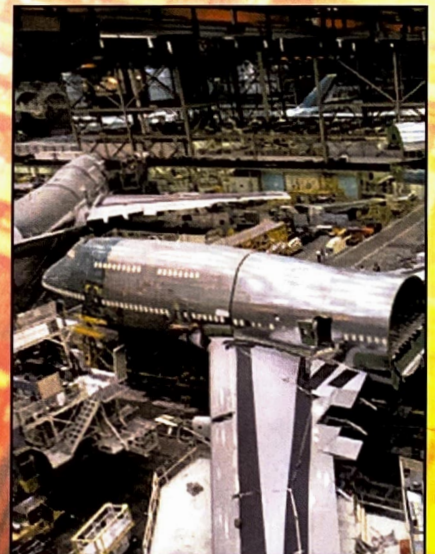


MANUFACTURING ENGINEERING AND TECHNOLOGY

FIFTH EDITION



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Manufacturing Engineering and Technology

FIFTH
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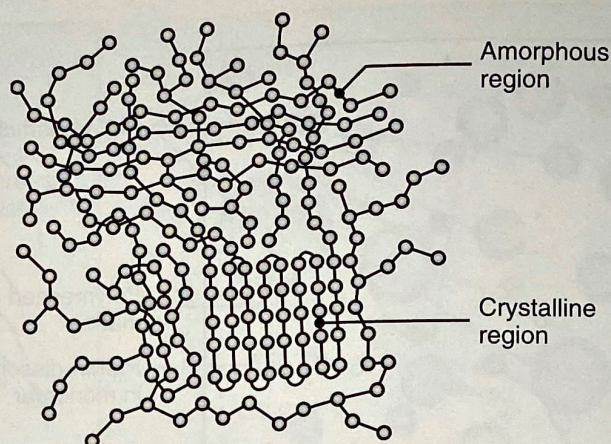


FIGURE 7.8 Amorphous and crystalline regions in a polymer. The crystalline region (crystallite) has an orderly arrangement of molecules. The higher the crystallinity, the harder, stiffer, and less ductile the polymer.

to solvents and heat (Fig. 7.6). The increase in density with increasing crystallinity is called *crystallization shrinkage* and is caused by a more efficient packing of the molecules in the crystal lattice. For example, the highly crystalline form of polyethylene, known as high-density polyethylene (HDPE), has a specific gravity in the range of from 0.941 to 0.970 (80 to 95% crystalline). It is stronger, stiffer, tougher, and less ductile than low-density polyethylene (LDPE), which is about 60 to 70% crystalline and has a specific gravity of about 0.910 to 0.925.

Optical properties of polymers also are affected by the degree of crystallinity. The reflection of light from the boundaries between the crystalline and the amorphous regions in the polymer causes opaqueness. Furthermore, because the index of refraction is proportional to density, the greater the density difference between the amorphous and crystalline phases, the greater is the opaqueness of the polymer. Polymers that are completely amorphous can be transparent, such as polycarbonate and acrylics.

7.2.3 Glass-transition temperature

Although amorphous polymers do not have a specific melting point, they undergo a distinct change in their mechanical behavior across a narrow range of temperature. At low temperatures, they are hard, rigid, brittle, and glassy; at high temperatures, they are rubbery or leathery. The temperature at which a transition occurs is called the *glass-transition temperature* (T_g), also called the *glass point* or *glass temperature*. The term glass is used in this description because glasses, which are amorphous solids, behave in the same manner (see *metallic glasses*, Section 6.14). Although most amorphous polymers exhibit this behavior, an exception is polycarbonate, which is neither rigid nor brittle below its glass-transition temperature. Polycarbonate is tough at ambient temperatures and is used for safety helmets and shields.

To determine T_g , the specific volume of the polymer is determined and plotted against temperature, and marked by a sharp change in the slope of the curve (Fig. 7.9). In the case of highly cross-linked polymers, the slope of the curve changes gradually near T_g , and hence, it can be difficult to determine T_g for these polymers. The

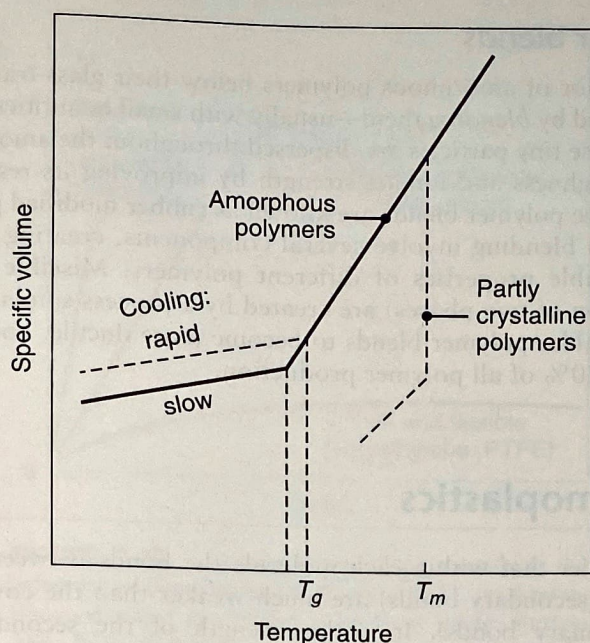


FIGURE 7.9 Specific volume of polymers as a function of temperature. Amorphous polymers, such as acrylic and polycarbonate, have a glass-transition temperature, T_g , but do not have a specific melting point, T_m . Partly crystalline polymers, such as polyethylene and nylons, contract sharply while passing through their melting temperatures during cooling.

glass-transition temperature varies with different polymers (Table 7.2). For example, room temperature is above T_g for some polymers and below it for others. Unlike amorphous polymers, partly crystalline polymers have a distinct melting point, T_m (Fig. 7.9; see also Table 7.2). Because of the structural changes (first-order changes) occurring, the specific volume of the polymer drops suddenly as its temperature is reduced.

TABLE 7.2

Glass-Transition and Melting Temperatures of Some Polymers

Material	T_g (°C)	T_m (°C)
Nylon 6,6	57	265
Polycarbonate	150	265
Polyester	73	265
Polyethylene		
High density	−90	137
Low density	−110	115
Polymethylmethacrylate	105	—
Polypropylene	−14	176
Polystyrene	100	239
Polytetrafluoroethylene	−90	327
Polyvinyl chloride	87	212
Rubber	−73	—

7.2.4 Polymer blends

The brittle behavior of amorphous polymers below their glass-transition temperature can be reduced by *blending* them—usually with small quantities of an **elastomer** (Section 7.9). These tiny particles are dispersed throughout the amorphous polymer, enhancing its toughness and impact strength by improving its resistance to crack propagation. These polymer blends are known as **rubber modified polymers**.

Advances in blending involve several components, creating **polyblends** that utilize the favorable properties of different polymers. **Miscible blends** (mixing without separation of two phases) are created by a process similar to the alloying of metals that enables polymer blends to become more ductile. Polymer blends account for about 20% of all polymer production.

7.3 Thermoplastics

It was noted earlier that within each molecule the bonds between adjacent long-chain molecules (secondary bonds) are much weaker than the covalent bonds between mers (primary bonds). It is the strength of the secondary bonds that determines the overall strength of the polymer; linear and branched polymers have weak secondary bonds.

As the temperature is raised above the glass-transition temperature, T_g , or melting point, T_m , certain polymers become easier to form or mold into desired shapes. The increased temperature weakens the secondary bonds (through thermal vibration of the long molecules), and the adjacent chains thus can move more easily when subjected to external shaping forces. When the polymer is cooled, it returns to its original hardness and strength; in other words, the process is reversible. Polymers that exhibit this behavior are known as **thermoplastics** (common examples of which are acrylics, cellulose, nylons, polyethylenes, and polyvinyl chloride).

The behavior of thermoplastics depends on other variables as well as their structure and their composition. Among the most important are temperature and rate of deformation. Below the glass-transition temperature, most polymers are *glassy* (brittle) and behave like an elastic solid (that is, the relationship between stress and strain is linear (see Fig. 2.2). For example, polymethylmethacrylate (PMMA) is glassy below its T_g , whereas polycarbonate is not glassy below its T_g . The glassy behavior can be represented by a spring whose stiffness is equivalent to the modulus of elasticity of the polymer.

When the applied stress is increased further, the polymer eventually fractures, just as a piece of glass does at ambient temperature. Plastics undergo fatigue and creep phenomena, just as metals do. Typical stress-strain curves for some thermoplastics and thermosets at room temperature are shown in Fig. 7.10. Note that these plastics exhibit various behaviors, which may be described as rigid, soft, brittle, flexible, and so on. The mechanical properties of several polymers listed in Table 7.1 indicate that thermoplastics are about two orders of magnitude less stiff than metals. Their ultimate tensile strength is about one order of magnitude lower than that of metals (see Table 2.1).

Effects of temperature. If the temperature of a thermoplastic polymer is raised above its T_g , it first becomes *leathery* and then, with increasing temperature, *rubbery* (Fig. 7.6). Finally, at higher temperatures (e.g., above T_m for crystalline thermoplastics), it becomes a *viscous fluid*: its viscosity decreases with increasing temperature. At still higher temperatures, the response of a thermoplastic can be likened to ice

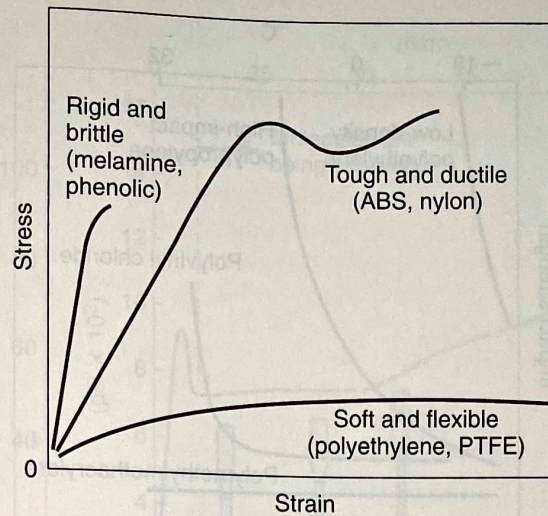


FIGURE 7.10 General terminology describing the behavior of three types of plastics. PTFE (polytetrafluoroethylene) has *Teflon* as its trade name. Source: After R. L. E. Brown.

cream: It can be softened, molded into shapes, refrozen, resoftened, and remolded a number of times. In practice, however, repeated heating and cooling cause **degradation**, or **thermal aging**, of thermoplastics.

The typical effect of temperature on the strength and elastic modulus of thermoplastics is similar to that of metals; with increasing temperature, the strength and the modulus of elasticity decrease and the toughness increases (Fig. 7.11). The effect of temperature on impact strength is shown in Fig. 7.12; note the large difference in the impact behaviors of various polymers.

Effect of rate of deformation. The behavior of thermoplastics is similar to the strain-rate sensitivity of metals, indicated by the strain-rate sensitivity

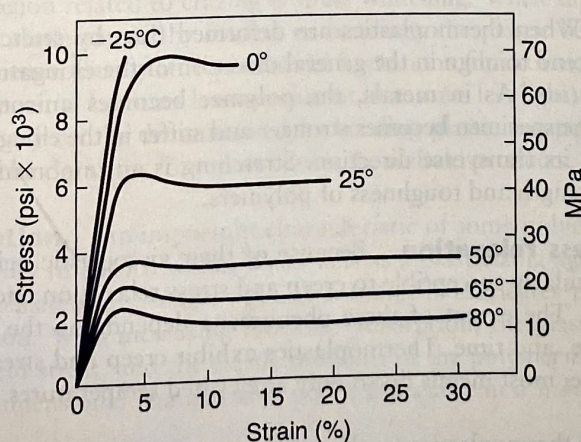


FIGURE 7.11 Effect of temperature on the stress-strain curve for cellulose acetate, a thermoplastic. Note the large drop in strength and the large increase in ductility with a relatively small increase in temperature. Source: After T. S. Carswell and H. K. Nason.

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