Define and differentiate polymers, plastics, and elastomers.

Chapter 10, Solution 1

A polymer is the long-chain molecule formed from monomer units.

Plastics are a large and varied group of synthetic materials which are produced through forming and molding processes and are classified as either thermoplastic or thermosetting.

Elastomers (rubbers) are highly flexible plastics: when subjected to stress, they are capable of withstanding large elastic deformation; once the stress is removed, these plastics regain, or nearly regain, their original shape and dimensions.

Chapter 10, Problem 2

(a) Describe the atomic structural arrangement of thermoplastics. (b) What types of atoms are bonded together in thermoplastic molecular chains? (c) What are the valences of these atoms in the molecular chains?

Chapter 10, Solution 2

- (a) Thermoplastics consist of very long molecular chains of covalently bonded carbon atoms.
- (b) The main molecular chains of thermoplastics are comprised of carbon, nitrogen, oxygen and sulfur atoms.
- (c) The valences of these atoms are: C (+4); N (-3); S (+2); O (-2).

Chapter 10, Problem 3

What is a pendant atom or group of atoms?

Chapter 10, Solution 3

A pendant atom or group of atoms is, respectively, an atom or group of atoms that is covalently bonded to the main carbon chain.

Chapter 10, Problem 4

- (a) What type of bonding exists within the molecular chains of thermoplastics?
- (b) What type of bonding exists between the molecular chains of thermoplastics?

Chapter 10, Solution 4

(a) Within thermoplastic molecular chains, covalent bonds exist.

(b) Between thermoplastic chains, permanent dipole bonds provide weak secondary bonding.

Chapter 10, Problem 5

(a) Define thermosetting plastics. (b) Describe the atomic structural arrangement of thermosetting plastics.

Chapter 10, Solution 5

- (a) Thermosetting plastics are plastics which can be formed into a shape and permanently cured or "set" by a chemical reaction. The cured product can not be melted and reused because these materials degrade at high temperatures.
- (b) Most thermosetting plastics consist of three-dimensional networks of covalently bonded atoms, as compared to the long chain-like molecules of thermoplastics.

Chapter 10, Problem 6

Define the following terms: chain polymerization, monomer, and polymer.

Chapter 10, Solution 6

Chain polymerization is the process by which monomers are chemically combined into long-chain molecular polymers.

A *monomer* is the simple molecule that is covalently bonded with other monomers to form long molecular chains.

A polymer is the long-chain molecule formed from monomer units.

Chapter 10, Problem 7

Describe the bonding structure within an ethylene molecule by using (a) the electron-dot-cross notation and (b) straight-line notation for the bonding electrons.

Chapter 10, Solution 7

Electron dot Notation:	Straight Line Notation
н н	н н
 C: :C	
C: :C	C == C
Н Н	Н Н

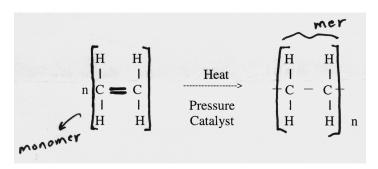
Chapter 10, Problem 8

(a) What is the repeating chemical unit of a polymer chain called? (b) What is the chemical repeating unit polyethylene? (c) Define the degree of polymerization for a polymer chain.

(a)

The chemical repeating unit is called a mer. The repeating unit for polyethylene is shown above right.

(b) Chapter 10, Problem 40.



(c) The degree of polymerization is equal to the number of subunits or mers within the polymer molecule.

Chapter 10, Problem 9

(a) What are the three major reactions that occur during chain polymerization? (b) What is the function of the initiator catalyst for chain polymerization? (c) What are two methods by which a linear chain polymerization reaction can be terminated?

Chapter 10, Solution 9

(a) The three major reactions that occur during chain polymerization are: initiation, propagation, and termination. (b) The initiator catalyst provides a free radical to a monomer and thus activates the monomer and allows the propagation stage of chain polymerization to begin. (c) A linear chain polymerization reaction can be terminated by reacting with a terminator free radical or by combining with another polymer chain.

Chapter 10, Problem 10

What is a free radical? Write a chemical equation for the formation of two free radicals from a hydrogen peroxide molecule by using (a) the electron-dot-cross notation and (b) straight-line notation for the bonding electrons.

- a) A free radical is a group of atoms having an unpaired electron which cancovalently bond to an unpaired electron of another molecule.
- b) H:0:0:H \rightarrow H:0'+'0:H free radical
 c) H-0-0-H \rightarrow 2H-0' free electron
 free radicals

Chapter 10, Problem 11

(a) Why must one consider the average degree of polymerization and the average molecular weight of a thermoplastic material? (b) Define the average molecular weight of a thermoplastic.

Chapter 10, Solution 11

- (a) Since thermoplastics consist of polymer chains of varying lengths, and thus different molecular weights, an average molecular mass must be assessed based upon the average degree of polymerization for the material.
- (b) The average molecular weight of a thermoplastic material, $M_{\it m}$, is defined as:

$$\overline{M}_m = \frac{\sum f_i M_i}{\sum f_i}$$

where

 M_i = mean molecular weight for each molecular weight range selected f_i = weight fraction of the material for a selected molecular weight range representative of the material

The average molecular weight is thus a weighted average based upon mean molecular weights, of weight ranges representative of the material, and the weight fractions of the respective ranges.

Chapter 10, Problem 12

What is the functionality of a monomer? Distinguish between a bifunctional and trifunctional monomer.

The functionality of a monomer is the number of active bonds the monomer has. A bifunctional monomer uses two active bonds for long-chain polymerization while a trifunctional monomer utilizes three active bonds.

Chapter 10, Problem 13

Write structural formulas for the mers of the following vinyl polymers:

(a) polyethylene, (b) polyvinyl chloride, (c) polypropylene, (d) polystyrene, (e) polyacrylonitrile, and (f) polyvinyl acetate.

Chapter 10, Solution 13

Chapter 10, Problem 14

Write structural formulas for the mers of the following vinylidene polymers: (a) polyvinylidene chloride and

(b) polymethyl methacrylate.

(a) Polyvinylidene Chloride

$$\begin{bmatrix}
H & Cl \\
| & | \\
Cx & Ca \\
| & | \\
H & Cl
\end{bmatrix}_{n}$$

(b) Polymethyl Methacrylate

Chapter 10, Problem 15

Distinguish between a homopolymer and a copolymer.

Chapter 10, Solution 15

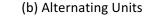
A homopolymer consists of polymer chains made up of a single repeating unit; whereas a copolymer consists of polymer chains containing two or more repeating units, of dissimilar chemical structure, that can form a variety of sequences.

Chapter 10, Problem 16

Illustrate the following types of copolymers by using filled and open circles for their mers: (a) random, (b) alternating, (c) block, and (d) graft.

Chapter 10, Solution 16

(a) Random Distributed Units



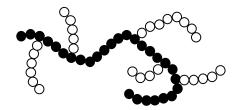




(c) Block Copolymer

(d) Graft Copolymer





Define stepwise polymerization of linear polymers. What by-products are commonly produced by stepwise polymerization?

Chapter 10, Solution 17

Heating &

Monomer(

s)

In stepwise polymerization, monomers chemically react with each of the individual monomers or as units of existing linear polymer chains, to produce linear polymers. These reactions, referred to as condensation polymerization reactions, often produce water as a by-product.

Chapter 10, Problem 18

What are three basic raw materials used to produce the basic chemicals needed for the polymerization of plastic materials?

Chapter 10, Solution 18

Natural gas, petroleum and coal are the three basic raw materials used to produce the basic chemicals needed for the polymerization of plastic materials.

Chapter 10, Problem 19

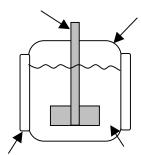
Describe and illustrate the following polymerization processes: (a) bulk, (b) solution, (c) suspension, and (d) emulsion.

Chapter 10, Solution 19

In the suspension process the heat of reaction is absorbed by water; whereas, the heat is absorbed by the solvent in the solution polymerization process. When the polymerization heat of reaction is low, the bulk polymerization process is used.

(a) Bulk Polymerization:

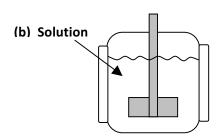
As shown schematically in Fig. 10.12a, bulk polymerization is accomplished by mixing the monomer and activator in a reactor that allows for heating and cooling, as required by the reaction. This process is used extensively for condensation polymerization because of the low heats of reaction associated with these reactions.



Monome

r Monomer(s) aroplets

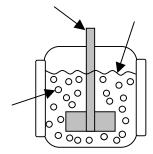
(c) Suspension



(b) Solution Polymerization:

In solution polymerization, a monomer is dissolved in a non-reactive solvent that contains a catalyst. Since the solvent absorbs the heat released by the reaction, the reaction rate is reduced. A schematic of this reaction is provided in Fig. 10.12b.

(c) Suspension Polymerization:
In this process (Fig. 10.12c), the mono-mer is mixed with a catalyst and then dispersed as a suspension in water. The particles are maintained in suspension through agitation while the water absorbs the heat released by the reaction. At the conclusion of polymerization, the product, typically a vinyl-type polymer, is separated and dried.



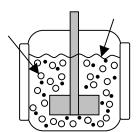
Monomer droplets with surfactant

Water

(d) Emulsion

(d) Emulsion Polymerization:

The emulsion polymerization process is similar to the suspension process in that it is carried out in water and uses an initiator. However, an emulsifier is also added to the suspension in order to disperse the monomer into very small particles. Fig. 10.12d schematically illustrates the emulsion process.



Chapter 10, Problem 20

Describe the Unipol process for producing low-density polyethylene. What are the advantages of this process?

Chapter 10, Solution 20

The Unipol process is a mass continuous type of polymerization process in which gaseous ethylene monomer and a comonomer are continuously fed into a fluidized-bed reactor to which a catalyst is added. The advantages of this process are temperature and pressure requirements that are one-third lower than other polymerization processes.

- (a) Define the glass transition temperature T_g for a thermoplastic? (b) What are measured T_g values for
- (i) polyethylene, (ii) polyvinyl chloride, and (iii) polymethyl methacrylate? Are the T_q values constants?

Chapter 10, Solution 21

- (a) A glassy material like a thermoplastic has no sharp freezing point; the plastic liquid gradually transitions from a viscous liquid to a soft plastic and finally becomes hard and brittle. The glass transition temperature is therefore defined as the average temperature at which the specific volume versus temperature curve changes slope. This change in gradient indicates the onset of solidification.
- (b) The measured T_g values are:
 - (a) -110°C for polyethylene;
 - (b) 82°C for polyvinyl chloride;
 - (c) 72°C for polymethyl methacrylate.

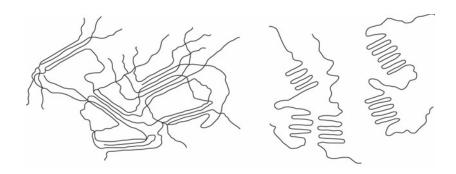
Glass transition temperatures are not material constants since they depend upon variables such as degree of crystallinity, rate of cooling of the thermoplastic, and the average molecular weight of the polymer chains.

Chapter 10, Problem 22

Describe and illustrate the fringed-micelle and folded-chain models for the structure of partly crystalline thermoplastics.

Chapter 10, Solution 22

According to the fringed-micelle model, long polymer chains, approximately 5000 nm in length, pass through ordered and disordered regions along the molecule's length. These regions correspond to the areas of crystalline and noncrystalline thermoplastic material. A more recent model, the folded-chain model, predicts that sections of the molecular chains fold upon themselves and thus allow the formation of crystalline and noncrystalline regions.



Describe the spherulitic structure found in some partly crystalline thermoplastics.

Chapter 10, Solution 23

The spherulitic structure is observed in some partly crystalline thermoplastics having the folded-chain type of structure. The spherulitic regions consist of crystalline lamellae which represent individual layers of the folded-chain structure. The spherulites grow within an otherwise noncrystalline structure and appear roughly spherical in shape.

Chapter 10, Problem 24

(a) What are stereoisomers with respect to chemical molecules? (b) Describe and draw structural models for the following stereoisomers of polypropylene: (i) atactic, (ii) isotactic, and (iii) syndiotactic.

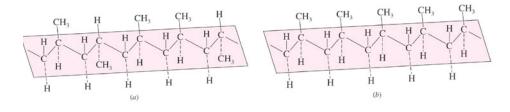
Chapter 10, Solution 24

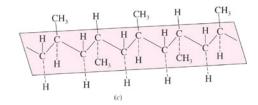
(a) Stereoisomers have identical chemical formulas but different structural arrangements.

(b)

(i) In the atactic stereoisomer of polypropylene, the pendant methyl group (CH_3) is randomly arranged on either side of the main-carbon chain.

- (ii) In the isotactic stereoisomer, the pendant group is always on the same side of the maincarbon chain.
- (iii) The syndiotactic stereoisomer has an alternating arrangement of the pendant group, from one side of the main chain to the other.





What is a stereospecific catalyst? How did the development of a stereospecific catalyst for the polymerization of polypropylene affect the usefulness of commercial polypropylene?

Chapter 10, Solution 25

A stereospecific catalyst is one that enables a polymer to be polymerized such that it consists of an individual stereoisomeric structure. The development of a stereospecific catalyst for the polymerization of isotactic polypropylene significantly affected the polymer's usefulness commercially; the catalyst provided a cost-effective method of mass production.

Chapter 10, Problem 26

In general how does the processing of thermoplastics into the desired shape differ from the processing of thermosetting plastics?

Chapter 10, Solution 26

In general, thermoplastics are heated to a softened state and then reshaped prior to cooling; whereas, thermosetting plastics are shaped prior to a final polymerization process in which the polymer chains are cross-linked into a polymeric network.

Chapter 10, Problem 27

(a) Describe the injection-molding process for thermoplastics. (b) Describe the operation of the reciprocating-screw injection-molding machine. (c) What are some advantages and disadvantages of the injection-molding process for molding thermoplastics? (d) What are the advantages of the reciprocating-screw injection-molding machine over the old plunger type?

Chapter 10, Solution 27

- (a) In the injection-molding process, thermoplastics material, in either powder or pellet form, is melted and then forced (injected) into a mold and allowed to form a rigid solid through cooling. This process is similar to the die casting of metals.
- (b) The reciprocating-screw injection-molding machine is a modern design which incorporates a reciprocating-screw mechanism for melting and injecting the plastic and a water-cooled mold for rapid solidification of the part.
- (c) Advantages of the injection-molding process include: potential for creating high quality parts at a high production rate; low labor costs; good surface finishes; capability for a highly automated process; ease of producing intricate shapes. The primary disadvantages of injection molding are: the large initial

investment required to purchase the machine necessitates a large volume of production; the process must be closely controlled to produce a high quality part.

(d) Compared to its predecessor, the plunger-type machine, the reciprocating-screw machine is more efficient and delivers a more homogeneous melt for injection.

Chapter 10, Problem 28

Describe the extrusion process for processing thermoplastics.

Chapter 10, Solution 28

In the extrusion process, thermoplastic resin is fed into a heated cylinder that contains a rotating screw mechanism. As the screw propels the material along the cylinder, the plastic is melted and then forced through a small opening into an accurately machined die where it is cooled below its glass transition temperature. This process is capable of forming a variety of continuous shapes such as pipes, rods, films, and sheets.

Chapter 10, Problem 29

Describe the blow molding and thermoforming processes for forming thermoplastics.

Chapter 10, Solution 29

In blow molding, a cylinder or tube of heated plastic (a parison) is placed between the jaws of a mold. The mold is then closed to pinch off the cylinder ends, and compressed air is blown into the mold, forcing the plastic against the mold walls. The result is a hollow part such as a bottle.

In thermoforming, a heated plastic sheet is forced into the contours of a mold by applying pressure – either mechanical, positive air pressure, or vacuum.

Chapter 10, Problem 30

(a) Describe the compression-molding process for thermosetting plastics. (b) What are some of the advantages and disadvantages of the compression-molding process?

Chapter 10, Solution 30

(a) In compression molding, preheated or room temperature plastic resin is placed between hot mold die plates that contain one or more cavities. The upper mold die is then forced down on the plastic

resin. This applied pressure, in conjunction with the mold's heat, causes the resin to melt and fill the cavity or cavities. Additional heat is then applied to the mold to complete the cross-linking of the resin.

(b) Advantages of the compression-molding process include: low initial mold costs; minimal wear and abrasion of molds due to relatively short material flow; ease of producing large parts; simplicity of mold design allows for more compact molds; means for expulsion of reaction gases during the molding process. The main disadvantages of this process are: difficulty in producing complicated part configurations; inability to achieve close tolerances on inserts; increased cost associated with trimming flash from molded parts.

Chapter 10, Problem 31

(a) Describe the transfer-molding process for thermosetting plastics. (b) What are some of the advantages of the transfer-molding process?

Chapter 10, Solution 31

- (a) In transfer molding, the plastic resin is fed into a chamber outside the mold cavities and forced, by a plunger, through a system of runners and gates into the closed mold. Once the resin has had time to cure into a rigid network polymeric material, the formed part is ejected from the mold.
- (b) Advantages of transfer molding are: the molded part requires less finishing since no flash is created; the runner system allows for molding many parts simultaneously; small intricate parts can be produced.

Chapter 10, Problem 32

What are the four major thermoplastic materials that account for about 60 percent of the sales tonnage of plastic materials in the United States? What were their prices per pound in 1988? In the year 2000? In the year 2009?

Chapter 10, Solution 32

The four major types of thermoplastic materials that account for approximately sixty percent of the sales tonnage of plastics in the U.S. are polyethylene, polyvinyl chloride, polypropylene, and polystyrene.

Chapter 10, Problem 33

Define an engineering thermoplastic. Why is this definition arbitrary?

O H
P |
æ Cæ Næ

Chapter 10, Solution 33

In the current text, an engineering thermoplastic is defined A made times plastic having a set of properties that makes it especially useful for engineering applications. However, this is an arbitrary definition; virtually every plastic could be classified as an engineering plastic.

Chapter 10, Problem 34

What is the structural formula for the amide linkage in thermoplastics? What is the general name for polyamide thermoplastics?

Chapter 10, Solution 34

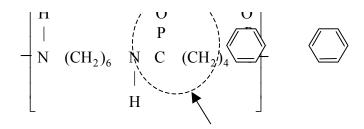
The general name for polyamide thermoplastics is *polyamides* or *nylons*. The structural formula for the amide linkage, present in all nylon thermo-plastics, is shown to the right.

Chapter 10, Problem 35

(a) In the designation nylon 6,6 what does the "6,6" stand for? (b) What is the repeating structural unit for nylon 6,6? (c) How can nylons 6,9, 6,10 and 6,12 be synthesized?

Chapter 10, Solution 35

- (a) The 6,6 of nylon 6,6 refers to the fact that there are six carbon atoms in the reacting diamine, hexamethylene diamine, and six carbon atoms in the reacting organic acid, adipic acid.
- (b) The repeating structure for nylon 6,6 is:



(c) Nylons 6,9, 6,10, and 6,12 can be synthesized using the same stepwise polymerization reaction as nylon 6,6 by replacing the adipic acid with azelaic acid (9 carbons), sebacic acid (10 carbons), and dodecanedioic acid (12 carbons), respectively.

Chapter 10, Problem 36

What is the basic repeating chemical structural unit for polycarbonates? What is the carbonate linkage? What are the common trade names for polycarbonate?

Chapter 10, Solution 36

Polycarbonates, manufactured under the trade names of Lexan and Merlon, have a carbonate linkage consisting of carbon-oxygen bonds as identified in below in the schematic of their repeating chemical structural unit.

Polyoxymethylene
$$CH_3$$
 H $Cæ$ O H H H H H

the trade names for these resins?

Chapter 10, Solution 37

Polyphenylene oxide-based resins, produced under the trade name Noryl, have the repeating chemical structural unit shown diagramed to the right.

Chapter 10, Problem 38

What is the repeating chemical structural unit for the acetal high-performance engineering thermoplastics? What are the two main types of acetals and what are their trade names?

Chapter 10, Solution 38

The two primary types of acetals are a homopolymer with trade name Delrin, and a copolymer with trade name Celcon. The repeating chemical structural unit for the high-performance acetals is diagramed to the right.

What are the two most important engineering thermoplastic polyesters? What are their repeating chemical structural units?

Chapter 10, Solution 39

The two most important engineering thermoplastic polyesters are polybutylene terephthalate (PBT) and polyethylene terephthalate (PET). The repeating mers of these plastics are shown below.

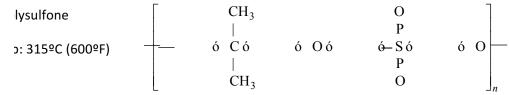
Chapter 10, Problem 40

What is the chemical structure of the ester linkage?

Chapter 10, Solution 40

The ester linkage consists of a carbon atom with a double bond to one oxygen atom and a single bond to a second oxygen atom. This linkage is depicted below in Prob. 10.156.

Chapter 10, Problem 156.



What are the two most important engineering thermoplastic polyesters? What are their repeating chemical structural units?

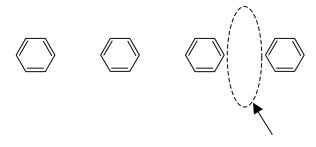
Sulfone linkage

The two most important engineering thermoplastic polyesters are polybutylene terephthalate (PBT) and polyethylene terephthalate (PET). The repeating mers of these plastics are shown below.

Chapter 10, Problem 41

What is the repeating chemical structural unit for polysulfone?

Chapter 10, Solution 41





Polyphenylene sulfide

Polyphenylene oxide

Chapter 10, Problem 42

What is the repeating chemical structural unit for polyphenylene sulfide? (b)What engineering thermoplastic has a similar structure? (c) What is the trade name for polyphenylene sulfide?

Chapter 10, Solution 42

The repeating chemical structural unit for polyphenylene sulfide is similar to the polyphenylene oxide mer; the oxygen atom is replaced with sulfur and the two —CH₃ groups are removed from the benzene ring. The molecular structures of these units are compared below.



(c) The trade name for polyphenylene sulfide (PPS) is Ryton.

What is the chemical structure of polyetherimide? What is its trade name?

Chapter 10, Solution 43

The imide linkage, shown to the right, gives polyetherimide high heat resistance, creep resistance and high rigidity.

Chapter 10, Problem 44

(a) What are polymer alloys? (b) How does their structure differ from copolymers? (c) What type of polymer alloy is (i) Xenoy 1000, (ii) Valox 815, and (iii) Bayblend MC2500?

Chapter 10, Solution 44

(a) Polymer alloys are mixtures of structurally different homopolymers or copolymers.

(b) The structure of polymer alloys differs from that of copolymers in terms of their components and bonds: alloys consist of different types of polymeric chains bonded by secondary intermolecular dipole forces; whereas copolymers consist of two different monomers bonded within a molecular chain by strong covalent bonds.

c)

- (i) Xenoy 1000 is a polymer alloy made of polycarbonate, PBT and elastomer.
- (ii) Valox 815 is a thermoplastic polyester alloy made of PBT and PET.
- (iii) Bayblend MC2500 is an ABS/polycarbonate alloy.

Chapter 10, Problem 45

(a) What are the major processing methods used for thermosets? (b) What are the two major ingredients of thermosetting molding compounds?

Chapter 10, Solution 45

- (a) Thermosets are typically processed using compression or transfer molding; however, special cases exist for which injection-molding techniques have been developed.
- (b) Two primary ingredients of thermosetting molding compounds are: a resin containing curing agents, hardeners, and plasticizers; and organic or inorganic fillers and/or reinforcing materials.

Chapter 10, Problem 46

What are elastomers? What are some elastomeric materials?

Chapter 10, Solution 46

Elastomers (rubbers) are polymeric materials whose dimensions can be significantly altered under stress yet return to nearly or exactly their original dimensions once the stress is removed. Examples of elastomeric materials include natural rubber, synthetic polyisoprene, styrene-butadiene rubber, nitrile rubbers, polychloroprene, and the silicones.

Chapter 10, Problem 47

From what tree is most natural rubber obtained? What countries have large plantations of these trees?

Most natural rubber is obtained from the latex of the *Hevea brasiliensis* tree. Tropical regions of southeast Asia, particularly Malaysia and Indonesia, have large plantations of the *Hevea brasiliensis* tree

Chapter 10, Problem 48

What is natural rubber latex? Briefly describe how natural rubber is produced in the bulk form?

Chapter 10, Solution 48

Natural rubber latex is a milky liquid, collected from trees and diluted to approximately 15 percent rubber content. This mixture is coagulated with formic acid, and the material is then compressed into sheets by rollers and dried. Subsequently, milling between heavy rolls is performed to break up some of the long polymer chains and thus reduce their average molecular weight.

Chapter 10, Problem 49

What is natural rubber mainly made of? What other components are present in natural rubber?

Chapter 10, Solution 49

Natural rubber is mainly made of *cis*-1,4 polyisoprene mixed with small quantities of components such as proteins, lipids, inorganic salts.

Chapter 10, Problem 50

To what structural arrangement is the coiling of the natural rubber polymer chains attributed? What is steric hindrance?

Chapter 10, Solution 50

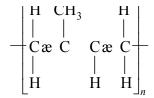
The coiling of the natural rubber polymer chains is attributed to the steric hindrance of the methyl group and the hydrogen atom. By definition, steric hindrance is the prevention or retardation of a chemical reaction, caused by the steric (spatial) arrangement of atoms. Here the term refers to the spatial interference of the methyl group and hydrogen atom, causing the molecule to coil.

Chapter 10, Problem 51

What are chemical structural isomers?

Chapter 10, Solution 51

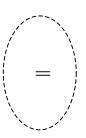
Structural isomers are compounds having identical chemical compositions but different structural arrangement of their atoms.



What is gutta-percha? What is the repeating chemical structural unit for gutta-percha? gutta-percha

Chapter 10, Solution 52

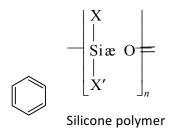
Gutta-percha is a structural isomer of polyisoprene also known as *trans*-1,4 polyisoprene. The repeating chemical structural unit for gutta-percha, shown to the right, is identical to the *cis*-1,4 except that the methyl group and hydrogen atom are on opposite sides of the carbon-carbon double bond. However, this material is not an elastomer.



What is the vulcanization process for natural rubber? Who discovered this process and when? Illustrate the cross-linking of *cis*-1,4 polyisoprene with divalent sulfur atoms.

Chapter 10, Solution 54

In the vulcanization process for natural rubber, the rubber polymer chains are cross-linked with sulfur atoms to restrict molecular mobility and thus increase the material's strength. Charles Goodyear discovered this process, through which a thermoplastic material is converted to an elastomeric material, in 1839. The rigid structure obtained by cross-linking cis-1,4 polyisoprene with divalent sulfur atoms is illustrated below.



What materials are used in the compounding of rubber and what is of each?

the function

Chapter 10, Solution 55

Fillers, plasticizers, accelerators and antioxidants are used in the compounding of rubber. Fillers, such as carbon black and silicas, lower the cost of production and increase the material's strength. Plasticizers impart greater flexibility while accelerators shorten the cure time at elevated temperatures. Antioxidants are added to retard oxidation and thus reduce brittleness.

Chapter 10, Problem 56

What is styrene-butadiene rubber (SBR)? What weight percent of it is styrene? What are the repeating chemical structural units for SBR?

Chapter 10, Solution 56

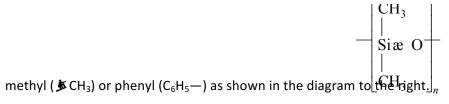
Styrene-butadiene rubber, the most important synthetic rubber, is a copolymer containing approximately 20 to 23 percent styrene. The repeating chemical structural unit for SBR is shown to the right.

Chapter 10, Problem 57

What are the silicones? What is the general repeating chemical structural unit for the silicones?

Chapter 10, Solution 57

The silicones are polymers which have repeating units of silicone and oxygen. Here, the X and X' may be hydrogen or groups such as



Polydimethyl siloxane

Chapter 10, Problem 58

What is a silicone elastomer? What is the chemical structural repeating unit of the most common type of silicone rubber? What is its technical name?

Chapter 10, Solution 58

A silicone elastomer is a silicone rubber based on the siliconoxygen repeating structure main chain with side groups on the silicon. The most common type of silicone elastomer is Polydimethyl siloxane, shown in the diagram to the right, which has methyl side groups.

Chapter 10, Problem 59

Describe the general deformation behavior of a thermoplastic plastic above and below its glass transition temperature.

Chapter 10, Solution 59

Below their glass transition temperatures, thermoplastics deform primarily by elastic deformation whereas above their glass transition temperatures, these plastics deform plastically.

What deformation mechanisms are involved during the elastic and plastic deformation of thermoplastics?

Chapter 10, Solution 60

During elastic deformation, the covalent bonds of the molecular chains stretch. Subsequently, the chains uncoil in a process that involves both elastic and plastic deformation. Finally, plastic deformation occurs as secondary dipole bonds are broken, allowing the chains to slide relative to each other and establish new dipole bonding forces.

Chapter 10, Problem 61

What is viscoelastic behavior of plastic materials?

Chapter 10, Solution 61

Above their glass transition temperatures, plastic materials experience viscoelastic behavior – a combination of both elastic and plastic deformation in which molecular chains are able to slide relative to each other.

Chapter 10, Problem 62

Define the creep modulus of a plastic material.

Chapter 10, Solution 62

The creep modulus of a plastic material is the ratio of the initial applied stress, σ_0 , at constant temperature to the resulting creep strain, U(t), after a specified time interval.

Chapter 10, Problem 63

What is a craze in a glassy thermoplastic?

Chapter 10, Solution 63

A craze is a highly stressed region consisting of aligned molecular chains with a high density of dispersed voids.

Chapter 10, Problem 64

Describe the structure of a craze in a thermoplastic.

Chapter 10, Solution 64

Refer to the answer below for Prob. 10.236.

What is a craze in a glassy thermoplastic?

A craze is a highly stressed region consisting of aligned molecular chains with a high density of dispersed voids.

Chapter 10, Problem 65

Describe the molecular structure changes that occur during the ductile fracturing of a thermoplastic.

Chapter 10, Solution 65

As the polymer is loaded and approaches the yield point, the molecular chains uncoil and slip past each other aligning in the direction of the applied load (see Fig 10.55). The process continues until the applied stress exceeds the strength of the covalent bonds inside the chain and the chain breaks.

Chapter 10, Problem 66

A high-molecular-weight polyethylene has an average molecular weight of 410,000 g/mol. What is its average degree of polymerization?

Chapter 10, Solution 66

To assess the average degree of polymerization (DP), the mass of the polyethylene mer is first calculated: $(4 \text{ hydrogen atoms} \times 1 \text{ g/mol}) + (2 \text{ carbon atoms} \times 12 \text{ g/mol}) = 28 \text{ g/mol}$.

The DP, defined in units of mers per mol, is:

$$DP = \frac{\text{molecular weight of polymer (g/mol)}}{\text{molecular weight of mer (g/mol/mer)}}$$
$$= \frac{410,000 \text{ g/mol}}{28 \text{ g/mol/mer}}$$
$$= 14,643 \text{ mers}$$

Chapter 10, Problem 67

If a type of polyethylene has an average degree of polymerization of 10,000, what is its average molecular weight?

$$\begin{aligned} MW_{av}(polymer) &= DP \times MW_{av}(mer) \\ &= (10,000 \text{ mers})(28 \text{ g/(mol · mer)}) \\ &= 280,000 \text{ g/mol} \end{aligned}$$

Chapter 10, Problem 68

A nylon 6,6 has an average molecular weight of 12,000 g/mol. Calculate the average degree of polymerization (see Sec. 10.7 for its mer structure M.W. = 226 g/mol).

Chapter 10, Solution 68

$$DP = \frac{\text{molecular weight of polymer (g/mol)}}{\text{molecular weight of mer (g/mol/mer})} = \frac{12,000 \text{ g/mol}}{226 \text{ g/mol/mer}} = 53 \text{ mers}$$

Chapter 10, Problem 69

An injection-molding polycarbonate material has an average molecular weight of 25,000 g/mol. Calculate its degree of polymerization (see Sec. 10.7 for the mer structure of polycarbonate.M.W. = 254 g/mol).

Chapter 10, Solution 69

$$DP = \frac{\text{molecular weight of polymer (g/mol)}}{\text{molecular weight of mer (g/mol/mer)}} = \frac{25,000 \text{ g/mol}}{254 \text{ g/mol/mer}} = 98 \text{ mers}$$

Chapter 10, Problem 70

Calculate the average molecular weight M_m for a thermoplastic that has the following weight fractions f_i for the molecular weight ranges listed:

Molecular Weight Range (g/mol)	f i	Molecular Weight Range (g/mol)	f i
0-5000	0.01	20,000-25,000	0.19
5000-10,000	0.04	25,000-30,000	0.21

10,000-15,000	0.16	30,000-35,000	0.15
15,000-20,000	0.17	35,000-40,000	0.07

The average molecular weight is calculated as, $\bar{M}_m = \frac{\sum f_i M_i}{\sum f_i}$	fi	M_i	Σ f _i M _i (g/mol)
$\sum f_i$	0.01	2500	25.0
Based on the results of summing the products of the weight fractions and the average range weights, $ \bar{M}_m = \frac{22,850 \text{ g/mol}}{1.00} $ $= 22,850 \text{ g/mol} $	0.04	7500	300.0
	0.16	12,500	2000.0
	0.17	17,500	2975.0
	0.19	22,500	4275.0
	0.21	27,500	5775.0
	0.15	32,500	4875.0
	0.07	37,500	2625.0
er 10, Problem 71	1.00		22,850.0

Chapte

A copolymer consists of 70 wt % polystyrene and 30 wt % polyacrylonitrile. Calculate the mole fraction of each component in this material.

Chapter 10, Solution 71

Using a basis of 100 g of copolymer, we have 70 g of polystyrene and 30 g of polyacrylonitrile. The corresponding number of moles of each component is:



Moles of polystyrene

$$MW_{polystyrene}$$
 = 9 H atoms × 1 g/mol + 8 C atoms × 12 g/mol = 105 g/mol

No. of moles of polystyrene in 100 g of copolymer =
$$\frac{70 \text{ g}}{105 \text{ g/mol}} = 0.667 \text{ mol}$$

Moles of polyacrylonitrile

$$MW_{PAN} = 3 \text{ H atoms} \times 1 \text{ g/mol} + 3 \text{ C atoms} \times 12 \text{ g/mol} + 1 \text{ N atom} \times 14 \text{ g/mol}$$

= 53 g/mol

No. of moles of polyacrylonitrile in 100 g of copolymer =
$$\frac{30 \text{ g}}{53 \text{ g/mol}} = 0.566 \text{ mol}$$

Thus, the mole fractions of the components are calculated as:

Mole fraction of polystyrene =
$$\frac{0.667 \text{ mol}}{0.667 \text{ mol} + 0.566 \text{ mol}} = \mathbf{0.541}$$

Mole fraction of polyacrylonitrile =
$$\frac{0.566 \text{ mol}}{0.667 \text{ mol} + 0.566 \text{ mol}} = \mathbf{0.459}$$

An ABS copolymer consists of 25 wt % polyacrylonitrile, 30 wt % polybutadiene, and 45 wt % polystyrene. Calculate the mole fraction of each component in this material.

Chapter 10, Solution 72

Using a basis of 100 g of copolymer, we have 25 g of polyacrylonitrile, 30 g of polybutadiene, and 45 g of polystyrene. The corresponding number of moles of each component is:

Moles of polyacrylonitrile

$$MW_{PAN} = 3 \text{ H atoms} \times 1 \text{ g/mol} + 3 \text{ C atoms} \times 12 \text{ g/mol} + 1 \text{ N atom} \times 14 \text{ g/mol}$$

= 53 g/mol

No. of moles of polyacrylonitrile in 100 g of copolymer =
$$\frac{25 \text{ g}}{53 \text{ g/mol}} = 0.472 \text{ mol}$$

Moles of polybutadiene

No. of moles of polybutadiene in 100 g of copolymer =
$$\frac{30 \text{ g}}{54 \text{ g/mol}} = 0.556 \text{ mol}$$

Moles of polystyrene

$$MW_{polystyrene} = 9 \text{ H atoms} \times 1 \text{ g/mol} + 8 \text{ C atoms} \times 12 \text{ g/mol} = 105 \text{ g/mol}$$

No. of moles of polystyrene in 100 g of copolymer =
$$\frac{45 \text{ g}}{105 \text{ g/mol}} = 0.429 \text{ mol}$$

Thus, the total number of moles is 0.472 + 0.556 + 0.429 = 1.457 mol. Then the mole fractions of the components are:

Mole fraction of polyacrylonitrile =
$$\frac{0.472 \text{ mol}}{1.457 \text{ mol}} = \mathbf{0.324}$$

Mole fraction of polybutadiene =
$$\frac{0.556 \text{ mol}}{1.457 \text{ mol}} = \mathbf{0.382}$$

Mole fraction of polystyrene =
$$\frac{0.429 \text{ mol}}{1.457 \text{ mol}} = \mathbf{0.294}$$

As a check, the mole fractions should add up to 1.00:

$$0.324 + 0.382 + 0.294 = 1.000$$
 checks

Chapter 10, Problem 73

Determine the mole fractions of polyvinyl chloride and polyvinyl acetate in a copolymer having a molecular weight of 11,000 g/mol and a degree of polymerization of 150.

Chapter 10, Solution 73

From Example Problem 10.3, the molecular weights of PVC and PVA are 62.5 g/mol and 86.0 g/mol, respectively. The mole fractions of these polymers can be determined based upon the average molecular weight of the copolymer mer.

$$MW_{av}(mer) = f_{PVC}MW_{PVC} + f_{PVA}MW_{PVA} = f_{PVC}MW_{PVC} + (1 - f_{PVC})MW_{PVA}$$

where the average molecular weight of the copolymer mer is,

$$MW_{av}(mer) = \frac{MW_{av}(polymer)}{DP} = \frac{11,000 \text{ g/mol}}{150 \text{ mers}} = 73.33 \text{ g/(mol · mer)}$$

The mole fraction of PVC can be obtained by equating these two equations.

$$f_{\text{PVC}}(62.5 \text{ g/mol/mer}) + (1 - f_{\text{PVC}})(86.0 \text{ g/mol/mer}) = 73.33 \text{ g/(mol · mer)}$$

 $f_{\text{PVC}} = \mathbf{0.539}$ and $f_{\text{PVA}} = 1 - f_{\text{PVC}} = \mathbf{0.461}$

Chapter 10, Problem 74

How much sulfur must be added to 70 g of butadiene rubber to cross-link 3.0 percent of the mers? (Assume all sulfur is used to cross-link the mers and that only one sulfur atom is involved in each cross-linking bond.)

Chapter 10, Solution 74

Assuming only one sulfur atom is involved in each cross-linking bond with butadiene, we know there is a one-to-one correspondence between the number of moles of sulfur and the number of moles of butadiene in the reaction. We are therefore able to assess the amount of sulfur required for 100% cross-linking.

$$\begin{aligned} \text{mass of S}\big|_{100\%} &= \text{MW}_\text{S} \times (\text{No. of moles of S}) = \text{MW}_\text{S} \times (\text{No. of moles of butadiene}) \\ &= \text{MW}_\text{S}\bigg(\frac{\text{mass of butadiene}}{\text{MW}_\text{butadiene}(\text{mer})}\bigg) \end{aligned}$$

The average molecular weight of the butadiene mer is:

 $MW_{polybutadiene} = 6 H atoms \times 1 g/mol + 4 C atoms \times 12 g/mol = 54 g/mol$

Substituting,

mass of S
$$|_{100\%}$$
 = (32 g/mol) $\left(\frac{70 \text{ g}}{54 \text{ g/mol}}\right)$ = 41.48 g S

Thus for only 3 percent cross-linking,

mass of
$$S|_{3\%} = 0.03 \times 41.48 \text{ g } S = 1.24 \text{ g } S$$

Chapter 10, Problem 75

If 5 g of sulfur is added to 90 g of butadiene rubber, what is the maximum fraction of the cross-link sites that can be connected?

Chapter 10, Solution 75

Assuming one sulfur atom is involved in cross-linking each butadiene mer, the fraction of cross-link sites is simply the ratio of the moles of sulfur to the moles of butadiene.

No. of moles of S =
$$\frac{5 \text{ g}}{32 \text{ g/mol}} = 0.156 \text{ mol S}$$

No. of moles of butadiene =
$$\frac{90 \text{ g}}{54 \text{ g/mol}} = 1.667 \text{ mol butadiene}$$

The fraction of cross-link sites is thus,

Fraction of cross-link sites =
$$\frac{0.156}{1.667} \times 100\% = 9.36\%$$

Chapter 10, Problem 76

How much sulfur must be added to cross-link 10 percent of the cross-link sites in 90 g of polyisoprene rubber?

Since there is a one-to-one correspondence between the number of moles of sulfur and the number of moles of polyisoprene in the reaction, we can determine the amount of sulfur required for 100% cross-linking.

$$\begin{aligned} \text{mass of S}\big|_{100\%} &= \text{MW}_{\text{S}} \times (\text{No. of moles of S}) \\ &= \text{MW}_{\text{S}} \left(\frac{\text{mass of polyisoprene}}{\text{MW}_{\text{polyisoprene}}} (\text{mer}) \right) \end{aligned}$$

The average molecular weight of the polyisoprene mer is:

Substituting,

mass of S
$$|_{100\%}$$
 = (32 g/mol) $\left(\frac{90.0 \text{ g}}{68.0 \text{ g/mol}}\right)$ = 42.35 g S

Thus for only 10 percent cross-linking,

mass of
$$S|_{10\%} = 0.10 \times 42.35 \text{ g S} = 4.24 \text{ g S}$$

Chapter 10, Problem 77

How many kilograms of sulfur are needed to cross-link 15 percent of the cross-link sites in 200 kg of polyisoprene rubber?

mass of
$$S|_{100\%} = MW_S \times (No. \text{ of moles of } S) = MW_S \times (No. \text{ of moles of polyisoprene})$$

$$= MW_{S} \left(\frac{\text{mass of polyisoprene}}{MW_{\text{polyisoprene}}(\text{mer})} \right)$$

The average molecular weight of the polyisoprene mer is 68.0 g/mol. Substituting,

mass of S
$$|_{100\%}$$
 = (32 g/mol) $\left(\frac{200,000.0 \text{ g}}{68.0 \text{ g/mol}}\right)$ = 94,117.6 g S

Thus for 15 percent cross-linking,

mass of
$$S|_{15\%} = 0.15 \times 94{,}117.6 \text{ g } S = 14{,}117.6 \text{ g } S = 14.1 \text{ kg } S$$

Chapter 10, Problem 78

If 3 kg of sulfur is added to 300 kg of butadiene rubber, what fraction of the cross-links are joined?

Chapter 10, Solution 78

Assuming one sulfur atom is involved in cross-linking each butadiene mer, the fraction of cross-link sites is simply the ratio of the moles of sulfur to the moles of butadiene.

No. of moles of S =
$$\frac{3000 \text{ g}}{32 \text{ g/mol}} = 93.75 \text{ mol S}$$

No. of moles of butadiene =
$$\frac{300,000 \text{ g}}{54 \text{ g/mol}} = 5555.56 \text{ mol butadiene}$$

The fraction of cross-link sites is thus,

Fraction of cross-link sites =
$$\frac{93.75}{5555.56} \times 100\% = 1.69\%$$

Chapter 10, Problem 79

A butadiene-styrene rubber is made by polymerizing one monomer of styrene with seven monomers of butadiene. If 20 percent of the cross-link sites are to be bonded with sulfur, what weight percent sulfur is required? (See EP 10.7.)

Since the copolymer has 1 mole of styrene for every 7 moles of polybutadiene, we have

7 moles polybutadiene
$$\times$$
 54 g/mol = 378 g
1 mole polystyrene \times 105 g/mol = $\underline{105 \text{ g}}$
Copolymer total mass = 483 g

However, in this reaction, only the butadiene can participate in the cross-linking with sulfur. We thus need the mass fraction of butadiene: 378 g / 483 g = 0.783. Using a basis of 100 g of copolymer, the number of moles of butadiene is,

moles butadiene =
$$\frac{\text{mass of butadiene}}{\text{MW(mer)}} = \frac{100 \text{ g} \times 0.783}{54 \text{ g/mol}} = 1.45 \text{ mol}$$

The mass of sulfur required for 20 percent cross-linking is therefore,

mass of S
$$|_{20\%}$$
 = (0.20)(1.45 mol)(32 g/mol) = 9.28 g

And the weight percent of sulfur required for this reaction is

Weight percent
$$S = \frac{9.28 \text{ g}}{100 \text{ g} + 9.28 \text{ g}} \times 100\% = 8.49\%$$

What weight percent sulfur must be added to polybutadiene to cross-link 20 percent of the possible cross-link sites?

Chapter 10, Solution 80

Using a basis of 100 g and recalling that the molecular weight of polybutadiene is 54.0 g/mol, the number of moles of rubber is:

No. of moles of polybutadiene =
$$\frac{100 \text{ g}}{54.0 \text{ g/mol}}$$
 = 1.85 mol

For 20 percent cross-linking, the mass of sulfur required is,

mass of
$$S|_{20\%} = (0.20)(1.85 \text{ mol})(32 \text{ g/mol}) = 11.84 \text{ g}$$

And the weight percent of sulfur required for this reaction is

Wt % S =
$$\frac{11.84 \text{ g}}{100 \text{ g} + 11.84 \text{ g}} \times 100\% = 10.59\%$$

Chapter 10, Problem 81

A butadiene-acrylonitrile rubber is made by polymerizing one acrylonitrile monomer with five butadiene monomers. How much sulfur is required to react with 200 kg of this rubber to cross-link 22 percent of the cross-link sites? (See EP 10.8)

First, note that only the polybutadiene cross-links with the sulfur in this reaction and recall that the molecular weights for butadiene and acrylonitrile are, respectively,

54 g/mol and 53 g/mol. Then, copolymer total mass based on a 5:1 mole ratio is,

5 moles polybutadiene
$$\times$$
 54 g/mol = 270 g
1 mole acrylonitrile \times 53 g/mol = $\underline{}$ 53 g
Copolymer total mass = 323 g

The mass fraction of butadiene is thus: 270 g / 323 g = 0.836. Thus in 200 kg of copolymer, the number of moles of polybutadiene is,

moles of butadiene =
$$\frac{\text{mass of butadiene}}{\text{MW(mer)}} = \frac{200,000 \text{ g} \times 0.836}{54 \text{ g/mol}} = 3096.3 \text{ mol}$$

The mass of sulfur required for 22 percent cross-linking is therefore,

mass of
$$S|_{22\%} = (0.22)(3096.3 \text{ mol})(32 \text{ g/mol}) = 21,798 \text{ g} = 21.8 \text{ kg}$$

And the weight percent of sulfur required for this reaction is

Wt % S =
$$\frac{21,798 \text{ g}}{200,000 \text{ g} + 21,798 \text{ g}} \times 100\% = 9.83\%$$

If 15 percent of the cross-link sites in isoprene rubber are to be bonded, what weight percent sulfur must the rubber contain?

Chapter 10, Solution 82

Using a basis of 100 g and recalling that the molecular weight of isoprene is 68.0 g/mol, the number of moles of isoprene is

No. of moles of isoprene =
$$\frac{100 \text{ g}}{68.0 \text{ g/mol}} = 1.47 \text{ mol}$$

For 15 percent cross-linking, the mass of sulfur required is,

mass of
$$S|_{15\%} = (0.15)(1.47 \text{ mol})(32 \text{ g/mol}) = 7.06 \text{ g S}$$

Thus the weight percent of sulfur required for this reaction is

Wt % S =
$$\frac{7.06 \text{ g}}{100 \text{ g} + 7.06 \text{ g}} \times 100\% = 6.56\%$$

Chapter 10, Problem 83

A stress of 9.0 MPa is applied to an elastomeric material at a constant stress at 20 $^{\circ}$ C. After 25 days, the stress decreases to 6.0 MPa. (a) What is the relaxation time τ for this material? (b) What will be the stress after 50 days?

Chapter 10, Solution 83

(a) The decrease in stress is given by $\sigma = \sigma_0 e^{-t/\tau}$. Thus,

$$\tau = \frac{-t}{\ln(\sigma/\sigma_0)} = \frac{-25 \text{ days}}{\ln(6 \text{ MPa}/9 \text{ MPa})} = 61.7 \text{ days}$$

(b) For a relaxation time constant of 61.7 days, the stress after 50 days will be,

$$\sigma = (9.0 \text{ MPa})e^{-(50 \text{ days}/61.7 \text{ days})} = 4.0 \text{ MPa}$$

Chapter 10, Problem 84

A polymeric material has a relaxation time of 60 days at 27°C when a stress of 7.0 MPa is applied. How many days will be required to decrease the stress to 6.0 MPa?

Chapter 10, Solution 84

The decrease in stress is given by $\sigma = \sigma_0 e^{-t/\tau}$. Thus,

$$t = -\tau [\ln(\sigma/\sigma_0)] = -(60 \text{ days}) [\ln(6 \text{ MPa}/7 \text{ MPa})] = 9.25 \text{ days}$$

Chapter 10, Problem 85

A stress of 1000 psi is applied to an elastomer at 27°C, and after 25 days the stress is reduced to 750 by stress relaxation. When the temperature is raised to 50°C, the stress is reduced from 1100 to 400 psi in 30 days. Calculate the activation energy for this relaxation process using an Arrhenius-type rate equation.

Chapter 10, Solution 85

First, the relaxation time must be calculated for each set of conditions:

$$\tau_1 = \frac{-t}{\ln(\sigma/\sigma_0)} = \frac{-25 \text{ days}}{\ln(750 \text{ psi}/1000 \text{ psi})} = 86.90 \text{ days}$$

$$\tau_2 = \frac{-t}{\ln(\sigma/\sigma_0)} = \frac{-30 \text{ days}}{\ln(400 \text{ psi}/1100 \text{ psi})} = 29.66 \text{ days}$$

Since the Arrhenius-type equation uses absolute temperature, we must next convert the temperatures to Kelvin: $T_1 = 27^\circ + 273^\circ = 300 \text{ K}$; $T_2 = 50^\circ + 273^\circ = 323 \text{ K}$. Applying the Arrhenius-type rate equation, $1/\tau = Ce^{-Q/RT}$, we obtain two equations in two unknowns.

$$\frac{1}{\tau_1} = Ce^{-Q/RT_1}$$
 and $\frac{1}{\tau_2} = Ce^{-Q/RT_2}$

Dividing these equations, we obtain a single equation with one unknown - Q

$$\frac{\tau_2}{\tau_1} = \exp\left[\frac{-Q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right]$$

Substituting the values provided and the calculated time constants,

$$\frac{29.66}{86.90} = \exp\left[\frac{-Q}{8.314 \text{ J/mol} \cdot \text{K}} \left(\frac{1}{300 \text{ K}} - \frac{1}{323 \text{ K}}\right)\right]$$

$$Q = \left(\frac{-8.314 \text{ J/mol} \cdot \text{K}}{2.3736 \times 10^{-4} \text{ / K}}\right) \ln\left(\frac{29.66}{86.90}\right) = 37,653 \text{ J/mol} = 37.65 \text{ kJ/mol}$$

Chapter 10, Problem 86

The stress on a sample of a rubber material at constant strain at 27°C decreases from 6.0 to 4.0 MPa in three days. (a) What is the relaxation time τ for this material? (b) What will be the stress on this material after (i) 15 days and (ii) after 40 days?

Chapter 10, Solution 86

(a) The decrease in stress is given by $\sigma = \sigma_0 e^{-t/\tau}$. Thus,

$$\tau = \frac{-t}{\ln(\sigma/\sigma_0)} = \frac{-3 \text{ days}}{\ln(4 \text{ MPa}/6 \text{ MPa})} = 7.4 \text{ days}$$

(b) For a relaxation time constant of 7.4 days, the stress will be,

(i)
$$\sigma = (6.0 \text{ MPa})e^{-(15 \text{ days}/7.4 \text{ days})} = 0.79 \text{ MPa} = 790.4 \text{ kPa}$$

(ii)
$$\sigma = (6.0 \text{ MPa})e^{-(40 \text{ days}/7.4 \text{ days})} = 0.02695 \text{ MPa} = 26.95 \text{ kPa}$$

Chapter 10, Problem 87

A polymeric material has a relaxation time of 100 days at 27°C when a stress of 6.0 MPa is applied. (a) How many days will be required to decrease the stress to 4.2 MPa? (b) What is the relaxation time at 40°C if the activation energy for this process is 25 kJ/mol?

Chapter 10, Solution 87

(a) The decrease in stress is given by $\sigma = \sigma_0 e^{-t/\tau}$. Thus,

$$t = -\tau [\ln(\sigma/\sigma_0)] = -(100 \text{ days})[\ln(4.2 \text{ MPa}/6 \text{ MPa})] = 35.7 \text{ days}$$

(b) By applying the Arrhenius-type rate equation, $1/\tau = Ce^{-Q/RT}$, for two sets of general conditions and dividing the resulting equations, we obtain

$$\frac{\tau_2}{\tau_1} = \exp\left[\frac{-Q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right]$$

Substituting the values provided and the τ_1 calculated above,

$$\frac{\tau_2}{100} = \exp\left[-\frac{25,000 \text{ J}}{8.314 \text{ J/mol} \cdot \text{K}} \left(\frac{1}{300 \text{ K}} - \frac{1}{313 \text{ K}}\right)\right]$$

$$\tau_2 = 65.95 \, \text{days}$$

What is the difference between a saturated and an unsaturated carbon-containing molecule?

Chapter 10, Solution 88

A saturated carbon-containing organic molecule has only single covalent bonds in its main chain. An unsaturated carbon-containing molecule has one or more double or triple bonds in its main chain.

Chapter 10, Problem 89

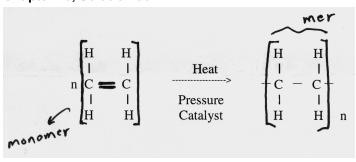
Describe the bonding structure of an activated ethylene molecule that is ready for covalent bonding with another activated molecule by using (a) the electron-dot-cross notation and (b) straight-line notation for the bonding electrons.

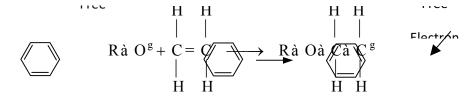
Chapter 10, Solution 89

Electron dot Notation:	Straight Line Notation		
н н	н н		
.C:C.	$-\frac{C}{I} - \frac{C}{I}$		
•• ••	1 1		
н н	н н		

Chapter 10, Problem 90

Write a general chemical reaction for the chain polymerization of ethylene monomer into the linear polymer polyethylene.





Write an equation for the formation of two free radicals from a molecule of benzoyl peroxide by using straight-line notation for the bonding electrons.

Chapter 10, Solution 91

Chapter 10, Problem 92

Write an equation for the reaction of an organic free radical (RO) with an ethylene molecule to form a new, longer-chain free radical.

Chapter 10, Solution 92



Chapter 10, Problem 93

Write a reaction for the free radical $R\grave{a}$ $CH_2\grave{a}$ CH_2 with an ethylene molecule to extend the free radical. What type of reaction is this?

Chapter 10, Solution 93

Rà
$$CH_2$$
à $CH_2^g + CH_2 = CH_2 \longrightarrow R$ à CH_2 à CH_2 à CH_2 à CH_2 à CH_2

This reaction is a polymerization process of degree two.

$$n \begin{bmatrix} \vdots & \vdots & \vdots \\ C = C \\ \vdots & \vdots \\ H & R_1 \end{bmatrix} \longrightarrow \begin{bmatrix} \vdots & \vdots & \vdots \\ C & C \\ \vdots & \vdots \\ H & R_1 \end{bmatrix}_n$$

(a) What causes a polyethylene molecular chain to have a zigzag configuration? (b) What type of chemical bonding is there between the polymer chains in polyethylene? (c) How do side branches on polyethylene main chains affect the packing of the molecular chains in a solid polymer? (d) How does branching of the polymer chains affect the tensile strength of solid bulk polyethylene?

Chapter 10, Solution 94

(a) A polyethylene molecular chain has a zigzag configuration because, at the microscopic level, the single carbon-carbon covalent bonds form an angle of approximately 109º. (b) Between the polymer chains of polyethylene, permanent dipoles bonds provide weak secondary bonding. (c) Side branches on polyethylene main chains reduce the packing of the molecular chains. (d) As a result of loose packing, the secondary bonds between chains are weakened and thus, the tensile strength of the solid bulk polyethylene is lowered.

Chapter 10, Problem 95

Write a general reaction for the polymerization of a vinyl-type polymer.

Chapter 10, Solution 95

Chapter 10, Problem 96

Write a general reaction for the polymerization of a vinylidene polymer.

monomer

Write a general polymerization reaction for the formation of a vinyl chloride and vinyl acetate copolymer.

Chapter 10, Solution 97

Chapter 10, Problem 98

Write the equation for the reaction of a molecule of hexamethylene diamine with one of adipic acid to produce a molecule of nylon 6,6. What is the by-product of this reaction?

dipamide	 Water	//		
dipamide		\		

Write the reaction for the stepwise polymerization of two phenol molecules with one of formaldehyde to produce a phenol formaldehyde molecule.

(a) Why is complete crystallinity in thermoplastics impossible? (b) How does the amount of crystallinity in a thermoplastic affect (i) its density and (ii) its tensile strength? Explain.

Chapter 10, Solution 100

(a) Complete crystallinity is impossible in thermoplastics because of molecular entanglements and crossovers which exist in all linear polymeric materials.

(b)

- (i) As the degree of crystallinity increases in a thermoplastic, the packing of polymer chains increases and thus the material density also increases.
- (ii) Similarly, since the polymer chains become closer with increased crystallinity, the bonding forces between polymers increase and thus the tensile strength of the material increases.

Chapter 10, Problem 101

How does the molecular-chain structure differ for the following types of polyethylene: (a) low-density, (b) high-density, and (c) linear-low-density?

Chapter 10, Solution 101

- (a) Low-density polyethylene (LDPE) has a fully branched-chain structure.
- (b) High-density polyethylene (HDPE) has a straight-chain structure.
- (c) Linear-low-density polyethylene (LLDPE) has a linear-chain structure with short, slanting side branches.

Chapter 10, Problem 102

How does chain branching affect the following properties of polyethylene: (a) amount of crystallinity, (b) strength, and (c) elongation?

Chapter 10, Solution 102

Chain branching:

- (a) decreases the degree of crystallinity;
- (b) decreases the strength;
- (c) increases elongation.

Chapter 10, Problem 103

(a) Write the general reaction for the polymerization of polyvinyl chloride. (b) How can the higher strength of polyvinyl chloride as compared to polyethylene be explained?

(b) Polyvinyl chloride has a higher strength than polyethylene because the chlorine atoms, in the PVC chain, create strong dipole moments which produce strong cohesive forces between the polymer chains.

Chapter 10, Problem 104

(a) Write the general reaction for the polymerization of polystyrene from styrene. (b) What effect does the presence of the phenyl group on every other carbon of the main chain have on the impact properties of polystyrene? (c) How can the low-impact resistance of polystyrene be improved by copolymerization? (d) What are some of the applications for polystyrene?

Chapter 10, Solution 104

(a)

- (b) The presence of the phenylene ring, on alternating carbon atoms of the main polystyrene chain, results in a rigid bulky steric configuration and thus an inflexible polymeric material having low-impact resistance.
- (c) Polystyrene's low-impact resistance can be improved through the addition of a copolymer with a rubber level between 3 and 12 percent. An example is the polybutadiene elastomer.
- (d) Polystyrene is typically used in automobile interior parts, appliance housings, dials and knobs, and housewares.

(a) How does the presence of the chlorine atom on every other carbon atom of the main chain of polychlorotrifluoroethylene modify the crystallinity and moldability of polytetrafluoroethylene? (b) What are some of the important applications of polychlorotrifluoroethylene?

Chapter 10, Solution 105

(a) The substitution of every fourth fluorine atom with a chlorine atom introduces irregularity in the polymer chains' structure. As a result, PCTFE is less crystalline and has a lower melting temperature and melt viscosity. Thus, unlike PTFE, PCTFE can be molded and extruded using conventional molding processes. (b) Important applications of extruded, molded and machined products of PCTFE are chemical processing equipment, electrical applications, gaskets, O-rings, seals, and electrical components.

Chapter 10, Problem 106

Write a chemical reaction for one molecule of a dibasic acid with a diamine to form an amide linkage. What is the by-product of this reaction?

Chapter 10, Solution 106

An example of a reaction involving one molecule of a dibasic acid with a diamine is polymerization of hexamethylene diamine and adipic acid which produces the most important nylon, Nylon 6,6, with water as the by-product.



Write a chemical reaction for one molecule of adipic acid and one molecule of hexamethylene diamine to form an amide linkage.

Chapter 10, Solution 107

See the solution to problem 10.133.

Chapter 10, Solution 133.

Write a chemical reaction for one molecule of a dibasic acid with a diamine to form an amide linkage. What is the by-product of this reaction?

An example of a reaction involving one molecule of a dibasic acid with a diamine is polymerization of hexamethylene diamine and adipic acid which produces the most important nylon, Nylon 6,6, with water as the by-product.



Write the reaction for the polymerization of nylon 6 from ∫-caprolactam.

Illustrate the bonding between polymer chains of nylon 6,6. Why is this bonding particularly strong? (See Fig. 10.35)

Figure 10.35

Chapter 10, Solution 109

The bonding between the nylon 6,6 chains is particularly strong because of the —NHO hydrogen bonds as shown schematically to the right.

Chapter 10, Problem 110

What part of the polycarbonate structure makes the molecule stiff? What part of the polycarbonate molecule provides molecular flexibility?

Chapter 10, Solution 110

The attachment of the two phenol groups and the two methyl groups to the same carbon atom makes the molecular structure very stiff. However, flexibility is provided by the single C—O bonds.

Chapter 10, Problem 111

What part of the structure of polyphenylene oxide provides its relatively high strength? What part of its structure provides its molecular flexibility?

The repeating phenylene rings provide for relatively high strength and rigidity while the oxygen linkage contributes to the molecular flexibility of the structure.

Chapter 10, Problem 112

What part of the structure of the acetals provides high strength?

Chapter 10, Solution 112

High strength is provided through the regularity, symmetry and flexibility of the acetal polymer molecules; high bonding strengths are thus achieved between the molecular chains with hydrogen and oxygen interaction.

Chapter 10, Problem 113

What part of the structure of the thermoplastic polyesters provides rigidity? What part provides molecular mobility?

Chapter 10, Solution 113

The phenylene ring structure provides rigidity to polyesters while the butylenes units in PBT provide for some molecular mobility which facilitates the melt process.

Chapter 10, Problem 114

What part of the polysulfone structure provides its high strength? What part provides chain flexibility and impact strength? What part provides high-oxidation stability?

Chapter 10, Solution 114

High strength and rigidity is provided through the phenylene rings of the polysulfone; these rings create rigidity and strong intermolecular attraction between polymer chains. The oxygen atom between the phenylene rings (ether linkage) imparts chain flexibility and impact strength. The para positions of the two oxygen atoms, with respect to the phenylene rings and the sulfone group, provide high-oxidation stability.

Chapter 10, Problem 115

What part of the structure of PPS provides its rigidity and strength? What part provides it high resistance to chemicals?

The compact structure of the phenylene rings separated by sulfur atoms produces the strong, rigid thermoplastic material. The sulfur atoms impart such high chemical resistance to PPS that no know chemical can dissolve this polymer.

Chapter 10, Problem 116

What is the function of the ether linkage in polyetherimide?

Chapter 10, Solution 116

The ether linkage, between the phenyl rings in polyetherimide, imparts the chain flexibility required for good melt and flow characteristics.

Chapter 10, Problem 117

What are some of the advantages of thermosetting plastics for engineering design applications? What is the major disadvantage of thermosets that thermoplastics do not have?

Chapter 10, Solution 117

General advantages of thermosetting plastics include one or more of the following: high thermal stability; high rigidity; high dimensional stability; resistance to creep and deformation under load; light weight; and high electrical and thermal insulating properties.

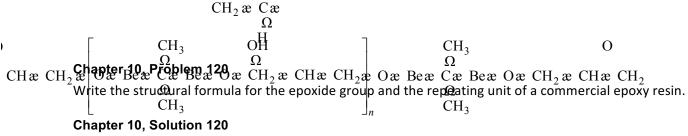
Chapter 10, Problem 118

Using structural formulas, write the reaction for phenol with formaldehyde to form a phenol-formaldehyde molecule (use two phenol molecules and one formaldehyde molecule). What kind of molecule is condensed off in the reaction?

Chapter 10, Solution 118

In the production of phenol-formaldehyde, water is formed as shown in the diagram below.

Chapter 10, Problem 119 Why are large percentages of fillers used in phenolic molding compounds? What types of fillers are used and for what purposes? Chapter 10, Solution 119 Phenolic molding compounds contain large percentages of fillers, as much as 50-80%, because the fillers reduce shrinkage during molding, lower cost and improve strength.



The chemical structure of the epoxide group is:

The general chemical structure of most commercial epoxy resins is:

Chapter 10, Problem 121

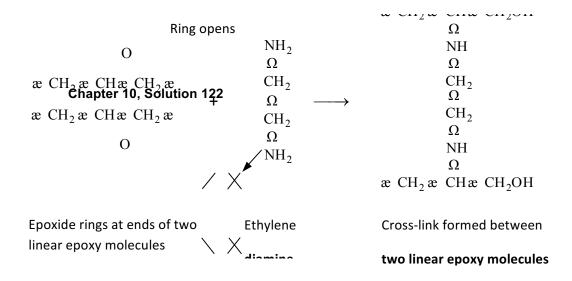
What are two types of reaction sites that are active in the cross-linking of commercial epoxy resins?

Chapter 10, Solution 121

The epoxy and hydroxyl (—OH) groups are the two active reaction sites in the cross-linking of commercial epoxy resins.

Chapter 10, Problem 122

Write the reaction for the cross-linking of two epoxy molecules with ethylene diamine.



What makes an unsaturated polyester resin "unsaturated"?

Chapter 10, Solution 123

An unsaturated polyester resin is "unsaturated" because it has reactive double carbon-carbon bonds available for the cross-linking necessary to form thermosets.

Chapter 10, Problem 124

How are linear unsaturated polyesters cross-linked? Write a structural formula chemical reaction to illustrate the cross-linking of an unsaturated polyester.

Chapter 10, Solution 124

Linear unsaturated polyesters are usually cross-linked with vinyl-type molecules such as styrene in the presence of a free-radical curing agent.

$$-\begin{bmatrix} H & H & O & O \\ \Omega & \Omega & P & P \\ O \circ & C \circ & C \circ & O \circ & C \circ & C & C \circ \\ \Omega & \Omega & \Omega & \Omega & \Omega \\ H & H & H & H & \end{bmatrix}_{n} + \begin{bmatrix} H & H \\ & & \\ &$$

Write the formula for *cis*-1,4 polyisoprene. What does the prefix *cis*- stand for? What is the significance of the 1,4 in the name *cis*-1,4 polyisoprene.

The formula for the *cis*-1,4 polyisoprene is shown

to the right.

The prefix *cis*- indicates that the methyl group and the hydrogen atom are on the same side of the carbon-carbon double bond while the notation "1,4" indicates that the mer is linear and that bonding occurs on the first and fourth carbon atoms of the polymer chain.

Chapter 10, Problem 126

Why does the trans isomer lead to a higher degree of crystallinity than the cis isomer for polyisoprene?

Chapter 10, Solution 126

The trans isomer leads to a higher degree of crystallinity because its steric arrangement is more symmetrical and thus does not cause interference between the methyl group and hydrogen atom.

Chapter 10, Problem 127

How does cross-linking with sulfur affect the tensile strength of natural rubber? Why is only about 3 wt % of sulfur used in the process?

Chapter 10, Solution 127

The cross-linking of natural rubber with sulfur increases the material's tensile strength significantly. Only about 3 wt % sulfur is used in the process because larger amounts cause greater cross-linking, resulting in a harder, less-flexible material.

Chapter 10, Problem 128

How can oxygen atoms cross-link the rubber molecules? How can the cross-linking of rubber molecules by oxygen atoms be retarded?

Chapter 10, Solution 128

Similar to sulfur atoms in vulcanization, oxygen atoms can cross-link the rubber molecules by reacting with the carbon double bonds. This process can be retarded through the addition of antioxidants in the rubber compounding process.

Can SBR be vulcanized? Explain.

Chapter 10, Solution 129

SBR can be vulcanized through cross-linking of the carbon double bonds in the butadiene mer with sulfur.

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Chapter 10, Problem 130

What is the composition of nitrile rubbers? What effect does the nitrile group have on the main carbon chain in nitrile rubber?

Chapter 10, Solution 130

Nitrile rubber is composed of 55 to 82 percent butadiene and 45 to 18 percent acrylonitrile copolymers, respectively. The nitrile group imparts good resistance to oils and solvents and improves the abrasion and heat resistance of the rubber, but also reduces the flexibility of the main carbon chain.

Chapter 10, Problem 131

Write the repeating chemical structural unit for polychloroprene. What common name is given to polychloroprene rubber? How does the presence of the chlorine atom in polychloroprene affect some of its properties?

Chapter 10, Solution 131

The repeating chemical structural unit for polychloroprene, better known as Neoprene, is shown schematically to the right. The presence of the chlorine atom in this mer increases the resistance of the unsaturated double bonds to attack by oxygen, ozone, light and weather conditions.

Chapter 10, Problem 132

How are polychloroprene elastomeric materials vulcanized?

Polychloroprene elastomeric materials can be vulcanized using metallic oxides. Zinc oxide is typically used as a catalyst for vulcanization which produces zinc chloride. Magnesium oxide is thus used as a stabilizer to remove the zinc chloride.

Chapter 10, Problem 133

How can a silicone rubber be cross-linked at room temperature?

Chapter 10, Solution 133

Polydimethyl siloxane silicone rubber is cross-linked using the initiator (benzoyl peroxide) at room temperature. It reacts with the two methyl groups to form $Si - CH_2 - CH_2 - Si$ bridges.

Chapter 10, Problem 134

How does the average molecular mass of a thermoplastic affect its strength?

Chapter 10, Solution 134

The average molecular mass of a thermoplastic directly affects its strength as it is indicative of the degree of polymerization of the solid; the plastic must attain a critical molecular mass to become a stable solid. However, increasing the mass beyond this minima does not appreciably increase the thermoplastic's strength.

Chapter 10, Problem 135

How does the amount of crystallinity within a thermoplastic material affect (a) its strength, (b) its tensile modulus of elasticity, and (c) its density?

Chapter 10, Solution 135

- (a) As the amount of crystallinity increases, the polymer chains become more tightly packed and the tensile strength increases.
- (b) The tensile modulus of elasticity is also directly related to crystallinity; the modulus increases with increasing crystallinity.
- (c) Increased crystallinity corresponds to an increase in density.

Chapter 10, Problem 136

Explain why low-density polyethylene is weaker than high-density polyethylene.

Chapter 10, Solution 136

Low-density polyethylene is weaker than high-density because the molecular chains are more branched and farther apart from each other, causing weaker bonding forces and thus lower strength.

Explain why bulky side groups strengthen thermoplastics.

Chapter 10, Solution 137

Bulky side groups strengthen thermoplastics because they impede chain slippage during permanent deformation.

Chapter 10, Problem 138

Explain how highly polar atoms bonded to the main carbon chain strengthen thermoplastics. Give examples.

Chapter 10, Solution 138

Highly polar pendant atoms of the main carbon chain greatly strengthen thermoplastics by increasing the molecular bonding forces between polymer chains.

Chapter 10, Problem 139

Explain how oxygen atoms covalently bonded in the main carbon chain strengthen thermoplastics. Give an example.

Chapter 10, Solution 139

The introduction of oxygen atoms in the main carbon chain strengthens a thermoplastic by increasing the rigidity and the permanent dipole bonds between polymer chains. Examples are polyoxy methylene (acetal) and polycarbonates.

Chapter 10, Problem 140

Explain how phenylene rings covalently bonded in the main carbon chain strengthen thermoplastics. Give an example.

Chapter 10, Solution 140

The covalent bonding of phenylene rings to the main carbon chain is an important means of producing high-strength engineering plastics such as polyphenylene oxide and polycarbonates. These rings increase the thermoplastic's strength by causing steric hindrance to rotation within the polymer chain and electronic attraction of resonating electrons between adjacent molecules.

Chapter 10, Problem 141

Explain why thermosetting plastics have in general high strengths and low ductilities.

In general, thermosetting plastics have high strengths and low ductilities because their molecular structure is comprised of a covalently bonded network produced by chemical reaction within the material after casting or during pressing under heat and pressure.

Chapter 10, Problem 142

How do the prices of engineering thermoplastics compare with those of the commodity plastics such as polyethylene, polyvinyl chloride, and polypropylene?

Chapter 10, Solution 142

In general, engineering thermoplastics cost more than commodity plastics.

Chapter 10, Problem 143

How do the densities and tensile strengths of engineering thermoplastics compare with those of polyethylene and polyvinyl chloride?

Chapter 10, Solution 143

The densities of engineering thermoplastics range from approximately $1.0-1.5 \text{ g/cm}^3$, and are thus higher than those of polyethylene ($0.92-0.96 \text{ g/cm}^3$) but lower than rigid PVC ($1.49-1.58 \text{ g/cm}^3$). The tensile strengths of engineering plastics are significantly higher than either high density or low density polyethylene and approximately equal to or greater than the strength of rigid PVC

Chapter 10, Problem 144

How does increasing the temperature of thermoplastics affect their strength? What changes in bonding structure occur as thermoplastics are heated?

Chapter 10, Solution 144

As the temperature of thermoplastics increases, the secondary bonding forces become weaker and the material softens.

Chapter 10, Problem 145

Why don't cured thermoset plastics become viscous and flow at elevated temperatures?

Chapter 10, Solution 146

As cured thermoset plastics are heated to elevated temperatures, the strong covalent bonds of their molecular network weaken but continue to prevent viscous flow; instead, the material degrades and chars.



Polytetrafluoroethylene Chapter 10, Problem 146

Polychlorotrifluoroethylene

How do increases in stress and temperature affect the creep resistance of thermoplastics?

Chapter 10, Solution 146

An increase in applied stress or temperature will increase the creep experienced by a thermoplastic.

Chapter 10, Problem 147

(a) What are the fluoroplastics? (b) What are the repeating chemical structural units for polytetrafluoroethylene and polychlorotrifluoroethylene? What are some of the important properties and applications of polytetrafluoroethylene?

Chapter 10, Solution 147

(a) Fluroplastics are plastics made from monomers having one or more fluorine atoms. Polytetrafluoroethylene (PTFE) and polychlorotrifluoroethylene (PCTFE), the two most widely used, have the following repeating chemical structural units.

(c) PTFE is a high density crystalline polymer with exceptional chemical resistance, high impact strength and a low coefficient of friction. It can be used over a wide range of temperatures (-200°C to 260°C) and can be strengthened by fillers. Applications of PTFE include: chemically resistant pipe and pump parts, high temperature cable insulation, molded electrical components, tape, and non-stick coatings. Filled PTFE compounds are used for bushings, bearings, O-rings, seals, packings and gaskets.

Chapter 10, Problem 148

How can the creep modulus of a thermoplastic be increased?

The creep modulus of thermoplastics can be increased by reinforcing the material with glass fibers.

Chapter 10, Problem 149

How can the extra energy required to fracture glassy thermoplastics, as compared to inorganic glasses, be explained?

Chapter 10, Solution 149

The additional energy required to fracture glassy thermoplastics, as compared to inorganic glasses, is attributed to the energy required for the development of crazes in glassy plastics prior to fracture.

Chapter 10, Problem 150

How is it possible for a polymer chain such as a polyethylene one to keep growing spontaneously during polymerization?

Chapter 10, Solution 150

The polymer chains in chain polymerization keep growing spontaneously because the energy of the chemical system is lowered by the chain polymerization process; the total energy of newly created polymers is lower than the total energy of the monomers that have reacted to form them.

Chapter 10, Problem 151

During the solidification of thermoplastics, how does the specific volume versus temperature plots differ for noncrystalline and partly crystalline thermoplastics?

Chapter 10, Solution 151

A noncrystalline thermoplastic experiences a gradual change in specific volume as the material is cooled from its melting point to its glass transition temperature. Conversely, partly crystalline thermoplastics display an abrupt decrease in specific volume as it solidifies. This sudden reduction is attributed to the increased packing of polymer chains into crystalline regions.

Chapter 10, Problem 152

(a) What are some of the properties that make polyethylene such an industrially important plastic material? (b) What are some of its industrial applications?

- (a) Some of the properties of that make polyethylene industrially important are: toughness at room temperature and low temperature, good flexibility over a wide temperature range, excellent corrosion resistance, excellent insulating properties, odorless, tasteless, and low water-vapor transmission.
- (b) Polyethylene is used to make containers, electrical insulation, chemical tubing, housewares, and blow-molded bottles.

Chapter 10, Problem 153

(a) How is the flexibility of bulk polyvinyl chloride increased? (b) What are some of the properties of polyvinyl chloride that make it an important industrial material?

Chapter 10, Solution 153

- (a) The flexibility of bulk polyvinyl chloride is increased through the addition of a plasticizer.
- (b) Polyvinyl chloride is important to industry primarily because of its high chemical resistance and its distinct ability to serve as the base material for a large number of compounds having a wide range of physical and chemical properties.

Chapter 10, Problem 154

(a) What are plasticizers? (b) Why are they used in some polymeric materials? (c) How do plasticizers usually affect the strength and flexibility of polymeric materials? (d) What types of plasticizers are commonly used for PVC?

Chapter 10, Solution 154

Plasticizers are high-molecular-weight compounds selected to be completely miscible and compatible with the base material. (b) They are used to impart flexibility, softness and extensibility to polymeric materials and (c) consequently decrease tensile strength. (d) Phthalate esters are commonly used in the production of PVC.

Chapter 10, Problem 155

(a) How is the processibility of PVC improved to produce rigid PVC? (b) What are some of the applications for plasticized PVC?

Chapter 10, Solution 155

(a) In the production of rigid PVC, rubbery resins, added to the PVC, improve the melt flow by forming a dispersion of small, soft rubbery particles.

(b) Plasticized PVC is used in a wide range of applications which include: furniture, interior wall coverings, rainwear, shoes, electrical wire insulation, garden hoses, refrigerator gaskets, appliance components, housewares and automobile upholstery, floor mats, and top coverings.

Chapter 10, Problem 156

(a) What are SAN resins? (b) What desirable properties do SAN thermoplastics have? (c) What are some of the applications for SAN thermoplastics?

Chapter 10, Solution 156

(a) SAN (styrene-acrylonitrile) resins are random, amorphous copolymers of styrene and acrylonitrile. (b) SAN thermoplastics are high performance members of the styrene family which possess improved chemical resistance, heat-deflection temperatures, toughness and load-bearing characteristics than standard polystyrene. But like polystyrene, these plastics are rigid, hard, easily processed, and exceptionally clear. (c) SANS are used in automotive instrument lenses, dash board components, glass-filled support panels, appliance knobs, blender and mixer bowls, medical syringes, blood aspirators, construction safety glazing, and houseware mugs.

Chapter 10, Problem 157

(a) What do the letters A, B, and S stand for in the ABS thermoplastic? (b) Why is ABS sometimes referred to as a terpolymer? (c) What important property advantages does each of the components in ABS contribute? (d) Describe the structure of ABS. (e) How can the impact properties of ABS be improved? (f) What are some of the applications for ABS plastics?

Chapter 10, Solution 157

- (a) The letters A, B, and S of the ABS acronym stand for the monomers α crylonitrile, butadiene, and styrene.
- (b) ABS is referred to as a terpolymer because it is produced from three polymers.
- (c) Acrylonitrile contributes toughness and good heat and chemical resistance, butadiene provides impact strength and low-property retention, and styrene add surface gloss, rigidity, and ease of processing.
- (d) ABS is not a random terpolymer but a blend of a glassy copolymer (styrene-acrylonitrile) and rubbery domains created from a butadiene polymer or copolymer.
- (e) The impact properties can be further improved by grafting the styrene-acrylonitrile copolymer matrix to the rubber domains. This technique produces a two-phase structure
- (f) The primary applications for ABS plastic are pipe and fittings for building construction. However, ABS is also used in automotive parts, appliance parts, business machines, computer and telephone housings, and electrical conduits.

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Chapter 10, Problem 158	(

(a) What is the repeating chemical structural unit for polymethyl methacrylate? (b) By what trade names is PMMA commonly known? (c) What are some of the important properties of PMMA that make it an important industrial plastic?

Chapter 10, Solution 158

Polymethyl methacrylate, commonly called Plexiglas and Lucite, has the following mer:

PMMA is hard, rigid and transparent and has good chemical resistance to outdoor environments.

Chapter 10, Problem 159

What properties do nylons have that make them useful for engineering applications? What is an important undesirable property of nylon?

Chapter 10, Solution 159

Nylons have high strength and heat-deflection temperatures. The flexibility of the main chain leads to low melt viscosity, and thus ease of processing, as well as high lubricity, low surface friction and good abrasion resistance. The polyamides also have good chemical resistance. However, nylon also exhibits high water absorption which results in dimensional changes with increasing moisture content.

Chapter 10, Problem 160

What are some of the engineering applications for nylons?

Chapter 10, Solution 160

Nylons are used throughout industry. Their high lubricity provides for use in applications such as unlubricated gears, bearings, and antifriction parts while their high temperature endurance, in conjunction with their chemical resistance, permits them to be used in mechanical and electrical parts designed for severe thermal-chemical environments. In addition, nylons are utilized in high-impact parts, and when reinforced with glass, in engine fan blades, valve covers, and steering column housings.

What are some engineering applications for polycarbonates?

Chapter 10, Solution 161

Some engineering applications for polycarbonates are safety shields, cams and gears, helmets, electrical relay covers, aircraft components, boat propellers, traffic light housings and lenses, window glazings, and housings for handheld power tools, small appliances, and computers terminals.

Chapter 10, Problem 162

What are some of the properties of polycarbonates that make them useful engineering thermoplastics?

Chapter 10, Solution 162

Properties of polycarbonate that make them useful engineering thermoplastics include relatively high impact and tensile strengths, thermal resistance, good electrical insulation, and transparency.

Chapter 10, Problem 163

What are some of the engineering applications for polyphenylene oxide resins?

Chapter 10, Solution 163

Common applications of polyphenylene oxide resins are electrical connectors, television tuners and deflection yoke components, small appliance and business machine housings, and automobile dashboards, grills and exterior body parts.

Chapter 10, Problem 164

What are some of the properties that make polyphenylene oxide resins important engineering thermoplastics?

Chapter 10, Solution 164

Polyphenylene oxide-based resins are important to engineering applications because of their excellent dimensional stability with low creep, high modulus, low water absorption, good dielectric properties, excellent resistance to impact and aqueous chemical environments, and good mechanical properties over a wide range of temperatures (-40°C to 150°C).

Chapter 10, Problem 165

What are some of the properties of acetals that make them important engineering thermoplastics?

Chapter 10, Solution 165

Acetals have exceptionally high melting points, long-term load carrying properties (low wear and friction and exceptional fatigue resistance) and dimensional stability. The homopolymer is particularly hard and rigid with high tensile and flexural strengths, as compared to the copolymer. In contrast, the copolymer is more stable for long-term, high-temperature applications and has a higher elongation.

Chapter 10, Problem 166

What outstanding property advantage do the acetals have over nylons?

Chapter 10, Solution 166

Unlike nylons, homopolymer acetals have low moisture absorption and thus good dimensional stability.

Chapter 10, Problem 167

What are some of the engineering applications for acetals?

Chapter 10, Solution 167

Acetals have replaced many metal castings and stampings, where high strength is not required in such applications as automobile seat belt, fuel system and window handle components and in such machinery applications as mechanical couplings, pump impellers, gears, cans, and housings. They are also used in many consumer products like zippers, fishing reels, and writing instruments.

Chapter 10, Problem 168

What types of materials have acetals commonly replaced?

Chapter 10, Solution 168

Acetals have replaced metal zinc, brass and aluminum castings and steel stampings due to their manufacturing cost-effectiveness; finishing and assembly operations costs have been reduced or eliminated in many applications.

Chapter 10, Problem 169

What are some of the properties of thermoplastic polyesters that make them important engineering thermoplastics?

Chapter 10, Solution 169

Thermoplastic polyesters crystallize readily, have good strength, chemical resistance and electrical insulation properties, and have low moisture-absorption characteristics.

What are some engineering applications for PBT thermoplastics?

Chapter 10, Solution 170

PBT is used in electrical applications such as connectors, switches, relays, TV tuner components, high-voltage components, terminal boards, integrated circuit boards, motor brush holders and housings. In industry, pump impellers, housings and support brackets, irrigation valves and bodies, and water meter components are made of PBT. Automotive applications include large exterior-body components, high-energy ignition caps and rotors, ignition coil caps, coil bobbins, and speedometer frames and gears.

Chapter 10, Problem 171

What are some of the properties of polysulfone that are important for engineering designs?

Chapter 10, Solution 171

Significant properties of polysulfone are its high heat-deflection temperature of 174°C at 1.68 MPa and its endurance at temperatures of 150°C to 174°C. In addition, polysulfone has excellent tensile strengths for a thermoplastic 70 MPa (10.2 ksi), a relatively low creep rate, and hydrolysis resistance in both aqueous acid and alkaline environments due to the hydrolytically stable oxygen linkages between the phenylene rings.

Chapter 10, Problem 172

What are some of the engineering applications for polysulfone?

Chapter 10, Solution 172

Because polysulfone can withstand high temperatures, it is widely used in medical instruments and trays which require autoclave sterilization. This hydrolysis resistant polyester is also used for corrosion-resistant piping, pumps, tower packing and filter modules and plates.

Chapter 10, Problem 173

What properties make PPS a useful engineering thermoplastic?

Chapter 10, Solution 173

Additional properties which make PPS useful in engineering designs include: high degree of crystallinity which affords a gradual decrease in strength up to 200°C; capability for nearly doubling of strength to 120 MPa (17 ksi) through glass filler.

What are some engineering applications for PPS?

Chapter 10, Solution 174

PPS is used in industrial-mechanical applications such as chemical process equipment – submersible, centrifugal, van and gear-type pumps. Other applications which take advantage of PPS' excellent corrosion resistance are automobile emission-control systems, coatings for oil field pipes, valves, fittings and couplings, and petroleum processing equipment. Electrical-electronic applications include computer components and thermostats requiring heat-resistant, insulating materials.

Chapter 10, Problem 175

What special properties does polyetherimide have for (a) electrical engineering designs and (b) mechanical engineering designs?

Chapter 10, Solution 175

Polyetherimide has good electrical insulation properties over a wide range of temperatures and frequencies.

Properties of polyetherimide which are valuable to mechanical engineering designs are its high heat resistance, creep resistance and rigidity.

Chapter 10, Problem 176

What are some applications for polyetherimide?

Chapter 10, Solution 176

Applications for polyetherimide include electrical-electronic, automotive, aerospace and specialty applications.

Chapter 10, Problem 177

Why are polymer alloys of great importance for engineering applications?

Chapter 10, Solution 177

Polymer alloys are particularly important to engineering applications because materials can now tailored to have specific properties and thus material performance and cost can be optimized.

Chapter 10, Problem 178

What are the major advantages of phenolic plastics for industrial applications?

Chapter 10, Solution 178

Phenolic plastics are low cost materials with good electrical and heat insulating properties, as well as, good mechanical properties.

Chapter 10, Problem 179

What are some of the applications for phenolic compounds?

Chapter 10, Solution 179

Typical applications of phenolic compounds include wiring devices, electrical switchgear, connectors, telephone relay systems, and heat resistant parts for small appliances such as handles, knobs and end panels. They are also used for lamination of some plywood and particle boards and as a binder for sand in foundry and molding processes.

Chapter 10, Problem 180

What are some of the advantages of epoxy thermoset resins? What are some of their applications?

Chapter 10, Solution 180

Advantageous properties of epoxy resins include: good chemical and environmental resistance, good mechanical properties, good electrical insulating properties, low cure shrinkage, strong adhesive properties and exceptional wetting characteristics. This set of attributes makes epoxies a natural choice for a wide variety of protective and decorative coatings, adhesives, fiber-reinforced matrix materials, electrical potting and encapsulating applications.

Chapter 10, Problem 181

How are most unsaturated polyesters reinforced?

Chapter 10, Solution 181

Most unsaturated polyesters are reinforced with glass fibers; the content of glass-fiber reinforcement may be as high as 80 percent and the resulting strength up to 172 to 344 MPa (25 to 50 ksi).

Chapter 10, Problem 182

What are some applications for reinforced polyesters?

Chapter 10, Solution 182

Applications for reinforced polyesters include automobile panels and body parts, small boat hulls, building panels, bathroom components, and pipes, tanks and ducts designed for corrosive environments.

What are some applications for nitrile rubbers?

Chapter 10, Solution 183

Nitrile rubbers are costly and thus their applications are limited to parts such as fuel hoses and gaskets for which high resistance to oils and solvents are essential.

Chapter 10, Problem 184

What are some engineering applications for neoprene rubbers?

Chapter 10, Solution 184

Neoprene rubbers are better strength than ordinary rubbers and fair fuel and oil

resistance. However, they are costly and have poor low-temperature flexibility.

Consequently, their application is restricted to parts such as wire and cable covering, industrial hoses and belts, and automotive seals and diaphragms.

Chapter 10, Problem 185

What are some of the engineering applications for silicone rubber?

Chapter 10, Solution 185

Typical applications of silicone rubber include sealants, gaskets, electrical insulation, automobile ignition cable, and spark plug boots.

Chapter 10, Problem 186

What are some of the advantages and disadvantages of SBR? Natural rubber?

Chapter 10, Solution 186

Advantages of SBR over natural rubber are lower cost, better wear resistance, and greater elasticity; however, SBR generates greater frictional heat. Both SBR and natural rubber have the disadvantage of absorbing organic solvents such as gasoline and oil.

Chapter 10, Problem 187

Select the material to serve as an insulating cover to a conducting copper wire in an automobile engine. What factors must you consider in your selection? What is the best choice? Use chapter tables and the appendices in the back of the book.

Chapter 10, Solution 187

The insulating cover must be flexible to match the contour of the wire. It must have reasonable strength and durability against cold temperatures (in cold regions) and the engine's hot environment. It must be inexpensive.

Polyethylene is the best choice since it has both high temperature and low temperature flexibility.

PVC is another good choice but does not perform as well in lower temperatures.

Note: Depending on the geographic location and time of the year, the insulating cover may experience temperatures as low as -30°C to as high as 90°C.

Chapter 10, Problem 188

Using Fig. 10.47, (α) estimate and compare the moduli of elasticity of high and low density polyethylene, (b) estimate and compare the toughness of the two, and (c) explain what causes these differences.

Chapter 10, Solution 188

Using figure 10.45, the slope of the elastic region for LDPE is $\sim \frac{1000 \text{ psi}}{0}.05 \cong 20 \text{ ksi}$

and for HDPE
$$\sim \frac{2800 \text{ psi}}{0}.05 \cong 56 \text{ ksi}$$

HDPE has a significantly higher modulus indicating that it is stiffer.

Toughness may be estimated by estimating the area under the curve.

LDPE: ~ 10 rectangular units,

Each unit is (1000 psi)(0.2 in/in)

Toughness = $(1000)(0.2)(10) = 2000 \text{ lb.in/in}^3$

LDPE: ~ 16 rectangular units,

Toughness = $(16)(1000)(0.2) = 3200 \text{ lb.in/in}^3$

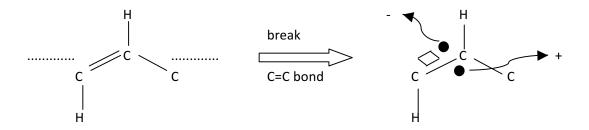
HDPE is much tougher.

The increase in stiffness and toughness is directly a result of increase in molecular mass of chains in HDPE and amount of crystallinity.

Some polymers such as trans-polyacetylene can conduct electricity (similar to a semiconductor). The structure of the molecule is given below. Suggest, theoretically, how electrical conductivity could be initiated a single chain.

Chapter 10, Solution 189

Conductivity may be initiated by cracking one of the double bonds between C atoms. The free electron produced carries a charge and the electron hole produced can also carry a positive charge.



Chapter 10, Problem 190

(a) Create a list of the required properties of the materials to be selected in the design and manufacturing of a large travel suitcase. (b) Propose a number of candidate materials. (c) Identify your best choice and explain why. Use chapter tables and the appendices.

Chapter 10, Solution 190

The material used in a travel suitcase must possess the following characteristics:

- * 1 lightweight (low density)
 - 2 strong (high UTS)
 - 3 reasonable stiffness (modulus of elasticity)
- * 4 impact resistant (high impact strength)
 - 5 be reasonably affordable

From table 10.5 and the appendix, PVC, polycarbonate and polypropylene seem to be suitable for this application, especially from a combination of high strength, low density, and high impact strength point of view.

There are also suitcases made of nylon textile materials. These may be less durable than the hard suitcase materials.

Polypropylene has a good combination of low density (0.9 g/cm³), UTS (5.5 ksi), impact strength (2.2 lb.ft/in), and cost (12.5/ lb).

Chapter 10, Problem 191

Suggest a way of making a standard polymer self-lubricating.

Chapter 10, Solution 191

One can create a polymer composite with self lubricating properties. Addition of polymers such as PTFE and materials such as graphite to the standard polymer will create self-lubricating properties. Load and ambient conditions are important considerations in selection of the lubricating additive.

Chapter 10, Problem 192

An engineer has identified epoxy, a thermoset, as an effective candidate for a specific application in humid and lightly corrosive conditions. However, the low stiffness or low modulus of elasticity of epoxy is a potential problem. Can you offer a solution?

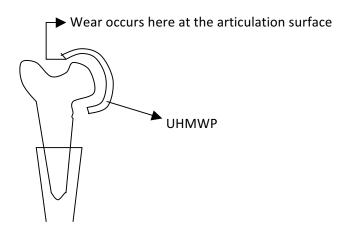
Chapter 10, Solution 192

The stiffness of epoxy can be increased by adding fiber to it. For instance, addition of glass fiber can significantly increase the stiffness of epoxy.

Chapter 10, Problem 193

In Total Hip Replacement surgery, the femur head is replaced with a metal component, usually a Co-Cr alloy, and the Acetabular Cup is replaced with Ultra High Molecular Weight Polyethylene (UHMWP). (a) Investigate this material and give reasons for the suitability of UHMWP for this application in comparison to a metal cup. (b) Investigate the advantage of UHMWP over low-density polyethylene.

Chapter 10, Solution 193



UHMWP – ultra high molecular weight polyethylene

UHMWP is a strong material with suitable modulus of elasticity and ductility.

a) Its main characteristic is that it has reduced wear particle generation when compared to conventional (low density) polyethylene.

Chapter 10, Problem 194

(a) In selecting the materials for the infant milk bottle, what factors should you consider? (b) Would polystyrene be a good choice? (c) What material would you select for this application? Use chapter tables and the appendices in the back.

Chapter 10, Solution 194

- a) In addition to strength and ductility, one must make sure that the material behaves appropriately at high temperatures (when the bottles are being washed in a washing machine). The material must not degrade as a result of repeated washing with hot water. The material should be safe and not react with the liquids that it stores.
- b) Polystyrene has a maximum use temperature of 60 104°C. The material will break down if its range is exceeded. This material is not a good choice.
- c) Polycarbonate has a slightly higher max-use temperature and is thus safer. However, there are chemicals in PC that may not be safe if ingested.

In general, materials used for the food industry must be completely non-toxic. Thus, the safest choice for baby bottle would be glass.

Chapter 10, Problem 195

Explain why is PMMA a good material to use for glazing of boats. What is the purpose of glazing on a boat?

Chapter 10, Solution 195

PMMA protects the boat from corrosion and staining. It protects against salt water, UV rays and air pollutants.

PMMA is a good glazing material because it can be easily applied; it is strong and environmentally stable and resistant.

Chapter 10, Problem 196

PTFE is used in cookware as non-stick coating. Examine its properties in Table 10.2. Should the manufacturers give a warning to the users?

Chapter 10, Solution 196

- 1. From table 10.2, polytetrafluoroethylene (PTFE) has a maximum use temperature of 288°C. Above this temperature, it could break down and toxify the food. Thus, the manufacturer must warn against excessively high temperatures.
- 2. All polymers are chemicals and must not be digested. Thus, use a wooden spatula to avoid scratching of the Teflon coating.

(a) In selecting the materials for compact disks, what factors should you consider? (b) What material would you select for this application? Use chapter tables and the appendices in the back.

Chapter 10, Solution 197

(neglecting electro optical properties)

- a) The material for compact disk must have reasonable strength and stiffness. It must be durable, lightweight and economical. The material should resist damage under high daily temperatures; for instance if left under sun light.
- b) Polycarbonate is a good choice since it is easily moldable and has a good strength (9 ksi) and impact resistance properties (12 − 16 ft.lb/in). It is fairly UV resistant. It has good elongation prior to fracture property (~ 80 -150 %). Its glass transition temperature is 150°C.

Chapter 10, Problem 198

(a) In selecting the materials for surgical gloves, what factors should you consider? (b) What material would you select for this application? Use chapter tables and the appendices.

Chapter 10, Solution 198

The gloves protect the surgeons from contact with patient's bodily fluids and they also protect the patient from infectious matter possibly carried by the surgeon.

The material must match the surface contour of the hand tightly to create excellent "touch" for the surgeon. It must be easy to clean.

Latex is commonly used for this purpose. Some show allergy to latex, in which case vinyl can be used.

Chapter 10, Problem 199

(a) In selecting the materials for keyboards, terminals, and other computer equipment that house the electronic components, what factors should you consider? (b) What material would you select for the above applications? Use chapter tables and the appendices.

Chapter 10, Solution 199

- a)Materials used in keyboards, terminals, and towers must be lightweight, strong, tough and have dimensional stability (dimensions won't change with heat and loading). The material must have excellent electrical insulation properties.
- b) Polycarbonate is an excellent choice for such applications.

Chapter 10, Problem 200

(a) In selecting the materials for a football helmet, what factors should you consider? (b) What material would you select for the above applications? Use chapter tables and the appendices.

Chapter 10, Solution 200

- a) Materials used in a football helmet must be lightweight, hard and tough. It must not break under impact, thus it must have high impact strength.
- b) Polycarbonate is the most often used plastic in helmets (ABS is also used)

The shock absorption ability of the helmet is due to the foam padding below the polycarbonate shell. The combination of the hard cover and foamy padding will alternate the shock due to impact.

Chapter 10, Problem 201

(a) In selecting the materials for a bungee cord, what factors should you consider? (b) What material do you suggest? Once you have selected the materials, what mechanical (or other) factors should you consider? Use chapter tables and the appendices in the back.

Chapter 10, Solution 201

- a) The material used in a bungee cord must have high tensile strength; excellent deformation (extension) capability and excellent resilience (regain its shape after loading).
- b) The best choices are natural or synthetic rubber. Natural rubber is stronger than synthetic rubber, but it is less resistant to environmental damage.
- c) The bungee cord becomes weaker (damaged) with usage and aging. Periodic inspections for damage detection must be made.

Chapter 10, Problem 202

Investigate the role of polymers in the ophthalmic lens manufacturing industry. Which polymers are used and what characteristics do they have?

Chapter 10, Solution 202

Hard lenses are mostly made of plexiglass (PMMA). However, PMMA does not allow for oxygen transmission to the cornea which can cause a number of eye-health problems.

Hard gas-permeable lenses are produced from a blend of PMMA and siloxanylalkyl methacrylates.

Chapter 10, Problem 203

Investigate the importance of polymers in heart-valve replacement surgery. What is the role of the polymer in this surgery? What polymer is used for this purpose?

Chapter 10, Solution 203

In heart-valve surgery, polymers are used to connect the artificial valve (usually made of metal) to the soft tissue of heart.

The heart valve is surrounded by a polymeric sewing ring made of expanded PTFE or PET (Dacron). The sewing ring is then sutured to the tissue. The suture material is either nylon or absorbable (PGA).

Chapter 10, Problem 204

In orthopedic applications related to knee and hip replacement, often cement is used to provide adhesion between the bone and the implant. What is this adhesive?

Chapter 10, Solution 204

The adhesive used is PMMA. Plexiglass is an excellent adhesive for inside the human body applications.