15.21 This question asks us to choose from a list of materials those which would be expected to be elastomers and those which would be thermosetting polymers.

(a) Linear and crystalline polyethylene would be neither an elastomer nor a thermoset since it is a linear polymer.

(b) Phenol-formaldehyde having a network structure would be a thermosetting polymer since it has a network structure. It would not be an elastomer since it does not have a crosslinked chain structure.

(c)   Heavily crosslinked polyisoprene having a glass transition temperature of 50°C would be a thermosetting polymer because it is heavily crosslinked. It would not be an elastomer since it is heavily crosslinked and room temperature is below its T_g.

(d) Lightly crosslinked polyisoprene having a glass transition temperature of –60°C is both an elastomer and a thermoset. It is an elastomer because it is lightly crosslinked and has a T_g below room temperature. It is a thermoset because it is crosslinked.

(e) Linear and partially amorphous poly(vinyl chloride) is neither an elastomer nor a thermoset. In order to be either it must have some crosslinking.

15.23 For an alternating acrylonitrile-butadiene copolymer, we are asked to compute the weight percent sulfur necessary for complete crosslinking, assuming that, on the average, four sulfur atoms participate in each crosslink. The acrylonitrile and butadiene repeat units are shown in Table 14.5, from which it may be noted that there are two possible crosslink sites on each butadiene repeat unit (one site at each of the two carbon atoms that are doubly bonded), and no possible sites for acrylonitrile; also, since it is an alternating copolymer, the ratio of butadiene to acrylonitrile repeat units is 1:1. Thus, for each pair of combined butadiene-acrylonitrile repeat units which crosslink, eight sulfur atoms are required, or, for complete crosslinking, the sulfur-to-(acrylonitrile-butadiene) ratio is 4:1.

Now, let us consider as our basis, one mole of the combined acrylonitrile-butadiene repeat units. In order for complete crosslinking, four moles of sulfur are required. Thus, for us to convert this composition to weight percent, it is necessary to convert moles to mass. The acrylonitrile repeat unit consists of three carbon atoms, three hydrogen atoms, and one nitrogen atom; the butadiene repeat unit is composed of four carbons and six hydrogens. This gives a molecular weight for the combined repeat unit of

$$m(\text{acrylonitrile-butadiene}) = 3(A_C) + 3(A_H) + A_N + 4(A_C) + 6(A_H)$$

$$= 7(12.01 \text{ g/mol}) + 9(1.008 \text{ g/mol}) + 14.007 \text{ g/mol} = 107.15 \text{ g/mol}$$

Or, in one mole of this combined repeat unit, there are 107.15 g. Furthermore, for complete crosslinking 4.0 mol of sulfur is required, which amounts to (4.0 mol)(32.06 g/mol) = 128.24 g. Thus, the concentration of S in weight percent C_S (using Equation 4.3) is just

$$C_S = \frac{128.24 \text{ g}}{128.24 \text{ g} + 107.15 \text{ g}} \times 100 = 54.5 \text{ wt\%}$$

15.25 We are asked what weight percent of sulfur must be added to polyisoprene in order to ensure that 10% of possible sites are crosslinked, assuming that, on the average, 3.5 sulfur atoms are associated with each crosslink. Table 14.5 shows the chemical repeat unit for isoprene. For each of these units there are two possible crosslink sites; one site is associated with each of the two carbon atoms that are involved in the chain double bond. Since 10% of the possible sites are crosslinked, for each 100 isoprene repeat units 10 of them are crosslinked; actually there are two crosslink sites per repeat unit, but each crosslink is shared by two chains. Furthermore, on the average we assume that each crosslink is composed of 3.5 sulfur atoms; thus, there must be 3.5 x 10 or 35 sulfur atoms added for every 100 isoprene repeat units. In terms of moles, it is necessary to add 35 moles of sulfur to 100 moles of isoprene. The atomic weight of sulfur is 32.06 g/mol, while the molecular weight of isoprene is

$$A(\text{isoprene}) = 5(A_C) + 8(A_H)$$

$$= (5)(12.01 \text{ g/mol}) + (8)(1.008 \text{ g/mol}) = 68.11 \text{ g/mol}$$

The mass of sulfur added (m_S) is

$$m_S = (35 \text{ mol})(32.06 \text{ g/mol}) = 1122 \text{ g}$$

While for isoprene

$$m_{ip} = (100 \text{ mol})(68.11 \text{ g/mol}) = 6811 \text{ g}$$

Or, the concentration of sulfur in weight percent (Equation 4.3) is just

$$C_S = \frac{m_S}{m_S + m_{ip}} \times 100 = \frac{1122 \text{ g}}{1122 \text{ g} + 6811 \text{ g}} \times 100 = 14.1 \text{ wt\%}$$

15.28 This question asks us to name which, of several polymers, would be suitable for the fabrication of cups to contain hot coffee. At its glass transition temperature, an amorphous polymer begins to soften. The maximum temperature of hot coffee is probably slightly below 100°C (212°F). Of the polymers listed, only polystyrene and polycarbonate have glass transition temperatures of 100°C or above (Table 15.2), and would be suitable for this application.

15.31 (a) Yes, it is possible to determine which polymer has the higher melting temperature. The linear polyethylene will most likely have a higher percent crystallinity, and, therefore, a higher melting temperature than the branched polyethylene. The molecular weights of both materials are the same and, thus, molecular weight is not a consideration.

(b) Yes, it is possible to determine which polymer has the higher melting temperature. Of these two polytetrafluoroethylene polymers, the PTFE with the higher density (2.20 g/cm^3) will have the higher percent crystallinity, and, therefore, a higher melting temperature than the lower density PTFE. The molecular weights of both materials are the same and, thus, molecular weight is not a consideration.

(c) Yes, it is possible to determine which polymer has the higher melting temperature. The linear polyethylene will have the greater melting temperature inasmuch as it will have a higher degree of crystallinity; polymers having a syndiotactic structure do not crystallize as easily as those polymers having identical single-atom side groups. With regard to molecular weight, or rather, degree of polymerization, it is about the same for both materials (8000), and therefore, is not a consideration.

(d) No, it is not possible to determine which of the two polymers has the higher melting temperature. The syndiotactic polypropylene will have a higher degree of crystallinity than the atactic material. On the basis of this effect alone, the syndiotactic PP should have the greater T_m, since melting temperature increases with degree of crystallinity. However, the molecular weight for the syndiotactic polypropylene (500,000 g/mol) is less than for the atactic material (750,000 g/mol); and this factor leads to a lowering of the melting temperature

15.32 For an amorphous polymer, the elastic modulus may be enhanced by increasing the number of crosslinks (while maintaining the molecular weight constant); this will also enhance the glass transition temperature. Thus, the modulus-glass transition temperature behavior would appear as
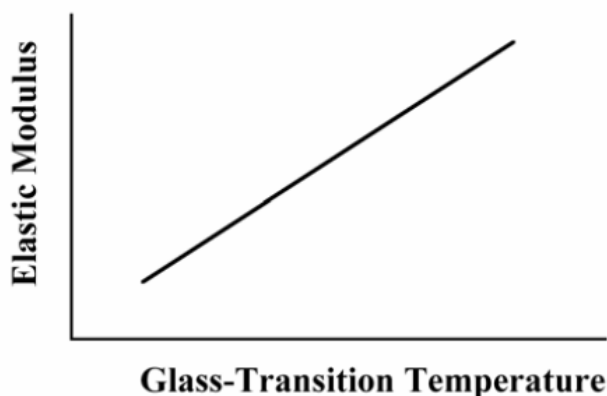
15.33 The backbone chain of most polymers consists of carbon atoms that are linked together. For the silicone polymers, this backbone chain is composed of silicon and oxygen atoms that alternate positions.

15.34 Two important characteristics for polymers that are to be used in fiber applications are: (1) they must have high molecular weights, and (2) they must have chain configurations/structures that will allow for a high degrees of crystallinity.

15.35 Five important characteristics for polymers that are to be used in thin-film applications are: (1) low density; (2) high flexibility; (3) high tensile and tear strengths; (4) resistance to moisture/chemical attack; and (5) low gas permeability.

15.36 For addition polymerization, the reactant species have the same chemical composition as the monomer species in the molecular chain. This is not the case for condensation polymerization, wherein there is a chemical reaction between two or more monomer species, producing the repeating unit. There is often a low molecular weight by-product for condensation polymerization; such is not found for addition polymerization.

15.37 (a) This problem asks that we determine how much ethylene glycol must be added to 20.0 kg of terephthalic acid to produce a linear chain structure of poly(ethylene terephthalate) according to Equation 15.9. Since the chemical formulas are provided in this equation we may calculate the molecular weights of each of these materials as follows:

$$MW(\text{ethylene glycol}) = 2(A_C) + 6(A_H) + 2(A_O)$$

$$= 2(12.01 \text{ g/mol}) + 6(1.008 \text{ g/mol}) + 2(16.00 \text{ g/mol}) = 62.07 \text{ g/mol}$$

$$MW(\text{terephthalic acid}) = 8(A_C) + 6(A_H) + 4(A_O)$$

$$= 8 (12.01 \text{ g/mol}) + 6(1.008 \text{ g/mol}) + 4(16.00 \text{ g/mol}) = 166.13 \text{ g/mol}$$

The 20.0 kg mass of terephthalic acid equals 20,000 g or $\dfrac{20{,}000 \text{ g}}{166.13 \text{ g}/\text{mol}} = 120.39$ mol. Since, according to Equation 15.9, each mole of terephthalic acid used requires one mole of ethylene glycol, which is equivalent to (120.39 mol)(62.07 g/mol) = 7473 g = 7.473 kg.

(b) Now we are asked for the mass of the resulting polymer. Inasmuch as one mole of water is given off for every repeat unit produced, this corresponds to 120.39 moles or (120.39 mol)(18.02 g/mol) = 2169 g or 2.169 kg since the molecular weight of water is 18.02 g/mol. The mass of poly(ethylene terephthalate) is just the sum of the masses of the two reactant materials [as computed in part (a)] minus the mass of water released, or

$$\text{mass [poly(ethylene terephthalate)]} = 20.0 \text{ kg} + 7.473 \text{ kg} - 2.169 \text{ kg} = 25.304 \text{ kg}$$

15.39 The distinction between dye and pigment colorants is that a dye dissolves within and becomes a part of the polymer structure, whereas a pigment does not dissolve, but remains as a separate phase.

15.40 Four factors that determine what fabrication technique is used to form polymeric materials are: (1) whether the polymer is thermoplastic or thermosetting; (2) if thermoplastic, the softening temperature; (3) atmospheric stability; and (4) the geometry and size of the finished product.

15.41 This question requests that we compare polymer molding techniques. For compression molding, both heat and pressure are applied after the polymer and necessary additives are situated between the mold members. For transfer molding, the solid materials (normally thermosetting in nature) are first melted in the transfer chamber prior to being forced into the die. And, for injection molding (normally used for thermoplastic materials), the raw materials are impelled by a ram through a heating chamber, and finally into the die cavity.

15.42 Fiber materials that are melt spun must be thermoplastic because: (1) In order to be melt spun, they must be capable of forming a viscous liquid when heated, which is not possible for thermosets. (2) During drawing, mechanical elongation must be possible; inasmuch as thermosetting materials are, in general, hard and relatively brittle, they are not easily elongated.

15.43 Of the two polymers cited, the one that was formed by extrusion and then rolled would have the higher strength. Both blown and extruded materials would have roughly comparable strengths; however the rolling operation would further serve to enhance the strength of the extruded material.