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Of the three basic types of materials, polymers are the newest and at the same time the oldest known to man. Polymers form the living organisms and vital processes of all life on earth. To ancient man, biological polymers were the source of food, shelter, and many of his implements. However, the focus in this chapter is on polymers other than biological. With the exception of natural rubber, nearly all of the polymeric materials used in engineering today are synthetic. The materials themselves are made by chemical processing, and most of the products are made by solidification processes.

A **polymer** is a compound consisting of long-chain molecules, each molecule made up of repeating units connected together. There may be thousands, even millions of units in a single polymer molecule. The word is derived from the Greek words **poly**, meaning many, and **meros** (reduced to **mer**), meaning part. Most polymers are based on carbon and are therefore considered organic chemicals.

Polymers can be separated into **plastics** and **rubbers**. As engineering materials, they are relatively new compared to metals and ceramics, dating only from around the mid-1800s (Historical Note 8.1). For the purpose of covering polymers as a technical subject, it is appropriate to divide them into three categories, where (1) and (2) are plastics and (3) is the rubber category:

1. **Thermoplastic polymers**, also called **thermoplastics** (TP), are solid materials at room temperature, but they become viscous liquids when heated to temperatures of only a few hundred degrees. This characteristic allows them to be easily and economically shaped into products. They can be subjected to this heating and cooling cycle repeatedly without significant degradation of the polymer.
2. **Thermosetting polymers**, or **thermosets** (TS), cannot tolerate repeated heating cycles as thermoplastics can. When initially heated, they soften and flow for molding, but the elevated temperatures also produce a chemical reaction that hardens the

## Historical Note 8.1 History of polymers

Certainly one of the milestones in the history of polymers was Charles Goodyear's discovery of vulcanization of rubber in 1839 (Historical Note 8.2). In 1851, his brother Nelson patented hard rubber, called **ebonite**, which in reality is a thermosetting polymer. It was used for many years for combs, battery cases, and dental prostheses.

At the 1862 International Exhibition in London, an English chemist Alexander Parkes demonstrated the possibilities of the first thermoplastic, a form of **cellulose nitrate** (cellulose is a natural polymer in wood and cotton). He called it **Parkesine** and described it as a replacement for ivory and tortoiseshell. The material became commercially important due to the efforts of American John W. Hyatt, Jr., who combined cellulose nitrate and camphor (which acts as a plasticizer) together with heat and pressure to form the product he called **Celluloid**. His patent was issued in 1870. Celluloid plastic was transparent, and the applications subsequently developed for it included photographic and motion picture film and windshields for carriages and early motorcars.

Several additional products based on cellulose were developed around the turn of the last century. Cellulose fibers, called **Rayon**, were first produced around 1890. Packaging film, called **Cellophane**, was first marketed around 1910. **Cellulose acetate** was adopted as the base for photographic film around the same time. This material was to become an important thermoplastic for injection molding during the next several decades.

The first synthetic plastic was developed in the early 1900s by the Belgian-born American chemist L. H. Baekeland. It involved the reaction and polymerization

of phenol and formaldehyde to form what its inventor called **Bakelite**. This thermosetting resin is still commercially important today. It was followed by other similar polymers: urea-formaldehyde in 1918 and melamine-formaldehyde in 1939.

The late 1920s and 1930s saw the development of a number of thermoplastics of major importance today. A Russian I. Ostromislensky had patented **polyvinylchloride** in 1912, but it was first commercialized in 1927 as a wall covering. Around the same time, **polystyrene** was first produced in Germany. In England, fundamental research was started in 1932 that led to the synthesis of **polyethylene**; the first production plant came on line just before the outbreak of World War II. This was low density polyethylene. Finally, a major research program initiated in 1928 under the direction of W. Carothers at DuPont in the United States led to the synthesis of the polyamide **nylon**; it was commercialized in the late 1930s. Its initial use was in ladies' hosiery; subsequent applications during the war included low friction bearings and wire insulation. Similar efforts in Germany provided an alternative form of nylon in 1939.

Several important special-purpose polymers were developed in the 1940s: **fluorocarbons (Teflon)**, **silicones**, and **polyurethanes** in 1943; **epoxy** resins in 1947, and **acrylonitrile-butadiene-styrene** copolymer (ABS) in 1948. During the 1950s: **polyester** fibers in 1950; and **polypropylene**, **polycarbonate**, and **high-density polyethylene** in 1957. **Thermoplastic elastomers** were first developed in the 1960s. The ensuing years have witnessed a tremendous growth in the use of plastics.

material into an infusible solid. If reheated, thermosetting polymers degrade and char rather than soften.

3. **Elastomers** are the rubbers. Elastomers (E) are polymers that exhibit extreme elastic extensibility when subjected to relatively low mechanical stress. Some elastomers can be stretched by a factor of 10 and yet completely recover to their original shape. Although their properties are quite different from thermosets, they have a similar molecular structure that is different from the thermoplastics.

Thermoplastics are commercially the most important of the three types, constituting around 70% of the tonnage of all synthetic polymers produced. Thermosets and elastomers share the remaining 30% about evenly, with a slight edge for the former. Common TP polymers include polyethylene, polyvinylchloride, polypropylene, polystyrene, and nylon. Examples of TS polymers are phenolics, epoxies, and certain polyesters. The most common example given for elastomers is natural (vulcanized) rubber; however, synthetic rubbers exceed the tonnage of natural rubber.

Although the classification of polymers into the TP, TS, and E categories suits the purpose of organizing the topic in this chapter, note that the three types sometimes overlap. Certain polymers that are normally thermoplastic can be made into thermosets. Some polymers can be either thermosets or elastomers (recall that their molecular structures are similar). And some elastomers are thermoplastic. However, these are exceptions to the general classification scheme.

The growth in applications of synthetic polymers is truly impressive. On a volumetric basis, current annual usage of polymers exceeds that of metals. There are several reasons for the commercial and technological importance of polymers:

- Plastics can be formed by molding into intricate part geometries, usually with no further processing required. They are very compatible with *net shape* processing.
- Plastics possess an attractive list of properties for many engineering applications where strength is not a factor: (1) low density relative to metals and ceramics; (2) good strength-to-weight ratios for certain (but not all) polymers; (3) high corrosion resistance; and (4) low electrical and thermal conductivity.
- On a volumetric basis, polymers are cost competitive with metals.
- On a volumetric basis, polymers generally require less energy to produce than metals. This is generally true because the temperatures for working these materials are much lower than for metals.
- Certain plastics are translucent and/or transparent, which makes them competitive with glass in some applications.
- Polymers are widely used in composite materials (Chapter 9).

On the negative side, polymers in general have the following limitations: (1) strength is low relative to metals and ceramics; (2) modulus of elasticity or stiffness is also low — in the case of elastomers, of course, this may be a desirable characteristic; (3) service temperatures are limited to only a few hundred degrees because of the softening of thermoplastic polymers or degradation of thermosetting polymers and elastomers; (4) some polymers degrade when subjected to sunlight and other forms of radiation; and (5) plastics exhibit viscoelastic properties (Section 3.5), which can be a distinct limitation in load bearing applications.

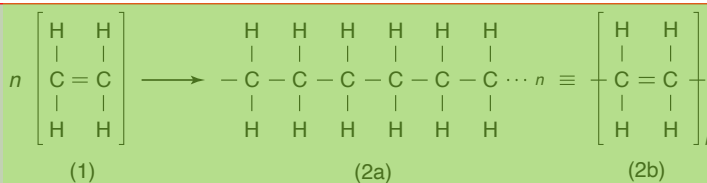
This chapter examines the technology of polymeric materials. The first section is devoted to an introductory discussion of polymer science and technology. Subsequent sections survey the three basic categories of polymers: thermoplastics, thermosets, and elastomers.

## 8.1

# Fundamentals of Polymer Science and Technology

Polymers are synthesized by joining many small molecules together to form very large molecules, called *macromolecules*, that possess a chain-like structure. The small units, called *monomers*, are generally simple unsaturated organic molecules such as ethylene  $C_2H_4$ . The atoms in these molecules are held together by covalent bonds; and when joined to form the polymer, the same covalent bonding holds the links of the chain together. Thus, each large molecule is characterized by strong primary bonding. Synthesis of the polyethylene molecule is depicted in Figure 8.1.

**FIGURE 8.1** Synthesis of polyethylene from ethylene monomers: (1)  $n$  ethylene monomers yields (2a) polyethylene of chain length  $n$ ; (2b) concise notation for depicting the polymer structure of chain length  $n$ .



As its structure is described here, polyethylene is a linear polymer; its mers form one long chain.

A mass of polymer material consists of many macromolecules; the analogy of a bowl of just-cooked spaghetti (without sauce) is sometimes used to visualize the relationship of the individual molecules to the bulk material. Entanglement among the long strands helps to hold the mass together, but atomic bonding is more significant. The bonding between macromolecules in the mass is due to van der Waals and other secondary bonding types. Thus, the aggregate polymer material is held together by forces that are substantially weaker than the primary bonds holding the molecules together. This explains why plastics in general are not nearly as stiff and strong as metals or ceramics.

When a thermoplastic polymer is heated, it softens. The heat energy causes the macromolecules to become thermally agitated, exciting them to move relative to each other within the polymer mass (here, the wet spaghetti analogy loses its appeal). The material begins to behave like a viscous liquid, viscosity decreasing (fluidity increasing) with rising temperature.

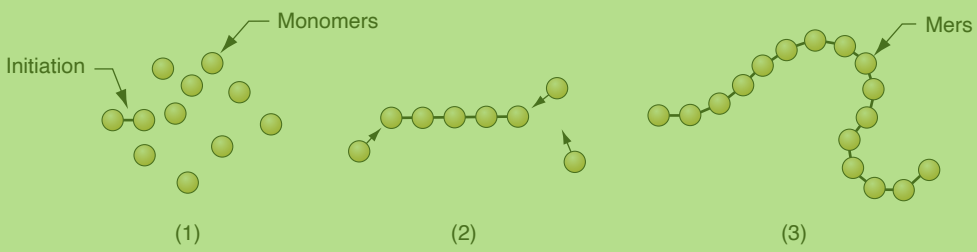
The following discussion will expand on these opening remarks, tracing how polymers are synthesized and examining the characteristics of the materials that result from the synthesis.

### 8.1.1 POLYMERIZATION

As a chemical process, the synthesis of polymers can occur by either of two methods: (1) addition polymerization and (2) step polymerization. Production of a given polymer is generally associated with one method or the other.

**Addition Polymerization** In this process, exemplified by polyethylene, the double bonds between carbon atoms in the ethylene monomers are induced to open so that they join with other monomer molecules. The connections occur on both ends of the expanding macromolecule, developing long chains of repeating mers. Because of the way the molecules are formed, the process is also known as **chain polymerization**. It is initiated using a chemical catalyst (called an **initiator**) to open the carbon double bond in some of the monomers. These monomers, which are now highly reactive because of their unpaired electrons, then capture other monomers to begin forming chains that are reactive. The chains propagate by capturing still other monomers, one at a time, until large molecules have been produced and the reaction is terminated. The process proceeds as indicated in Figure 8.2. The entire polymerization reaction takes only seconds for any given macromolecule. However, in the industrial process, it may take many minutes or even hours to complete

**FIGURE 8.2** Model of addition (chain) polymerization: (1) initiation, (2) rapid addition of monomers, and (3) resulting long-chain polymer molecule with *n* mers at termination of reaction.

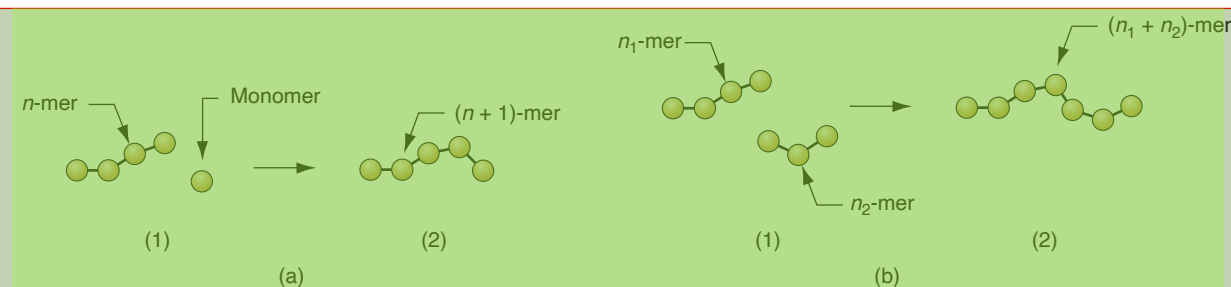


the polymerization of a given batch, since all of the chain reactions do not occur simultaneously in the mixture.

Other polymers typically formed by addition polymerization are presented in Figure 8.3, along with the starting monomer and the repeating mer. Note that the chemical formula for the monomer is the same as that of the mer in the polymer. This is a characteristic of this method of polymerization. Note also that many of the common polymers involve substitution of some alternative atom or molecule in place of one of the H atoms in polyethylene. Polypropylene, polyvinylchloride, and polystyrene are examples of this substitution. Polytetrafluoroethylene replaces all four H atoms in the structure with atoms of fluorine (F). Most addition polymers are thermoplastics. The exception in Figure 8.3 is polyisoprene, the polymer of natural rubber. Although formed by addition polymerization, it is an elastomer.

Polymer	Monomer	Repeating mer	Chemical formula
Polypropylene	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{C} = \text{C} \\   \quad   \\ \text{H} \quad \text{CH}_3 \end{array}$	$\left[ \begin{array}{cc} \text{H} & \text{H} \\   &   \\ -\text{C} & - \text{C}- \\   &   \\ \text{H} & \text{CH}_3 \end{array} \right]_n$	$(\text{C}_3\text{H}_6)_n$
Polyvinyl chloride	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{C} = \text{C} \\   \quad   \\ \text{H} \quad \text{Cl} \end{array}$	$\left[ \begin{array}{cc} \text{H} & \text{H} \\   &   \\ -\text{C} & - \text{C}- \\   &   \\ \text{H} & \text{Cl} \end{array} \right]_n$	$(\text{C}_2\text{H}_3\text{Cl})_n$
Polystyrene	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{C} = \text{C} \\   \quad   \\ \text{H} \quad \text{C}_6\text{H}_5 \end{array}$	$\left[ \begin{array}{cc} \text{H} & \text{H} \\   &   \\ -\text{C} & - \text{C}- \\   &   \\ \text{H} & \text{C}_6\text{H}_5 \end{array} \right]_n$	$(\text{C}_8\text{H}_8)_n$
Polytetrafluoroethylene (Teflon)	$\begin{array}{c} \text{F} \quad \text{F} \\   \quad   \\ \text{C} = \text{C} \\   \quad   \\ \text{F} \quad \text{F} \end{array}$	$\left[ \begin{array}{cc} \text{F} & \text{F} \\   &   \\ -\text{C} & - \text{C}- \\   &   \\ \text{F} & \text{F} \end{array} \right]_n$	$(\text{C}_2\text{F}_4)_n$
Polyisoprene (natural rubber)	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \\ \text{C} - \text{C} = \text{C} - \text{C} \\   \quad   \quad   \\ \text{H} \quad \text{CH}_3 \quad \text{H} \end{array}$	$\left[ \begin{array}{cccc} \text{H} & \text{H} & & \text{H} \\   &   & &   \\ -\text{C} & - \text{C} = & \text{C} - & \text{C}- \\   & &   &   \\ \text{H} & & \text{CH}_3 & \text{H} \end{array} \right]_n$	$(\text{C}_5\text{H}_8)_n$

**FIGURE 8.3** Some typical polymers formed by addition (chain) polymerization.



**FIGURE 8.4** Model of step polymerization showing the two types of reactions occurring: (a)  $n$ -mer attaching a single monomer to form a  $(n + 1)$ -mer; and (b)  $n_1$ -mer combining with  $n_2$ -mer to form a  $(n_1 + n_2)$ -mer. Sequence is shown by (1) and (2).

**Step Polymerization** In this form of polymerization, two reacting monomers are brought together to form a new molecule of the desired compound. In most (but not all) step polymerization processes, a byproduct of the reaction is also produced. The byproduct is typically water, which condenses; hence, the term **condensation polymerization** is often used for processes that yield the condensate. As the reaction continues, more molecules of the reactants combine with the molecules first synthesized to form polymers of length  $n = 2$ , then polymers of length  $n = 3$ , and so on. Polymers of increasing  $n$  are created in a slow, stepwise fashion. In addition to this gradual elongation of the molecules, intermediate polymers of length  $n_1$  and  $n_2$  also combine to form molecules of length  $n = n_1 + n_2$ , so that two types of reactions are proceeding simultaneously once the process is under way, as illustrated in Figure 8.4. Accordingly, at any point in the process, the batch contains polymers of various lengths. Only after sufficient time has elapsed are molecules of adequate length formed.

It should be noted that water is not always the byproduct of the reaction; for example, ammonia ( $\text{NH}_3$ ) is another simple compound produced in some reactions. Nevertheless, the term condensation polymerization is still used. It should also be noted that although most step polymerization processes involve condensation of a byproduct, some do not. Examples of commercial polymers produced by step (condensation) polymerization are given in Figure 8.5. Both thermoplastic and thermosetting polymers are synthesized by this method; nylon-6,6 and polycarbonate are TP polymers, while phenol formaldehyde and urea formaldehyde are TS polymers.

**Degree of Polymerization and Molecular Weight** A macromolecule produced by polymerization consists of  $n$  repeating mers. Since molecules in a given batch of polymerized material vary in length,  $n$  for the batch is an average; its statistical distribution is normal. The mean value of  $n$  is called the **degree of polymerization** (DP) for the batch. The degree of polymerization affects the properties of the polymer: higher DP increases mechanical strength but also increases viscosity in the fluid state, which makes processing more difficult.

The **molecular weight** (MW) of a polymer is the sum of the molecular weights of the mers in the molecule; it is  $n$  times the molecular weight of each repeating unit. Since  $n$  varies for different molecules in a batch, the molecule weight must be interpreted as an average. Typical values of DP and MW for selected polymers are presented in Table 8.1.

Polymer	Repeating unit	Chemical formula	Condensate
Nylon-6, 6	$\left[ \begin{array}{c} \text{H} \\   \\ \text{---} \left( \text{C} \right) \text{---} \\   \\ \text{H}_6 \end{array} \text{---} \text{N} \text{---} \text{C} \begin{array}{c} \text{O} \\    \\ \text{---} \left( \text{C} \right) \text{---} \\   \\ \text{H}_4 \end{array} \text{---} \text{C} \begin{array}{c} \text{O} \\    \\ \text{---} \left( \text{C} \right) \text{---} \\   \\ \text{H} \end{array} \text{---} \text{N} \right]_n$	$[(\text{CH}_2)_6 (\text{CONH})_2 (\text{CH}_2)_4]_n$	$\text{H}_2\text{O}$
Polycarbonate	$\text{---} \left( \text{C}_6\text{H}_4 \right) \text{---} \text{C} \begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3 \end{array} \text{---} \left( \text{C}_6\text{H}_4 \right) \text{---} \text{O} \text{---} \text{C} \begin{array}{c} \text{O} \\    \\ \text{O} \end{array} \text{---} \text{O} \text{---}$	$(\text{C}_3\text{H}_6 (\text{C}_6\text{H}_4)_2 \text{CO}_3)_n$	$\text{HCl}$
Phenol formaldehyde	$\text{---} \text{C}_6\text{H}_4 \text{---} \text{C} \begin{array}{c} \text{H} \\   \\ \text{OH} \end{array} \text{---}$	$[(\text{C}_6\text{H}_4)\text{CH}_2\text{OH}]_n$	$\text{H}_2\text{O}$
Urea formaldehyde	$\text{---} \text{C} \begin{array}{c} \text{NH} \\   \\ \text{NH} \end{array} \text{=O} \text{---} \text{C} \begin{array}{c} \text{H} \\   \\ \text{H} \end{array} \text{---}$	$(\text{CO}(\text{NH})_2 \text{CH}_2)_n$	$\text{H}_2\text{O}$

**FIGURE 8.5** Some typical polymers formed by step (condensation) polymerization (simplified expression of structure and formula; ends of polymer chain are not shown).

8.1.2 POLYMER STRUCTURES AND COPOLYMERS

There are structural differences among polymer molecules, even molecules of the same polymer. This section examines three aspects of molecular structure: (1) stereoregularity, (2) branching and cross-linking, and (3) copolymers.

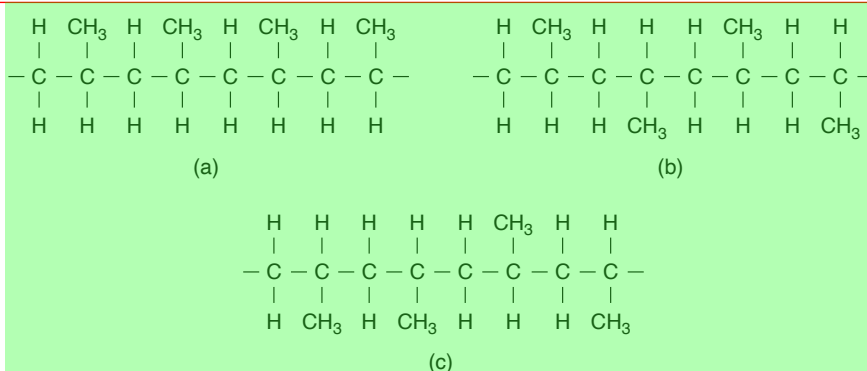
**Stereoregularity** Stereoregularity is concerned with the spatial arrangement of the atoms and groups of atoms in the repeating units of the polymer molecule. An important aspect of stereoregularity is the way the atom groups are located along the chain for a polymer that has one of the H atoms in its mers replaced by some

**TABLE • 8.1** Typical values of degree of polymerization and molecular weight for selected thermoplastic polymers.

Polymer	Degree of Polymerization ( <i>n</i> )	Molecular Weight
Polyethylene	10,000	300,000
Polystyrene	3000	300,000
Polyvinylchloride	1500	100,000
Nylon	120	15,000
Polycarbonate	200	40,000

Compiled from [7].





**FIGURE 8.6** Possible arrangement of atom groups in polypropylene: (a) isotactic, (b) syndiotactic, and (c) atactic.

other atom or atom group. Polypropylene is an example; it is similar to polyethylene except that CH<sub>3</sub> is substituted for one of the four H atoms in the mer. Three tactic arrangements are possible, illustrated in Figure 8.6: (a) **isotactic**, in which the odd atom groups are all on the same side; (b) **syndiotactic**, in which the atom groups alternate on opposite sides; and (c) **atactic**, in which the groups are randomly along either side.

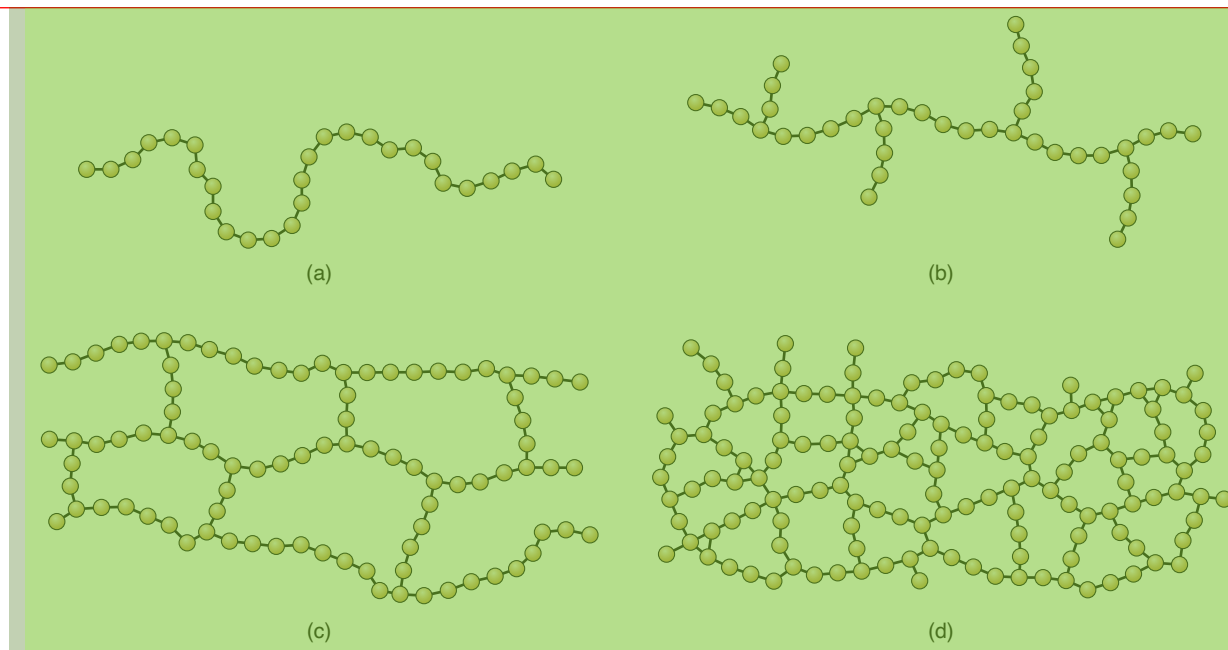
The tactic structure is important in determining the properties of the polymer. It also influences the tendency of a polymer to crystallize (Section 8.1.3). Continuing with the polypropylene example, this polymer can be synthesized in any of the three tactic structures. In its isotactic form, it is strong and melts at 175°C (347°F); the syndiotactic structure is also strong, but melts at 131°C (268°F); but atactic polypropylene is soft and melts at around 75°C (165°F) and has little commercial use [6], [9].

**Linear, Branched, and Cross-Linked Polymers** The polymerization process has been described as yielding macromolecules of a chain-like structure, called a **linear polymer**. This is the characteristic structure of a thermoplastic polymer. Other structures are possible, as portrayed in Figure 8.7. One possibility is for side branches to form along the chain, resulting in the **branched polymer** shown in Figure 8.7(b). In polyethylene, this occurs because hydrogen atoms are replaced by carbon atoms at random points along the chain, initiating the growth of a branch chain at each location. For certain polymers, primary bonding occurs between branches and other molecules at certain connection points to form **cross-linked polymers** as pictured in Figure 8.7(c) and (d). Cross-linking occurs because a certain proportion of the monomers used to form the polymer are capable of bonding to adjacent monomers on more than two sides, thus allowing branches from other molecules to attach. Lightly cross-linked structures are characteristic of elastomers. When the polymer is highly cross-linked, this is referred to as **network structure**, as in (d); in effect, the entire mass is one gigantic macromolecule. Thermosetting plastics take this structure after curing.

The presence of branching and cross-linking in polymers has a significant effect on properties. It is the basis of the difference between the three categories of polymers: TP, TS, and E. Thermoplastic polymers always possess linear or branched structures, or a mixture of the two. Branching increases entanglement among the molecules, usually making the polymer stronger in the solid state and more viscous at a given temperature in the plastic or liquid state.

Thermosetting plastics and elastomers are cross-linked polymers. Cross-linking causes the polymer to become chemically set; the reaction cannot be reversed.

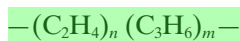




**FIGURE 8.7** Various structures of polymer molecules: (a) linear, characteristic of thermoplastics; (b) branched; (c) loosely cross-linked as in an elastomer; and (d) tightly cross-linked or networked structure as in a thermoset.

The effect is to permanently change the structure of the polymer; upon heating, it degrades or burns rather than melts. Thermosets possess a high degree of cross-linking, while elastomers possess a low degree of cross-linking. Thermosets are hard and brittle, while elastomers are elastic and resilient.

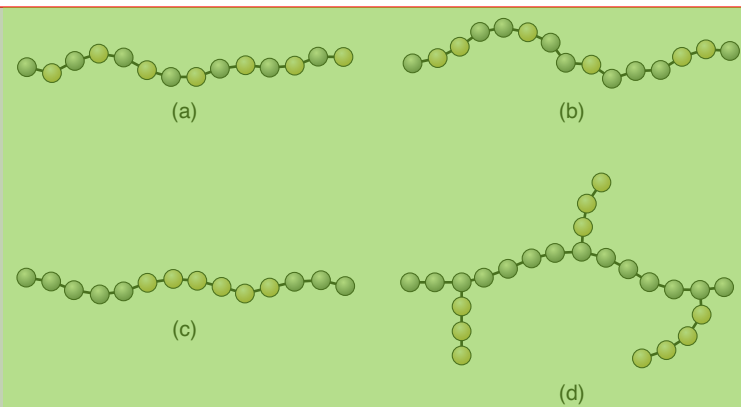
**Copolymers** Polyethylene is a *homopolymer*; so are polypropylene, polystyrene, and many other common plastics; their molecules consist of repeating mers that are all the same type. **Copolymers** are polymers whose molecules are made of repeating units of two different types. An example is the copolymer synthesized from ethylene and propylene to produce a copolymer with elastomeric properties. The ethylene-propylene copolymer can be represented as follows:



where  $n$  and  $m$  range between 10 and 20, and the proportions of the two constituents are around 50% each. For example, the combination of polyethylene and polypropylene with small amounts of diene is an important synthetic rubber (Section 8.4.3).

Copolymers can possess different arrangements of their constituent mers. The possibilities are shown in Figure 8.8: (a) **alternating copolymer**, in which the mers repeat every other place; (b) **random**, in which the mers are in random order, the frequency depending on the relative proportions of the starting monomers; (c) **block**, in which mers of the same type tend to group themselves into long segments along the chain; and (d) **graft**, in which mers of one type are attached as branches to a main backbone of mers of the other type. The ethylene-propylene diene rubber, mentioned previously, is a block type.

**FIGURE 8.8** Various structures of copolymers: (a) alternating, (b) random, (c) block, and (d) graft.



Synthesis of copolymers is analogous to alloying of metals to form solid solutions. As with metallic alloys, differences in the ingredients and structure of copolymers can have a substantial effect on properties. An example is the polyethylene–polypropylene mixture discussed above. Each of these polymers alone is fairly stiff; yet a 50–50 mixture forms a copolymer of random structure that is rubbery.

It is also possible to synthesize *ternary polymers*, or *terpolymers*, which consist of mers of three different types. An example is the plastic ABS (acrylonitrile–butadiene–styrene—no wonder they call it ABS).

### 8.1.3 CRYSTALLINITY

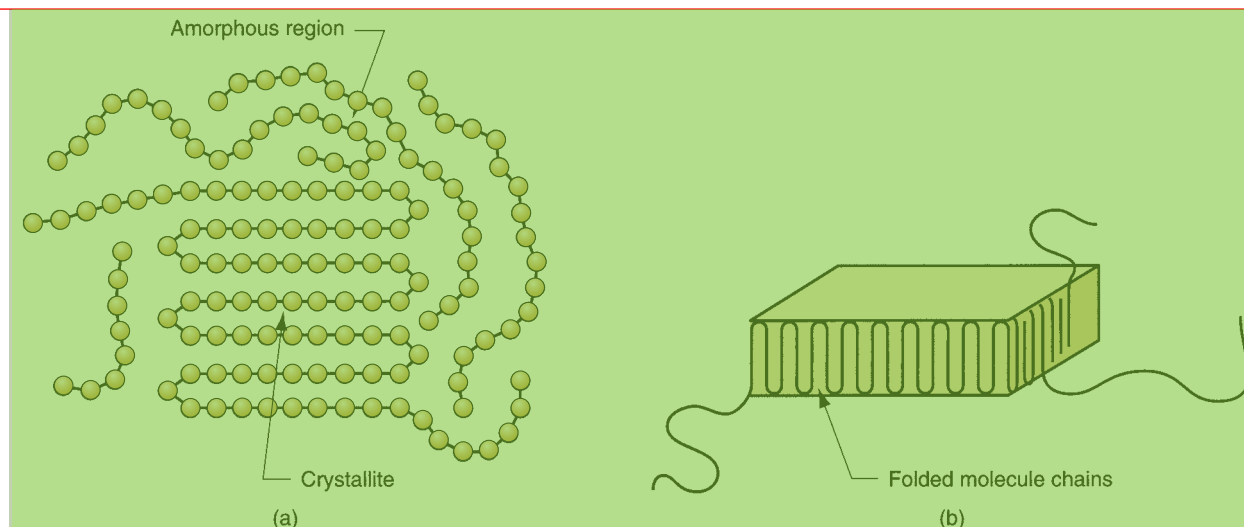
Both amorphous and crystalline structures are possible with polymers, although the tendency to crystallize is much less than for metals or nonglass ceramics. Not all polymers can form crystals. For those that can, the *degree of crystallinity* (the proportion of crystallized material in the mass) is always less than 100%. As crystallinity is increased in a polymer, so are (1) density, (2) stiffness, strength, and toughness, and (3) heat resistance. In addition, (4) if the polymer is transparent in the amorphous state, it becomes opaque when partially crystallized. Many polymers are transparent, but only in the amorphous (glassy) state. Some of these effects can be illustrated by the differences between low-density and high-density polyethylene, presented in Table 8.2. The underlying reason for the property differences between these materials is the degree of crystallinity.

Linear polymers consist of long molecules with thousands of repeated mers. Crystallization in these polymers involves the folding back and forth of the long chains

**TABLE • 8.2** Comparison of low-density polyethylene and high-density polyethylene.

Polyethylene Type	Low Density	High Density
Degree of crystallinity	55%	92%
Specific gravity	0.92	0.96
Modulus of elasticity	140 MPa (20,000 lb/in <sup>2</sup> )	700 MPa (100,000 lb/in <sup>2</sup> )
Melting temperature	115°C (239°F)	135°C (275°F)

Compiled from [6]. Values given are typical.



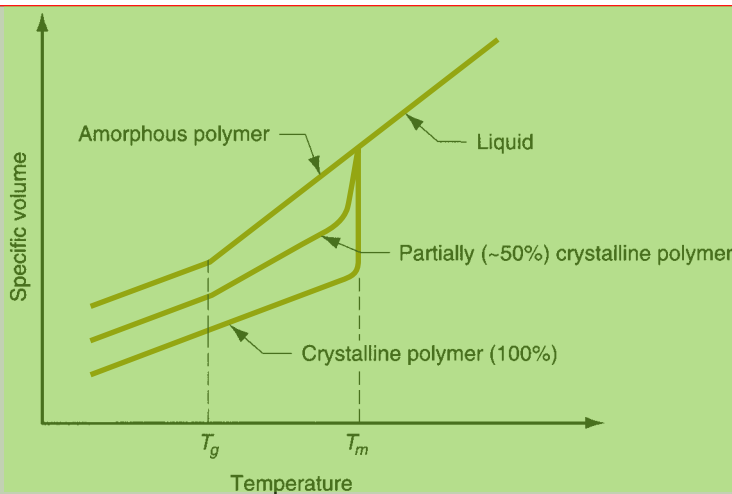
**FIGURE 8.9** Crystallized regions in a polymer: (a) long molecules forming crystals randomly mixed in with the amorphous material; and (b) folded chain lamella, the typical form of a crystallized region.

upon themselves to achieve a very regular arrangement of the mers, as pictured in Figure 8.9(a). The crystallized regions are called **crystallites**. Owing to the tremendous length of a single molecule (on an atomic scale), it may participate in more than one crystallite. Also, more than one molecule may be combined in a single crystal region. The crystallites take the form of lamellae, as pictured in Figure 8.9(b), that are randomly mixed in with the amorphous material. Thus, a polymer that crystallizes is a two-phase system—crystallites interspersed throughout an amorphous matrix.

A number of factors determine the capacity and/or tendency of a polymer to form crystalline regions within the material. The factors can be summarized as follows: (1) as a general rule, only linear polymers can form crystals; (2) stereoregularity of the molecule is critical [15]: isotactic polymers always form crystals; syndiotactic polymers sometimes form crystals; atactic polymers never form crystals; (3) copolymers, due to their molecular irregularity, rarely form crystals; (4) slower cooling promotes crystal formation and growth, as it does in metals and ceramics; (5) mechanical deformation, as in the stretching of a heated thermoplastic, tends to align the structure and increase crystallization; and (6) plasticizers (chemicals added to a polymer to soften it) reduce the degree of crystallinity.

#### 8.1.4 THERMAL BEHAVIOR OF POLYMERS

The thermal behavior of polymers with crystalline structures is different from that of amorphous polymers (Section 2.4). The effect of structure can be observed on a plot of specific volume (reciprocal of density) as a function of temperature, as plotted in Figure 8.10. A highly crystalline polymer has a melting point  $T_m$  at which its volume undergoes an abrupt change. Also, at temperatures above  $T_m$ , the thermal expansion of the molten material is greater than for the solid material below  $T_m$ . An amorphous polymer does not undergo the same abrupt changes at  $T_m$ . As it is cooled from the liquid, its coefficient of thermal expansion continues to decline along the



**FIGURE 8.10** Behavior of polymers as a function of temperature.

same trajectory as when it was molten, and it becomes increasingly viscous with decreasing temperature. During cooling below  $T_m$ , the polymer changes from liquid to rubbery. As temperature continues to drop, a point is finally reached at which the thermal expansion of the amorphous polymer suddenly becomes lower. This is the **glass-transition temperature**,  $T_g$  (Section 3.5), seen as the change in slope. Below  $T_g$ , the material is hard and brittle.

A partially crystallized polymer lies between these two extremes, as indicated in Figure 8.10. It is an average of the amorphous and crystalline states, the average depending on the degree of crystallinity. Above  $T_m$  it exhibits the viscous characteristics of a liquid; between  $T_m$  and  $T_g$  it has viscoelastic properties; and below  $T_g$  it has the conventional elastic properties of a solid.

What is described in this section applies to thermoplastic materials, which can move up and down the curve of Figure 8.10 multiple times. The manner in which they are heated and cooled may change the path that is followed. For example, fast cooling rates may inhibit crystal formation and increase the glass-transition temperature. Thermosets and elastomers cooled from the liquid state behave like an amorphous polymer until cross-linking occurs. Their molecular structure restricts the formation of crystals. And once their molecules are cross-linked, they cannot be reheated to the molten state.

## 8.1.5 ADDITIVES

The properties of a polymer can often be beneficially changed by combining them with additives. Additives either alter the molecular structure of the polymer or add a second phase to the plastic, in effect transforming a polymer into a composite material. Additives can be classified by function as (1) fillers, (2) plasticizers, (3) colorants, (4) lubricants, (5) flame retardants, (6) cross-linking agents, (7) ultraviolet light absorbers, and (8) antioxidants.

**Filler** *Fillers* are solid materials added to a polymer usually in particulate or fibrous form to alter its mechanical properties or to simply reduce material cost. Other reasons for using fillers are to improve dimensional and thermal stability. Examples

of fillers used in polymers include cellulosic fibers and powders (e.g., cotton fibers and wood flour, respectively); powders of silica ( $\text{SiO}_2$ ), calcium carbonate ( $\text{CaCO}_3$ ), and clay (hydrous aluminum silicate); and fibers of glass, metal, carbon, or other polymers. Fillers that improve mechanical properties are called **reinforcing agents**, and composites thus created are referred to as **reinforced plastics**; they have higher stiffness, strength, hardness, and toughness than the original polymer. Fibers provide the greatest strengthening effect.

**Plasticizers** *Plasticizers* are chemicals added to a polymer to make it softer and more flexible, and to improve its flow characteristics during forming. The plasticizer works by reducing the glass transition temperature to below room temperature. Whereas the polymer is hard and brittle below  $T_g$ , it is soft and tough above it. Addition of a plasticizer<sup>1</sup> to polyvinylchloride (PVC) is a good example; depending on the proportion of plasticizer in the mix, PVC can be obtained in a range of properties, from rigid and brittle to flexible and rubbery.

**Colorants** An advantage of many polymers over metals or ceramics is that the material itself can be obtained in most any color. This eliminates the need for secondary coating operations. Colorants for polymers are of two types: pigments and dyes. **Pigments** are finely powdered materials that are insoluble in and must be uniformly distributed throughout the polymer in very low concentrations, usually less than 1%. They often add opacity as well as color to the plastic. **Dyes** are chemicals, usually supplied in liquid form, that are generally soluble in the polymer. They are normally used to color transparent plastics such as styrene and acrylics.

**Other Additives** *Lubricants* are sometimes added to the polymer to reduce friction and promote flow at the mold interface. Lubricants are also helpful in releasing the part from the mold in injection molding. Mold release agents, sprayed onto the mold surface, are often used for the same purpose.

Nearly all polymers burn if the required heat and oxygen are supplied. Some polymers are more combustible than others. **Flame retardants** are chemicals added to polymers to reduce flammability by any or a combination of the following mechanisms: (1) interfering with flame propagation, (2) producing large amounts of incombustible gases, and/or (3) increasing the combustion temperature of the material. The chemicals may also function to (4) reduce the emission of noxious or toxic gases generated during combustion.

Additives that cause cross-linking in thermosetting polymers and elastomers should be included in the discussion here. The term **cross-linking agent** refers to a variety of ingredients that cause a cross-linking reaction or act as a catalyst to promote such a reaction. Important commercial examples are (1) sulfur in vulcanization of natural rubber, (2) formaldehyde for phenolics to form phenolic thermosetting plastics, and (3) peroxides for polyesters.

Many polymers are susceptible to degradation by ultraviolet light (e.g., from sunlight) and oxidation. The degradation manifests itself as the breaking of links in the long chain molecules. Polyethylene, for example, is vulnerable to both types of degradation, which lead to a loss of mechanical strength. **Ultraviolet light absorbers** and **antioxidants** are additives that reduce the susceptibility of the polymer to these forms of attack.

<sup>1</sup>The common plasticizer in PVC is dioctyl phthalate, a phthalate ester.

## 8.2 Thermoplastic Polymers

This section discusses the properties of the thermoplastic polymer group and provides a survey of its important members.

### 8.2.1 PROPERTIES OF THERMOPLASTIC POLYMERS

The defining property of a thermoplastic polymer is that it can be heated from a solid state to a viscous liquid state and then cooled back down to solid, and that this heating and cooling cycle can be applied multiple times without degrading the polymer. The reason for this property is that TP polymers consist of linear (and/or branched) macromolecules that do not cross-link when heated. By contrast, thermosets and elastomers undergo a chemical change when heated, which cross-links their molecules and permanently sets these polymers.

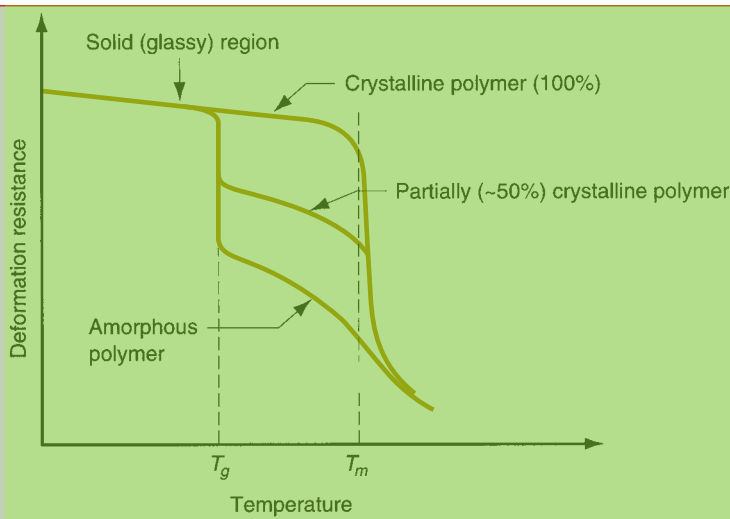
In truth, thermoplastics do deteriorate chemically with repeated heating and cooling. In plastic molding, a distinction is made between new or *virgin* material, and plastic that has been previously molded (e.g., sprues, defective parts) and therefore has experienced thermal cycling. For some applications, only virgin material is acceptable. Thermoplastic polymers also degrade gradually when subjected to continuous elevated temperatures below  $T_m$ . This long-term effect is called **thermal aging** and involves slow chemical deterioration. Some TP polymers are more susceptible to thermal aging than others, and for a given material the rate of deterioration depends on temperature.

**Mechanical Properties** In the discussion of mechanical properties in Chapter 3, polymers were compared with metals and ceramics. The typical thermoplastic at room temperature is characterized by the following: (1) much lower stiffness, the modulus of elasticity being two (in some cases, three) orders of magnitude lower than metals and ceramics; (2) lower tensile strength, about 10% of the metals; (3) much lower hardness; and (4) greater ductility on average, but there is a tremendous range of values, from 1% elongation for polystyrene to 500% or more for polypropylene.

Mechanical properties of thermoplastics depend on temperature. The functional relationships must be discussed in the context of amorphous and crystalline structures. Amorphous thermoplastics are rigid and glass-like below their glass transition temperature  $T_g$  and flexible or rubber-like just above it. As temperature increases above  $T_g$ , the polymer becomes increasingly soft, finally becoming a viscous fluid (it never becomes a thin liquid due to its high molecular weight). The effect on mechanical behavior can be portrayed as in Figure 8.11, in which mechanical behavior is defined as deformation resistance. This is analogous to modulus of elasticity but it allows us to observe the effect of temperature on the amorphous polymer as it transitions from solid to liquid. Below  $T_g$ , the material is elastic and strong. At  $T_g$ , a rather sudden drop in deformation resistance is observed as the material transforms into its rubbery phase; its behavior is viscoelastic in this region. As temperature increases, it gradually becomes more fluid-like.

A theoretical thermoplastic with 100% crystallinity would have a distinct melting point  $T_m$  at which it transforms from solid to liquid, but would show no perceptible  $T_g$  point. Of course, real polymers have less than 100% crystallinity. For partially crystallized polymers, the resistance to deformation is characterized by the curve that lies between the two extremes, its position determined by the relative proportions of the

**FIGURE 8.11** Relationship of mechanical properties, portrayed as deformation resistance, as a function of temperature for an amorphous thermoplastic, a 100% crystalline (theoretical) thermoplastic, and a partially crystallized thermoplastic.



two phases. The partially crystallized polymer exhibits features of both amorphous and fully crystallized plastics. Below  $T_g$ , it is elastic with deformation resistance sloping downward with rising temperatures. Above  $T_g$ , the amorphous portions of the polymer soften, while the crystalline portions remain intact. The bulk material exhibits properties that are generally viscoelastic. As  $T_m$  is reached, the crystals now melt, giving the polymer a liquid consistency; resistance to deformation is now due to the fluid's viscous properties. The degree to which the polymer assumes liquid characteristics at and above  $T_m$  depends on molecular weight and degree of polymerization. Higher DP and MW reduces flow of the polymer, making it more difficult to process by molding and similar shaping methods. This is a dilemma faced by those who select these materials because higher MW and DP mean higher strength.

**Physical Properties** Physical properties of materials are discussed in Chapter 4. In general, thermoplastic polymers have the following characteristics: (1) lower densities than metals or ceramics—typical specific gravities for polymers are around 1.2, for ceramics around 2.5, and for metals around 7.0; (2) much higher coefficient of thermal expansion—roughly five times the value for metals and 10 times the value for ceramics; (3) much lower melting temperatures; (4) specific heats that are two to four times those of metals and ceramics; (5) thermal conductivities that are about three orders of magnitude lower than those of metals; and (6) insulating electrical properties.

### 8.2.2 IMPORTANT COMMERCIAL THERMOPLASTICS

Thermoplastic products include molded and extruded items, fibers, films, sheets, packaging materials, paints, and varnishes. The starting raw materials for these products are normally supplied to the fabricator in the form of powders or pellets in bags, drums, or larger loads by truck or rail car. The most important TP polymers are discussed in alphabetical order in this section. For each plastic, Table 8.3 lists the chemical formula and selected properties. Approximate market share is given relative to all plastics (thermoplastic and thermosetting).



**TABLE • 8.3** Important commercial thermoplastic polymers: (a) acetal<sup>a</sup>.

Polymer:	Polyoxymethylene, also known as polyacetal $(\text{OCH}_2)_n$	Elongation:	25%–75%
Symbol:	POM	Specific gravity:	1.42
Polymerization method:	Step (condensation)	Glass transition temperature:	$-80^\circ\text{C}$ ( $-112^\circ\text{F}$ )
Degree of crystallinity:	75% typical	Melting temperature:	$180^\circ\text{C}$ ( $356^\circ\text{F}$ )
Modulus of elasticity:	3500 MPa (500,000 lb/in <sup>2</sup> )	Approximate market share:	Much less than 1%
Tensile strength:	70 MPa (10,000 lb/in <sup>2</sup> )		

<sup>a</sup>Table 8.3 is compiled from [2], [4], [6], [7], [9], [16], and other sources.

**Acetals** *Acetal* is the popular name given to **polyoxymethylene**, an engineering polymer prepared from formaldehyde ( $\text{CH}_2\text{O}$ ) with high stiffness, strength, toughness, and wear resistance. In addition, it has a high melting point, low moisture absorption, and is insoluble in common solvents at ambient temperatures. Because of this combination of properties, acetal resins are competitive with certain metals (e.g., brass and zinc) in automotive components such as door handles, pump housings, and similar parts; appliance hardware; and machinery components.

**Acrylics** The acrylics are polymers derived from acrylic acid ( $\text{C}_3\text{H}_4\text{O}_2$ ) and compounds originating from it. The most important thermoplastic in the acrylics group is **polymethylmethacrylate** (PMMA) or Plexiglas (Rohm & Haas's trade name for PMMA). Data on PMMA are listed in Table 8.3(b). It is an amorphous linear polymer. Its outstanding property is excellent transparency, which makes it competitive with glass in optical applications. Examples include automotive tail-light lenses, optical instruments, and aircraft windows. Its limitation when compared with glass is a much lower scratch resistance. Other uses of PMMA include floor waxes and emulsion latex paints. Another important use of acrylics is in fibers for textiles; polyacrylonitrile (PAN) is an example that goes by the more familiar trade names Orlon (DuPont) and Acrilan (Monsanto).

**Acrylonitrile–Butadiene–Styrene** ABS is called an engineering plastic due to its excellent combination of mechanical properties, some of which are listed in Table 8.3(c). ABS is a two-phase terpolymer, one phase being the hard copolymer styrene–acrylonitrile, while the other phase is styrene–butadiene copolymer that is rubbery. The name of the plastic is derived from the three starting monomers, which may be mixed in various proportions. Typical applications include components for automotive, appliances, and business machines; and pipes and fittings.

**TABLE • 8.3** (continued): (b) acrylics (thermoplastic).

Representative polymer:	Polymethylmethacrylate $(\text{C}_5\text{H}_8\text{O}_2)_n$	Elongation:	5
Symbol:	PMMA	Specific gravity:	1.2
Polymerization method:	Addition	Glass transition temperature:	$105^\circ\text{C}$ ( $221^\circ\text{F}$ )
Degree of crystallinity:	None (amorphous)	Melting temperature:	$200^\circ\text{C}$ ( $392^\circ\text{F}$ )
Modulus of elasticity:	2800 MPa (400,000 lb/in <sup>2</sup> )	Approximate market share:	About 1%
Tensile strength:	55 MPa (8,000 lb/in <sup>2</sup> )		

TABLE • 8.3 (continued): (c) acrylonitrile–butadiene–styrene.

Polymer:	Terpolymer of acrylonitrile ( $C_3H_3N$ ), butadiene ( $C_4H_6$ ), and styrene ( $C_8H_8$ ).		
Symbol:	ABS	Tensile strength:	50 MPa (7,000 lb/in <sup>2</sup> )
Polymerization method:	Addition	Elongation:	10%–30%
Degree of crystallinity:	None (amorphous)	Specific gravity:	1.06
Modulus of elasticity:	2100 MPa (300,000 lb/in <sup>2</sup> )	Approximate market share:	About 3%

**Cellulosics** *Cellulose* ( $C_6H_{10}O_5$ ) is a carbohydrate polymer commonly occurring in nature. Wood and cotton fibers, the chief industrial sources of cellulose, contain about 50% and 95% of the polymer, respectively. When cellulose is dissolved and reprecipitated during chemical processing, the resulting polymer is called *regenerated cellulose*. When this is produced as a fiber for apparel it is known as *rayon* (of course, cotton itself is a widely used fiber for apparel). When it is produced as a thin film, it is *cellophane*, a common packaging material. Cellulose itself cannot be used as a thermoplastic because it decomposes before melting when its temperature is increased. However, it can be combined with various compounds to form several plastics of commercial importance; examples are *cellulose acetate* (CA) and *cellulose acetate-butyrate* (CAB). CA, data for which are given in Table 8.3(d), is produced in the form of sheets (for wrapping), film (for photography), and molded parts. CAB is a better molding material than CA and has greater impact strength, lower moisture absorption, and better compatibility with plasticizers. The cellulosic thermoplastics share about 1% of the market.

**Fluoropolymers** *Polytetrafluorethylene* (PTFE), commonly known as *Teflon*, accounts for about 85% of the family of polymers called *fluoropolymers*, in which F atoms replace H atoms in the hydrocarbon chain. PTFE is extremely resistant to chemical and environmental attack, is unaffected by water, good heat resistance,

TABLE • 8.3 (continued): (d) cellulosics.

Representative polymer:	Cellulose acetate ( $C_6H_9O_5-COCH_3$ ) <sub>n</sub>		
Symbol:	CA	Elongation:	10%–50%
Polymerization method:	Step (condensation)	Specific gravity:	1.3
Degree of crystallinity:	Amorphous	Glass transition temperature:	105°C (221°F)
Modulus of elasticity:	2800 MPa (400,000 lb/in <sup>2</sup> )	Melting temperature:	306°C (583°F)
Tensile strength:	30 MPa (4,000 lb/in <sup>2</sup> )	Approximate market share:	Less than 1%

TABLE • 8.3 (continued): (e) fluoropolymers.

Representative polymer:	Polytetrafluorethylene ( $C_2F_4$ ) <sub>n</sub>		
Symbol:	PTFE	Elongation:	100%–300%
Polymerization method:	Addition	Specific gravity:	2.2
Degree of crystallinity:	About 95% crystalline	Glass transition temperature:	127°C (260°F)
Modulus of elasticity:	425 MPa (60,000 lb/in <sup>2</sup> )	Melting temperature:	327°C (620°F)
Tensile strength:	20 MPa (2500 lb/in <sup>2</sup> )	Approximate market share:	Less than 1%

TABLE • 8.3 (continued): (f) polyamides.

Representative polymer:	Nylon–6,6 ((CH <sub>2</sub> ) <sub>6</sub> (CONH) <sub>2</sub> (CH <sub>2</sub> ) <sub>4</sub> ) <sub>n</sub>	
Symbol:	PA–6,6	Elongation: 300%
Polymerization method:	Step (condensation)	Specific gravity: 1.14
Degree of crystallinity:	Highly crystalline	Glass transition temperature: 50°C (122°F)
Modulus of elasticity:	700 MPa (100,000 lb/in <sup>2</sup> )	Melting temperature: 260°C (500°F)
Tensile strength:	70 MPa (10,000 lb/in <sup>2</sup> )	Approximate market share: 1% for all polyamides

and very low coefficient of friction. These latter two properties have promoted its use in nonstick household cookware. Other applications that rely on the same property include nonlubricating bearings and similar components. PTFE also finds applications in chemical equipment and food processing.

**Polyamides** An important polymer family that forms characteristic amide linkages (CO–NH) during polymerization is the polyamides (PA). The most important members of the PA family are *nylons*, of which the two principal grades are nylon–6 and nylon 6,6 (the numbers are codes that indicate the number of carbon atoms in the monomer). The data given in Table 8.3(f) are for nylon–6,6, which was developed at DuPont in the 1930s. Properties of nylon-6, developed in Germany are similar. Nylon is strong, highly elastic, tough, abrasion resistant, and self-lubricating. It retains good mechanical properties at temperatures up to about 125°C (250°F). One shortcoming is that it absorbs water with an accompanying degradation in properties. The majority of applications of nylon (about 90%) are in fibers for carpets, apparel, and tire cord. The remainder (10%) are in engineering components; nylon is commonly a good substitute for metals in bearings, gears, and similar parts where strength and low friction are needed.

A second group of polyamides is the *aramids* (aromatic polyamides) of which **Kevlar** (DuPont trade name) is gaining in importance as a fiber in reinforced plastics. The reason for the interest in Kevlar is that its strength is the same as steel at 20% of the weight.

**Polycarbonate** Polycarbonate (PC) is noted for its generally excellent mechanical properties, which include high toughness and good creep resistance. It is one of the best thermoplastics for heat resistance—it can be used to temperatures around 125°C (250°F). In addition, it is transparent and fire resistant. Applications include molded machinery parts, housings for business machines, pump impellers, safety helmets, and compact disks (e.g., audio, video, and computer). It is also widely used in glazing (window and windshield) applications.

TABLE • 8.3 (continued): (g) polycarbonate.

Polymer:	Polycarbonate (C <sub>3</sub> H <sub>6</sub> (C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> ) <sub>n</sub>	
Symbol:	PC	Elongation: 110%
Polymerization method:	Step (condensation)	Specific gravity: 1.2
Degree of crystallinity:	Amorphous	Glass transition temperature: 150°C (302°F)
Modulus of elasticity:	2500 MPa (350,000 lb/in <sup>2</sup> )	Melting temperature: 230°C (446°F)
Tensile strength:	65 MPa (9500 lb/in <sup>2</sup> )	Approximate market share: Less than 1%

TABLE • 8.3 (continued): (h) polyesters (thermoplastic).

Representative polymer:	Polyethylene terephthalate ( $C_2H_4-C_8H_4O_4$ ) <sub>n</sub>	
Symbol:	PET	Elongation: 200%
Polymerization method:	Step (condensation)	Specific gravity: 1.3
Degree of crystallinity:	Amorphous to 30% crystalline	Glass transition temperature: 70°C (158°F)
Modulus of elasticity:	2300 MPa (325,000 lb/in <sup>2</sup> )	Melting temperature: 265°C (509°F)
Tensile strength:	55 MPa (8000 lb/in <sup>2</sup> )	Approximate market share: About 2%

**Polyesters** The polyesters form a family of polymers made up of the characteristic ester linkages (CO–O). They can be either thermoplastic or thermosetting, depending on whether cross-linking occurs. Of the thermoplastic polyesters, a representative example is *polyethylene terephthalate* (PET), data for which are compiled in the table. It can be either amorphous or partially crystallized (up to about 30%), depending on how it is cooled after shaping. Fast cooling favors the amorphous state, which is highly transparent. Significant applications include blow-molded beverage containers, photographic films, and magnetic recording tape. In addition, PET fibers are widely used in apparel. Polyester fibers have low moisture absorption and good deformation recovery, both of which make them ideal for “wash and wear” garments that resist wrinkling. The PET fibers are almost always blended with cotton or wool. Familiar trade names for polyester fibers include Dacron (DuPont) and Fortrel (Celanese).

**Polyethylene** Polyethylene (PE) was first synthesized in the 1930s, and today it accounts for the largest volume of all plastics. The features that make PE attractive as an engineering material are low cost, chemical inertness, and easy processing. Polyethylene is available in several grades, the most common of which are *low-density polyethylene* (LDPE) and *high-density polyethylene* (HDPE). The low-density grade is a highly branched polymer with lower crystallinity and density. Applications include squeezable bottles, frozen food bags, sheets, film, and wire insulation. HDPE has a more linear structure, with higher crystallinity and density. These differences make HDPE stiffer and stronger and give it a higher melting temperature. HDPE is used to produce bottles, pipes, and housewares. Both grades can be processed by most polymer shaping methods (Chapter 13). Properties for the two grades are given in Table 8.3(i).

TABLE • 8.3 (continued): (i) polyethylene.

Polyethylene:	( $C_2H_4$ ) <sub>n</sub> (low density)	( $C_2H_4$ ) <sub>n</sub> (high density)
Symbol:	LDPE	HDPE
Polymerization method:	Addition	Addition
Degree of crystallinity:	55% typical	92% typical
Modulus of elasticity:	140 MPa (20,000 lb/in <sup>2</sup> )	700 MPa (100,000 lb/in <sup>2</sup> )
Tensile strength:	15 MPa (2000 lb/in <sup>2</sup> )	30 MPa (4000 lb/in <sup>2</sup> )
Elongation:	100–500%	20–100%
Specific gravity:	0.92	0.96
Glass transition temperature:	–100°C (–148°F)	–115°C (–175°F)
Melting temperature:	115°C (240°F)	135°C (275°F)
Approximate market share:	About 20%	About 15%

TABLE • 8.3 (continued): (j) polypropylene.

Polymer:	Polypropylene (C <sub>3</sub> H <sub>6</sub> ) <sub>n</sub>	Elongation:	10%–500% <sup>a</sup>
Symbol:	PP	Specific gravity:	0.90
Polymerization method:	Addition	Glass transition temperature:	–20°C (–4°F)
Degree of crystallinity:	High, varies with processing	Melting temperature:	176°C (249°F)
Modulus of elasticity:	1400 MPa (200,000 lb/in <sup>2</sup> )	Approximate market share:	About 13%
Tensile strength:	35 MPa (5000 lb/in <sup>2</sup> )		

<sup>a</sup>Elongation depends on additives.

**Polypropylene** Polypropylene (PP) has become a major plastic, especially for injection molding, since its introduction in the late 1950s. PP can be synthesized in isotactic, syndiotactic, or atactic structures, the first of these being the most important and for which the characteristics are given in the table. It is the lightest of the plastics, and its strength-to-weight ratio is high. PP is frequently compared with HDPE because its cost and many of its properties are similar. However, the high melting point of polypropylene allows certain applications that preclude use of polyethylene—for example, components that must be sterilized. Other applications are injection molded parts for automotive and houseware, and fiber products for carpeting. A special application suited to polypropylene is one-piece hinges that can be subjected to a high number of flexing cycles without failure.

**Polystyrene** There are several polymers, copolymers, and terpolymers based on the monomer styrene (C<sub>8</sub>H<sub>8</sub>), of which polystyrene (PS) is used in the highest volume. It is a linear homopolymer with amorphous structure that is generally noted for its brittleness. PS is transparent, easily colored, and readily molded, but degrades at elevated temperatures and dissolves in various solvents. Because of its brittleness, some PS grades contain 5% to 15% rubber and the term *high-impact polystyrene* (HIPS) is used for these types. They have higher toughness, but transparency and tensile strength are reduced. In addition to injection molding applications (e.g., molded toys, housewares), polystyrene also finds uses in packaging in the form of PS foams.

**Polyvinylchloride** Polyvinylchloride (PVC) is a widely used plastic whose properties can be varied by combining additives with the polymer. In particular, plasticizers are used to achieve thermoplastics ranging from rigid PVC (no plasticizers) to flexible PVC (high proportions of plasticizer). The range of properties makes PVC a versatile polymer, with applications that include rigid pipe (used in construction, water and

TABLE • 8.3 (continued): (k) polystyrene.

Polymer:	Polystyrene (C <sub>8</sub> H <sub>8</sub> ) <sub>n</sub>	Elongation:	1%
Symbol:	PS	Specific gravity:	1.05
Polymerization method:	Addition	Glass transition temperature:	100°C (212°F)
Degree of crystallinity:	None (amorphous)	Melting temperature:	240°C (464°F)
Modulus of elasticity:	3200 MPa (450,000 lb/in <sup>2</sup> )	Approximate market share:	About 10%
Tensile strength:	50 MPa (7000 lb/in <sup>2</sup> )		

TABLE • 8.3 (continued): (I) polyvinylchloride.

Polymer:	Polyvinylchloride (C <sub>2</sub> H <sub>3</sub> Cl) <sub>n</sub>	Elongation:	2% with no plasticizer
Symbol:	PVC	Specific gravity:	1.40
Polymerization method:	Addition	Glass transition temperature:	81°C (178°F) <sup>a</sup>
Degree of crystallinity:	None (amorphous structure)	Melting temperature:	212°C (414°F)
Modulus of elasticity:	2800 MPa (400,000 lb/in <sup>2</sup> ) <sup>a</sup>	Approximate market share:	About 16%
Tensile strength:	40 MPa (6000 lb/in <sup>2</sup> )		

<sup>a</sup>With no plasticizer.

sewer systems, irrigation), fittings, wire and cable insulation, film, sheets, food packaging, flooring, and toys. PVC by itself is relatively unstable to heat and light, and stabilizers must be added to improve its resistance to these environmental conditions. Care must be taken in the production and handling of the vinyl chloride monomer used to polymerize PVC, due to its carcinogenic nature.

## 8.3 Thermosetting Polymers

Thermosetting (TS) polymers are distinguished by their highly cross-linked structure. In effect, the formed part (e.g., the pot handle or electrical switch cover) becomes one large macromolecule. Thermosets are always amorphous and exhibit no glass transition temperature. This section examines the general characteristics of the TS plastics and identify the important materials in this category.

### 8.3.1 GENERAL PROPERTIES AND CHARACTERISTICS

Owing to differences in chemistry and molecular structure, properties of thermosetting plastics are different from those of thermoplastics. In general, thermosets are (1) more rigid—modulus of elasticity is two to three times greater; (2) brittle—they possess virtually no ductility; (3) less soluble in common solvents; (4) capable of higher service temperatures; and (5) not capable of being remelted—instead they degrade or burn.

The differences in properties of the TS plastics are attributable to cross-linking, which forms a thermally stable, three-dimensional, covalently bonded structure within the molecule. Cross-linking is accomplished in three ways [7]:

1. **Temperature-activated systems**—In the most common systems, the changes are caused by heat supplied during the part shaping operation (e.g., molding). The starting material is a linear polymer in granular form supplied by the chemical plant. As heat is added, the material softens for molding; continued heating results in cross-linking of the polymer. The term *thermosetting* is most aptly applied to these polymers.
2. **Catalyst-activated systems**—Cross-linking in these systems occurs when small amounts of a catalyst are added to the polymer, which is in liquid form. Without the catalyst, the polymer remains stable; once combined with the catalyst, it changes into solid form.

3. **Mixing-activated systems**—Most epoxies are examples of these systems. The mixing of two chemicals results in a reaction that forms a cross-linked solid polymer. Elevated temperatures are sometimes used to accelerate the reactions.

The chemical reactions associated with cross-linking are called **curing** or **setting**. Curing is done at the fabrication plants that shape the parts rather than the chemical plants that supply the starting materials to the fabricator.

8.3.2 IMPORTANT THERMOSETTING POLYMERS

Thermosetting plastics are not as widely used as the thermoplastics, perhaps because of the added processing complications involved in curing the TS polymers. The largest volume thermosets are phenolic resins, whose annual volume is about 6% of the total plastics market. This is significantly less than polyethylene, the leading thermoplastic, whose volume is about 35% of the total. Technical data for these materials are given in Table 8.4. Market share data refer to total plastics (TP plus TS).

**Amino Resins** Amino plastics, characterized by the amino group (NH<sub>2</sub>), consist of two thermosetting polymers, urea-formaldehyde and melamine-formaldehyde, which are produced by the reaction of formaldehyde (CH<sub>2</sub>O) with either urea (CO(NH<sub>2</sub>)<sub>2</sub>) or melamine (C<sub>3</sub>H<sub>6</sub>N<sub>6</sub>), respectively. In commercial importance, the amino resins rank just below the other formaldehyde resin, phenol-formaldehyde, discussed below. **Urea-formaldehyde** is competitive with the phenols in certain applications, particularly as a plywood and particle-board adhesive. The resins are also used as a molding compound. It is slightly more expensive than the phenol material. **Melamine-formaldehyde** plastic is water resistant and is used for dishware and as a coating in laminated table and counter tops (Formica, trade name of Cyanamid Co.). When used as molding materials, amino plastics usually contain significant proportions of fillers, such as cellulose.

**Epoxies** Epoxy resins are based on a chemical group called the **epoxides**. The simplest formulation of epoxide is ethylene oxide (C<sub>2</sub>H<sub>3</sub>O). Epichlorohydrin (C<sub>3</sub>H<sub>5</sub>OCl) is a much more widely used epoxide for producing epoxy resins. Uncured, epoxides have a low degree of polymerization. To increase molecular weight and to cross-link the epoxide, a curing agent must be used. Possible curing agents include polyamines

TABLE • 8.4 Important commercial thermosetting polymers: (a) amino resins.

Representative polymer:	Melamine-formaldehyde		
Monomers:	Melamine (C <sub>3</sub> H <sub>6</sub> N <sub>6</sub> ) and formaldehyde (CH <sub>2</sub> O)		
Polymerization method:	Step (condensation)	Elongation:	Less than 1%
Modulus of elasticity:	9000 MPa (1,300,000 lb/in <sup>2</sup> )	Specific gravity:	1.5
Tensile strength:	50 MPa (7000 lb/in <sup>2</sup> )	Approx. market share:	About 4% for urea-formaldehyde and melamine-formaldehyde.

Table 8.4 is compiled from [2], [4], [6], [7], [9], [16], and other sources.



TABLE • 8.4 (continued): (b) epoxy.

Example chemistry:	Epichlorohydrin (C <sub>3</sub> H <sub>5</sub> OCl) plus curing agent such as triethylamine (C <sub>6</sub> H <sub>5</sub> –CH <sub>2</sub> N–(CH <sub>3</sub> ) <sub>2</sub> )	
Polymerization method:	Condensation	Elongation: 0%
Modulus of elasticity:	7000 MPa (1,000,000 lb/in <sup>2</sup> )	Specific gravity: 1.1
Tensile strength:	70 MPa (10,000 lb/in <sup>2</sup> )	Approx. market share: About 1%

TABLE • 8.4 (continued): (c) phenol formaldehyde.

Monomer ingredients:	Phenol (C <sub>6</sub> H <sub>5</sub> OH) and formaldehyde (CH <sub>2</sub> O)	
Polymerization method:	Step (condensation)	Elongation: Less than 1%
Modulus of elasticity:	7000 MPa (1,000,000 lb/in <sup>2</sup> )	Specific gravity: 1.4
Tensile strength:	70 MPa (10,000 lb/in <sup>2</sup> )	Approx. market share: 6%

and acid anhydrides. Cured epoxies are noted for strength, adhesion, and heat and chemical resistance. Applications include surface coatings, industrial flooring, glass fiber-reinforced composites, and adhesives. Insulating properties of epoxy thermosets make them useful in various electronic applications, such as encapsulation of integrated circuits and lamination of printed circuit boards.

**Phenolics** Phenol (C<sub>6</sub>H<sub>5</sub>OH) is an acidic compound that can be reacted with aldehydes (dehydrogenated alcohols), formaldehyde (CH<sub>2</sub>O) being the most reactive. **Phenol-formaldehyde** is the most important of the phenolic polymers; it was first commercialized around 1900 under the trade name **Bakelite**. It is almost always combined with fillers such as wood flour, cellulose fibers, and minerals when used as a molding material. It is brittle, possesses good thermal, chemical, and dimensional stability. Its capacity to accept colorants is limited—it is available only in dark colors. Molded products constitute only about 10% of total phenolics use. Other applications include adhesives for plywood, printed circuit boards, counter tops, and bonding material for brake linings and abrasive wheels.

**Polyesters** Polyesters, which contain the characteristic ester linkages (CO–O), can be thermosetting as well as thermoplastic. Thermosetting polyesters are used largely in reinforced plastics (composites) to fabricate large items such as pipes, tanks, boat hulls, auto body parts, and construction panels. They can also be used in various molding processes to produce smaller parts. Synthesis of the starting polymer involves reaction of an acid or anhydride such as maleic anhydride (C<sub>4</sub>H<sub>2</sub>O<sub>3</sub>) with a glycol such as ethylene glycol (C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>). This produces an **unsaturated polyester** of

TABLE • 8.4 (continued): (d) unsaturated polyester.

Example chemistry:	Maleic anhydride (C <sub>4</sub> H <sub>2</sub> O <sub>3</sub> ) and ethylene glycol (C <sub>2</sub> H <sub>6</sub> O <sub>2</sub> ) plus styrene (C <sub>8</sub> H <sub>8</sub> )	
Polymerization method:	Step (condensation)	Elongation: 0%
Modulus of elasticity:	7000 MPa (1,000,000 lb/in <sup>2</sup> )	Specific gravity: 1.1
Tensile strength:	30 MPa (4000 lb/in <sup>2</sup> )	Approx. market share: 3%

**TABLE • 8.4** (continued): (e) polyimides.

Starting monomers:	Pyromellitic dianhydride (C <sub>6</sub> H <sub>2</sub> (C <sub>2</sub> O <sub>3</sub> ) <sub>2</sub> ), 4,4'-oxydianiline (O(C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub> ) <sub>2</sub> )	
Polymerization method:	Condensation	Elongation: 5%
Modulus of elasticity:	3200 MPa (460,000 lb/in <sup>2</sup> )	Specific gravity: 1.43
Tensile strength:	80 MPa (12,000 lb/in <sup>2</sup> )	Approx. market share: <1%

relatively low molecular weight (MW = 1000 to 3000). This ingredient is mixed with a monomer capable of polymerizing and cross-linking with the polyester. Styrene (C<sub>8</sub>H<sub>8</sub>) is commonly used for this purpose, in proportions of 30% to 50%. A third component, called an inhibitor, is added to prevent premature cross-linking. This mixture forms the polyester resin system that is supplied to the fabricator. Polyesters are cured either by heat (temperature-activated systems), or by means of a catalyst added to the polyester resin (catalyst-activated systems). Curing is done at the time of fabrication (molding or other forming process) and results in cross-linking of the polymer.

An important class of polyesters are the *alkyd* resins (the name derived by abbreviating and combining the words alcohol and *acid* and changing a few letters). They are used primarily as bases for paints, varnishes, and lacquers. Alkyd molding compounds are also available, but their applications are limited.

**Polyimides** These plastics are available as both thermoplastics and thermosets, but the TS types are more important commercially. They are available under brand names such as Kapton (Dupont) and Kaptrex (Professional Plastics) in several forms including tapes, films, coatings, and molding resins. TS polyimides (PI) are noted for chemical resistance, high tensile strength and stiffness, and stability at elevated temperatures. They are called high-temperature polymers due to their excellent heat resistance. Applications that exploit these properties include insulating films, molded parts used in elevated temperature service, flexible cables in laptop computers, medical tubing, and fibers for protective clothing.

**Polyurethanes** This includes a large family of polymers, all characterized by the urethane group (NHCOO) in their structure. The chemistry of the polyurethanes is complex, and there are many chemical varieties in the family. The characteristic feature is the reaction of a *polyol*, whose molecules contain hydroxyl (OH) groups,

**TABLE • 8.4** (continued): (f) polyurethane.

Polymer:	Polyurethane is formed by the reaction of a polyol and an isocyanate. Chemistry varies significantly.	
Polymerization method:	Step (condensation)	Elongation: Depends on cross-linking.
Modulus of elasticity:	Depends on chemistry and processing.	Specific gravity: 1.2
Tensile strength:	30 MPa (4000 lb/in <sup>2</sup> ) <sup>a</sup>	Approx. market share: About 4%, including elastomers

<sup>a</sup>Typical for highly cross-linked polyurethane.

TABLE • 8.4 (continued): (g) silicone thermosetting resins.

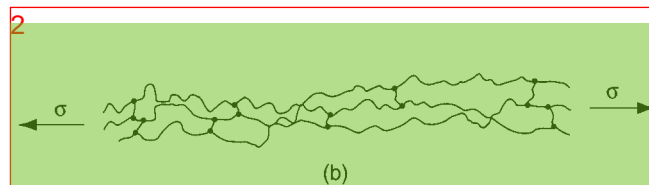
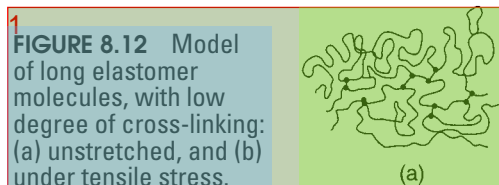
2	Example chemistry: $((\text{CH}_3)_6\text{-SiO})_n$ Polymerization method: Step (condensation), usually Tensile strength: 30 MPa (4000 lb/in <sup>2</sup> )	3	Elongation: 0% Specific gravity: 1.65 Approx. market share: Less than 1%
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such as butylene ether glycol ( $\text{C}_4\text{H}_{10}\text{O}_2$ ); and an *isocyanate*, such as diphenylmethane diisocyanate ( $\text{C}_{15}\text{H}_{10}\text{O}_2\text{N}_2$ ). Through variations in chemistry, cross-linking, and processing, polyurethanes can be thermoplastic, thermosetting, or elastomeric materials, the latter two being the most important commercially. The largest application of polyurethane is in foams. These can range between elastomeric and rigid, the latter being more highly cross-linked. Rigid foams are used as a filler material in hollow construction panels and refrigerator walls. In these types of applications, the material provides excellent thermal insulation, adds rigidity to the structure, and does not absorb water in significant amounts. Many paints, varnishes, and similar coating materials are based on urethane systems. Polyurethane elastomers are discussed in Section 8.4.

**Silicones** Silicones are inorganic and semi-inorganic polymers, distinguished by the presence of the repeating siloxane link ( $\text{-Si-O-}$ ) in their molecular structure. A typical formulation combines the methyl radical ( $\text{CH}_3$ ) with ( $\text{SiO}$ ) in various proportions to obtain the repeating unit  $\text{--}((\text{CH}_3)_m\text{-SiO})\text{--}$ , where *m* establishes the proportionality. By variations in composition and processing, polysiloxanes can be produced in three forms: (1) fluids, (2) elastomers, and (3) thermosetting resins. Fluids are low molecular weight polymers used for lubricants, polishes, waxes, and other liquid products—not really polymers in the sense of this chapter, but important commercially nevertheless. Silicone elastomers, covered in Section 8.4, and thermosetting silicones, treated here, are cross-linked. When highly cross-linked, polysiloxanes form rigid resin systems used for paints, varnishes, and other coatings; and laminates such as printed circuit boards. They are also used as molding materials for electrical parts. Curing is accomplished by heating or by allowing the solvents containing the polymers to evaporate. Silicones are noted for their good heat resistance and water repellence, but their mechanical strength is not as great as other cross-linked polymers. Data in Table 8.4(g) are for a typical silicone thermosetting polymer.

8.4 Elastomers

Elastomers are polymers capable of large elastic deformation when subjected to relatively low stresses. Some elastomers can withstand extensions of 500% or more and still return to their original shape. The more popular term for elastomer is, of course, rubber. Rubbers can be divided into two categories: (1) natural rubber, derived from certain biological plants; and (2) synthetic elastomers, produced by polymerization processes similar to those used for thermoplastic and thermosetting polymers. Before discussing natural and synthetic rubbers, consider the general characteristics of elastomers.



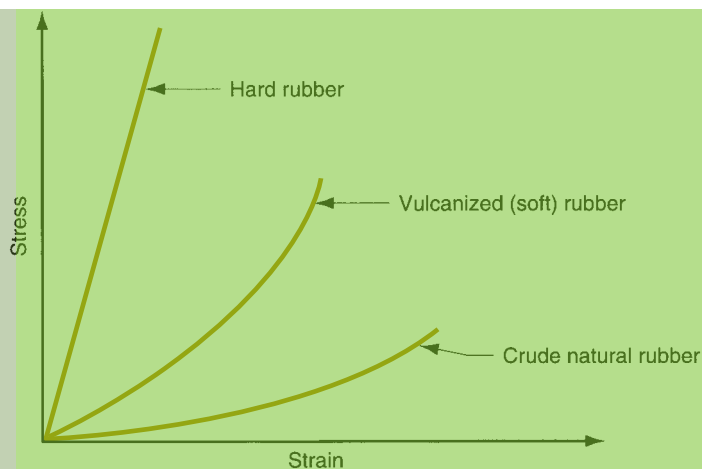
### 8.4.1 CHARACTERISTICS OF ELASTOMERS

Elastomers consist of long-chain molecules that are cross-linked. They owe their impressive elastic properties to the combination of two features: (1) the long molecules are tightly kinked when unstretched, and (2) the degree of cross-linking is substantially below that of the thermosets. These features are illustrated in the model of Figure 8.12(a), which shows a tightly kinked cross-linked molecule under no stress.

When the material is stretched, the molecules are forced to uncoil and straighten as shown in Figure 8.12(b). The molecules' natural resistance to uncoiling provides the initial elastic modulus of the aggregate material. As further strain is experienced, the covalent bonds of the cross-linked molecules begin to play an increasing role in the modulus, and the stiffness increases as illustrated in Figure 8.13. With greater cross-linking, the elastomer becomes stiffer and its modulus of elasticity is more linear. These characteristics are shown in the figure by the stress-strain curves for three grades of rubber: natural crude rubber, whose cross-linking is very low; cured (vulcanized) rubber with low-to-medium cross-linking; and hard rubber (ebonite), whose high degree of cross-linking transforms it into a thermosetting plastic.

For a polymer to exhibit elastomeric properties, it must be amorphous in the unstretched condition, and its temperature must be above  $T_g$ . If below the glass transition temperature, the material is hard and brittle; above  $T_g$  the polymer is in the "rubbery" state. Any amorphous thermoplastic polymer will exhibit elastomeric properties above  $T_g$  for a short time, because its linear molecules are always coiled to some extent, thus allowing for elastic extension. It is the absence of cross-linking in TP polymers that prevents them from being truly elastic; instead they exhibit viscoelastic behavior.

Curing is required to effect cross-linking in most of the common elastomers today. The term for curing used in the context of natural rubber (and certain synthetic rubbers) is **vulcanization**, which involves the formation of chemical cross-links between the polymer chains. Typical cross-linking in rubber is 1 to 10 links per 100 carbon



**FIGURE 8.13** Increase in stiffness as a function of strain for three grades of rubber: natural rubber, vulcanized rubber, and hard rubber.

atoms in the linear polymer chain, depending on the degree of stiffness desired in the material. This is considerably less than the degree of cross-linking in thermosets.

An alternative method of curing involves the use of starting chemicals that react when mixed (sometimes requiring a catalyst or heat) to form elastomers with relatively infrequent cross-links between molecules. These synthetic rubbers are known as **reactive system elastomers**. Certain polymers that cure by this means, such as urethanes and silicones, can be classified as either thermosets or elastomers, depending on the degree of cross-linking achieved during the reaction.

A relatively new class of elastomers, called **thermoplastic elastomers**, possesses elastomeric properties that result from the mixture of two phases, both thermoplastic. One is above its  $T_g$  at room temperature while the other is below its  $T_g$ . Thus, the polymer includes soft rubbery regions intermixed with hard particles that act as cross-links. The composite material is elastic in its mechanical behavior, although not as extensible as most other elastomers. Because both phases are thermoplastic, the aggregate material can be heated above its  $T_m$  for forming, using processes that are generally more economical than those used for rubber.

The elastomers are discussed in the following two sections. The first deals with natural rubber and how it is vulcanized to create a useful commercial material; the second examines the synthetic rubbers.

## 8.4.2 NATURAL RUBBER

Natural rubber (NR) consists primarily of polyisoprene, a high-molecular-weight polymer of isoprene ( $C_5H_8$ ). It is derived from latex, a milky substance produced by various plants, the most important of which is the rubber tree (*Hevea brasiliensis*) that grows in tropical climates (Historical Note 8.2). Latex is a water emulsion of polyisoprene (about one third by weight), plus various other ingredients. Rubber is extracted from the latex by various methods (e.g., coagulation, drying, and spraying) that remove the water.

### Historical Note 8.2 *Natural rubber*

The first use of natural rubber seems to have been in the form of rubber balls used for sport by the natives of Central and South America at least 500 hundred years ago. Columbus noted this during his second voyage to the New World in 1493–96. The balls were made from the dried gum of a rubber tree. The first white men in South America called the tree **caoutchouc**, which was their way of pronouncing the Indian name for it. The name **rubber** came from the English chemist Joseph Priestley, who discovered (around 1770) that gum rubber would “rub” away pencil marks.

Early rubber goods were less than satisfactory; they melted in summer heat and hardened in winter cold. One of those in the business of making and selling rubber goods was American Charles Goodyear. Recognizing the deficiencies of the natural material, he experimented with ways to improve its properties and discovered that rubber could be cured by heating

with sulfur. This was in 1839, and the process, later called **vulcanization**, was patented by him in 1844.

Vulcanization and the emerging demand for rubber products led to tremendous growth in rubber production and the industry that supported it. In 1876, Henry Wickham collected thousands of rubber tree seeds from the Brazilian jungle and planted them in England; the sprouts were later transplanted to Ceylon and Malaya (then British colonies) to form rubber plantations. Soon, other countries in the region followed the British example. Southeast Asia became the base of the rubber industry.

In 1888, a British veterinary surgeon named John Dunlop patented pneumatic tires for bicycles. By the twentieth century, the motorcar industry was developing in the United States and Europe. Together, the automobile and rubber industries grew to occupy positions of unimagined importance.

**TABLE • 8.5** Characteristics and typical properties of vulcanized rubber.

Polymer: Polyisoprene (C <sub>5</sub> H <sub>8</sub> ) <sub>n</sub>	Specific gravity: 0.93
Symbol: NR	High temperature limit: 80°C (180°F)
Modulus of elasticity: 18 MPa (2500 lb/in <sup>2</sup> ) at 300% elongation	Low temperature limit: −50°C (−60°F)
Tensile strength: 25 MPa (3500 lb/in <sup>2</sup> )	Approx. market share: 22%
Elongation: 700% at failure	

Compiled from [2], [6], [9], and other sources.

Natural crude rubber (without vulcanization) is sticky in hot weather, but stiff and brittle in cold weather. To form an elastomer with useful properties, natural rubber must be vulcanized. Traditionally, vulcanization has been accomplished by mixing small amounts of sulfur and other chemicals with the crude rubber and heating. The chemical effect of vulcanization is cross-linking; the mechanical result is increased strength and stiffness, yet maintenance of extensibility. The dramatic change in properties caused by vulcanization can be seen in the stress-strain curves of Figure 8.13.

Sulfur alone can cause cross-linking, but the process is slow, taking hours to complete. Other chemicals are added to sulfur during vulcanization to accelerate the process and serve other beneficial functions. Also, rubber can be vulcanized using chemicals other than sulfur. Today, curing times have been reduced significantly compared to the original sulfur curing of years ago.

As an engineering material, vulcanized rubber is noted among elastomers for its high tensile strength, tear strength, resilience (capacity to recover shape after deformation), and resistance to wear and fatigue. Its weaknesses are that it degrades when subjected to heat, sunlight, oxygen, ozone, and oil. Some of these limitations can be reduced through the use of additives. Typical properties and other data for vulcanized natural rubber are listed in Table 8.5. Market share is relative to total annual rubber volume, natural plus synthetic. Rubber volume is about 15% of total polymer market.

The largest single market for natural rubber is automotive tires. In tires, carbon black is an important additive; it reinforces the rubber, serving to increase tensile strength and resistance to tearing and abrasion. Other products made of rubber include shoe soles, bushings, seals, and shock-absorbing components. In each case, the rubber is compounded to achieve the specific properties required in the application. Besides carbon black, other additives used in rubber and some of the synthetic elastomers include clay, kaolin, silica, talc, and calcium carbonate, as well as chemicals that accelerate and promote vulcanization.

### 8.4.3 SYNTHETIC RUBBERS

Today, the tonnage of synthetic rubbers is more than three times that of natural rubber. Development of these synthetic materials was motivated largely by the world wars when NR was difficult to obtain (Historical Note 8.3). The most important of the synthetics is styrene-butadiene rubber (SBR), a copolymer of butadiene (C<sub>4</sub>H<sub>6</sub>) and styrene (C<sub>8</sub>H<sub>8</sub>). As with most other polymers, the predominant raw material for the synthetic rubbers is petroleum. Only the synthetic rubbers of greatest commercial

Historical Note 8.3 Synthetic rubbers

In 1826, Faraday recognized the formula of natural rubber to be  $C_5H_8$ . Subsequent attempts at reproducing this molecule over many years were generally unsuccessful. Regrettably, it was the world wars that created the necessity which became the mother of invention for synthetic rubber. In World War I, the Germans, denied access to natural rubber, developed a methyl-based substitute. This material was not very successful, but it marks the first large-scale production of synthetic rubber.

After World War I, the price of natural rubber was so low that many attempts at fabricating synthetics were abandoned. However, the Germans, perhaps anticipating a future conflict, renewed their development efforts. The firm I.G. Farben developed two synthetic rubbers, starting in the early 1930s, called Buna-S and Buna-N. **Buna** is derived from **butadiene** ( $C_4H_6$ ), which has become the critical ingredient in many modern synthetic rubbers, and **Na**, the symbol for sodium, used to accelerate or catalyze the polymerization process (**Natrium** is the

German word for sodium). The symbol **S** in Buna-S stands for styrene. Buna-S is the copolymer known today as **styrene-butadiene rubber**, or SBR. The **N** in Buna-N stands for acryloNitrile, and the synthetic rubber is called **nitrile rubber** in current usage.

Other efforts included the work at the DuPont Company in the United States, which led to the development of polychloroprene, first marketed in 1932 under the name Duprene, later changed to **Neoprene**, its current name.

During World War II, the Japanese cut off the supply of natural rubber from Southeast Asia to the United States. Production of Buna-S synthetic rubber was begun on a large scale in America. The federal government preferred to use the name **GR-S** (Government Rubber-Styrene) rather than Buna-S (the German name). By 1944, the United States was outproducing Germany in SBR 10-to-1. Since the early 1960s, worldwide production of synthetic rubbers has exceeded that of natural rubbers.

importance are discussed here. Technical data are presented in Table 8.6. Market share data are for total volume of natural and synthetic rubbers. About 10% of total volume of rubber production is reclaimed; thus, total tonnages in Tables 8.5 and 8.6 do not sum to 100%.

**Butadiene Rubber** *Polybutadiene* (BR) is important mainly in combination with other rubbers. It is compounded with natural rubber and with styrene (styrene-butadiene rubber is discussed later) in the production of automotive tires. Without compounding, the tear resistance, tensile strength, and ease of processing of polybutadiene are less than desirable.

**Butyl Rubber** Butyl rubber is a copolymer of polyisobutylene (98–99%) and polyisoprene (1–2%). It can be vulcanized to provide a rubber with very low air permeability, which has led to applications in inflatable products such as inner tubes, liners in tubeless tires, and sporting goods.

TABLE • 8.6 Characteristics and typical properties of synthetic rubbers: (a) butadiene rubber.

5	Polymer: Polybutadiene ( $C_4H_6$ ) <sub>n</sub> Symbol: BR Tensile strength: 15 MPa (2000 lb/in <sup>2</sup> ) Elongation: 500% at failure	6	Specific gravity: 0.93 High temperature limit: 100°C (210°F) Low temperature limit: –50°C (–60°F) Approx. market share: 12%
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Table 8.6 is compiled from [2], [6], [9], [11], and other sources.



**TABLE • 8.6** (continued): (b) butyl rubber.

Polymer: Copolymer of isobutylene (C <sub>4</sub> H <sub>8</sub> ) <sub>n</sub> and isoprene (C <sub>5</sub> H <sub>8</sub> ) <sub>n</sub>	
Symbol: PIB	Specific gravity: 0.92
Modulus of elasticity: 7 MPa (1000 lb/in <sup>2</sup> ) at 300% elongation	High temperature limit: 110°C (220°F)
Tensile strength: 20 MPa (3000 lb/in <sup>2</sup> )	Low temperature limit: −50°C (−60°F)
Elongation: 700%	Approx. market share: about 3%

**TABLE • 8.6** (continued): (c) chloroprene rubber (neoprene).

Polymer:	Polychloroprene (C <sub>4</sub> H <sub>5</sub> Cl) <sub>n</sub>		
Symbol:	CR	Specific gravity:	1.23
Modulus of elasticity:	7 MPa (1000 lb/in <sup>2</sup> ) at 300% elongation	High temperature limit:	120°C (250°F)
Tensile strength:	25 MPa (3500 lb/in <sup>2</sup> )	Low temperature limit:	−20°C (−10°F)
Elongation:	500% at failure	Approx. market share:	2%

**Chloroprene Rubber** Polychloroprene was one of the first synthetic rubbers to be developed (early 1930s). Commonly known today as **Neoprene**, it is an important special-purpose rubber. It crystallizes when strained to provide good mechanical properties. Chloroprene rubber (CR) is more resistant to oils, weather, ozone, heat, and flame (chlorine makes this rubber self-extinguishing) than NR, but somewhat more expensive. Its applications include fuel hoses (and other automotive parts), conveyor belts, and gaskets, but not tires.

**Ethylene–Propylene Rubber** Polymerization of ethylene and propylene with small proportions (3–8%) of a diene monomer produces the terpolymer ethylene–propylene–diene (EPDM), a useful synthetic rubber. Applications are for parts mostly in the automotive industry other than tires. Other uses are wire and cable insulation.

**Isoprene Rubber** Isoprene can be polymerized to synthesize a chemical equivalent of natural rubber. Synthetic (unvulcanized) **polyisoprene** is softer and more easily molded than raw natural rubber. Applications of the synthetic material are similar to those of its natural counterpart, car tires being the largest single market. It is also used for footwear, conveyor belts, and caulking compound. Cost per unit weight is about 35% higher than for NR.

**TABLE • 8.6** (continued): (d) ethylene–propylene–diene rubber.

Representative polymer:		Terpolymer of ethylene (C <sub>2</sub> H <sub>4</sub> ), propylene (C <sub>3</sub> H <sub>6</sub> ), and a diene monomer (3–8%) for cross-linking.			
2	Symbol:	EPDM	3	Specific gravity:	0.86
	Tensile strength:	15 MPa (2000 lb/in <sup>2</sup> )		High temperature limit:	150°C (300°F)
	Elongation:	300% at failure		Low temperature limit:	–50°C (–60°F)
				Approx. market share:	5%

TABLE • 8.6 (continued): (e) isoprene rubber (synthetic).

Polymer:	Polyisoprene ( $C_5H_8$ ) <sub>n</sub>	Specific gravity:	0.93
Symbol:	IR	High temperature limit:	80°C (180°F)
Modulus of elasticity:	17 MPa (2500 lb/in <sup>2</sup> ) at 300% elongation	Low temperature limit:	−50°C (−60°F)
Tensile strength:	25 MPa (3500 lb/in <sup>2</sup> )	Approx. market share:	2%
Elongation:	500% at failure		

TABLE • 8.6 (continued): (f) nitrile rubber.

Polymer:	Copolymer of butadiene ( $C_4H_6$ ) and acrylonitrile ( $C_3H_3N$ )	Specific gravity:	1.00 (without fillers)
Symbol:	NBR	High temperature limit:	120°C (250°F)
Modulus of elasticity:	10 MPa (1500 lb/in <sup>2</sup> ) at 300% elongation	Low temperature limit:	−50°F (−60°F)
Tensile strength:	30 MPa (4000 lb/in <sup>2</sup> )	Approx. market share:	2%
Elongation:	500% at failure		

**Nitrile Rubber** This is a vulcanizable copolymer of butadiene (50–75%) and acrylonitrile (25–50%). Its more technical name is *butadiene-acrylonitrile rubber*. It has good strength and resistance to abrasion, oil, gasoline, and water. These properties make it ideal for applications such as gasoline hoses and seals, and also for footwear.

**Polyurethanes** Thermosetting polyurethanes with minimum cross-linking are elastomers, most commonly produced as flexible foams. In this form, they are widely used as cushion materials for furniture and automobile seats. Unfoamed polyurethane can be molded into products ranging from shoe soles to car bumpers, with cross-linking adjusted to achieve the desired properties for the application. With no cross-linking, the material is a thermoplastic elastomer that can be injection molded. As an elastomer or thermoset, reaction injection molding and other shaping methods are used.

**Silicones** Like the polyurethanes, silicones can be elastomeric or thermosetting, depending on the degree of cross-linking. Silicone elastomers are noted for the wide temperature range over which they can be used. Their resistance to oils is poor. The silicones possess various chemistries, the most common being *polydimethylsiloxane*, Table 8.6(h). To obtain acceptable mechanical properties, silicone elastomers must

TABLE • 8.6 (continued): (g) polyurethane.

4	Polymer:	Polyurethane (chemistry varies)	5	Specific gravity:	1.25
	Symbol:	PUR		High temperature limit:	100°C (210°F)
	Modulus of elasticity:	10 MPa (1200 lb/in <sup>2</sup> ) at 300% elongation		Low temperature limit:	−50°C (−60°F)
	Tensile strength:	60 MPa (8000 lb/in <sup>2</sup> )		Approx. market share:	listed under thermosets, Table 8.4(e)
	Elongation:	700% at failure			

**TABLE • 8.6** (continued): (h) silicone rubber.

Representative polymer:	Polydimethylsiloxane (SiO(CH <sub>3</sub> ) <sub>2</sub> ) <sub>n</sub>	
Symbol:	VMQ	Specific gravity: 0.98
Tensile strength:	10 MPa (1500 lb/in <sup>2</sup> )	High temperature limit: 230°C (450°F)
Elongation:	700% at failure	Low temperature limit: −50°C (−60°F)
		Approx. market share: Less than 1%

**TABLE • 8.6** (continued): (i) styrene–butadiene rubber

Polymer:	Copolymer of styrene (C <sub>8</sub> H <sub>8</sub> ) and butadiene (C <sub>4</sub> H <sub>6</sub> )	
Symbol:	SBR	Specific gravity: 0.94
Modulus of elasticity:	17 MPa (2500 lb/in <sup>2</sup> ) at 300% elongation	High temperature limit: 110°C (230°F)
Tensile strength:	20 MPa (3000 lb/in <sup>2</sup> ) reinforced	Low temperature limit: −50°C (−60°F)
Elongation:	700% at failure	Approx. market share: Slightly less than 30%

be reinforced, usually with fine silica powders. Owing to their high cost, they are considered special-purpose rubbers for applications such as gaskets, seals, wire and cable insulation, prosthetic devices, and bases for caulking materials.

**Styrene–Butadiene Rubber** SBR is a random copolymer of styrene (about 25%) and butadiene (about 75%). It was originally developed in Germany as Buna-S rubber before World War II. Today, it is the largest tonnage elastomer, totaling about 40% of all rubbers produced (natural rubber is second in tonnage). Its attractive features are low cost, resistance to abrasion, and better uniformity than NR. When reinforced with carbon black and vulcanized, its characteristics and applications are very similar to those of natural rubber. Cost is also similar. A close comparison of properties reveals that most of its mechanical properties except wear resistance are inferior to NR, but its resistance to heat aging, ozone, weather, and oils is superior. Applications include automotive tires, footwear, and wire and cable insulation. A material chemically related to SBR is styrene–butadiene–styrene block copolymer, a thermoplastic elastomer discussed below.

**Thermoplastic Elastomers** As previously described, a thermoplastic elastomer (TPE) is a thermoplastic that behaves like an elastomer. It constitutes a family of polymers that is a fast-growing segment of the elastomer market. TPEs derive their elastomeric properties not from chemical cross-links, but from physical connections between soft and hard phases that make up the material. Thermoplastic elastomers include *styrene–butadiene–styrene* (SBS), a block copolymer as opposed to styrene–butadiene rubber (SBR) which is a random copolymer (Section 8.1.2); *thermoplastic polyurethanes*; *thermoplastic polyester copolymers*; and other copolymers and polymer blends. Table 8.6(j) gives data on SBS. The chemistry and structure of these materials are generally complex, involving two materials that are incompatible so that they form distinct phases whose room temperature properties are different. Owing to their thermoplasticity, the TPEs cannot match conventional cross-linked elastomers in elevated temperature strength and creep resistance. Typical applications include

**TABLE • 8.6** (continued): (j) thermoplastic elastomers (TPE).

Representative polymer:	Styrene–butadiene–styrene block copolymer		
Symbol:	SBS (also YSBR)	Specific gravity:	1.0
Tensile strength:	14 MPa (2000 lb/in <sup>2</sup> )	High temperature limit:	65°C (150°F)
Elongation:	400%	Low temperature limit:	–50°C (–60°F)
		Approx. market share:	12%

footwear, rubber bands, extruded tubing, wire coating, and molded parts for automotive and other uses in which elastomeric properties are required. TPEs are not suitable for tires.

8.5

Polymer Recycling and Biodegradability

It is estimated that since the 1950s, 1 billion tons of plastic have been discarded as garbage.<sup>2</sup> This plastic trash could be around for centuries, because the primary bonds that make plastics so durable also make them resistant to degradation by the environmental and biological processes of nature. This section considers two polymer topics related to environmental concerns: (1) recycling of polymer products and (2) biodegradable plastics.

8.5.1

POLYMER RECYCLING

Approximately 200 million tons of plastic products are made annually throughout the world, more than one-eighth of which are produced in the United States.<sup>3</sup> Only about 6% of the U.S. tonnage is recycled as plastic waste; the rest either remains in products and/or ends up in garbage landfills. **Recycling** means recovering the discarded plastic items and reprocessing them into new products, in some cases products that are quite different from the original discarded items.

In general the recycling of plastics is more difficult than recycling of glass and metal products. There are several reasons for this: (1) compared to plastic parts, many recycled metal items are much larger and heavier (e.g., structural steel from buildings and bridges, steel car body frames), so the economics of recycling are more favorable for recycling metals; most plastic items are lightweight; (2) compared to plastics, which come in a variety of chemical compositions that do not mix well, glass products are all based on silicon dioxide; and (3) many plastic products contain fillers, dyes, and other additives that cannot be readily separated from the polymer itself. Of course, a common problem in all recycling efforts is the fluctuation in prices of recycled materials.

To cope with the problem of mixing different types of plastics and to promote recycling of plastics, the Plastic Identification Code (PIC) was developed by the Society of the Plastics Industry. The code is a symbol consisting of a triangle formed by three bent arrows enclosing a number. It is printed or molded on the plastic item.

<sup>2</sup>[en.wikipedia.org/wiki/Plastic](http://en.wikipedia.org/wiki/Plastic).

<sup>3</sup>According to the Society of Plastics Engineers, as reported in [en.wikipedia.org/wiki/Biodegradable\\_plastic](http://en.wikipedia.org/wiki/Biodegradable_plastic).

The number identifies the plastic for recycling purposes. The seven plastics (all thermoplastics) used in the PIC recycling program are (1) polyethylene terephthalate, used in 2-liter beverage containers; (2) high-density polyethylene, used in milk jugs and shopping bags; (3) polyvinyl chloride, used in juice bottles and PVC pipes; (4) low-density polyethylene, used in squeezable bottles and flexible container lids; (5) polypropylene, used in yogurt and margarine containers; (6) polystyrene, used in egg cartons, disposable plates, cups, and utensils, and as foamed packing materials; and (7) other, such as polycarbonate or ABS. The PIC facilitates the separation of items made from the different types of plastics for reprocessing. Nevertheless, sorting the plastics is a labor-intensive activity.

Once separated, the thermoplastic items can be readily reprocessed into new products by remelting. This is not the case with thermosets and rubbers because of the cross-linking in these polymers. Thus, these materials must be recycled and reprocessed by different means. Recycled thermosets are typically ground up into particulate matter and used as fillers, for example, in molded plastic parts. Most recycled rubber comes from used tires. While some of these tires are retreaded, others are ground up into granules in forms such as chunks and nuggets that can be used for landscape mulch, playgrounds, and similar purposes.

### 8.5.2 BIODEGRADABLE POLYMERS

Another approach that addresses the environmental concerns about plastics involves the development of biodegradable plastics, which are defined as plastics that are decomposed by the actions of microorganisms occurring in nature, such as bacteria and fungi. Conventional plastic products usually consist of a combination of a petroleum-based polymer and a filler (Section 8.1.5). In effect, the material is a polymer-matrix composite (Section 9.4). The purpose of the filler is to improve mechanical properties and/or reduce material cost. In many cases, neither the polymer nor the filler are biodegradable. Distinguished from these non-biodegradable plastics are two forms of biodegradable plastics: (1) partially degradable and (2) completely degradable.

**Partially biodegradable plastics** consist of a conventional polymer and a natural filler. The polymer matrix is petroleum-based, which is non-biodegradable, but the natural filler can be consumed by microorganisms (e.g., in a landfill), thus converting the polymer into a sponge-like structure and possibly leading to its degradation over time.

The plastics of greatest interest from an environmental viewpoint are the **completely biodegradable plastics** (a.k.a. **bioplastics**) consisting of a polymer and filler that are both derived from natural and renewable sources. Various agricultural products are used as the raw materials for biodegradable plastics. A common polymeric starting material is starch, which is a major component in corn, wheat, rice, and potatoes. It consists of the two polymers amylose and amylopectin. Starch can be used to synthesize several thermoplastic materials that are processable by conventional plastic shaping methods, such as extrusion and injection molding (Chapter 13). Another starting point for biodegradable plastics involves fermentation of either corn starch or sugar cane to produce lactic acid, which can be polymerized to form polylactide, another thermoplastic material. A common filler used in bioplastics is cellulose, often in the form of reinforcing fibers in the polymer-matrix composite. Cellulose is grown as flax or hemp. It is inexpensive and possesses good mechanical strength.