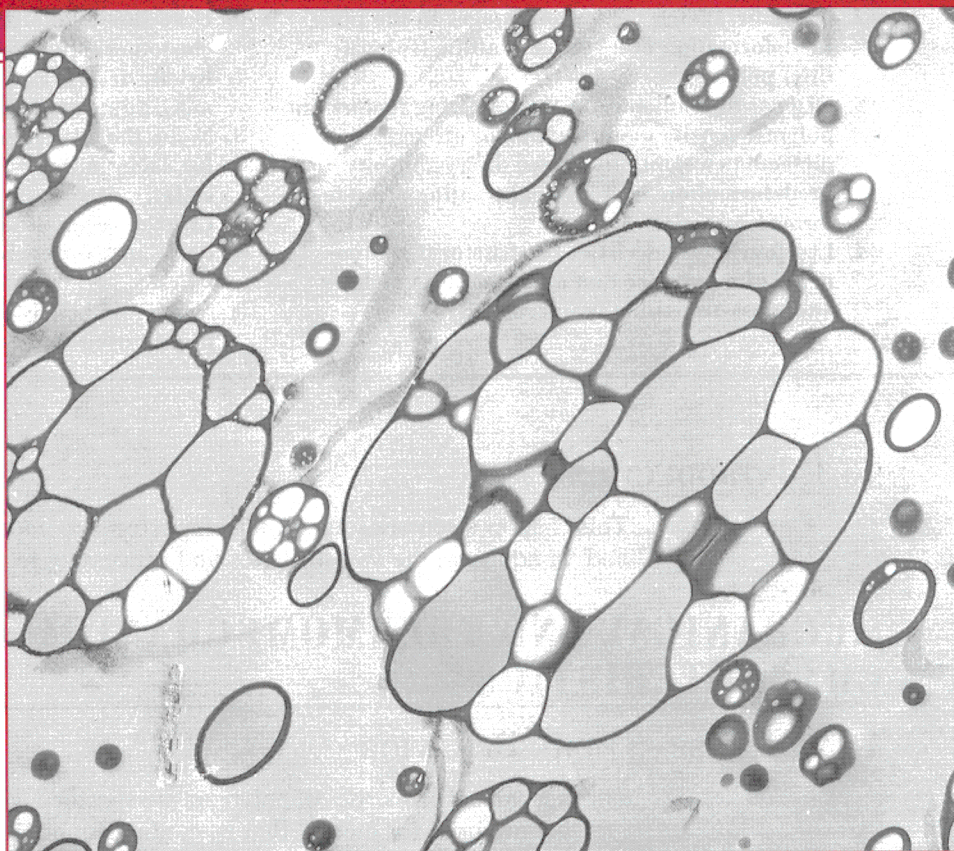


# Chapter 16 / Characteristics, Applications, and Processing of Polymers

**S**canning electron micrograph of a polystyrene that has been made more impact resistant by the addition of a rubber phase. The continuous matrix phase (gray) is polystyrene; the fine dispersed structure consists of particles of both polystyrene and rubber (white). 15,000 $\times$ . (From E. R. Wagner and L. M. Robeson, *Rubber Chemistry and Technology*, **43**, 1129, 1970. Reprinted with permission.)



## 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. Understanding the mechanisms by which polymers elastically and plastically deform allows one to alter and control their moduli of elasticity and strengths

(Sections 16.3 and 16.4). 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 16.12).

## 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 plastic deformation 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. List four characteristics or structural components of a polymer that affect both its melting and glass-transition temperatures.
5. Cite the differences in behavior and molecular structure for thermoplastic and thermosetting polymers.
6. Describe the molecular mechanism by which elastomeric polymers deform elastically.
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. Cite the seven different polymer application types and, for each, note its general characteristics.
10. Name and briefly describe five fabrication techniques used for plastic polymers.

## 16.1 INTRODUCTION

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

## MECHANICAL AND THERMOMECHANICAL CHARACTERISTICS

### 16.2 STRESS-STRAIN BEHAVIOR

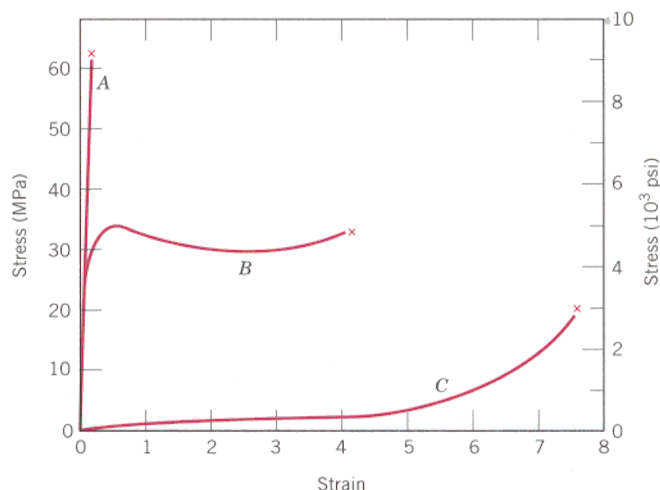
The mechanical properties of polymers are specified with many of the same parameters that are used for metals, that is, modulus of elasticity, and tensile, impact, and fatigue strengths. For many polymeric materials, the simple stress-strain test is employed for the characterization of some of these mechanical parameters.<sup>1</sup> 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.



Three typically different types of stress-strain behavior are found for polymeric materials, as represented in Figure 16.1. Curve *A* illustrates the stress-strain character for a brittle polymer, inasmuch as it fractures while deforming elastically. The behavior for the plastic material, curve *B*, is similar to that found 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 rubberlike 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

<sup>1</sup> ASTM Standard D 638, "Standard Test Method for Tensile Properties of Plastics."

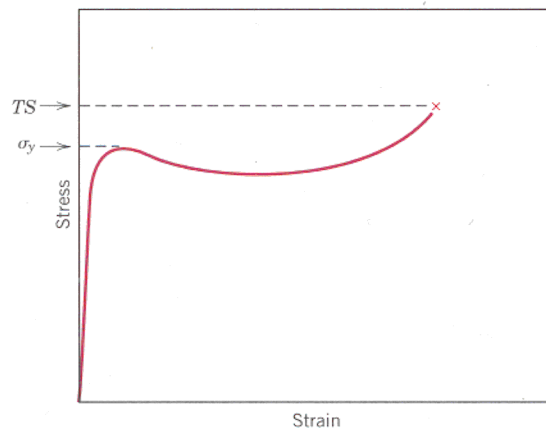


**FIGURE 16.1** The stress–strain behavior for brittle (curve A), plastic (curve B), and highly elastic (elastomeric) (curve C) polymers.

same manner as for metals (Section 6.6). For plastic polymers (curve B, Figure 16.1), the yield point is taken as a maximum on the curve, which occurs just beyond the termination of the linear-elastic region (Figure 16.2); the stress at this maximum is the yield strength ( $\sigma_y$ ). Furthermore, tensile strength (TS) corresponds to the stress at which fracture occurs (Figure 16.2); TS may be greater than or less than  $\sigma_y$ . Strength, for these plastic polymers, is normally taken as tensile strength. Table 16.1 gives these mechanical properties for several polymeric materials; more comprehensive lists are provided in Appendices B.2, B.3, and B.4.

Polymers are, in many respects, mechanically dissimilar to metals. 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 ( $0.6 \times 10^6$  psi) for some of the very stiff polymers; modulus values for metals are much larger and range between 48 and 410 GPa ( $7 \times 10^6$  to  $60 \times 10^6$  psi). Maximum tensile strengths for polymers are on the order of 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 as much as 1000%.

In addition, the mechanical characteristics of polymers are much more sensitive to temperature changes within the vicinity of room temperature. Consider the stress–strain behavior for polymethyl methacrylate (Plexiglas) at several tempera-



**FIGURE 16.2** Schematic stress–strain curve for a plastic polymer showing how yield and tensile strengths are determined.



**Table 16.1** Room-Temperature Mechanical Characteristics of Some of the More Common Polymers

<i>Material</i>	<i>Specific Gravity</i>	<i>Tensile Modulus</i> [GPa (ksi)]	<i>Tensile Strength</i> [MPa (ksi)]	<i>Yield Strength</i> [MPa (ksi)]	<i>Elongation at Break (%)</i>
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
Polyvinyl 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
Polymethyl 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

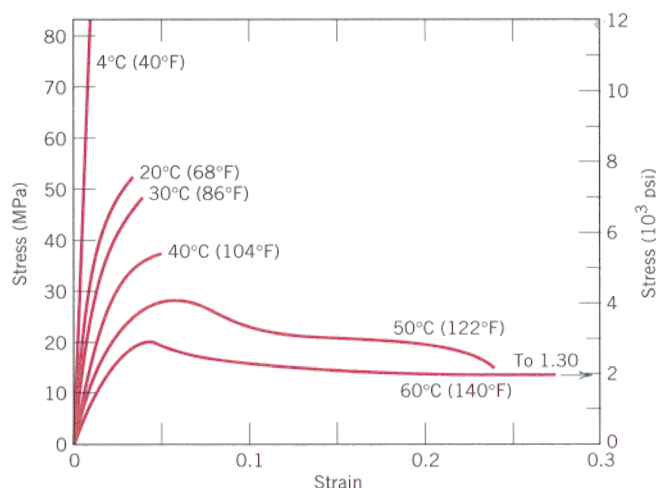
**Source:** *Modern Plastics Encyclopedia '96*. Copyright 1995, The McGraw-Hill Companies. Reprinted with permission.

tures between 4 and 60°C (40 and 140°F) (Figure 16.3). Several features of this figure are worth noting, as follows: 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, whereas considerable plastic deformation is realized at both 50 and 60°C (122 and 140°F).

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.

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 16.4. On the other hand, elastomers are utilized on the basis of their unusual elastic properties; the deformation mechanism of these polymers is treated in Section 16.8.





**FIGURE 16.3** The influence of temperature on the stress-strain characteristics of polymethyl 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.)

## 16.3 DEFORMATION OF SEMICRYSTALLINE POLYMERS

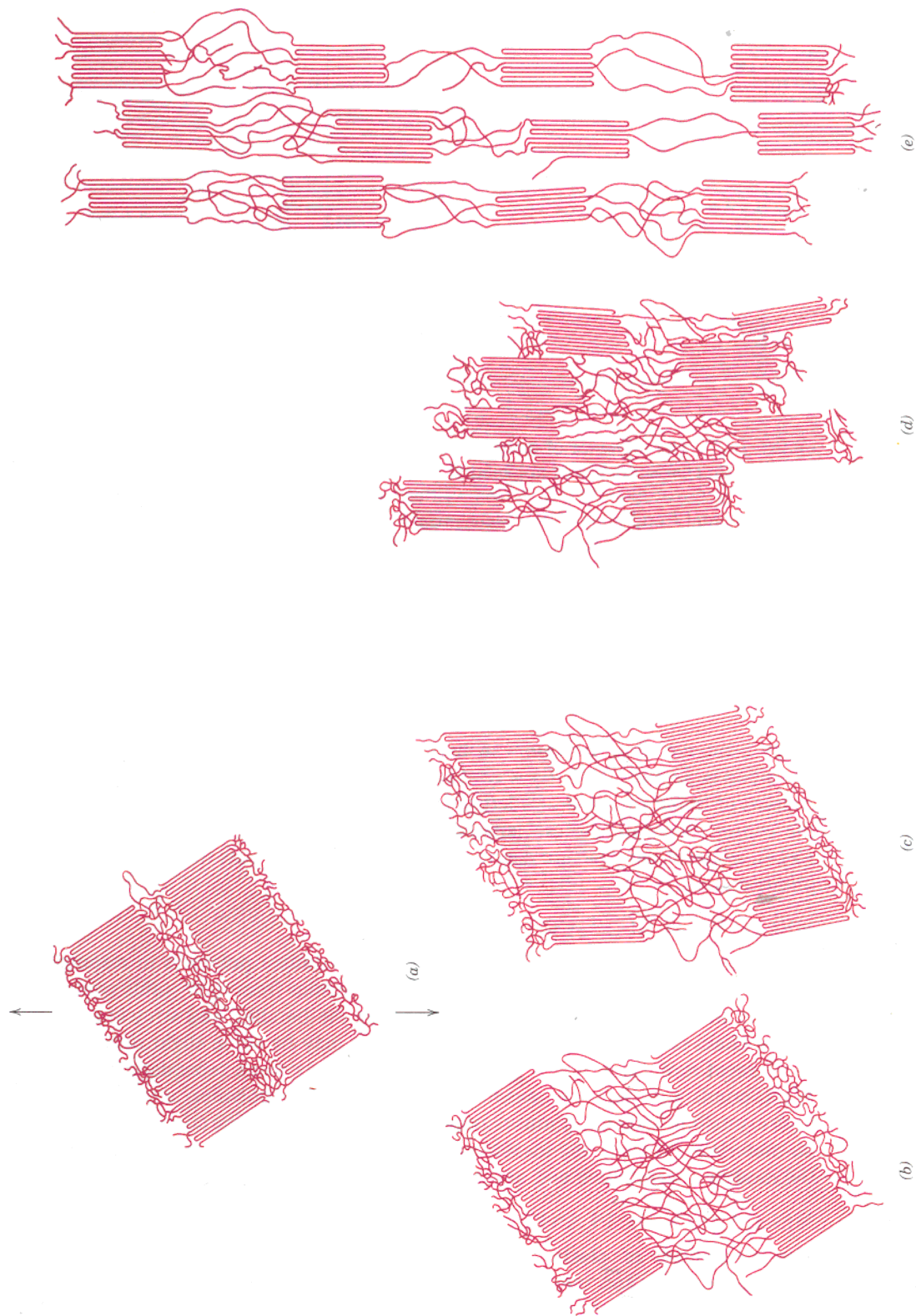
Many semicrystalline polymers in bulk form will have the spherulitic structure described in Section 15.11. By way of review, let us repeat here that each spherulite consists of numerous chain-folded ribbons, or lamellae, that radiate outward from the center. Separating these lamellae are areas of amorphous material (Figure 15.14); adjacent lamellae are connected by tie chains that pass through these amorphous regions.

### MECHANISM OF ELASTIC DEFORMATION

The mechanism of elastic deformation in semicrystalline polymers in response to tensile stresses is the elongation of the chain molecules from their stable conformations, in the direction of the applied stress, by the bending and stretching of the strong chain covalent bonds. In addition, there may be some slight displacement of adjacent molecules, which is resisted by relatively weak secondary or van der Waals bonds. Furthermore, 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 mechanism of plastic deformation is best described by the interactions between lamellar and intervening amorphous regions in response to an applied tensile load. This process occurs in several stages, which are schematically diagrammed in Figure 16.4. Two adjacent chain-folded lamellae and the interlamellar amorphous material, prior to deformation, are shown in Figure 16.4a. During



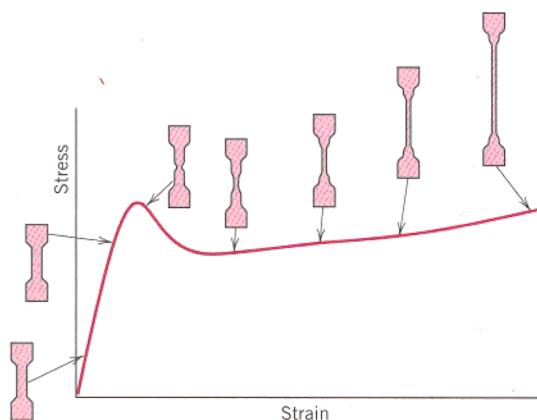
**FIGURE 16.4** Stages in the deformation of a semicrystalline polymer. (a) Two adjacent chain-folded lamellae and interlamellar amorphous material before deformation. (b) Elongation of amorphous tie chains during the first stage of deformation. (c) Tilting of lamellar chain folds during the second stage. (d) Separation of crystalline block segments during the third stage. (e) Orientation of block segments and tie chains with the tensile axis in the final deformation stage. (From Jerold M. Schultz, *Polymer Materials Science*, copyright © 1974, pp. 500–501. Reprinted by permission of Prentice-Hall, Inc., Englewood Cliffs, NJ.)

the initial stage of deformation (Figure 16.4*b*) the chains in the amorphous regions slip past each other and align in the loading direction. This causes the lamellar ribbons simply to slide past one another as the tie chains within the amorphous regions become extended. Continued deformation in the second stage occurs by the tilting of the lamellae so that the chain folds become aligned with the tensile axis (Figure 16.4*c*). Next, crystalline block segments separate from the lamellae, which segments remain attached to one another by tie chains (Figure 16.4*d*). In the final stage (Figure 16.4*e*), the blocks and tie chains become oriented in the direction of the tensile axis. Thus appreciable tensile deformation of semicrystalline polymers produces a highly oriented structure. During deformation the spherulites experience shape changes for moderate levels of elongation. However, for large deformations, the spherulitic structure is virtually destroyed. Also, it is interesting to note that, to a large degree, the processes represented in Figure 16.4 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., annealed), the material will revert back to having the spherulitic structure that was characteristic of its undeformed state. Furthermore, the specimen will tend to shrink back to the shape 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.



### MACROSCOPIC DEFORMATION

Some aspects of the macroscopic deformation of semicrystalline polymers deserve our attention. The tensile stress–strain curve for a semicrystalline material, which was initially unoriented, is shown in Figure 16.5; also included in the figure are schematic representations of specimen profile 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), 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 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.



**FIGURE 16.5** 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.)



## 16.4 FACTORS THAT INFLUENCE THE MECHANICAL PROPERTIES OF POLYMERS

A number of factors influence the mechanical characteristics of polymeric materials. For example, we have already discussed the effect of temperature and strain rate on stress-strain behavior (Section 16.2, Figure 16.3). 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 16.4; 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. 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

$$TS = TS_{\infty} - \frac{A}{M_n} \quad (16.1)$$

where  $TS_{\infty}$  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  $M_n$ .

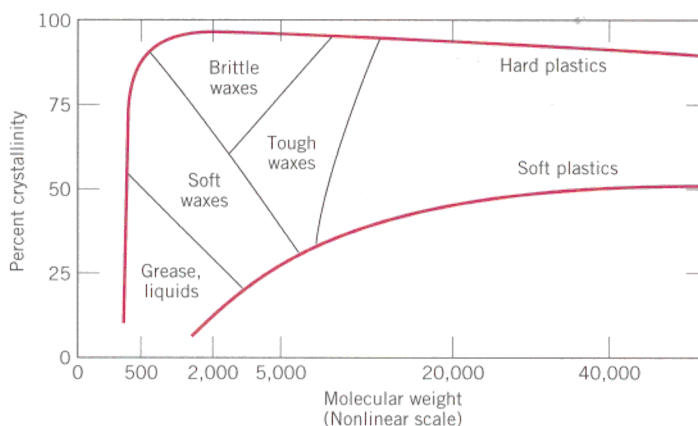
### DEGREE OF CRYSTALLINITY

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 15.

The effects of both percent crystallinity and molecular weight on the physical state of polyethylene are represented in Figure 16.6.

**FIGURE 16.6**  
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.)



### PREDEFORMATION BY DRAWING

On a commercial basis, one of the most important techniques used to improve mechanical strength and tensile modulus is permanently deforming the polymer in tension. This procedure is sometimes termed *drawing*, and corresponds to the neck extension process illustrated schematically in Figure 16.5. 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 16.4e.

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 of  $45^\circ$  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 leads to modifications in crystallite size and perfection, as well as 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. It should be noted 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—i.e., modulus decreases with increased annealing temperature due to a loss of chain orientation and strain-induced crystallinity.

## 16.5 CRYSTALLIZATION, MELTING, AND GLASS TRANSITION PHENOMENA

Inasmuch as the mechanical properties of polymers are highly sensitive to temperature changes, the several succeeding sections are devoted to discussions of thermal and thermomechanical characteristics of these materials. We begin with treatments of crystallization, melting, and glass-transition phenomena. 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 which, when cooled from a liquid melt, become rigid solids yet retain the disordered molecular structure that is characteristic of the liquid state; consequently, they may be considered frozen liquids (or amorphous solids). 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.

### CRYSTALLIZATION

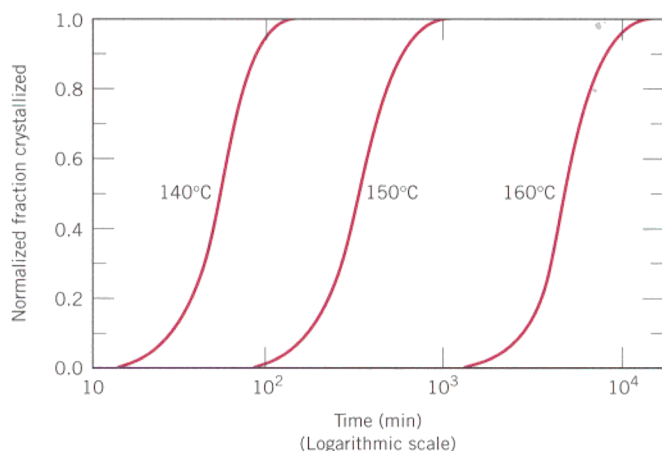
An understanding of the mechanism and kinetics of polymer crystallization is important inasmuch as the degree of crystallinity influences the mechanical and thermal properties of these materials. The crystallization of a molten polymer occurs by nucleation and growth processes, topics discussed in the 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 15.13. 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 increase in lateral dimensions, or, for spherulitic structures (Figure 15.14) there is an increase in spherulite radius.

The time dependence of crystallization is the same as for many solid-state transformations—Figure 10.1; 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 16.7 for the crystallization of polypropylene at three temperatures. Mathematically, fraction crystallized  $y$  is a function of time  $t$  according to the Avrami equation, Equation 10.1, as

$$y = 1 - \exp(-kt^n) \quad (10.1)$$

where  $k$  and  $n$  are time-independent constants, which 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





**FIGURE 16.7** 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.)

phases. Rate of crystallization may be specified in the same manner as for the transformations discussed in Section 10.3, and according to Equation 10.2; 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 16.7) and also on the molecular weight of the polymer; rate decreases with increasing molecular weight.

For polypropylene, the attainment of 100% crystallinity is not possible. Therefore, in Figure 16.7, 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.

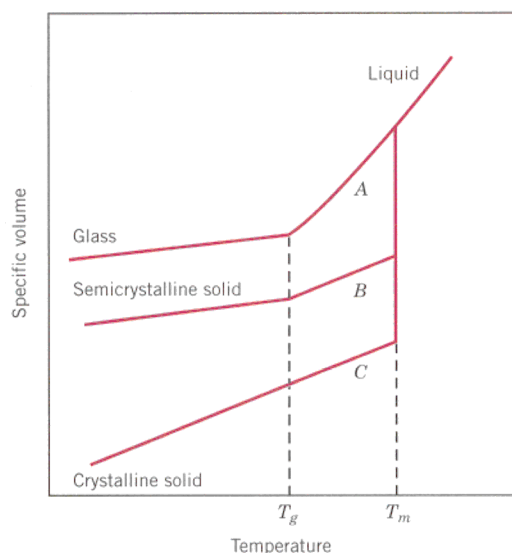
## MELTING

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. And 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 the 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 of the polymer.

## 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.



**FIGURE 16.8** Specific volume versus temperature, upon cooling from the liquid melt, for totally amorphous (curve A), semicrystalline (curve B), and crystalline (curve C) polymers.

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: e.g., stiffness (Figure 16.12), heat capacity, and coefficient of thermal expansion.

## 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 16.8 is such a plot, wherein curves A and C, for amorphous and crystalline polymers, respectively, have the same configurations as their ceramic counterparts (Figure 14.3).<sup>2</sup> 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 it 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 semicrystalline material. As discussed above, the behaviors represented in Figure 16.8 will depend on the rate of cooling or heating. Representative

<sup>2</sup> It should be noted that no engineering polymer is 100% crystalline; curve C is included in Figure 16.8 to illustrate the extreme behavior that would be displayed by a totally crystalline material.

**Table 16.2** Melting and Glass Transition Temperatures for Some of the More Common Polymeric Materials

<i>Material</i>	<i>Glass Transition Temperature [°C (°F)]</i>	<i>Melting Temperature [°C (°F)]</i>
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)
Polyvinyl chloride	87 (190)	212 (415)
Polystyrene	100 (212)	240 (465)
Polycarbonate	150 (300)	265 (510)

melting and glass transition temperatures of a number of polymers are contained in Table 16.2 and Appendix E.

## FACTORS THAT INFLUENCE MELTING AND GLASS TRANSITION TEMPERATURES

### *Melting Temperature*

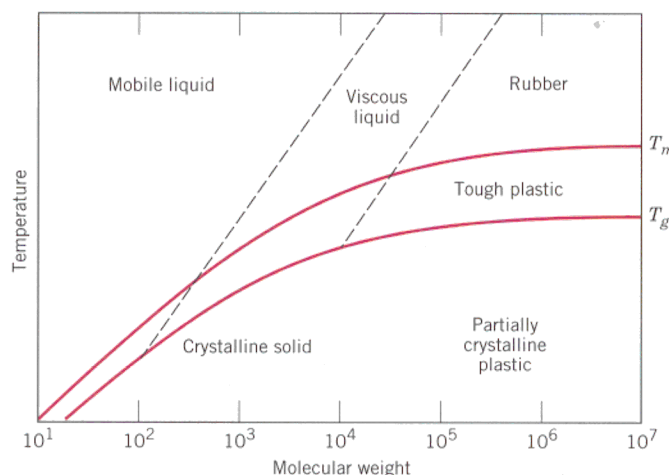
During melting of a polymer there will necessarily occur a rearrangement of the molecules in the transformation from ordered to disordered molecular states. Molecular chemistry and structure will influence the ability of the polymer chain molecules to make these rearrangements, and, therefore, will also 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-chain bonds and aromatic groups 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 16.2); the CH<sub>3</sub> methyl side group for polypropylene is larger than the H atom found on polyethylene. The presence of polar side groups (viz. Cl, OH, and CN), even though not excessively large, leads to significant intermolecular bonding forces and relatively high  $T_m$ s. This may be verified by comparing the melting temperatures of polypropylene (175°C) and polyvinyl chloride (212°C).

For a specific polymer, melting temperature will also depend on molecular weight. At relatively low molecular weights, increasing  $\bar{M}$  (or chain length) raises  $T_m$  (Figure 16.9). Furthermore, the melting of a polymer takes place over a range of temperatures, and, thus, there will exist a range of  $T_m$ s, rather than a single melting temperature. This is because, every polymer will be composed of molecules having a variety of molecular weights (Section 15.5), 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 16.2 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 16.9**  
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 16.2) 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 which 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 following:

1. The presence of bulky side groups; from Table 16.2, the respective values for polypropylene and polystyrene are  $-18^\circ\text{C}$  and  $100^\circ\text{C}$ .
2. Polar side atoms or groups of atoms; this may be confirmed by comparing  $T_g$  values for polyvinyl chloride and polypropylene ( $87^\circ\text{C}$  versus  $-18^\circ\text{C}$ ).
3. Double-chain bonds and aromatic chain groups which tend to stiffen the molecular backbone.

Increasing the molecular weight also tends to raise the glass transition temperature, as noted in Figure 16.9. 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.

## 16.6 THERMOPLASTIC AND THERMOSETTING POLYMERS

One classification scheme of polymeric materials is according to the mechanical response at elevated temperatures. *Thermoplasts* (or **thermoplastic polymers**) and *thermosets* (or **thermosetting polymers**) are the two subdivisions. Thermoplasts soften when heated (and eventually liquefy) and harden when cooled—processes that are totally reversible and may be repeated. These materials are normally fabricated by the simultaneous application of heat and pressure. On a molecular level, as the temperature is raised, secondary bonding forces are diminished (by increased molecular motion) so that the relative movement of adjacent chains is facilitated when a stress is applied. Irreversible degradation results when the temperature of a molten thermoplastic polymer is raised to the point at which molecular vibrations become violent enough to break the primary covalent bonds. In addition, thermoplasts are relatively soft and ductile. Most linear polymers and those having some branched structures with flexible chains are thermoplastic.

Thermosetting polymers become permanently hard when heat is applied and do not soften upon subsequent heating. During the initial heat treatment, covalent crosslinks are formed between adjacent molecular chains; these bonds anchor the chains together to resist the vibrational and rotational chain motions at high temperatures. Crosslinking is usually extensive, in that 10 to 50% of the chain mer units are crosslinked. Only heating to excessive temperatures will cause severance of these crosslink bonds and polymer degradation. Thermoset polymers are generally harder, stronger, and more brittle than thermoplastics, and have better dimensional stability. Most of the crosslinked and network polymers, which include vulcanized rubbers, epoxies, and phenolic and some polyester resins, are thermosetting.

## 16.7 VISCOELASTICITY

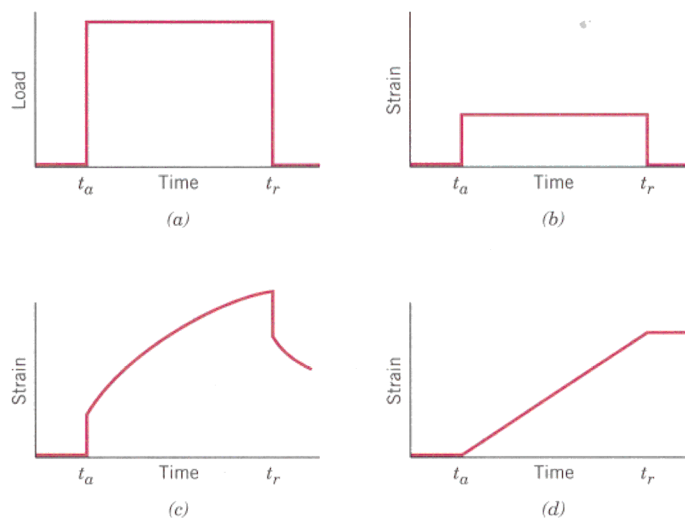
We know that an amorphous polymer may behave like a glass at low temperatures, a rubbery solid at intermediate temperatures (above the glass transition temperature), and a viscous liquid as the temperature is further raised. For relatively small deformations, the mechanical behavior at low temperatures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

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 16.10*b* as strain versus time for the instantaneous load–time curve, shown in Figure 16.10*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 16.10*d*.

For the intermediate viscoelastic behavior, the imposition of a stress in the manner of Figure 16.10*a* results in an instantaneous elastic strain, which is followed

**FIGURE 16.10** (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) behavior.



by a viscous, time-dependent strain, a form of anelasticity (Section 6.4); this behavior is illustrated in Figure 16.10c.

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

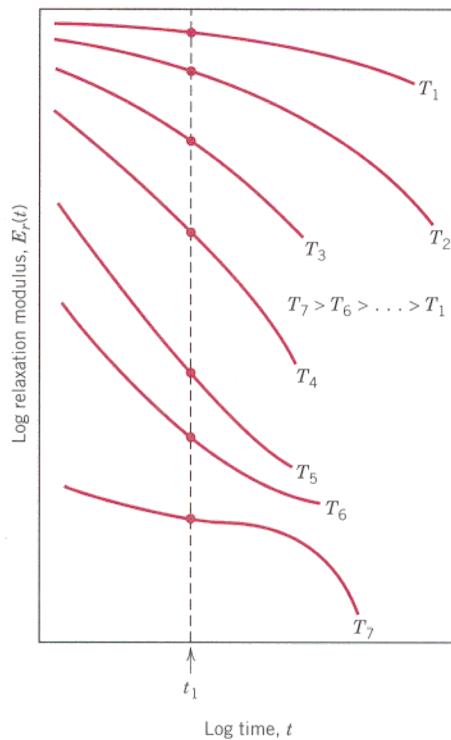
The viscoelastic behavior of polymeric materials is dependent on both time and temperature; several experimental techniques may be used to measure and quantify this behavior. *Stress relaxation* measurements represent one possibility. With these tests, a specimen is initially strained rapidly in tension 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

$$E_r(t) = \frac{\sigma(t)}{\epsilon_0} \quad (16.2)$$

where  $\sigma(t)$  is the measured time-dependent stress and  $\epsilon_0$  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 16.11 is a schematic log  $E_r(t)$ -versus-log time plot for a polymer that exhibits viscoelastic behavior; included are several curves generated at a variety of temperatures. Worth noting from this figure are (1) the decrease of  $E_r(t)$  with time (corre-





**FIGURE 16.11** 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.

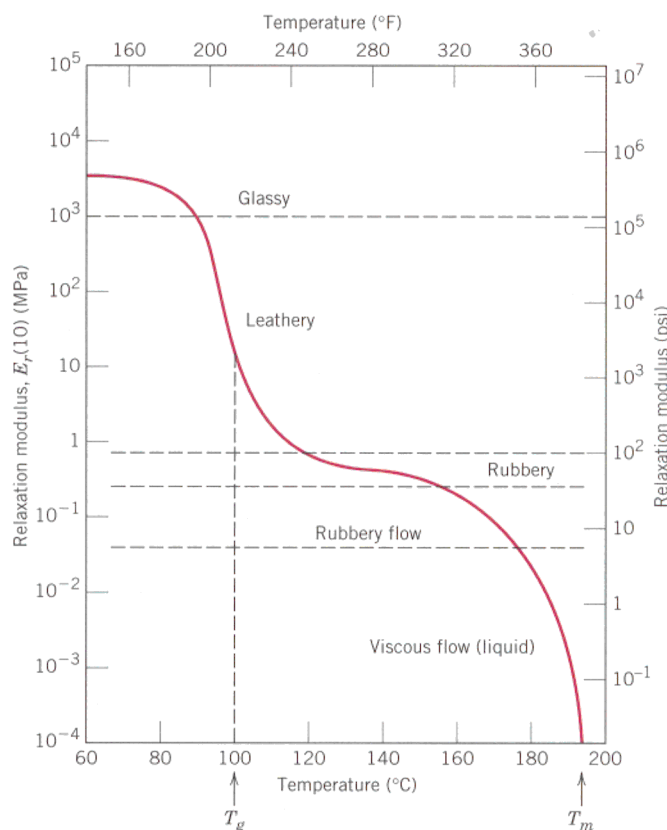
sponding to the decay of stress, Equation 16.2), and (2) the displacement of the curves to lower  $E_r(t)$  levels with increasing temperature.

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 16.11—and then cross-plotted as  $\log E_r(t_1)$  versus temperature. Figure 16.12 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. For the first, 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 16.10b. 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  $20^\circ\text{C}$  ( $35^\circ\text{F}$ ) temperature span; this is sometimes called the leathery, or glass transition, region, and  $T_g$  lies near the upper temperature extremity; for polystyrene (Figure 16.12),  $T_g = 100^\circ\text{C}$  ( $212^\circ\text{F}$ ). 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 depicted in Figure 16.10c.

Within the rubbery plateau temperature region (Figure 16.12), 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. Within the viscous flow region,



**FIGURE 16.12** 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.)

the modulus decreases dramatically with increasing temperature; and, again, the strain-time behavior is as represented in Figure 16.10d. From a molecular standpoint, chain motion intensifies so greatly that for viscous flow, the chain segments experience vibration and rotational motion quite independently of one another. At these temperatures, any deformation is entirely viscous.

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 13.9.

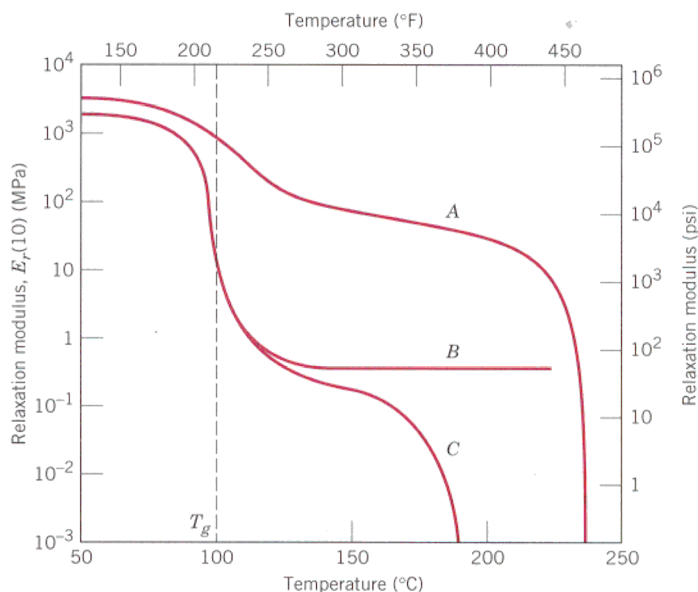
The rate of stress application also influences the viscoelastic characteristics. Increasing the loading rate has the same influence as lowering temperature.

The log  $E_r(10)$ -versus-temperature behavior for polystyrene materials having several molecular configurations is plotted in Figure 16.13. The curve for the amorphous material (curve C) is the same as in Figure 16.12. 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 also increase. Rubber or elastomeric materials display this type of behavior and are ordinarily utilized at temperatures within this plateau range.

Also shown in Figure 16.13 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

**FIGURE 16.13**

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.)



temperature until its melting temperature  $T_m$  is approached. From Figure 16.13, 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

$$E_c(t) = \frac{\sigma_0}{\epsilon(t)} \quad (16.3)$$

wherein  $\sigma_0$  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.

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.

## 16.8 DEFORMATION OF ELASTOMERS

One of the fascinating properties of the elastomeric materials is their rubberlike elasticity. That is, they have the ability to be deformed to quite large deformations, and then elastically spring back to their original form. This behavior was probably

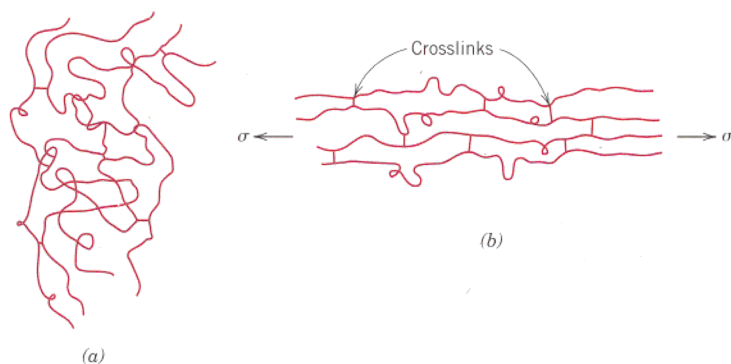


first observed in natural rubber; however, the past few years have brought about the synthesis of a large number of elastomers with a wide variety of properties. Typical stress-strain characteristics of elastomeric materials are displayed in Figure 16.1, curve C. Their moduli of elasticity are quite 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 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 16.14. Upon release of the stress, the chains spring back to their prestressed conformations, and the macroscopic piece returns to its original shape.

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 in order 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 in order 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 16.14. Crosslinking in many elastomers is carried out in a process called vulcanization, to be discussed in Section 16.15. (4) Finally, the elastomer must be above its glass transition temperature. The lowest temperature at which rubberlike behavior persists is  $T_g$  (Figure 16.12), which for many of the common elastomers is between



**FIGURE 16.14** 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.)

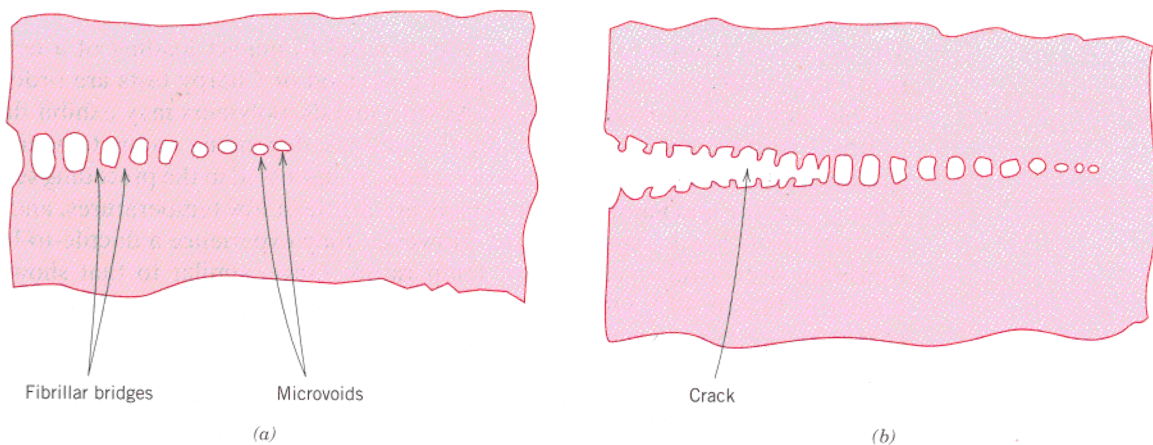
$-50$  and  $-90^{\circ}\text{C}$  ( $-60$  and  $-130^{\circ}\text{F}$ ). Below its glass transition temperature, an elastomer becomes brittle such that its stress-strain behavior resembles curve A in Figure 16.1.

## 16.9 FRACTURE OF POLYMERS

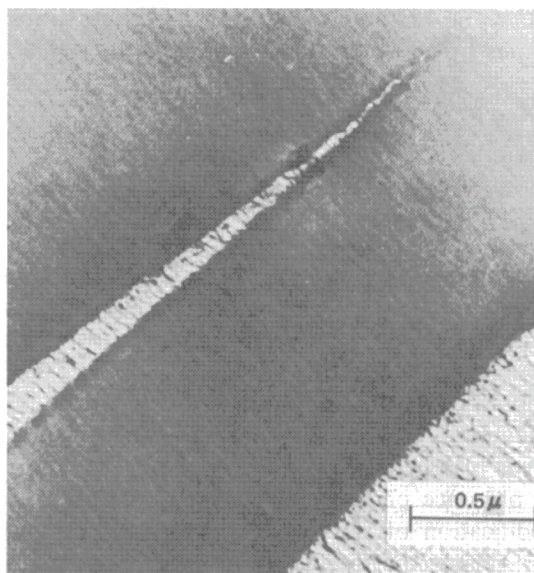
The fracture strengths of polymeric materials are low relative to those of metals and ceramics. As a general rule, the mode of fracture in thermosetting polymers is brittle. In simple terms, associated with the fracture process is the formation of cracks at regions where there is a localized stress concentration (i.e., scratches, notches, and sharp flaws). 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, in addition, a modification of the polymer structure (chemical, molecular, and/or microstructural). Glassy thermoplastics are brittle at relatively low temperatures; as the temperature is raised, they become ductile in the vicinity of their glass transition temperatures and experience plastic yielding prior to fracture. This behavior is demonstrated by the stress-strain characteristics of polymethyl methacrylate in Figure 16.3. At  $4^{\circ}\text{C}$ , PMMA is totally brittle, whereas at  $60^{\circ}\text{C}$  it becomes extremely ductile.

One phenomenon that frequently precedes fracture in some glassy thermoplastic polymers is *crazing*. Associated with crazes are regions of very localized yielding, which lead to the formation of small and interconnected microvoids (Figure 16.15a). Fibrillar bridges form between these microvoids wherein molecular chains become oriented. 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 16.15b. 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 frac-



**FIGURE 16.15** 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 16.16** Photomicrograph of a craze in polyphenylene 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.)

ture toughness of the polymer. 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  $5\text{ }\mu\text{m}$  or less thick. Figure 16.16 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 Appendix B.5.

## 16.10 MISCELLANEOUS CHARACTERISTICS

### IMPACT STRENGTH

The degree of resistance of a polymeric material to impact loading of a notched piece may be of concern in some applications. Izod or Charpy tests are ordinarily conducted to assess impact strength. 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 crystalline 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 a steel in Figure 8.17. 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



## POLYMER APPLICATIONS 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; specific forming procedures are discussed according to polymer type.

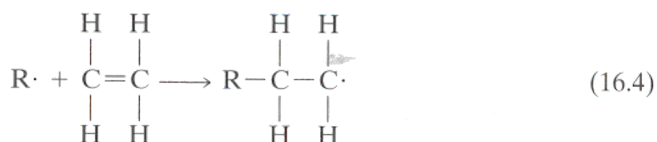
### 16.11 POLYMERIZATION

The synthesis of the large molecular weight polymers is termed *polymerization*; it is simply the process by which monomer units are joined over and over, to generate each of the constituent giant molecules. Most generally, the raw materials for synthetic polymers are derived from coal and petroleum products, which are composed of molecules having low molecular weights. The reactions by which polymerization occurs are grouped into two general classifications—addition and condensation—according to the reaction mechanism, as discussed below.

#### ADDITION POLYMERIZATION

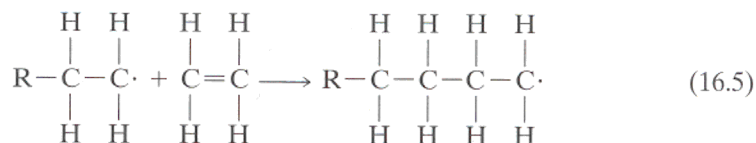
**Addition polymerization** (sometimes called *chain reaction polymerization*) is a process by which bifunctional monomer units are attached one at a time in chainlike fashion to form a linear macromolecule; the composition of the resultant product molecule is an exact multiple for that of the original 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 15.1), which is repeated as follows:



Again,  $\text{R}\cdot$  represents the active initiator, and  $\cdot$  is an unpaired electron.

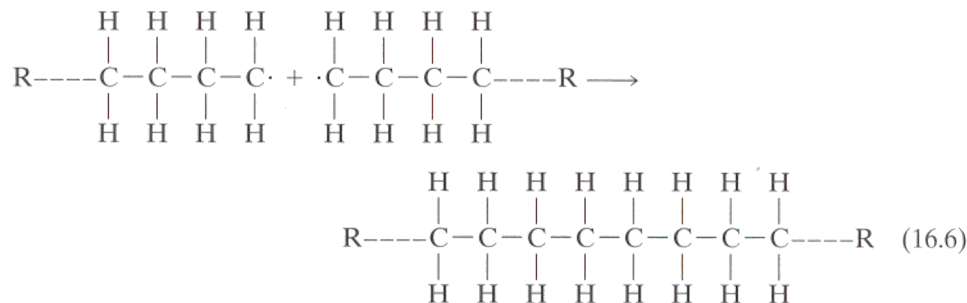
Propagation involves the linear growth of the molecule as monomer units become attached to one another in succession to produce the chain molecule, which is represented, again for polyethylene, as follows:



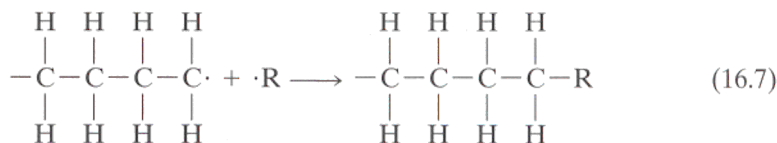
Chain growth is relatively rapid; the period required to grow a molecule consisting of, say, 1000 mer units is on the order of  $10^{-2}$  to  $10^{-3}$  s.

Propagation may end or terminate in different ways. First, the active ends of two propagating chains may react or link together to form a nonreactive molecule,

as follows:



thus terminating the growth of each chain. Or, an active chain end may react with an initiator or other chemical species having a single active bond, as follows:



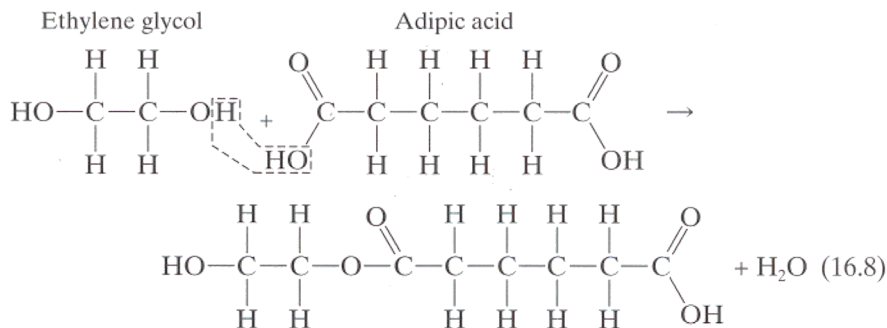
with the resultant cessation of chain growth.

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, polyvinyl chloride, and polystyrene, as well as many of the copolymers.

## CONDENSATION POLYMERIZATION

**Condensation** (or *step reaction*) **polymerization** is the formation of polymers by stepwise intermolecular chemical reactions that normally involve more than one monomer species; there is usually a small molecular weight by-product such as water, which is eliminated. No reactant species has the chemical formula of the mer repeat unit, and the intermolecular reaction occurs every time a mer repeat unit is formed. For example, consider the formation of a polyester from the reaction between ethylene glycol and adipic acid; the intermolecular reaction is as follows:



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

Condensation reactions often produce trifunctional 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.

## 16.12 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** 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. Because these inexpensive materials replace some volume of the more expensive polymer, the cost of the final product is reduced.

### PLASTICIZERS

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 polyvinyl chloride and some of the acetate copolymers. In effect, 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.

### STABILIZERS

Some polymeric materials, under normal environmental conditions, are subject to rapid deterioration, generally in terms of mechanical integrity. Most often, this deterioration is a result of exposure to light, in particular ultraviolet radiation, and also oxidation (Section 18.12). Ultraviolet radiation interacts with, and causes a severance of some of the covalent bonds along the molecular chain, which may also result in some crosslinking. Oxidation deterioration is a consequence of the chemical interaction between oxygen atoms and the polymer molecules. Additives that counteract these deteriorative processes are called **stabilizers**.

### COLORANTS

**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 and become part of the



molecular structure of the polymer. Pigments are filler materials that do not dissolve, but remain as a separate phase; normally they have a small particle size, are transparent, and have 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 polyvinyl chloride and polytetrafluoroethylene. The flammability 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 chemical reaction that causes a cooling of the combustion region and a cessation of burning.

## 16.13 POLYMER TYPES

There are many different polymeric materials that are familiar to us and find a wide variety of applications. These 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. In addition, for each, some of the common fabrication methods are noted.

## 16.14 PLASTICS

### CHARACTERISTICS AND APPLICATIONS

Possibly the largest number of different polymeric materials come under the plastic classification. Polyethylene, polypropylene, polyvinyl 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; others are flexible, exhibiting both elastic and plastic deformations when stressed, and sometimes experiencing considerable deformation before fracture.

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. The trade names, characteristics, and typical applications for a number of plastics are given in Table 16.3.

Several plastics exhibit especially outstanding properties. For applications in which optical transparency is critical, polystyrene and polymethyl 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 16.3** Trade Names, Characteristics, and Typical Applications for a Number of Plastic Materials

<i>Material Type</i>	<i>Trade Names</i>	<i>Major Application Characteristics</i>	<i>Typical Applications</i>
<b>Thermoplastics</b>			
Acrylonitrile-butadiene-styrene (ABS)	Abson Cyclocac 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 Halon Hostaflon TF	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 Durethan Heriox 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	Baylon Iupilon Lexan Makrolon Merlon Nuclon	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 Ethron Fortiflex Hi-fax Petrothene Rigidex 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
Polypropylene	Bexphane Herculon Meraklon Moplen Poly-pro Pro-fax 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 Celatron Hostyren Lustrex Styron Vestylon	Excellent electrical properties and optical clarity; good thermal and dimensional stability; relatively inexpensive	Wall tile, battery cases, toys, indoor lighting panels, appliance housings

**Table 16.3** (Continued)

<i>Material Type</i>	<i>Trade Names</i>	<i>Major Application Characteristics</i>	<i>Typical Applications</i>
Vinyls	Darvic Exon Geon Pee Vee Cee Pliovic Saran Tygon	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 Crastin Dacron Hylar Melinex Mylar Terylen	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
<b>Thermosetting Polymers</b>			
Epoxies	Araldite Epikote Epon Epi-rez Lekutherm Nepoxide	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 Aroclene 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 Laguval 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.

## FORMING TECHNIQUES

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.

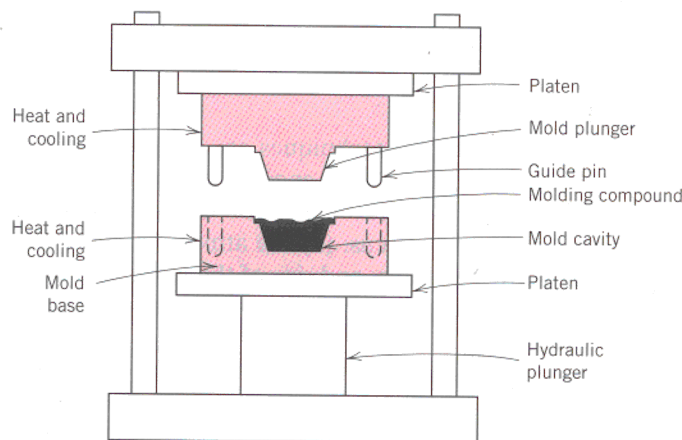
Fabrication of thermosetting polymers is ordinarily accomplished in two stages. First comes the preparation of a linear polymer (sometimes called a prepolymer) as a liquid, having a low molecular weight. This material is converted into the final hard and stiff product during the second stage, which is 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 more chemically inert.

**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 granulated 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 16.18. Both mold pieces are heated; however, only one is movable. The mold is closed, and heat and pressure are applied, causing the plastic material to become viscous and 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.

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 mold chamber, the pressure is distributed more uniformly over all surfaces.



**FIGURE 16.18**

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.

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This process is used with thermosetting polymers and for pieces having complex geometries.

### Injection Molding

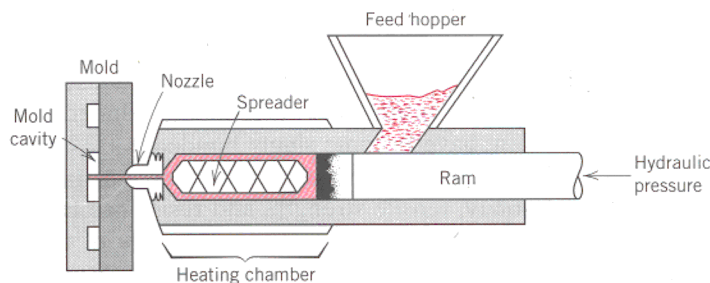
Injection molding, the polymer analogue of die casting for metals, is the most widely used technique for fabricating thermoplastic materials. A schematic cross section of the apparatus used is illustrated in Figure 16.19. The correct amount of pelletized material is fed from a loading hopper into a cylinder by the motion of a plunger or ram. This charge is pushed forward into a heating chamber, at which point 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).

### Extrusion

The extrusion process is simply injection molding of a viscous thermoplastic through an open-ended die, similar to the extrusion of metals (Figure 12.2c). A mechanical screw or auger propels through a chamber the pelletized material, which is successively compacted, melted, and formed into a continuous charge of viscous fluid. Extrusion takes place as this molten mass is forced through a die orifice. Solidification of the extruded length is expedited by blowers or a water spray just before passing onto a moving conveyor. 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 14.5. First, a parison, or



**FIGURE 16.19** 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.)

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

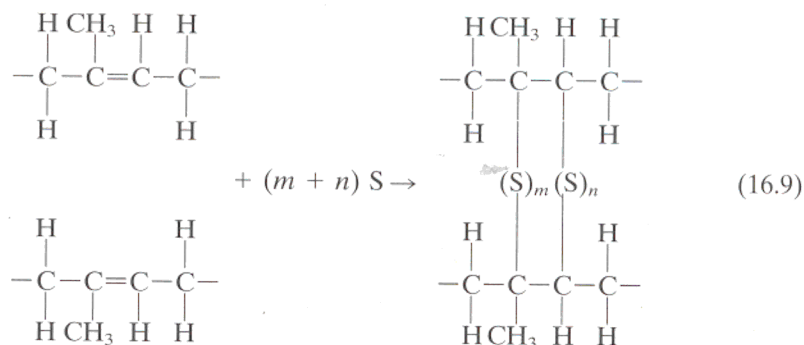
Like metals and ceramics, polymeric materials may be cast, as when a molten plastic material is poured into a mold and allowed to solidify. Both thermoplastic and thermosetting plastics may be cast. For thermoplastics, solidification occurs upon cooling from the molten state; however, for thermosets,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

## 16.15 ELASTOMERS

The characteristics of and deformation mechanism for elastomers were treated previously (Section 16.8). The present discussion, therefore, focuses on the processing and types of elastomeric materials.

### VULCANIZATION

One requisite characteristic for elastomeric behavior is that the molecular structure be lightly crosslinked. 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:

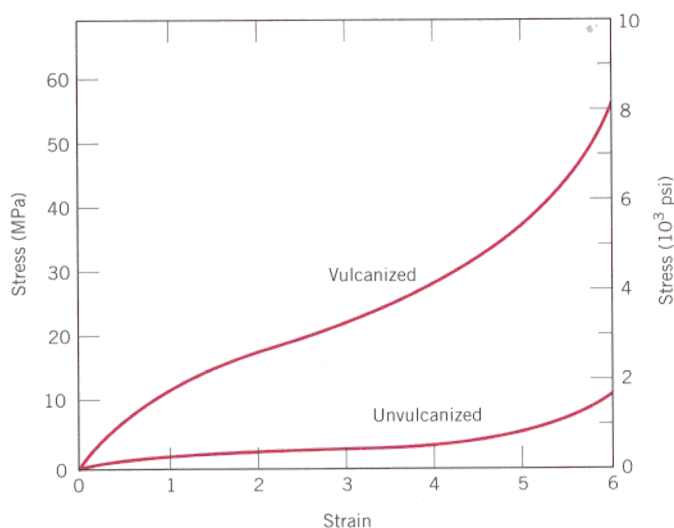


in which the two crosslinks shown consist of  $m$  and  $n$  sulfur atoms. Crosslink main chain sites are carbon atoms that were doubly bonded before vulcanization, but, after vulcanization, have become singly bonded.

Unvulcanized rubber 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 crosslinks. Stress-strain curves for vulcanized and unvulcanized natural rubber are presented in Figure 16.20. 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 is added to 100 parts of rubber. Increasing the sulfur content further hardens the rubber and also







**FIGURE 16.20**  
Stress-strain curves to 600% elongation for unvulcanized and vulcanized natural rubber.

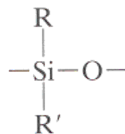
reduces its extensibility. Also, since they are crosslinked, elastomeric materials are thermosetting in nature.

### ELASTOMERIC TYPES

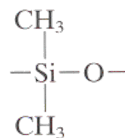
Table 16.4 lists properties and applications of common elastomers; these properties are typical and, of course, depend on the degree of vulcanization and on whether any reinforcement is used. Natural rubber is still utilized to a large degree because it has an outstanding combination of desirable properties. 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.

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 17.2). Furthermore, the 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.

Finally, some mention should be made of the silicone rubbers. For these materials, the backbone carbon chain is replaced by a chain that alternates silicon and oxygen atoms:



where R and R' represent side-bonded atoms such as hydrogen or groups of atoms such as CH<sub>3</sub>. For example, polydimethylsiloxane has the mer structure



Of course, as elastomers, these materials are crosslinked.

**Table 16.4** Tabulation of Important Characteristics and Typical Applications for Five Commercial Elastomers

<i>Chemical Type</i>	<i>Trade (Common) Name</i>	<i>Elongation (%)</i>	<i>Useful Temperature Range [°C (°F)]</i>	<i>Major Application Characteristics</i>	<i>Typical Applications</i>
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.

The silicone elastomers possess a high degree of flexibility at low temperatures [to  $-90^{\circ}\text{C}$  ( $-130^{\circ}\text{F}$ )] and yet are stable to temperatures as high as  $250^{\circ}\text{C}$  ( $480^{\circ}\text{F}$ ). In addition, they are resistant to weathering and lubricating oils. A further attractive characteristic is that some silicone rubbers vulcanize at room temperature (RTV rubbers).

## 16.16 FIBERS

### CHARACTERISTICS AND APPLICATIONS

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 17.8. 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. Also, since 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 regularly repeating mer units.

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.

### FORMING TECHNIQUES

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 down through a plate called a spinnerette, which contains numerous small, round holes. As the molten material passes through each of these orifices, a single fiber is formed, which solidifies almost immediately upon passing into the air.

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 16.4. Again, drawing is simply the 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 16.4e), such that the tensile strength, modulus of elasticity, and toughness are improved. Although the mechanical strength of a drawn fiber is improved in this axial direction, strength is reduced in a transverse or radial direction. However, since fibers are normally stressed only along the axis, this strength differential is not critical. The cross section of drawn fibers is nearly circular, and the properties are uniform throughout the cross section.

## 16.17 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.

### ADHESIVES

An **adhesive** is a substance used to join together the surfaces of two solid materials (termed “adherends”) to produce a joint with a high shear strength. The bonding forces between the adhesive and adherend surfaces are thought to be electrostatic, similar to the secondary bonding forces between the molecular chains in thermoplastic polymers. Even though the inherent strength of the adhesive may be much less than that of the adherend materials, nevertheless, a strong joint may be produced



if the adhesive layer is thin and continuous. If a good joint is formed, the adherend material may fracture or rupture before the adhesive.

Polymeric materials that fall within the classifications of thermoplastics, thermosetting resins, elastomeric compounds, and natural adhesives (animal glue, casein, starch, and rosin) may serve adhesive functions. Polymer adhesives may be used to join a large variety of material combinations: metal-metal, metal-plastic, metal-ceramic, and so on. The primary drawback is the service temperature limitation. Organic polymers maintain their mechanical integrity only at relatively low temperatures, and strength decreases rapidly with increasing temperature.

## FILMS

Within relatively recent times, 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. Some of the polymers that meet these criteria and are manufactured in film form are polyethylene, polypropylene, cellophane, and cellulose acetate.

There are several forming methods. Many films are simply extruded through a thin die slit; this may be followed by a rolling 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, wall thickness may be continuously reduced to produce a thin cylindrical film, which may be cut and laid flat. Some of the newer films are produced by coextrusion; that is, multilayers of more than one polymer type are extruded simultaneously.

## FOAMS

Very porous plastic materials are produced in a process called foaming. Both thermoplastic and thermosetting materials may be foamed by including in the batch a blowing agent that upon heating, decomposes with the liberation of a gas. Gas bubbles are generated throughout the now-fluid mass, which remain as pores upon cooling and give rise to a spongelike structure. The same effect is produced by bubbling an inert gas through a material while it is in a molten state. Some of the commonly foamed polymers are polyurethane, rubber, polystyrene, and polyvinyl chloride. **Foams** are commonly used as cushions in automobiles and furniture as well as in packaging and thermal insulation.

## 16.18 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)** is a linear polyethylene that has an extremely high molecular weight. Its typical  $\bar{M}_w$  is approximately  $4 \times 10^6$

g/mol, which is an order of magnitude (i.e., factor of ten) greater than that of high-density polyethylene. In fiber form, UHMWPE has the tradename Spectra. 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.

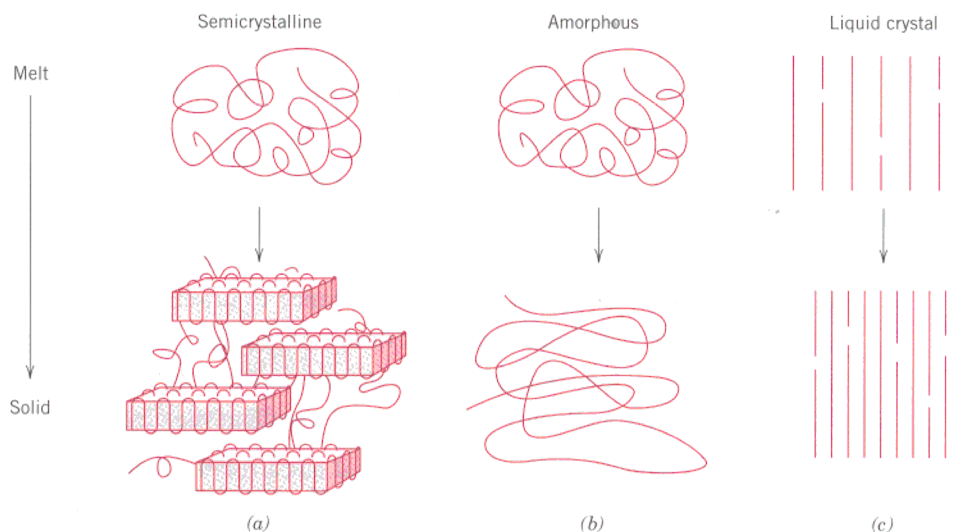
However, since this material has a relatively low melting temperature, its mechanical properties diminish rapidly with increasing temperature.

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 23.8), blood filters, marking pen nibs, bulk material handling equipment (for coal, grain, cement, gravel, etc.), bushings, pump impellers, and valve gaskets.

## LIQUID CRYSTAL POLYMERS

The **liquid crystal polymers (LCPs)** 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, 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 16.21. 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 (LCDs)*, on digital watches, laptop computers, and for 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 electrically conductive film; in addition, into this film on the side that is to be viewed are etched the character-forming number/letter elements. 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.



**FIGURE 16.21** 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.)

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 ( $1.4 \times 10^6$  and  $3.5 \times 10^6$  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 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

The **thermoplastic elastomers** (TPEs or TEs) are a type of polymeric material that, at ambient conditions, exhibits elastomeric (or rubbery) behavior, yet is thermoplastic in nature (Section 16.6). By way of contrast, most elastomers heretofore discussed are thermosets, since they become 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 mer (commonly styrene [S]), and a soft and flexible elastic mer (often butadiene [B] or isoprene [I]). These two block types alternate positions—for a common molecule, hard polymerized segments are located at chain ends, whereas the 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 16.22.

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 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. In Figure 16.23 is presented a schematic illustration for the structure of this TPE type.

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; for the styrenic block copolymers this range is between about  $-70^\circ\text{C}$  ( $-95^\circ\text{F}$ ) and  $100^\circ\text{C}$  ( $212^\circ\text{F}$ ).

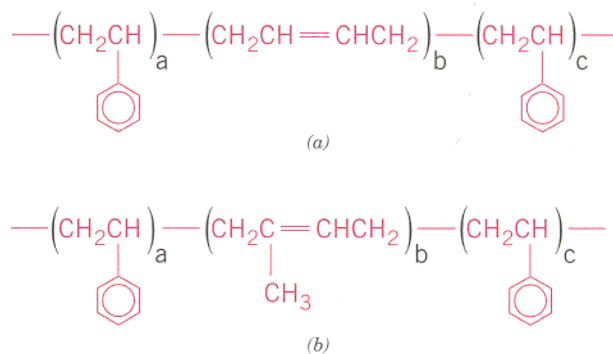
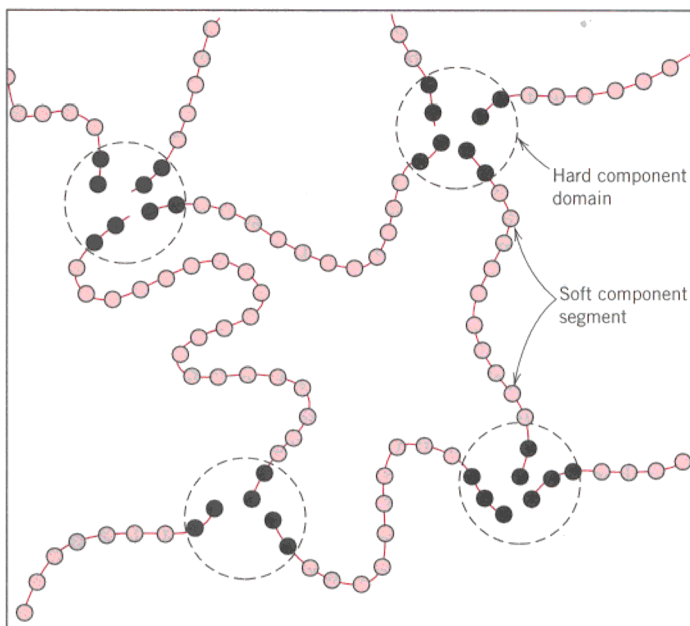


FIGURE 16.22

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

**FIGURE 16.23** Schematic representation of the molecular structure for a thermoplastic elastomer. This structure consists of “soft” (i.e., butadiene or isoprene) mer center-chain segments and “hard” (i.e., styrene) domains (chain ends), which act as physical crosslinks at room temperature. (Reprinted with permission of Brooks/Cole Publishing Company, a division of International Thomson Publishing Inc.; fax 800-730-2215. From *The Science and Engineering of Materials*, 3/e by D. Askeland © 1994.)



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.); 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, appliance parts, medical devices, and as components in sealants, caulking, and adhesives.

## SUMMARY

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.

During the elastic deformation of a semicrystalline polymer that is stressed in tension, the constituent molecules elongate in the stress direction by the bending

and stretching of covalent chain bonds. Slight molecular displacements are resisted by weak secondary bonds.

The mechanism of plastic deformation for semicrystalline polymers having the spherulitic structure was presented. Tensile deformation is thought to occur in several stages as both amorphous tie chains and chain-folded block segments (which separate from the ribbonlike 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. Furthermore, the predeformed spherulitic structure and macroscopic shape may be virtually restored by annealing at an elevated temperature below the polymer's  $T_m$ .

The mechanical behavior of a polymer will be influenced by both inservice 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.

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  $T_g$ .

With regard to mechanical behavior at elevated temperatures, polymers are classified as either thermoplastic or thermosetting. The former soften when heated and harden when cooled; this cycle is reversible and repeatable. In contrast, thermosets, once having hardened, will not soften upon heating.

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.

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.

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 glassy thermoplastics, the crack formation process may be preceded by crazing; crazing can lead to an increase in ductility and toughness of the material.

Synthesis of large molecular weight polymers is attained by polymerization, of which there are two types: addition and condensation. The various properties of polymers may be further modified by using additives; these include fillers, plasticizers, stabilizers, colorants, and flame retardants.

The plastic materials are perhaps the most widely used group of polymers. Fabrication is usually accomplished by plastic deformation at an elevated tempera-



ture, using at least one of several different molding techniques; casting is also possible.

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. Some fibers are spun from a viscous melt, after which they are plastically elongated during a drawing operation, which improves the mechanical strength.

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

This chapter concluded with discussions of 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.

## IMPORTANT TERMS AND CONCEPTS

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

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## QUESTIONS AND PROBLEMS

**16.1** From the stress–strain data for polymethyl methacrylate shown in Figure 16.3, determine the modulus of elasticity and tensile strength at room temperature [20°C (68°F)], and compare these values with those given in Table 16.1.

**16.2** 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.

**16.3** 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;
- (e)** annealing of a drawn material.

**16.4** 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.

**16.5** Normal butane and isobutane have boiling temperatures of  $-0.5$  and  $-12.3^{\circ}\text{C}$  ( $31.1$  and  $9.9^{\circ}\text{F}$ ), respectively. Briefly explain this behavior on the basis of their molecular structures, as presented in Section 15.2.

**16.6** The tensile strength and number-average molecular weight for two polymethyl methacrylate materials are as follows:

<i>Tensile Strength</i> (MPa)	<i>Number Average</i> <i>Molecular Weight</i> (g/mol)
107	40,000
170	60,000

Estimate the tensile strength at a number-average molecular weight of 30,000 g/mol.

**16.7** The tensile strength and number-average molecular weight for two polyethylene mate-

rials are as follows:

<i>Tensile Strength</i> (MPa)	<i>Number Average</i> <i>Molecular Weight</i> (g/mol)
85	12,700
150	28,500

Estimate the number-average molecular weight that is required to give a tensile strength of 195 MPa.

**16.8** For each of the following pairs 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.

**(a)** 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.

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

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

**(d)** 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.

**16.9** For each of the following pairs 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.

**(a)** 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.

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

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

(d) Network polyester; lightly branched polytetrafluoroethylene.

**16.10** 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?

**16.11** 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, c, and d).

(a) Isotactic and linear polypropylene having a weight-average molecular weight of 120,000 g/mol; atactic and linear polypropylene having a weight-average molecular weight of 100,000 g/mol.

(b) Branched polyvinyl chloride having a number-average degree of polymerization of 2000; heavily crosslinked polyvinyl chloride having a number-average degree of polymerization of 2000.

(c) 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.

(d) Polyisoprene, molecular weight of 100,000 g/mol having 10% of available sites crosslinked; polyisoprene, molecular weight of 100,000 g/mol having 20% of available sites crosslinked. *Hint:* polyisoprene is a natural rubber that may display elastomeric behavior.

**16.12** 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?

**16.13** 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) 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.

(b) Graft poly(styrene-butadiene) copolymer with 10% of available sites crosslinked; random poly(styrene-butadiene) copolymer with 15% of available sites crosslinked.

(c) Polyethylene having a density of 0.985 g/cm<sup>3</sup> and a number-average degree of polymerization of 2500; polyethylene having a density of 0.915 g/cm<sup>3</sup> and a degree of polymerization of 2000.

**16.14** 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) Isotactic polystyrene that has a density of 1.12 g/cm<sup>3</sup> and a weight-average molecular weight of 150,000 g/mol; syndiotactic polystyrene that has a density of 1.10 g/cm<sup>3</sup> and a weight-average molecular weight of 125,000 g/mol.

(b) Linear polyethylene that has a number-average degree of polymerization of 5,000; linear and isotactic polypropylene that has a number-average degree of polymerization of 6,500.

(c) Branched and isotactic polystyrene that has a weight-average degree of polymerization of 4,000; linear and isotactic polypropylene that has a weight-average degree of polymerization of 7,500.

**16.15** Make a schematic plot showing how the modulus of elasticity of an amorphous polymer depends on the glass transition tempera-



ture. Assume that molecular weight is held constant.

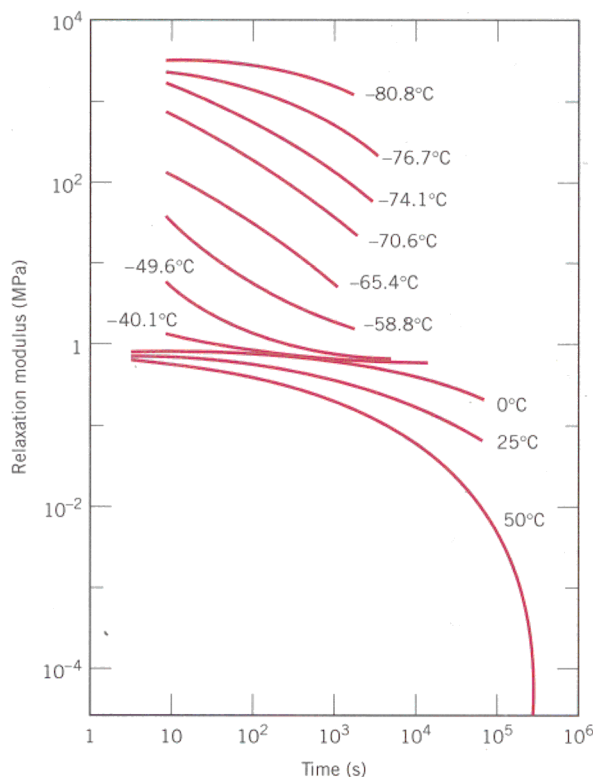
- 16.16** Name the following polymer(s) that would be suitable for the fabrication of cups to contain hot coffee: polyethylene, polypropylene, polyvinyl chloride, PET polyester, and polycarbonate. Why?
- 16.17** Of those polymers listed in Table 16.2, which polymer(s) would be best suited for use as ice cube trays? Why?
- 16.18** Make comparisons of thermoplastic and thermosetting polymers **(a)** on the basis of mechanical characteristics upon heating, and **(b)** according to possible molecular structures.
- 16.19** Some of the polyesters may be either thermoplastic or thermosetting. Suggest one reason for this.
- 16.20** **(a)** Is it possible to grind up and reuse phenol-formaldehyde? Why or why not?  
**(b)** Is it possible to grind up and reuse polypropylene? Why or why not?
- 16.21** In your own words, briefly describe the phenomenon of viscoelasticity.

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

$$\sigma(t) = \sigma(0) \exp\left(-\frac{t}{\tau}\right) \quad (16.10)$$

where  $\sigma(t)$  and  $\sigma(0)$  represent the time-dependent and initial (i.e., time = 0) stresses, respectively, and  $t$  and  $\tau$  denote elapsed time and the relaxation time;  $\tau$  is a time-independent constant characteristic of the material. A specimen of some viscoelastic polymer the stress relaxation of which obeys Equation 16.10 was suddenly pulled in tension to a measured strain of 0.6; 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 2.76 MPa (400 psi) and dropped to 1.72 MPa (250 psi) after 60 s.

- 16.23** In Figure 16.24, the logarithm of  $E_r(t)$  versus the logarithm of time is plotted for polyisobutylene at a variety of temperatures. Make a plot of  $E_r(10)$  versus temperature and then estimate  $T_g$ .



**FIGURE 16.24** Logarithm of relaxation modulus versus logarithm of time for polyisobutylene between  $-80$  and  $50^\circ\text{C}$ . (Adapted from E. Catsiff and A. V. Tobolsky, "Stress-Relaxation of Polyisobutylene in the Transition Region [1,2]," *J. Colloid Sci.*, **10**, 377 [1955]. Reprinted by permission of Academic Press, Inc.)

- 16.24** On the basis of the curves in Figure 16.10, sketch schematic strain-time plots for the following polystyrene materials at the specified temperatures:
- (a) Amorphous at 120°C.
  - (b) Crosslinked at 150°C.
  - (c) Crystalline at 230°C.
  - (d) Crosslinked at 50°C.
- 16.25** (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.
- 16.26** Make two schematic plots of the logarithm of relaxation modulus versus temperature for an amorphous polymer (curve *C* in Figure 16.13).
- (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.
- 16.27** For thermoplastic polymers, cite five factors that favor brittle fracture.
- 16.28** (a) Compare the fatigue limits for polystyrene (Figure 16.17) and the cast iron for which fatigue data are given in Problem 8.31.
- (b) Compare the fatigue strengths at  $10^6$  cycles for polyethylene terephthalate (PET, Figure 16.17) and red brass (Figure 8.42).
- 16.29** Cite the primary differences between addition and condensation polymerization techniques.
- 16.30** 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.
- 16.31** (a) How much adipic acid must be added to 50 kg of ethylene glycol to produce a linear chain structure of polyester according to Equation 16.8?
- (b) What is the mass of the resulting polymer?
- 16.32** Nylon 6,6 may be formed by means of a condensation polymerization reaction in which hexamethylene diamine [ $\text{NH}_2-(\text{CH}_2)_6-\text{NH}_2$ ] and adipic acid react with one another with the formation of water as a by-product. Write out this reaction in the manner of Equation 16.8.
- 16.33** It is desired to produce nylon 6,6 by condensation polymerization using hexamethylene diamine and adipic acid as described in Problem 16.32. What masses of these two components are necessary to yield 37.5 kg of completely linear nylon 6,6?
- 16.34** (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) Is it possible for a crosslinked polymer to be plasticized? Why or why not?
- (d) How does the addition of a plasticizer influence the tensile strength of a polymer? Why?
- 16.35** What is the distinction between dye and pigment colorants?
- 16.36** Cite four factors that determine what fabrication technique is used to form polymeric materials.
- 16.37** Contrast compression, injection, and transfer molding techniques that are used to form plastic materials.
- 16.38** Ten kilogram of polybutadiene is vulcanized with 4.8 kg sulfur. What fraction of the possible crosslink sites is bonded to sulfur crosslinks, assuming that, on the average, 4.5 sulfur atoms participate in each crosslink?
- 16.39** Compute the weight percent sulfur that must be added to completely crosslink an alternating chloroprene-acrylonitrile copolymer, assuming that five sulfur atoms participate in each crosslink.

- 16.40** The vulcanization of polyisoprene is accomplished with sulfur atoms according to Equation 16.9. If 57 wt% sulfur is combined with polyisoprene, how many crosslinks will be associated with each isoprene mer if it is assumed that, on the average, six sulfur atoms participate in each crosslink?
- 16.41** For the vulcanization of polyisoprene, compute the weight percent of sulfur that must be added to ensure that 8% of possible sites will be crosslinked; assume that, on the average, three sulfur atoms are associated with each crosslink.
- 16.42** It is desired that some rubber component in its final form be vulcanized. Should vulcanization be carried out prior or subsequent to the forming operation? Why?
- 16.43** List the two molecular characteristics that are essential for elastomers.
- 16.44** Which of the following would you expect to be elastomers and which thermosetting polymers at room temperature? Justify each choice.
- (a) Epoxy having a network structure.
  - (b) Lightly crosslinked poly(styrene-butadiene) random copolymer that has a glass-transition temperature of  $-50^{\circ}\text{C}$ .
  - (c) Lightly branched and semicrystalline polytetrafluoroethylene that has a glass-transition temperature of  $-100^{\circ}\text{C}$ .
  - (d) Heavily crosslinked poly(ethylene-propylene) random copolymer that has a glass-transition temperature of  $0^{\circ}\text{C}$ .
  - (e) Thermoplastic elastomer that has a glass-transition temperature of  $75^{\circ}\text{C}$ .
- 16.45** In terms of molecular structure, explain why phenol-formaldehyde (Bakelite) will not be an elastomer.
- 16.46** Demonstrate, in a manner similar to Equation 16.9, how vulcanization may occur in a chloroprene rubber.
- 16.47** During the winter months, the temperature in some parts of Alaska may go as low as  $-55^{\circ}\text{C}$  ( $-65^{\circ}\text{F}$ ). Of the elastomers natural isoprene, styrene-butadiene, acrylonitrile-butadiene, chloroprene, and polysiloxane, which would be suitable for automobile tires under these conditions? Why?
- 16.48** Briefly explain the difference in molecular chemistry between silicone polymers and other polymeric materials.
- 16.49** Silicone polymers may be prepared to exist as liquids at room temperature. Cite differences in molecular structure between them and the silicone elastomers.
- 16.50** Why must fiber materials that are melt spun and then drawn be thermoplastic? Cite two reasons.
- 16.51** List two important characteristics for polymers that are to be used in fiber applications.
- 16.52** Cite five important characteristics for polymers that are to be used in thin-film applications.
- 16.53** 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

- 16.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.
- 16.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.