much ethylene glycol must be added to 20.0 kg of terephthalic acid to produce a linear chain structure of poly(ethylene terephthalate) according to Equation 15.9?

(b) What is the mass of the resulting polymer?

15.38 Nylon 6,6 may be formed by means of a condensation polymerization reaction in which hexamethylene diamine [NH_2—$(CH_2)_6$—NH_2] and adipic acid react with one another with the formation of water as a byproduct. What masses of hexamethylene diamine and adipic acid are necessary to yield 20 kg of completely linear nylon 6,6? (*Note:* the chemical equation for this reaction is the answer to Concept Check 15.12.)

Polymer Additives

15.39 What is the distinction between dye and pigment colorants?

Forming Techniques for Plastics

15.40 Cite four factors that determine what fabrication technique is used to form polymeric materials.

15.41 Contrast compression, injection, and transfer molding techniques that are used to form plastic materials.

Fabrication of Fibers and Films

15.42 Why must fiber materials that are melt spun and then drawn be thermoplastic? Cite two reasons.

15.43 Which of the following polyethylene thin films would have the better mechanical characteristics: (1) formed by blowing, or (2) formed by extrusion and then rolled? Why?

DESIGN QUESTIONS

15.D1 **(a)** List several advantages and disadvantages of using transparent polymeric materials for eyeglass lenses.

(b) Cite four properties (in addition to being transparent) that are important for this application.

(c) Note three polymers that may be candidates for eyeglass lenses, and then tabulate values of the properties noted in part (b) for these three materials.

15.D2 Write an essay on polymeric materials that are used in the packaging of food products and drinks. Include a list of the general requisite characteristics of materials that are used for these applications. Now cite a specific material that is utilized for each of three different container types and the rationale for each choice.

15.D3 Write an essay on the replacement of metallic automobile components by polymers and composite materials. Address the following issues: (1) Which automotive components (e.g., crankshaft) now use polymers and/or composites? (2) Specifically what materials (e.g., high-density polyethylene) are now being used? (3) What are the reasons for these replacements?