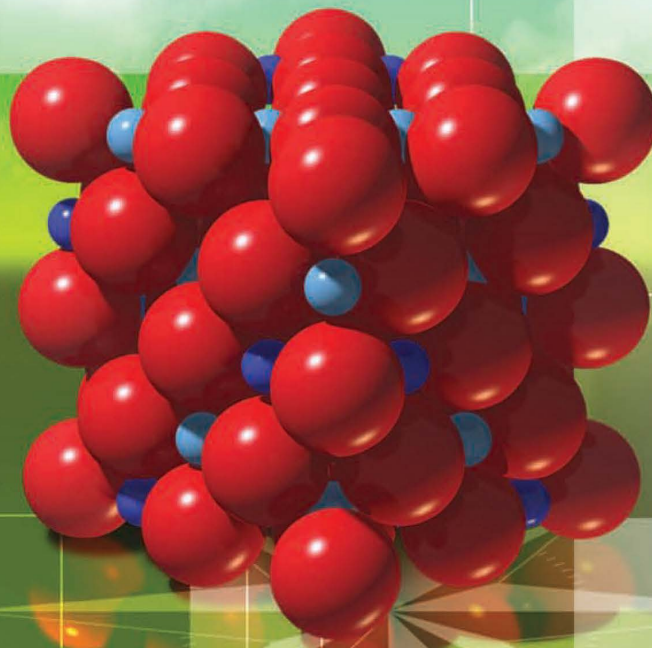


MATERIALS SCIENCE AND ENGINEERING AN INTRODUCTION

EIGHTH EDITION



William D. Callister, Jr.
David G. Rethwisch

EIGHTH EDITION

Materials Science and Engineering

An Introduction

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Front Cover: Depiction of a unit cell for the inverse spinel crystal structure. Red spheres represent O^{2-} oxygen ions; dark blue and light blue spheres denote Fe^{2+} and Fe^{3+} iron ions, respectively. (As discussed in Chapter 20, some of the magnetic ceramic materials have this inverse spinel crystal structure.)
Back Cover: The image on the right shows the ionic packing of a close-packed plane for the inverse spinel crystal structure. The relationship between this close-packed plane and the unit cell is represented by the image on the left; a section has been taken through the unit cell, which exposes this close-packed plane.

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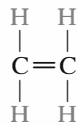
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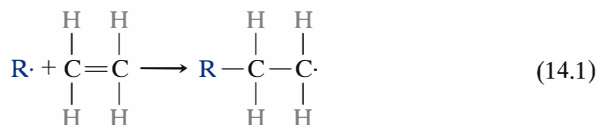
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14.4 THE CHEMISTRY OF POLYMER MOLECULES

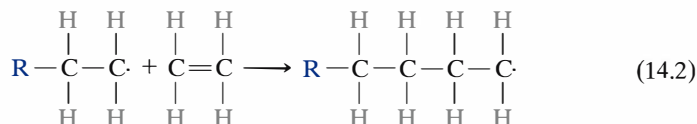
Consider again the hydrocarbon ethylene (C_2H_4), which is a gas at ambient temperature and pressure and has the following molecular structure:



If the ethylene gas is reacted under appropriate conditions, it will transform to polyethylene (PE), which is a solid polymeric material. This process begins when an active center is formed by the reaction between an initiator or catalyst species ($R\cdot$) and the ethylene monomer, as follows:

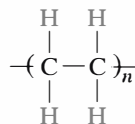


The polymer chain then forms by the sequential addition of monomer units to this active growing chain molecule. The active site, or unpaired electron (denoted by $\cdot$), is transferred to each successive end monomer as it is linked to the chain. This may be represented schematically as follows:

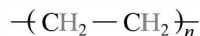


Repeat Unit Structures

The final result, after the addition of many ethylene monomer units, is the polyethylene molecule;² a portion of one such molecule and the polyethylene repeat unit are shown in Figure 14.1a. This polyethylene chain structure can also be represented as



or alternatively as



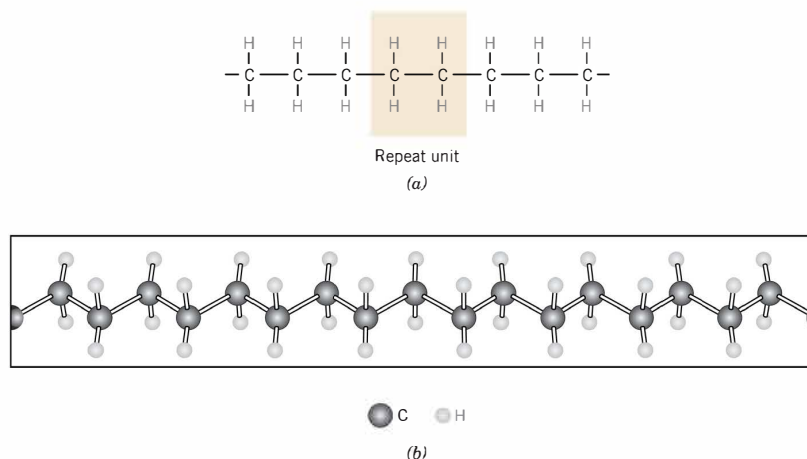
Here the repeat units are enclosed in parentheses, and the subscript n indicates the number of times it repeats.³

The representation in Figure 14.1a is not strictly correct in that the angle between the singly bonded carbon atoms is not 180° as shown, but rather close to 109° . A more accurate three-dimensional model is one in which the carbon atoms form a zigzag pattern (Figure 14.1b), the C—C bond length being 0.154 nm. In this

² A more detailed discussion of polymerization reactions, including both addition and condensation mechanisms, is given in Section 15.20.

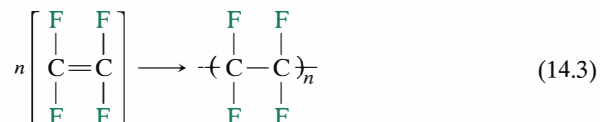
³ Chain ends/end groups (i.e., the Rs in Equation 14.2) are not normally represented in chain structures.

Figure 14.1 For polyethylene, (a) a schematic representation of repeat unit and chain structures, and (b) a perspective of the molecule, indicating the zigzag backbone structure.



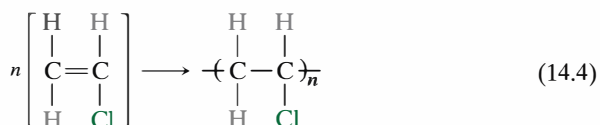
discussion, depiction of polymer molecules is frequently simplified using the linear chain model shown in Figure 14.1a.

Of course, polymer structures having other chemistries are possible. For example, the tetrafluoroethylene monomer, $\text{CF}_2=\text{CF}_2$ can polymerize to form *polytetrafluoroethylene* (PTFE) as follows:



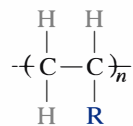
Polytetrafluoroethylene (having the trade name Teflon) belongs to a family of polymers called the fluorocarbons.

The vinyl chloride monomer ($\text{CH}_2=\text{CHCl}$) is a slight variant of that for ethylene, in which one of the four H atoms is replaced with a Cl atom. Its polymerization is represented as



and leads to *poly(vinyl chloride)* (PVC), another common polymer.

Some polymers may be represented using the following generalized form:



where the R depicts either an atom [i.e., H or Cl, for polyethylene or poly(vinyl chloride), respectively], or an organic group such as CH_3 , C_2H_5 , and C_6H_5 (methyl, ethyl, and phenyl). For example, when R represents a CH_3 group, the polymer is *polypropylene* (PP). Poly(vinyl chloride) and polypropylene chain structures are also represented in Figure 14.2. Table 14.3 lists repeat units for some of the more common polymers; as may be noted, some of them—for example, nylon, polyester,



Repeat Unit Structures



Repeat Unit Structures



Repeat Unit Structures

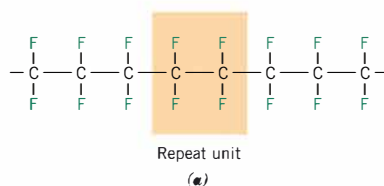


Figure 14.2 Repeat unit and chain structures for (a) polytetrafluoroethylene, (b) poly(vinyl chloride), and (c) polypropylene.

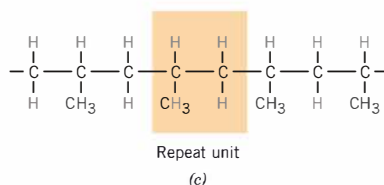
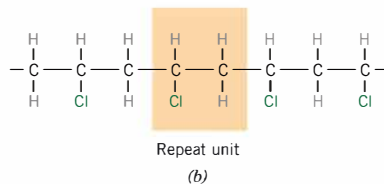


Table 14.3 A Listing of Repeat Units for 10 of the More Common Polymeric Materials

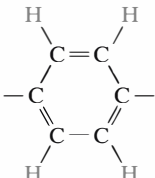
VMSE
Repeat Unit Structures



Polymer	Repeat Unit
Polyethylene (PE)	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{H} \end{array}$
Poly(vinyl chloride) (PVC)	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{Cl} \end{array}$
Polytetrafluoroethylene (PTFE)	$\begin{array}{c} \text{F} \quad \text{F} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{F} \quad \text{F} \end{array}$
Polypropylene (PP)	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{CH}_3 \end{array}$
Polystyrene (PS)	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{C}_6\text{H}_5 \end{array}$

(Continued)

Table 14.3 (Continued)

<i>Polymer</i>	<i>Repeat Unit</i>
 Poly(methyl methacrylate) (PMMA)	
 Phenol-formaldehyde (Bakelite)	
 Poly(hexamethylene adipamide) (nylon 6,6)	
 Poly(ethylene terephthalate) (PET, a polyester)	
 Polycarbonate (PC)	
^a The  symbol in the backbone chain denotes an aromatic ring as 	

and polycarbonate—are relatively complex. Repeat units for a large number of relatively common polymers are given in Appendix D.

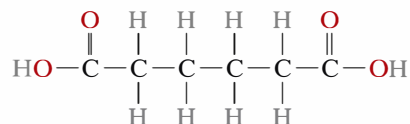
When all of the repeating units along a chain are of the same type, the resulting polymer is called a **homopolymer**. Chains may be composed of two or more different repeat units, in what are termed **copolymers** (see Section 14.10).

The monomers discussed thus far have an active bond that may react to form two covalent bonds with other monomers forming a two-dimensional chainlike molecular structure, as indicated earlier for ethylene. Such a monomer is termed **bifunctional**. In general, the **functionality** is the number of bonds that a given monomer can form. For example, monomers such as phenol-formaldehyde (Table 14.3) are **trifunctional**; they have three active bonds, from which a three-dimensional molecular network structure results.

homopolymer**copolymer****bifunctional****functionality****trifunctional**

**Concept Check 15.12**

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 15.9. *Note:* the structure for adipic acid is



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

15.21 POLYMER ADDITIVES

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

Fillers**filler**

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

Plasticizers**plasticizer**

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

**Concept Check 15.13**

- (a) Why must the vapor pressure of a plasticizer be relatively low?
- (b) How will the crystallinity of a polymer be affected by the addition of a plasticizer? Why?
- (c) How does the addition of a plasticizer influence the tensile strength of a polymer? Why?

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

Stabilizers**stabilizer**

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

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

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

Colorants**colorant**

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

Flame Retardants**flame retardant**

The flammability of polymeric materials is a major concern, especially in the manufacture of textiles and children's toys. Most polymers are flammable in their pure form; exceptions include those containing significant contents of chlorine and/or fluorine, such as poly(vinyl chloride) and polytetrafluoroethylene. The flammability resistance of the remaining combustible polymers may be enhanced by additives called **flame retardants**. These retardants may function by interfering with the combustion process through the gas phase, or by initiating a different combustion reaction that generates less heat, thereby reducing the temperature; this causes a slowing or cessation of burning.

15.22 FORMING TECHNIQUES FOR PLASTICS

Quite a variety of different techniques are employed in the forming of polymeric materials. The method used for a specific polymer depends on several factors: (1) whether the material is thermoplastic or thermosetting; (2) if thermoplastic, the

temperature at which it softens; (3) the atmospheric stability of the material being formed; and (4) the geometry and size of the finished product. There are numerous similarities between some of these techniques and those used 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 re-formed 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, because they are now dimensionally stable. Thermosets are difficult to recycle, do not melt, are usable at higher temperatures than thermoplastics, and are often more chemically inert.

molding

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

Compression and Transfer Molding

For compression molding, the appropriate amounts of thoroughly mixed polymer and necessary additives are placed between male and female mold members, as illustrated in Figure 15.23. Both mold pieces are heated; however, only one is movable. The mold is closed, and heat and pressure are applied, causing the plastic to become viscous and flow to conform to the mold shape. Before molding, raw materials may be mixed and cold-pressed into a disc, which is called a *preform*. Preheating of the preform reduces molding time and pressure, extends the die lifetime, and produces a more uniform finished piece. This molding technique lends

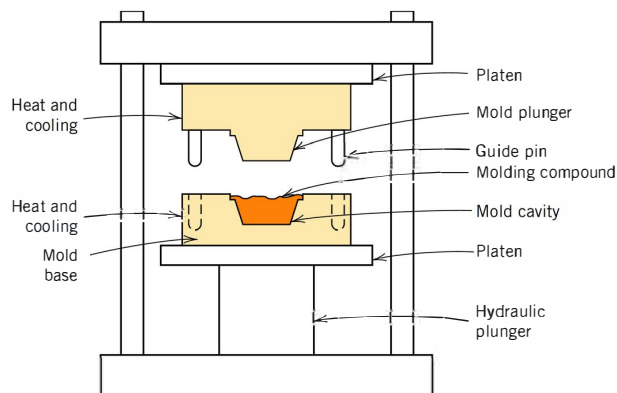


Figure 15.23 Schematic diagram of a compression molding apparatus. (From F. W. Billmeyer, Jr., *Textbook of Polymer Science*, 3rd edition. Copyright © 1984 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

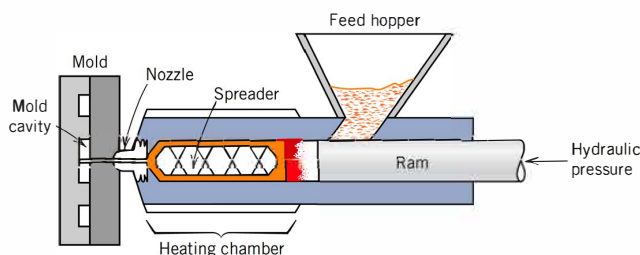


Figure 15.24 Schematic diagram of an injection molding apparatus. (Adapted from F. W. Billmeyer, Jr., *Textbook of Polymer Science*, 2nd edition. Copyright © 1971 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

itself to the fabrication of both thermoplastic and thermosetting polymers; however, its use with thermoplastics is more time-consuming and expensive than the more commonly used extrusion or injection molding techniques discussed next.

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

Injection Molding

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

Extrusion

The extrusion process is the molding of a viscous thermoplastic under pressure through an open-ended die, similar to the extrusion of metals (Figure 11.8c). 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 (Figure 15.25). Extrusion takes place as this molten mass is forced through a die orifice. Solidification of the extruded length is expedited by blowers, a water spray, or bath. The technique is especially adapted to producing continuous lengths having constant cross-sectional geometries—for example, rods, tubes, hose channels, sheets, and filaments.

Blow Molding

The blow-molding process for the fabrication of plastic containers is similar to that used for blowing glass bottles, as represented in Figure 13.8. First, a parison, or length of polymer tubing, is extruded. While still in a semimolten state, the parison

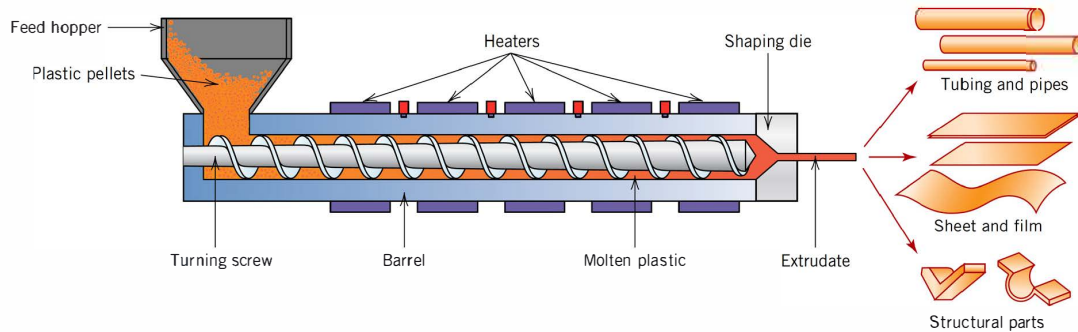


Figure 15.25 Schematic diagram of an extruder. (Reprinted with permission from *Encyclopædia Britannica*, © 1997 by Encyclopædia Britannica, Inc.)

is placed in a two-piece mold having the desired container configuration. The hollow piece is formed by blowing air or steam under pressure into the parison, forcing the tube walls to conform to the contours of the mold. Of course the temperature and viscosity of the parison must be carefully regulated.

Casting

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

15.23 FABRICATION OF ELASTOMERS

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



Concept Check 15.14

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

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

15.24 FABRICATION OF FIBERS AND FILMS

Fibers

spinning

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