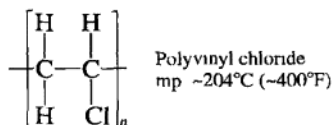


10.6.2 Polyvinyl Chloride and Copolymers

Polyvinyl chloride (PVC) is a widely used synthetic plastic that has the second largest sales tonnage in the world. The widespread use of PVC is attributed mainly to its high chemical resistance and its unique ability to be mixed with additives to produce a large number of compounds with a wide range of physical and chemical properties.

Repeating Chemical Structural Unit



Structure and Properties The presence of the large chlorine atom on every other carbon atom of the main chain of polyvinyl chloride produces a polymeric material that is essentially amorphous and does *not* recrystallize. The strong cohesive forces between the polymer chains in PVC are due mainly to the strong dipole moments caused by the chlorine atoms. The large negative chlorine atoms, however, cause some steric hindrance and electrostatic repulsion, which reduces the flexibility of the polymer chains. This molecular immobility results in difficulty in the processing of the homopolymer, and only in a few applications can PVC be used without being compounded with a number of additives so that it can be processed and converted into finished products.

PVC homopolymer has a relatively high strength (7.5 to 9.0 ksi), along with brittleness. PVC has a medium heat-deflection temperature (57°C to 82°C [135°F to 180°F] at 66 psi), good electrical properties (425 to 1300 V/mil dielectric strength), and high solvent resistance. The high chlorine content of PVC produces flame and chemical resistance.

Polyvinyl Chloride Compounding Polyvinyl chloride can only be used for a few applications without the addition of a number of compounds to the basic material so that it can be processed and converted into a finished product. Compounds added to PVC include plasticizers, heat stabilizers, lubricants, fillers, and pigments.

Plasticizers impart flexibility to polymeric materials. They are usually high-molecular-weight compounds that are selected to be completely miscible and compatible with the basic material. For PVC, phthalate esters are commonly used as plasticizers. The effect of some plasticizers on the tensile strength of PVC is shown in Fig. 10.30.

Heat stabilizers are added to PVC to prevent thermal degradation during processing and may also help to extend the life of the finished product. Typical stabilizers used may be all organic or inorganic but are usually organometallic compounds based on tin, lead, barium-cadmium, calcium, and zinc.

Lubricants aid the melt flow of PVC compounds during processing and prevent adhesion to metal surfaces. Waxes, fatty esters, and metallic soaps are commonly used lubricants.

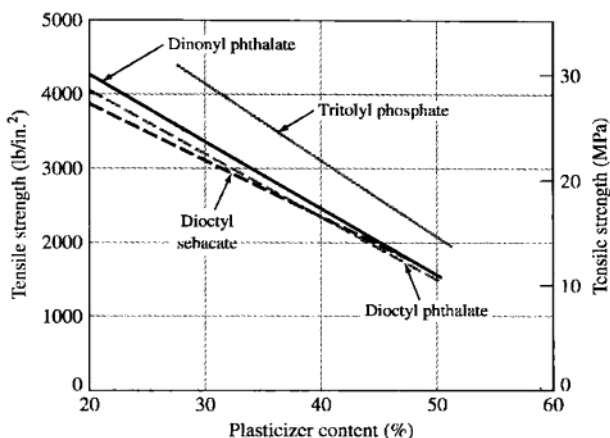


Figure 10.30

Effect of different plasticizers on the tensile strength of polyvinyl chloride.

[From C.A. Brighton, "Vinyl Chloride Polymers (Compounding)," in "Encyclopedia of Polymer Science and Technology," vol. 14, Interscience, 1971, p. 398. Reprinted with permission of John Wiley & Sons, Inc.]

Fillers such as calcium carbonate are mainly added to lower the cost of PVC compounds.

Pigments, both inorganic and organic, are used to give color, opacity, and weatherability to PVC compounds.

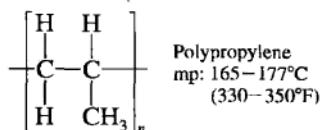
Rigid Polyvinyl Chloride Polyvinyl chloride alone can be used for some applications but is difficult to process and has low impact strength. The addition of rubbery resins can improve melt flow during processing by forming a dispersion of small, soft rubbery particles in the matrix of rigid PVC. The rubbery material serves to absorb and disperse impact energy so that the impact resistance of the material is increased. With improved properties, rigid PVC is used for many applications. In building construction, rigid PVC is used for pipe, siding, window frames, gutters, and interior molding and trim. PVC is also used for electrical conduit.

Plasticized Polyvinyl Chloride The addition of plasticizers to PVC produces softness, flexibility, and extensibility. These properties can be varied over a wide range by adjusting the plasticizer-polymer ratio. Plasticized polyvinyl chloride is used in many applications where it outperforms rubber, textiles, and paper. Plasticized PVC is used for furniture and auto upholstery, interior wall coverings, rainwear, shoes, luggage, and shower curtains. In transportation, plasticized PVC is used for auto top coverings, electrical wire insulation, floor mats, and interior and exterior trim. Other applications include garden hoses, refrigerator gaskets, appliance components, and housewares.

10.6.3 Polypropylene

Polypropylene is the third most important plastic from a sales tonnage standpoint and is one of the lowest in cost since it can be synthesized from low-cost petrochemical raw materials using a Ziegler-type catalyst.

Repeating Chemical Structural Unit



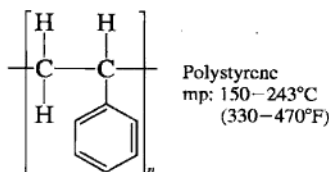
Structure and Properties In going from polyethylene to polypropylene, the substitution of a methyl group on every second carbon atom of the polymer main chain restricts rotation of the chains, producing a stronger but less flexible material. The methyl groups on the chains also increase the glass transition temperature, and thus polypropylene has higher melting and heat-deflection temperatures than polyethylene. With the use of stereospecific catalysts, isotactic polypropylene can be synthesized with a melting point in the 165°C to 177°C (330°F to 350°F) range. This material can be subjected to temperatures of about 120°C (250°F) without deformation.

Polypropylene has a good balance of attractive properties for producing many manufactured goods. These include good chemical, moisture, and heat resistance, along with low density (0.900 to 0.910 g/cm³), good surface hardness, and dimensional stability. Polypropylene also has outstanding flex life as a hinge and can be used for products with an integral hinge. Along with the low cost of its monomer, polypropylene is a very competitive thermoplastic material.

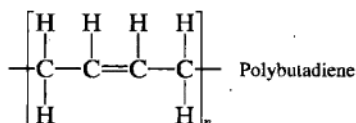
Applications The major applications for polypropylene are housewares, appliance parts, packaging, laboratory ware, and bottles of various types. In transportation, high-impact polypropylene copolymers have replaced hard rubber for battery housings. Similar resins are used for fender liners and splash shrouds. Filled polypropylene finds application for automobile fan shrouds and heater ducts, where high resistance to heat deflection is needed. Also, polypropylene homopolymer is used extensively for primary carpet backing and as a woven material is used for shipping sacks for many industrial products. In the film market, polypropylene is used as a bag and overwrap film for soft goods because of its luster, gloss, and good stiffness. In packaging, polypropylene is used for screw closures, cases, and containers.

10.6.4 Polystyrene

Polystyrene is the fourth-largest tonnage thermoplastic. Homopolymer polystyrene is a clear, odorless, and tasteless plastic material that is relatively brittle unless modified. Besides crystal polystyrene, other important grades are rubber-modified, impact-resistant, and expandable polystyrenes. Styrene also is used to produce many important copolymers.

Repeating Chemical Structural Unit

Structure and Properties The presence of the phenylene ring on every other carbon atom of the main chain of polystyrene produces a rigid bulky configuration with sufficient steric hindrance to make the polymer very inflexible at room temperature. The homopolymer is characterized by its rigidity, sparkling clarity, and ease of processibility but tends to be brittle. The impact properties of polystyrene can be improved by copolymerization with the polybutadiene elastomer, which has the following chemical structure:



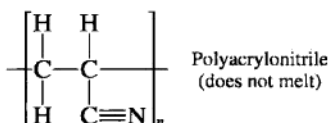
Copolymers of impact styrene usually have rubber levels between 3 and 12 percent. The addition of the rubber to polystyrene lowers the rigidity and heat-deflection temperature of the homopolymer.

In general, polystyrenes have good dimensional stability and low-mold shrinkage and are easily processed at a low cost. However, they have poor weatherability and are chemically attacked by organic solvents and oils. Polystyrenes have good electrical insulating properties and adequate mechanical properties within operating temperature limits.

Applications Typical applications include automobile interior parts, appliance housings, dials and knobs, and housewares.

10.6.5 Polyacrylonitrile

This acrylic-type polymeric material is often used in the form of fibers, and because of its strength and chemical stability, it is also used as a comonomer for some engineering thermoplastics.

Repeating Chemical Structural Unit

Structure and Properties The high electronegativity of the nitrile group on every other carbon atom of the main chain exerts mutual electrical repulsion, causing the

molecular chains to be forced into extended, stiff, rodlike structures. The regularity of the rodlike structures allows them to orient themselves to produce strong fibers by hydrogen bonding between the polymer chains. As a result, the acrylonitrile fibers have high strength and good resistance to moisture and solvents.

Applications Acrylonitrile is used in fiber form for woollike applications such as sweaters and blankets. Acrylonitrile is also used as a comonomer for producing *styrene-acrylonitrile copolymers* (SAN resins) and *acrylonitrile-butadiene-styrene terpolymers* (ABS resins).

10.6.6 Styrene-Acrylonitrile (SAN)

Styrene-acrylonitrile thermoplastics are high-performance members of the styrene family.

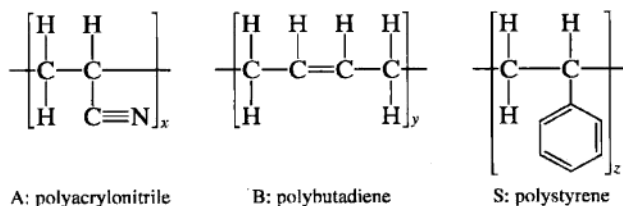
Structure and Properties SAN resins are random, amorphous copolymers of styrene and acrylonitrile. This copolymerization creates polarity and hydrogen-bond attractive forces between the polymer chains. As a result, SAN resins have better chemical resistance, higher heat-deflection temperatures, toughness, and load-bearing characteristics than polystyrene alone. SAN thermoplastics are rigid and hard, process easily, and have the gloss and clarity of polystyrene.

Applications Major applications for SAN resins include automotive instrument lenses, dash components, and glass-filled support panels; appliance knobs and blender and mixer bowls; medical syringes and blood aspirators; construction safety glazing; and houseware tumblers and mugs.

10.6.7 ABS

ABS is the name given to a family of thermoplastics. The acronym is derived from the three monomers used to produce ABS: *acrylonitrile*, *butadiene*, and *styrene*. ABS materials are noted for their engineering properties such as good impact and mechanical strength combined with ease of processing.

Chemical Structural Units ABS contains the following three chemical structural units:



Structure and Properties of ABS The wide range of useful engineering properties exhibited by ABS is due to the contributing properties of each of its components. Acrylonitrile contributes heat and chemical resistance and toughness, butadiene

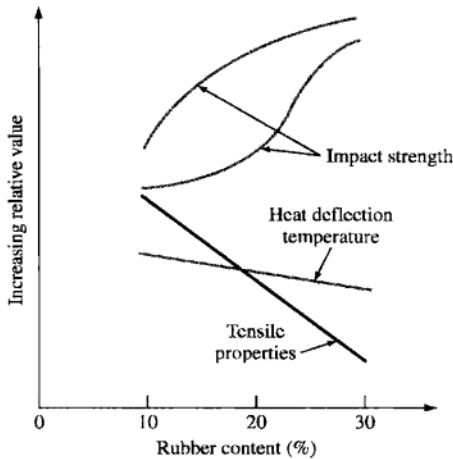


Figure 10.31
Percent rubber versus some properties of ABS.
(From G.E. Teer, "ABS and Related Multipolymers," in "Modern Plastics Encyclopedia," McGraw-Hill, 1981–1982. Reprinted by permission of Modern Plastics.)

Table 10.4 Some typical properties of ABS plastics (23°C)

	High-impact	Medium-impact	Low-impact
Impact strength (Izod):			
ft · lb/in.	7–12	4–7	2–4
J/m	375–640	215–375	105–320
Tensile strength:			
×1000 psi	4.8–6.0	6.0–7.0	6.0–7.5
MPa	33–41	41–48	41–52
Elongation (%)	15–70	10–50	5–30

provides impact strength and low-property retention, and styrene provides surface gloss, rigidity, and ease of processing. The impact strengths of ABS plastics are increased as the percent rubber content is increased, but the tensile-strength properties and heat-deflection temperatures are decreased (Fig. 10.31). Table 10.4 lists some of the properties of high-, medium-, and low-impact ABS plastics.

The structure of ABS is *not* that of a random terpolymer. ABS can be considered a blend of a glassy copolymer (styrene-acrylonitrile) and rubbery domains (primarily a butadiene polymer or copolymer). Simply blending rubber with the glassy copolymer does not produce optimal impact properties. The best impact strength is obtained when the styrene-acrylonitrile copolymer matrix is grafted to the rubber domains to produce a two-phase structure (Fig. 10.32).

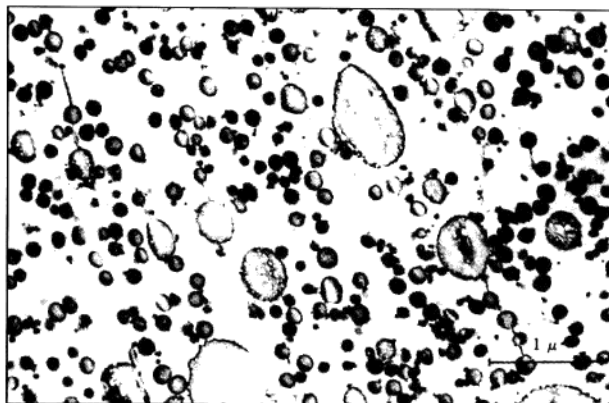


Figure 10.32

Electron micrograph of an ultrathin section of a type G ABS resin showing the rubbery particles in a copolymer of styrene-acrylonitrile.

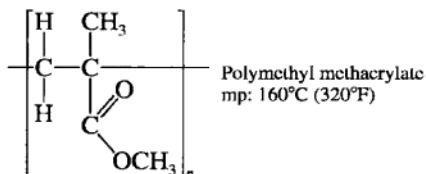
[After M. Matsuo, *Polym. Eng. Sci.*, 9:206(1969).]

Applications The major use for ABS is for pipe and fittings, particularly drain-waste-and-vent pipe in building. Other uses for ABS are for automotive parts, appliance parts such as refrigerator door liners and inner liners, business machines, computer housings and covers, telephone housings, electrical conduit, and electromagnetic interference-radio-frequency shielding applications.

10.6.8 Polymethyl Methacrylate (PMMA)

Polymethyl methacrylate (PMMA) is a hard, rigid transparent thermoplastic that has good outdoor weatherability and is more impact-resistant than glass. This material is better known by the trade names Plexiglas or Lucite and is the most important material of the group of thermoplastics known as the *acrylics*.

Repeating Chemical Structural Unit



Structure and Properties The substitution of the methyl and methacrylate groups on every other carbon atom of the main carbon chain provides considerable steric hindrance and thus makes PMMA rigid and relatively strong. The random configuration of the asymmetrical carbon atoms produces a completely amorphous structure that

has a high transparency to visible light. PMMA also has good chemical resistance to outdoor environments.

Applications PMMA is used for glazing for aircraft and boats, skylights, exterior lighting, and advertising signs. Other uses include auto taillight lenses, safety shields, protective goggles, and knobs and handles.

10.6.9 Fluoroplastics

These materials are plastics or polymers made from monomers containing one or more atoms of fluorine. The fluoroplastics have a combination of special properties for engineering applications. As a class, they have a high resistance to hostile chemical environments and outstanding electrical insulating properties. Those fluoroplastics containing a large percentage of fluorine have low coefficients of friction, which give them self-lubricating and nonstick properties.

There are many fluoroplastics produced, but the two most widely used ones, *polytetrafluoroethylene* (PTFE) (Fig. 10.33) and *polychlorotrifluoroethylene* (PCTFE), will be discussed in this subsection.

Polytetrafluoroethylene

Repeating Chemical Structural Unit

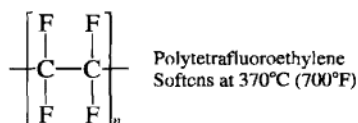


Figure 10.33
Structure of
polytetrafluoroethylene

Chemical Processing PTFE is a completely fluorinated polymer formed by the free-radical chain polymerization of tetrafluoroethylene gas to produce linear-chain polymers of $-\text{CF}_2-$ units. The original discovery of the polymerization of tetrafluoroethylene gas into polytetrafluoroethylene (Teflon) was made by R.J. Plunkett in 1938 in a Du Pont laboratory.

Structure and Properties PTFE is a crystalline polymer with a crystalline melting point of 327°C (620°F). The small size of the fluorine atom and the regularity of the fluorinated carbon chain polymer results in a highly dense crystalline polymeric material. The density of PTFE is high for plastic materials, 2.13 to 2.19 g/cm³.

PTFE has exceptional resistance to chemicals and is insoluble in all organics with the exception of a few fluorinated solvents. PTFE also has useful mechanical properties from cryogenic temperatures (−200°C [−330°F]) to 260°C (550°F). Its impact strength is high, but its tensile strength, wear, and creep resistance are low when compared with other engineering plastics. Fillers such as glass fibers can be

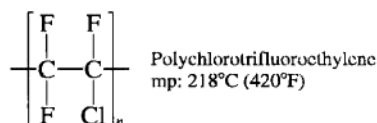
used to increase strength. PTFE is slippery and waxy to the touch and has a low coefficient of friction.

Processing Since PTFE has such a high melt viscosity, conventional extrusion and injection-molding processes cannot be used. Parts are molded by compressing granules at room temperature at 2000 to 10,000 psi (14 to 69 MPa). After compression, the performed materials are sintered at 360°C to 380°C (680°F to 716°F).

Applications PTFE is used for chemically resistant pipe and pump parts, high-temperature cable insulation, molded electrical components, tape, and nonstick coatings. Filled PTFE compounds are used for bushings, packings, gaskets, seals, O rings, and bearings.

Polychlorotrifluoroethylene

Repeating Chemical Structural Unit



Structure and Properties The substitution of a chlorine atom for every fourth fluorine atom produces some irregularity in the polymer chains, making the material less crystalline and more moldable. Thus, PCTFE has a lower melting point (218°C [420°F]) than PTFE and can be extruded and molded by conventional processes.

Applications Extruded, molded, and machined products of PCTFE polymeric materials are used for chemical processing equipment and electrical applications. Other applications include gaskets, O rings, seals, and electrical components.

10.7 ENGINEERING THERMOPLASTICS

In this section some important aspects of the structure, properties, and applications of engineering thermoplastics will be discussed. The definition of an engineering plastic is arbitrary since there is virtually no plastic that cannot in some form be considered an engineering plastic. A thermoplastic in this book will be considered an engineering thermoplastic if it has a balance of properties that makes it especially useful for engineering applications. In this discussion, the following families of thermoplastics have been selected as engineering thermoplastics: polyamides (nylons), polycarbonates, phenylene oxide-based resins, acetals, thermoplastic polyesters, polysulfone, polyphenylene sulfide, and polyetherimide.

Sales tonnages of engineering thermoplastics are a relatively small percentage in total compared to the general-purpose plastics. An exception might be the nylons because of their special properties. However, the figures are not available and so will not be quoted. The bulk list prices are available.

Some Basic Properties of Selected Engineering Thermoplastics Table 10.5 lists the densities, tensile strengths, impact strengths, dielectric strengths, and maximum-use

Table 10.5 Some properties of selected engineering thermoplastics

Material	Density (g/cm ³)	Tensile strength (×1000 psi)*	Impact strength, Izod (ft · lb/in)†	Dielectric strength (V/mil)‡	Max-use temp. (no load)	
					°F	°C
Nylon 6,6	1.13–1.15	9–12	2.0	385	180–300	82–150
Polyacetal, homo.	1.42	10	1.4	320	195	90
Polycarbonate	1.2	9	12–16	380	250	120
Polyester:						
PET	1.37	10.4	0.8	...	175	80
PBT	1.31	8.0–8.2	1.2–1.3	590–700	250	120
Polyphenylene oxide	1.06–1.10	7.8–9.6	5.0	400–500	175–220	80–105
Polysulfone	1.24	10.2	1.2	425	300	150
Polyphenylene sulfide	1.34	10	0.3	595	500	260

*1000 psi = 6.9 MPa.

†Notched Izod test: 1 ft · lb/in. = 53.38 J/m.

‡1 V/mil = 39.4 V/mm.

temperatures for some selected engineering thermoplastics. The densities of the engineering thermoplastics listed in Table 10.5 are relatively low, ranging from 1.06 to 1.42 g/cm³. The low densities of these materials are an important property advantage for many engineering designs. As for almost all plastic materials, their tensile strengths are relatively low, with those in Table 10.5 ranging from 8000 to 12,000 psi (55 to 83 MPa). These low strengths are usually an engineering design disadvantage. As for the impact strengths of the engineering thermoplastics, polycarbonate has an outstanding impact strength, having values from 12 to 16 ft · lb/in. The low values of 1.4 and 2.0 ft · lb/in. for polyacetal and nylon 6,6 are somewhat misleading since these materials are “tough” plastic materials but are notch-sensitive, as the notched Izod impact test indicates.

The electrical insulation strengths of the engineering thermoplastics listed in Table 10.5 are high, as is the case for most plastic materials, and range from 320 to 700 V/mil. The maximum-use temperatures for the engineering thermoplastics listed in Table 10.5 are from 180°F to 500°F (82°C to 260°C). Of the engineering thermoplastics in Table 10.5, polyphenylene sulfide has the highest use temperature of 500°F (260°C).

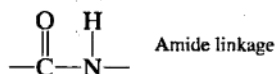
There are many other properties of engineering thermoplastics that make these materials industrially important. Engineering thermoplastics are relatively easy to process into a near-finished or finished shape, and their processing can be automated in most cases. Engineering thermoplastics have good corrosion resistance to many environments. In some cases, engineering plastics have superior resistance to chemical attack. For example, polyphenylene sulfide has no known solvents below 400°F (204°C).

10.7.1 Polyamides (Nylons)

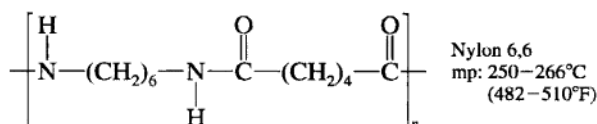
Polyamides or *nylons* are melt-processible thermoplastics whose main-chain structure incorporates a repeating amide group. Nylons are members of the engineering

plastics family and offer superior load-bearing capability at elevated temperatures, good toughness, low-frictional properties, and good chemical resistance.

Chemical Repeating Linkage There are many types of nylons, and the repeating unit is different for each type. They all, however, have the *amide linkage* in common:

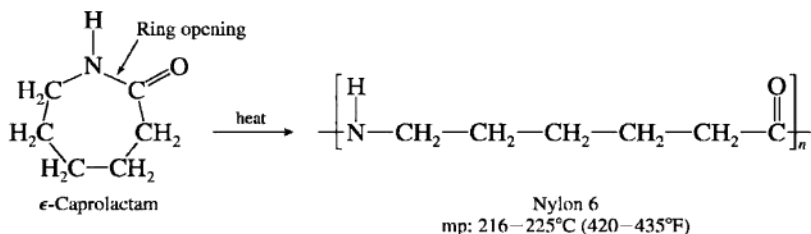


Chemical Processing and Polymerization Reactions Some types of nylons are produced by a stepwise polymerization of a dibasic organic acid with a diamine. Nylon 6,6,⁵ which is the most important of the nylon family, is produced by a polymerization reaction between hexamethylene diamine and adipic acid to produce polyhexamethylene diamine (Fig. 10.10). The repeating chemical structural unit for nylon 6,6 is



Other important commercial nylons made by the same type of reaction are nylons 6,9, 6,10, and 6,12, which are made with hexamethylene diamine and azelaic (9 carbons), sebacic (10 carbons), or dodecanedioic (12 carbons) acids, respectively.

Nylons can also be produced by chain polymerization of ring compounds that contain both organic acid and amine groups. For example, nylon 6 can be polymerized from ϵ -caprolactam (6 carbons) as shown in the following diagram:



Structure and Properties Nylons are highly crystalline polymeric materials because of the regular symmetrical structure of their main polymer chains. The high crystallizability of the nylons is apparent by the fact that under controlled solidification conditions spherulites can be produced. Figure 10.34 shows an excellent example of the formation of a complex spherulitic structure in nylon 9,6 grown at 210°C.

The high strength of the nylons is partly due to the hydrogen bonding between the molecular chains (Fig. 10.35). The amide linkage makes possible a NHO type of hydrogen bond between the chains. As a result, the nylon polyamides have high strength,

⁵The designation "6,6" of nylon 6,6 refers to the fact that there are 6 carbon atoms in the reacting diamine (hexamethylene diamine) and also 6 carbon atoms in the reacting organic acid (adipic acid).

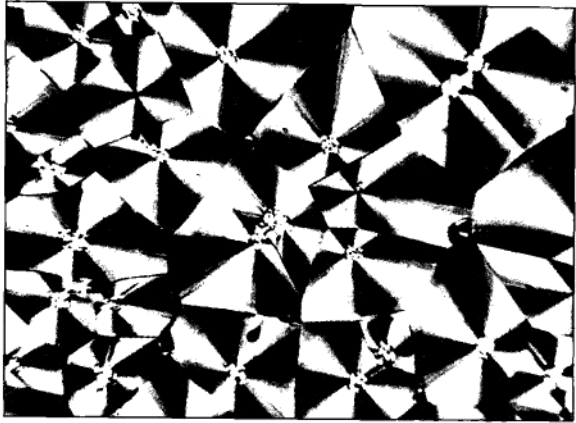


Figure 10.34
Complex spherulitic structure of nylon 9,6 grown at 210°C. The fact that spherulites can be grown in this nylon material emphasizes the capability of nylon materials to crystallize.
(Courtesy of J.H. Magill, University of Pittsburgh.)

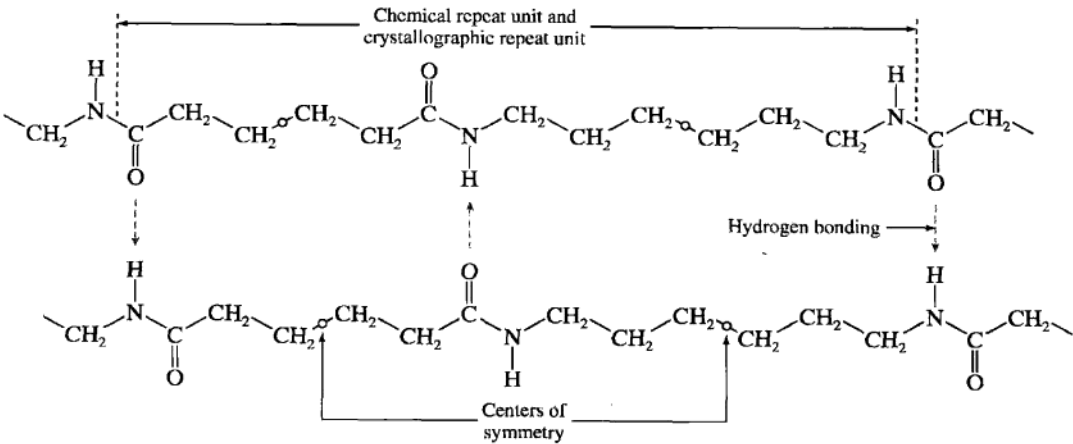


Figure 10.35
Schematic representation of hydrogen bonding between two molecular chains.
[M.I. Kohan (ed.), "Nylon Plastics," Wiley, 1973, p. 274. Reprinted by permission of Dr. Melvin I. Kohan.]

high heat-deflection temperatures, and good chemical resistance. The flexibility of the main carbon chains produces molecular flexibility, which leads to low melt viscosity and easy processibility. The flexibility of the carbon chains contributes to high lubricity, low surface friction, and good abrasion resistance. However, the polarity and hydrogen bonding of the amide groups causes high water absorption, which results in dimensional changes with increasing moisture content. Nylons 11 and 12 with their longer carbon chains between amide groups are less sensitive to water absorption.

Processing Most nylons are processed by conventional injection-molding or extrusion methods.

Applications Applications for nylons are found in almost all industries. Typical uses are for unlubricated gears, bearings, and antifriction parts, mechanical parts that must function at high temperatures and resist hydrocarbons and solvents, electrical parts subjected to high temperatures, and high-impact parts requiring strength and rigidity. Automobile applications include speedometer and windshield wiper gears and trim clips. Glass-reinforced nylon is used for engine fan blades, brake and power-steering fluid reservoirs, valve covers, and steering column housings. Electrical and/or electronic applications include connectors, plugs, hookup wire insulation, antenna mounts, and terminals. Nylon is also used in packaging and for many general-purpose applications.

Nylons 6,6 and 6 make up most of the U.S. nylon sales tonnage because they offer the most favorable combination of price, properties, and processibility. However, nylons 6,10 and 6,12 and nylons 11 and 12 as well as others are produced and sold at a premium price when their special properties are required.

10.7.2 Polycarbonate

Polycarbonates form another class of engineering thermoplastics because some of their special high-performance characteristics such as high strength, toughness, and dimensional stability are required for some engineering designs. Polycarbonate resins are manufactured in the United States by General Electric under the trade name Lexan and by Mobay under the trade name Merlon.

Basic Repeating Chemical Structural Unit

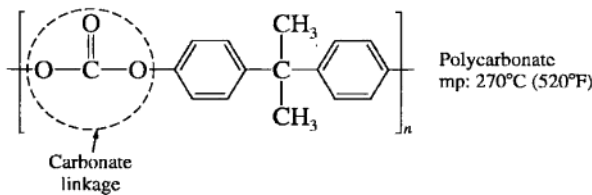


Figure 10.36
Structure of polycarbonate thermoplastic.

Structure and Properties The two phenyl and two methyl groups attached to the same carbon atom in the repeating structural unit (Fig. 10.36) produce considerable

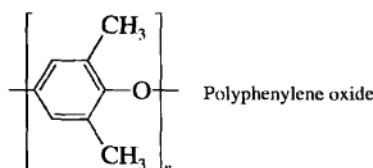
steric hindrance and make a very stiff molecular structure. However, the carbon-oxygen single bonds in the carbonate linkage provide some molecular flexibility for the overall molecular structure, which produces high-impact energy. The tensile strengths of the polycarbonates at room temperature are relatively high at about 9 ksi (62 MPa), and their impact strengths are very high at 12 to 16 ft · lb/in. (640 to 854 J/m) as measured by the Izod test. Other important properties of polycarbonates for engineering designs are their high heat-deflection temperatures, good electrical insulating properties, and transparency. The creep resistance of these materials is also good. Polycarbonates are resistant to a variety of chemicals but are attacked by solvents. Their high dimensional stability enables them to be used in precision engineering components where close tolerances are required.

Applications Typical applications for polycarbonates include safety shields, cams and gears, helmets, electrical relay covers, aircraft components, boat propellers, traffic light housings and lenses, glazing for windows and solar collectors, and housings for handheld power tools, small appliances, and computer terminals.

10.7.3 Phenylene Oxide-Based Resins

The phenylene oxide-based resins form a class of engineering thermoplastic materials.

Basic Repeating Chemical Structural Unit

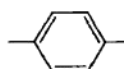


Chemical Processing A patented process for the oxidative coupling of phenolic monomers is used to produce phenylene oxide-based thermoplastic resins that have the trade name Noryl (General Electric).

Structure and Properties The repeating phenylene rings⁶ create steric hindrance to rotation of the polymer molecule and electronic attraction due to the resonating electrons in the benzene rings of adjacent molecules. These factors lead to a polymeric material with high rigidity, strength, chemical resistance to many environments, dimensional stability, and heat-deflection temperature.

There are many different grades of these materials to meet the requirements of a wide range of engineering design applications. Among the principal design advantages of the polyphenylene oxide resins are excellent mechanical properties over the temperature range from -40°C to 150°C (-40°F to 302°F), excellent

⁶A phenylene ring is a benzene ring chemically bonded to other atoms as, for example,



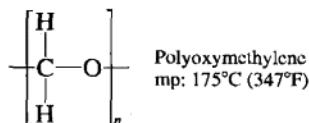
dimensional stability with low creep, high modulus, low water absorption, good dielectric properties, excellent impact properties, and excellent resistance to aqueous chemical environments.

Applications Typical applications for polyphenylene oxide resins are electrical connectors, TV tuners and deflection yoke components, small appliance and business machine housings, and automobile dashboards, grills, and exterior body parts.

10.7.4 Acetals

Acetals are a class of high-performance engineering thermoplastic materials. They are among the strongest (tensile strength of 10 ksi [68.9 MPa]) and stiffest (modulus in flexure of 410 ksi [2820 MPa]) thermoplastics and have excellent fatigue life and dimensional stability. Other important characteristics include low friction coefficients, good processibility, good solvent resistance, and high heat resistance to about 90°C (195°F) with no load.

Repeating Chemical Structural Unit



Types of Acetals At present there are two basic types of acetals: a homopolymer (Du Pont's Delrin) and a copolymer (Celanese's Celcon).

Structure and Properties The regularity, symmetry, and flexibility of the acetal polymer molecules produce a polymeric material with high regularity, strength, and heat-deflection temperature. Acetals have excellent long-term load-carrying properties and dimensional stability and thus can be used for precision parts such as gears, bearings, and cams. The homopolymer is harder and more rigid, and has higher tensile strength and flexural strength than the copolymer. The copolymer is more stable for long-term, high-temperature applications and has a higher elongation.

The low moisture absorption of unmodified acetal homopolymer provides it with good dimensional stability. Also, the low wear and friction characteristics of acetal make it useful for moving parts. In all moving parts, acetal's excellent fatigue resistance is an important property. However, acetals are flammable, and so their use in electrical and/or electronic applications is limited.

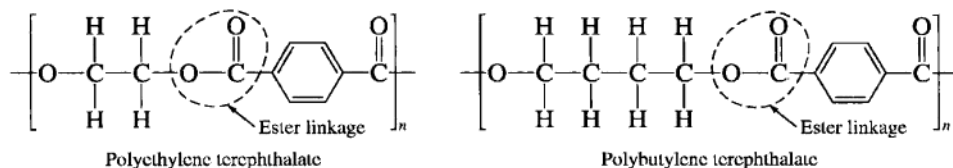
Applications Acetals have replaced many metal castings of zinc, brass, and aluminum and stampings of steel because of lower cost. Where the higher strength of the metals is not required, finishing and assembly operation costs can be reduced or eliminated by using acetals for many applications.

In automobiles, acetals are used for components in fuel systems, seat belts, and window handles. Machinery applications for acetals include mechanical couplings, pump impellers, gears, cams, and housings. Acetals are also used in a wide variety of consumer products such as zippers, fishing reels, and writing pens.

10.7.5 Thermoplastic Polyesters

Polybutylene Terephthalate and Polyethylene Terephthalate Two important engineering thermoplastic polyesters are *polybutylene terephthalate* (PBT) and *polyethylene terephthalate* (PET). PET is widely used for film for food packaging and as a fiber for clothing, carpeting, and tire cord. Since 1977, PET has been used as a container resin. PBT, which has a higher-molecular-weight repeating unit in its polymer chains, was introduced in 1969 as a replacement material for some applications where thermosetting plastics and metals were used. The use of PBT is continuing to expand because of its properties and relatively low cost.

Repeating Chemical Structural Units

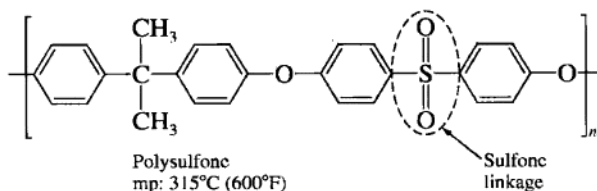


Structure and Properties The phenylene rings along with the carbonyl groups ($C=O$) in PBT form large, flat, bulky units in the polymer chains. This regular structure crystallizes quite readily in spite of its bulkiness. The phenylene ring structure provides rigidity to this material, and the butylene units provide some molecular mobility for melt processing. PBT has good strength (7.5 ksi [52 MPa] for unreinforced grades and 19 ksi [131 MPa] for 40 percent glass-reinforced grades). Thermoplastic polyester resins also have low moisture-absorption characteristics. The crystalline structure of PBT makes it resistant to most chemicals. Most organic compounds have little effect on PBT at moderate temperatures. PBT also has good electrical insulation properties that are nearly independent of temperature and humidity.

Applications Electrical-electronic applications for PBT include connectors, switches, relays, TV tuner components, high-voltage components, terminal boards, integrated circuit boards, motor brush holders, end bells, and housings. Industrial uses for PBT include pump impellers, housings and support brackets, irrigation valves and bodies, and water meter chambers and components. PBT is also used for appliance housings and handles. Automotive applications include large exterior-body components, high-energy ignition caps and rotors, ignition coil caps, coil bobbins, fuel injection controls, and speedometer frames and gears.

Polysulfone

Repeating Chemical Structural Unit



Structure and Properties The phenylene rings of the polysulfone repeating unit restrict rotation of the polymer chains and create strong intermolecular attraction to provide high strength and rigidity to this material. An oxygen atom in para⁷ position of the phenylene ring with respect to the sulfone group provide the high-oxidation stability of the sulfone polymers. The oxygen atoms between the phenylene rings (ether linkage) provide chain flexibility and impact strength.

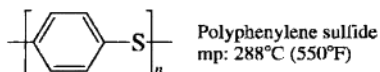
Properties of polysulfone of special significance to the design engineer are its high heat-deflection temperature of 174°C (345°F) at 245 psi (1.68 MPa) and its ability to be used for long times at 150°C to 174°C (300°F to 345°F). Polysulfone has a high tensile strength (for thermoplastics) of 10.2 ksi (70 MPa) and a relatively low tendency to creep. Polysulfones resist hydrolysis in aqueous acid and alkaline environments because the oxygen linkages between the phenylene rings are hydrolytically stable.

Applications Electrical-electronic applications include connectors, coil bobbins and cores, television components, capacitor film, and structural circuit boards. Polysulfone's resistance to autoclave sterilization makes it widely used for medical instruments and trays. In chemical-processing and pollution-control equipment, polysulfone is used for corrosion-resistant piping, pumps, tower packing, and filter modules and support plates.

10.7.6 Polyphenylene Sulfide

Polyphenylene sulfide (PPS) is an engineering thermoplastic that is characterized by outstanding chemical resistance along with good mechanical properties and stiffness at elevated temperatures. PPS was first produced in 1973 and is manufactured by Phillips Chemical Co. under the trade name Ryton.

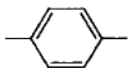
Repeating Chemical Structural Unit Polyphenylene sulfide has a repeating structural unit in its main chain of para-substituted benzene rings and divalent sulfur atoms:



Structure and Properties The compact symmetrical structure of the phenylene rings separated by sulfur atoms produces a rigid and strong polymeric material. The compact molecular structure also promotes a high degree of crystallinity. Because of the presence of the sulfur atoms, PPS is highly resistant to attack by chemicals. In fact, no chemical has been found to dissolve PPS readily below 200°C (392°F). Even at high temperatures, few materials react chemically with PPS.

Unfilled PPS has a room-temperature strength of 9.5 ksi (65 MPa), whereas when 40 percent glass-filled, its strength is raised to 17 ksi (120 MPa). Because of its crystalline structure, the loss of strength with increasing temperature is gradual, and even at 200°C (392°F) considerable strength is retained.

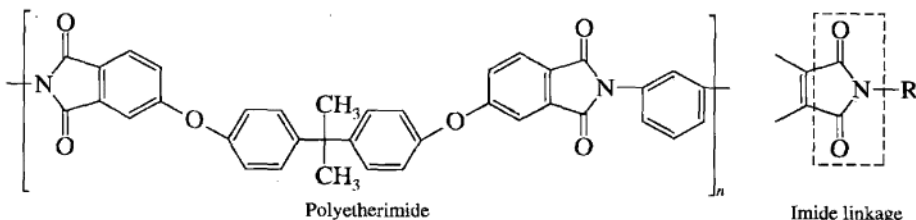
⁷Para positions are at opposite ends of the benzene ring.



Applications Industrial-mechanical applications include chemical process equipment such as submersible, centrifugal, vane, and gear-type pumps. PPS compounds are specified for many under-the-hood automobile applications such as emission-control systems because they are impervious to the corrosive effects of engine exhaust gases as well as to gasoline and other automotive fluids. Electrical-electronic applications include computer components such as connectors, coil forms, and bobbins. Corrosive-resistant and thermally stable coatings of PPS are used for oil field pipe, valves, fittings, couplings, and other equipment in the petroleum- and chemical-processing industries.

10.7.7 Polyetherimide

Polyetherimide is one of the newer amorphous high-performance engineering thermoplastics. It was introduced in 1982 and is commercially available from General Electric Co. under the trademark Ultem. Polyetherimide has the following chemical structure:



The stability of the imide linkage gives this material high heat resistance, creep resistance, and high rigidity. The ether linkage between the phenyl rings provides the necessary degree of chain flexibility required for good melt processability and flow characteristics. This material has good electrical insulation properties that are stable over a wide range of temperatures and frequencies. Uses for polyetherimide include electrical-electronic, automotive, aerospace, and specialty applications. Electrical-electronic applications include high-voltage circuit breaker housings, pin connectors, high-temperature bobbins and coils, and fuse blocks. Printed wiring boards made of reinforced polyetherimide offer dimensional stability for vapor-phase soldering conditions.

10.7.8 Polymer Alloys

Polymer alloys consist of mixtures of structurally different homopolymers or copolymers. In thermoplastic polymer alloys, different types of polymer molecular chains are bonded together by secondary intermolecular dipole forces. By contrast, in a copolymer two structurally different monomers are bonded together in a molecular chain by strong covalent bonds. The components of a polymer alloy must have some degree of compatibility or adhesion to prevent phase separation during processing. Polymer alloys are becoming more important today since plastic materials with specific properties can be created and cost and performance can be optimized.

Some of the early polymer alloys were made by adding rubbery polymers such as ABS to rigid polymers such as polyvinyl chloride. The rubbery material improves

Table 10.6 Some commercial polymer alloys

Polymer alloy	Trade name of material	Supplier
ABS/polycarbonate	Bayblend MC2500	Mobay
ABS/polyvinyl chloride	Cycovin K-29	Borg-Warner Chemicals
Acetal/elastomer	Celcon C-400	Celanese
Polycarbonate/polyethylene	Lexan EM	General Electric
Polycarbonate/PBT/elastomer	Xenoy 1000	General Electric
PBT/PET	Valox 815	General Electric

Source: "Modern Plastics Encyclopedia," 1984-85, McGraw-Hill.

the toughness of the rigid material. Today, even the newer thermoplastics are alloyed together. For example, polybutylene terephthalate is alloyed with some polyethylene terephthalate to improve surface gloss and reduce cost. Table 10.6 lists some commercial polymer alloys.

10.8 THERMOSETTING PLASTICS (THERMOSETS)

Thermosetting plastics or thermosets are formed with a network molecular structure of primary covalent bonds. Some thermosets are cross-linked by heat or a combination of heat and pressure. Others may be cross-linked by a chemical reaction that occurs at room temperature (cold-setting thermosets). Although cured parts made from thermosets can be softened by heat, their covalent-bonding cross-links prevent them from being restored to the flowable state that existed before the plastic resin was cured. Thermosets, therefore, cannot be reheated and remelted as can thermoplastics. This is a disadvantage for thermosets since scrap produced during the processing cannot be recycled and reused.

In general, the advantages of thermosetting plastics for engineering design applications are one or more of the following:

1. High thermal stability
2. High rigidity
3. High dimensional stability
4. Resistance to creep and deformation under load
5. Light weight
6. High electrical and thermal insulating properties

Thermosetting plastics are usually processed by using compression or transfer molding. However, in some cases thermoset injection-molding techniques have been developed so that the processing cost is lowered.

Many thermosets are used in the form of molding compounds consisting of two major ingredients: (1) a resin containing curing agents, hardeners, and plasticizers and (2) fillers and/or reinforcing materials that may be organic or inorganic materials. Wood flour, mica, glass, and cellulose are commonly used filler materials.

Let us first look at the bulk list prices in the United States and at some of the important properties of some selected thermoset materials as a group for comparative purposes.

Table 10.7 Some properties of selected thermoset plastics

Material	Density (g/cm ³)	Tensile strength (× 1000 psi)*	Impact strength, Izod (ft · lb/in.)†	Dielectric strength (V/mil)‡	Max-use temp. (no load)	
					°F	°C
Phenolic:						
Wood-flour-filled	1.34–1.45	5–9	0.2–0.6	260–400	300–350	150–177
Mica-filled	1.65–1.92	5.5–7	0.3–0.4	350–400	250–300	120–150
Glass-filled	1.69–1.95	5–18	0.3–18	140–400	350–550	177–288
Polyester:						
Glass-filled SMC	1.7–2.1	8–20	8–22	320–400	300–350	150–177
Glass-filled BMC	1.7–2.3	4–10	15–16	300–420	300–350	150–177
Melamine:						
Cellulose-filled	1.45–1.52	5–9	0.2–0.4	350–400	250	120
Flock-filled	1.50–1.55	7–9	0.4–0.5	300–330	250	120
Glass-filled	1.8–2.0	5–10	0.6–18	170–300	300–400	150–200
Urea, cellulose-filled	1.47–1.52	5.5–13	0.2–0.4	300–400	170	77
Alkyd:						
Glass-filled	2.12–2.15	4–9.5	0.6–10	350–450	450	230
Mineral-filled	1.60–2.30	3–9	0.3–0.5	350–450	300–450	150–230
Epoxy (bis A):						
No filler	1.06–1.40	4–13	0.2–10	400–650	250–500	120–260
Mineral-filled	1.6–2.0	5–15	0.3–0.4	300–400	300–500	150–260
Glass-filled	1.7–2.0	10–30	...	300–400	300–500	150–260

*1000 psi = 6.9 MPa.

†Notched Izod test: 1 ft · lb/in. = 53.38 J/m.

‡1 V/mil = 39.4 V/mm.

Source: *Materials Engineering*, May 1972.

Bulk List Prices of Some Thermoset Plastics The bulk list prices of the commonly used thermosets are in the low to medium range for plastics, ranging from \$0.55 to \$1.26 (2000 prices). Of all the thermosets listed, the phenolics are the lowest in price and have the largest sales tonnage. Unsaturated polyesters are also relatively low in price and have a relatively large sales tonnage. Epoxy resins, which have special properties for many industrial applications, command a premium price.

Some Basic Properties of Selected Thermoset Plastics Table 10.7 lists the densities, tensile strengths, impact strengths, dielectric strengths, and maximum-use temperatures for some selected thermoset plastics. The densities of thermoset plastics tend to be slightly higher than most plastic materials, with those listed in Table 10.7 ranging from 1.34 to 2.3 g/cm³. The tensile strengths of most thermosets are relatively low, with most strengths ranging from 4000 to 15,000 psi (28 to 103 MPa). However, with a high amount of glass filling, the tensile strength of some thermosets can be increased to as high as 30,000 psi (207 MPa). Glass-filled thermosets also have much higher impact strengths, as indicated in Table 10.7. The thermosets also have good dielectric strengths, ranging from 140 to 650 V/mil. Like all plastic materials, however, their maximum-use temperature is limited. The maximum-use temperature for the thermosets listed in Table 10.7 ranges from 170°F to 550°F (77°C to 288°C).

Let us now examine some of the important aspects of the structure, properties, and applications of the following thermosets: phenolics, epoxy resins, unsaturated polyesters, and amino resins.

10.8.1 Phenolics

Phenolic thermosetting materials were the first major plastic material used by industry. The original patents for the reaction of phenol with formaldehyde to make the phenolic plastic Bakelite were issued to L.H. Baekeland in 1909. Phenolic plastics are still used today because they are low in cost and have good electrical and heat insulating properties along with good mechanical properties. They are easily molded but are limited in color (usually black or brown).

Chemistry Phenolic resins are most commonly produced by the reaction of phenol and formaldehyde by condensation polymerization, with water as a by-product. However, almost any reactive phenol or aldehyde can be used. Two-stage (novolac) phenolic resins are commonly produced for convenience for molding. In the first stage, a brittle thermoplastic resin is produced that can be melted but cannot cross-link to form a network solid. This material is prepared by reacting less than a mole of formaldehyde with a mole of phenol in the presence of an acid catalyst. The polymerization reaction is shown in Fig. 10.11.

The addition of *hexamethylenetetramine* (hexa), which is a basic catalyst, to the first-stage phenolic resin makes it possible to create methylene cross-linkages to form a thermosetting material. When heat and pressure are applied to the hexa-containing novolac resin, the hexa decomposes, producing ammonia, which provides methylene cross-linkages to form a network structure.

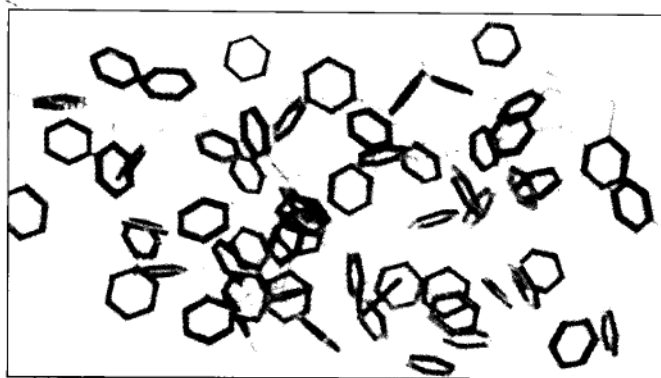
The temperature required for the cross-linking (curing) of the novolac resin ranges from 120°C to 177°C (250°F to 350°F). Molding compounds are made by combining the resin with various fillers, which sometimes account for up to 50 to 80 percent of the total weight of the molding compounds. The fillers reduce shrinkage during molding, lower cost, and improve strength. They also can be used to increase electrical and thermal insulating properties.

Structure and Properties The high cross-linking of the aromatic structure (Fig. 10.37) produces high hardness, rigidity, and strength combined with good heat and electrical insulating properties and chemical resistance.

Some of the various types of phenolic molding compounds manufactured are:

1. *General-purpose compounds.* These materials are usually wood flour-filled to increase impact strength and lower cost.
2. *High-impact-strength compounds.* These compounds are filled with cellulose (cotton flock and chopped fabric), mineral, and glass fibers to provide impact strengths of up to 18 ft · lb/in. (961 J/m).
3. *High electrical insulating compounds.* These materials are mineral- (e.g., mica) filled to increase electrical resistance.
4. *Heat-resistant compounds.* These are mineral- (e.g., asbestos) filled and are able to withstand long-term exposure to temperatures of 150°C to 180°C (300°F to 350°F).

Applications Phenolic compounds are widely used in wiring devices, electrical switchgear, connectors, and telephone relay systems. Automotive engineers use phenolic molding compounds for power-assist brake components and transmission parts. Phenolics are widely used for handles, knobs, and end panels for small

**Figure 10.37**

Three-dimensional model of polymerized phenolic resin.

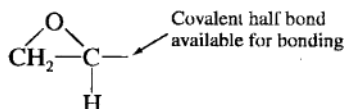
(After E. G. K. Pritchett, in "Encyclopedia of Polymer Science and Technology," vol. 10, Wiley, 1969, p. 30.)

appliances. Because they are good high-temperature and moisture-resistant adhesives, phenolic resins are used in laminating some types of plywood and in particleboard. Large amounts of phenolic resins are also used as a binder material for sand in the foundry and for shell molding.

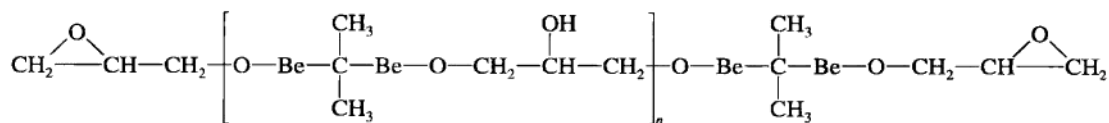
10.8.2 Epoxy Resins

Epoxy resins are a family of thermosetting polymeric materials that do not give off reaction products when they cure (cross-link) and so have low cure shrinkage. They also have good adhesion to other materials, good chemical and environmental resistance, good mechanical properties, and good electrical insulating properties.

Chemistry Epoxy resins are characterized by having two or more epoxy groups per molecule. The chemical structure of an epoxide group is



Most commercial epoxy resins have the following general chemical structure:



where Be = benzene ring. For liquids, the n in the structure is usually less than 1. For solid resins, n is 2 or greater. There are also many other kinds of epoxy resins that have different structures than the one shown here.

To form solid thermosetting materials, epoxy resins must be cured by using cross-linking agents and/or catalysts to develop the desired properties. The epoxy

and hydroxyl groups (—OH) are the reaction sites for cross-linking. Cross-linking agents include amines, anhydrides, and aldehyde condensation products.

For curing at room temperature when the heat requirements for the epoxy solid materials are low (under about 100°C), amines such as diethylene triamine and triethylene tetramine are used as curing agents. Some epoxy resins are cross-linked by using a curing reagent, while others can react with their own reaction sites if an appropriate catalyst is present. In an epoxy reaction, the epoxide ring is opened and a donor hydrogen from, for example, an amine or hydroxyl group bonds with the oxygen atom of the epoxide group. Figure 10.38 shows the reaction of epoxide groups at the ends of two linear epoxy molecules with ethylene diamine.

In the reaction of Fig. 10.38 the epoxy rings are opened up and hydrogen atoms from the diamine form —OH groups, which are reaction sites for further cross-linking. An important characteristic of this reaction is that no by-product is given off. Many different kinds of amines can be used for cross-linking epoxy resins.

Structure and Properties The low molecular weight of uncured epoxide resins in the liquid state gives them exceptionally high molecular mobility during processing. This property allows the liquid epoxy resin to quickly and thoroughly wet surfaces. This wetting action is important for epoxies used for reinforced materials and adhesives. Also the ability to be poured into final form is important for electrical potting and encapsulating. The high reactivity of the epoxide groups with curing agents such as amines provides a high degree of cross-linking and produces good hardness, strength, and chemical resistance. Since no by-product is given off during the curing reaction, there is low shrinkage during hardening.

Applications Epoxy resins are used for a wide variety of protective and decorative coatings because of their good adhesion and good mechanical and chemical resistance. Typical uses are can and drum linings, automotive and appliance primers, and wire coatings. In the electrical and electronics industry epoxy resins are used because of their dielectric strength, low shrinkage on curing, good adhesion, and ability to retain

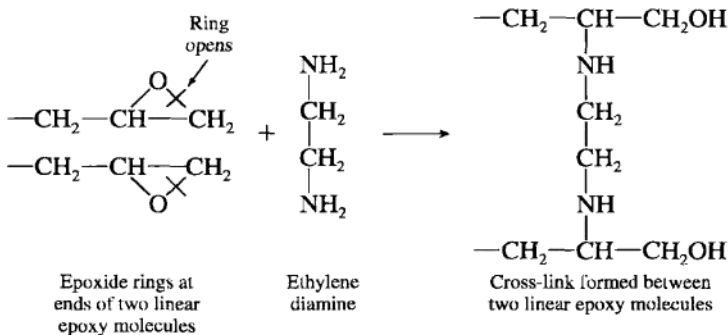


Figure 10.38

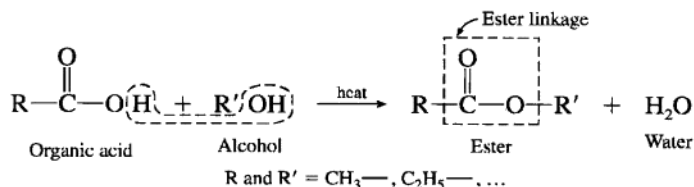
Reaction of epoxy rings at the ends of two linear epoxy molecules with ethylene diamine to form a cross-link. Note that no by-product is given off.

properties under a variety of environments such as wet and high-humidity conditions. Typical applications include high-voltage insulators, switchgear, and encapsulation of transistors. Epoxy resins are also used for laminates and for fiber-reinforced matrix materials. Epoxy resins are the predominate matrix material for most high-performance components such as those made with high-modulus fibers (e.g., graphite).

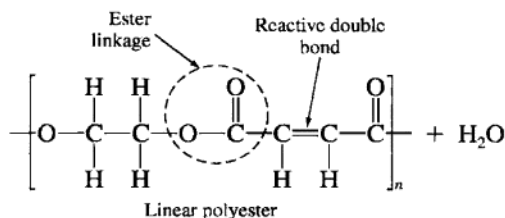
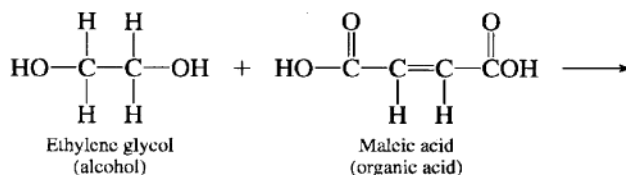
10.8.3 Unsaturated Polyesters

Unsaturated polyesters have reactive double carbon-carbon covalent bonds that can be cross-linked to form thermosetting materials. In combination with glass fibers, unsaturated polyesters can be cross-linked to form high-strength reinforced composite materials.

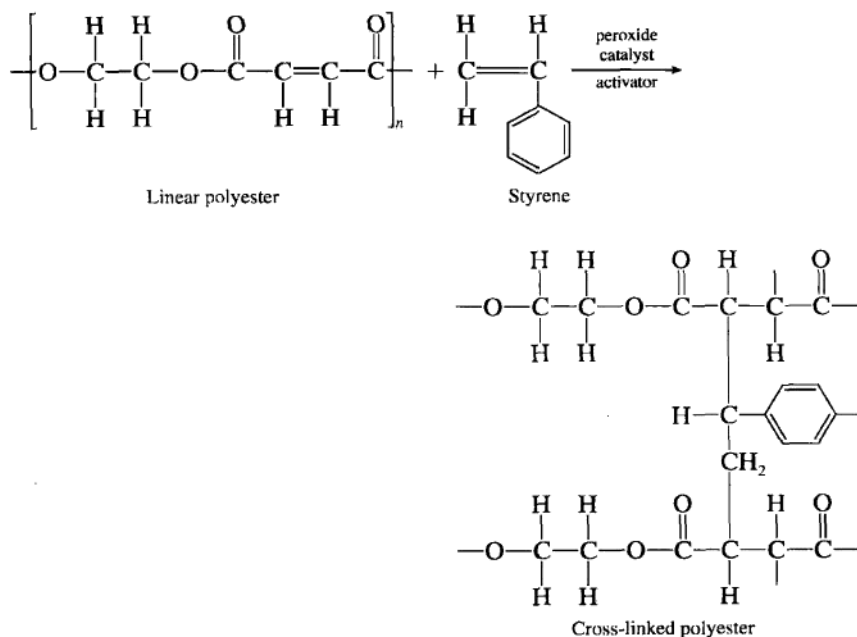
Chemistry The ester linkage can be produced by reacting an alcohol with an organic acid, as



The basic unsaturated polyester resin can be formed by the reaction of a diol (an alcohol with two —OH groups) with a diacid (an acid with two —COOH groups) that contains a reactive double carbon-carbon bond. Commercial resins may have mixtures of different diols and diacids to obtain special properties, for example, ethylene glycol can be reacted with maleic acid to form a linear polyester:



The linear unsaturated polyesters are usually cross-linked with vinyl-type molecules such as styrene in the presence of a free-radical curing agent. Peroxide-curing agents are most commonly used, with *methyl ethyl ketone* (MEK) peroxide usually being used for the room-temperature curing of polyesters. The reaction is commonly activated with a small amount of cobalt naphthanate.



Structure and Properties The unsaturated polyester resins are low-viscosity materials that can be mixed with high amounts of fillers and reinforcements. For example, unsaturated polyesters may contain as high as about 80 percent by weight of glass-fiber reinforcement. Glass-fiber-reinforced unsaturated polyesters when cured have outstanding strength, 25 to 50 ksi (172 to 344 MPa), and good impact and chemical resistance.

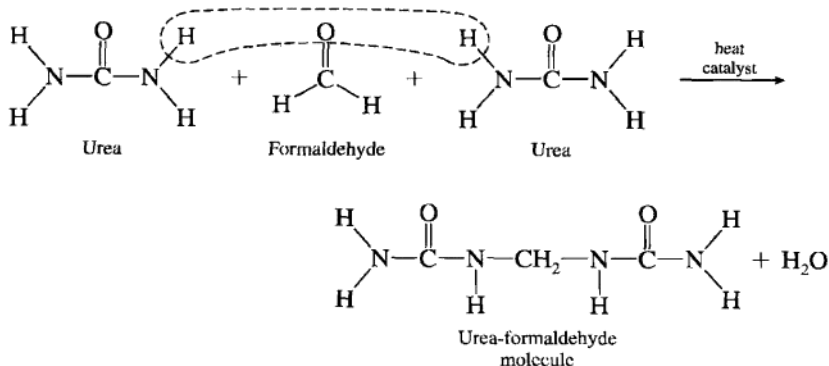
Processing Unsaturated polyester resins can be processed by many methods, but in most cases they are molded in some way. Open-mold lay-up or spray-up techniques are used for many small-volume parts. For high-volume parts such as automobile panels, compression molding is usually used. In recent years *sheet-molding compounds* (SMCs) that combine resin, reinforcement, and other additives have been produced to speed up the feeding of material into molding presses made of matched metal dies.

Applications Glass-reinforced unsaturated polyesters are used for making automobile panels and body parts. This material is also used for small boat hulls and in the construction industry for building panels and bathroom components. Unsaturated reinforced polyesters are also used for pipes, tanks, and ducts where good corrosion resistance is required.

10.8.4 Amino Resins (Ureas and Melamines)

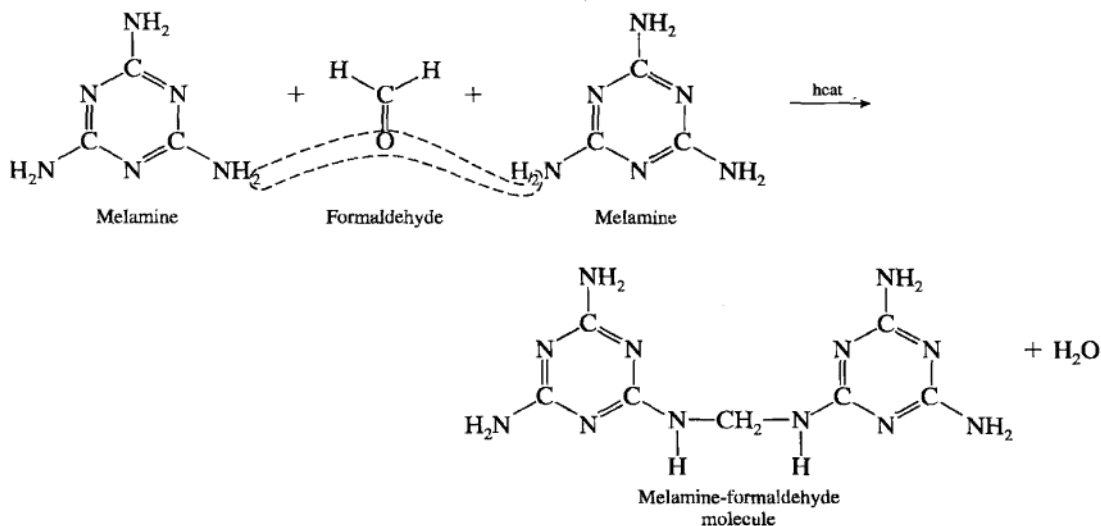
The amino resins are thermosetting polymeric materials formed by the controlled reaction of formaldehyde with various compounds that contain the amine group —NH_2 . The two most important types of amino resins are urea-formaldehyde and melamine-formaldehyde.

Chemistry Both urea and melamine react with formaldehyde by condensation polymerization reactions that produce water as a by-product. The condensation reaction of urea with formaldehyde is



The amine groups at the ends of the molecule shown here react with more formaldehyde molecules to produce a highly rigid network polymer structure. As in the case of the phenolic resins, urea and formaldehyde are first only partially polymerized to produce a low-molecular-weight polymer that is ground into a powder and compounded with fillers, pigments, and a catalyst. The molding compound can then be compression-molded into the final shape by applying heat (127°C to 171°C [260°F to 340°F]) and pressure (2 to 8 ksi [14 to 55 MPa]).

Melamine also reacts with formaldehyde by a condensation reaction, resulting in polymerized melamine-formaldehyde molecules with water being given off as a by-product:⁸



⁸Only one hydrogen atom is removed from each NH_2 group and one oxygen atom from a formaldehyde molecule to form the H_2O molecule.

Structure and Properties The high reactivity of the urea-formaldehyde and melamine-formaldehyde low-molecular-weight prepolymers enable highly cross-linked thermoset products to be made. When these resins are combined with cellulose (wood flour) fillers, low-cost products are obtained that have good rigidity, strength, and impact resistance. Urea-formaldehyde costs less than melamine-formaldehyde but does not have as high a heat resistance and surface hardness as melamine.

Applications Cellulose-filled molding compounds of urea-formaldehyde are used for electrical wall plates and receptacles and for knobs and handles. Applications for cellulose-filled melamine compounds include molded dinnerware, buttons, control buttons, and knobs. Both urea and melamine water-soluble resins find application as adhesives and bonding resins for wood particleboard, plywood, boat hulls, flooring, and furniture assemblies. The amino resins are also used in binders for foundry cores and shell molds.

10.9 SUMMARY

Plastics and elastomers are important engineering materials primarily because of their wide range of properties, relative ease of forming into a desired shape, and relatively low cost. Plastic materials can be conveniently divided into two classes: *thermoplastics* and *thermosetting plastics* (*thermosets*). Thermoplastics require heat to make them formable, and after cooling they retain the shape they were formed into. These materials can be reheated and reused repeatedly. Thermosetting plastics are usually formed into a permanent shape by heat and pressure during which time a chemical reaction takes place that bonds the atoms together to form a rigid solid. However, some thermosetting reactions take place at room temperature without the use of heat and pressure. Thermosetting plastics cannot be remelted after they are "set" or "cured," and upon heating to a high temperature, they degrade or decompose.

The chemicals required for producing plastics are derived mainly from petroleum, natural gas, and coal. Plastic materials are produced by the polymerizing of many small molecules called *monomers* into very large molecules called *polymers*. Thermoplastics are composed of long-molecular-chain polymers, with the bonding forces between the chains being of the secondary permanent dipole type. Thermosetting plastics are covalently bonded throughout with strong covalent bonding between all the atoms.

The most commonly used processing methods for thermoplastics are *injection molding*, *extrusion*, and *blow molding*, whereas the most commonly used methods for thermosetting plastics are *compression and transfer molding* and *casting*.

There are many families of thermoplastics and thermosetting plastics. Examples of some general-purpose thermoplastics are polyethylene, polyvinyl chloride, polypropylene, and polystyrene. Examples of engineering plastics are polyamides (nylons), polyacetal, polycarbonate, saturated polyesters, polyphenylene oxide, and polysulfone. (Note that the separation of thermoplastics into general-purpose and engineering plastics is arbitrary.) Examples of thermosetting plastics are phenolics, unsaturated polyesters, melamines, and epoxies.

Elastomers or *rubbers* form a large subdivision of polymeric materials and are of great engineering importance. Natural rubber is obtained from tree plantations and is still much in demand (about 30 percent of the world's rubber supply) because of its superior elastic properties. Synthetic rubbers account for about 70 percent of the world's rubber supply, with styrene-butadiene being the most commonly used type. Other synthetic rubbers such as nitrile and polychloroprene (neoprene) are used for applications where

special properties such as resistance to oils and solvents are required.

Thermoplastics have a *glass transition temperature* above which these materials behave as viscous or rubbery solids and below which they behave as brittle, glasslike solids. Above the glass transition temperature, permanent deformation occurs by molecular chains sliding past each other, breaking and remaking secondary bonds. Thermoplastics used above the glass transition temperature can be strengthened by intermolecular bonding forces by using polar pendant atoms such as chlorine in polyvinyl chloride or by hydrogen bonding as in the case of the nylons. Thermosetting plastics, because they are covalently bonded throughout, allow little deformation before fracture.

10.10 DEFINITIONS

Sec. 10.1

Thermoplastic (noun): a plastic material that requires heat to make it formable (plastic) and upon cooling, retains its shape. Thermoplastics are composed of chain polymers with the bonds between the chains being of the secondary permanent dipole type. Thermoplastics can be repeatedly softened when heated and harden when cooled. Typical thermoplastics are polyethylenes, vinyls, acrylics, cellulose, and nylons.

Thermosetting plastic (thermoset): a plastic material that has undergone a chemical reaction by the action of heat, catalysis, etc., leading to a cross-linked network macromolecular structure. Thermoset plastics cannot be remelted and reprocessed since when they are heated they degrade and decompose. Typical thermoset plastics are phenolics, unsaturated polyesters, and epoxies.

Sec. 10.2

Monomer: a simple molecular compound that can be covalently bonded together to form long molecular chains (polymers). Example: ethylene.

Chain polymer: a high-molecular-mass compound whose structure consists of a large number of small repeating units called *mers*. Carbon atoms make up most of the mainchain atoms in most polymers.

Chain polymerization: the polymerization mechanism whereby each polymer molecule increases in size at a rapid rate once growth has started. This type of reaction occurs in three steps: (1) chain initiation, (2) chain propagation, and (3) chain termination. The name implies a chain reaction and is usually initiated by some external source. Example: the chain polymerization of ethylene into polyethylene.

Mer: a repeating unit in a chain polymer molecule.

Degree of polymerization: the molecular mass of a polymer chain divided by the molecular mass of its mer.

Functionality: the number of active bonding sites in a monomer. If the monomer has two bonding sites, it is said to be *bifunctional*.

Homopolymer: a polymer consisting of only one type of monomeric unit.

Copolymer: a polymer chain consisting of two or more types of monomeric units.

Copolymerization: the chemical reaction in which high-molecular-mass molecules are formed from two or more monomers.

Stepwise polymerization: the polymerization mechanism whereby the growth of the polymer molecule proceeds by a stepwise intermolecular reaction. Only one type of reaction is involved. Monomer units can react with each other or with any size polymer molecule. The active group on the end of a monomer is assumed to have the same reactivity no matter

what the polymer length is. Often a by-product such as water is condensed off in the polymerization process. Example: the polymerization of nylon 6,6 from adipic acid and hexamethylene diamine.

Polymerization: the chemical reaction in which high-molecular-mass molecules are formed from monomers.

Cross-linking: the formation of primary valence bonds between polymer chain molecules. When extensive cross-linking occurs as in the case of thermosetting resins, cross-linking makes one supermolecule of all the atoms.

Sec. 10.3

Bulk polymerization: the direct polymerization of liquid monomer to polymer in a reaction system in which the polymer remains soluble in its own monomer.

Solution polymerization: in this process, a solvent is used that dissolves the monomer, the polymer, and the polymerization initiator. Diluting the monomer with the solvent reduces the rate of polymerization, and the heat released by the polymerization reaction is absorbed by the solvent.

Suspension polymerization: in this process, water is used as the reaction medium, and the monomer is dispersed rather than being dissolved in the medium. The polymer products are obtained in the form of small beads that are filtered, washed, and dried in the form of molding powders.

Emulsion polymerization: a type of polymerization process which deals with mixing of unblended phases.

Sec. 10.4

Crystallinity (in polymers): the packing of molecular chains into a stereoregular arrangement with a high degree of compactness. Crystallinity in polymeric materials is never 100 percent and is favored in polymeric materials whose polymer chains are symmetrical. Example: high-density polyethylene can be 95 percent crystalline.

Glass transition temperature: the center of the temperature range where a heated thermoplastic upon cooling changes from a rubbery, leathery state to that of brittle glass.

Stereoisomers: molecules that have the same chemical composition but different structural arrangements.

Atactic stereoisomer: this isomer has pendant groups of atoms *randomly arranged* along a vinyl polymer chain. Example: atactic polypropylene.

Isotactic stereoisomer: this isomer has pendant groups of atoms all on the *same side* of a vinyl polymer chain. Example: isotactic polypropylene.

Syndiotactic stereoisomer: this isomer has pendant groups of atoms *regularly alternating* in positions on both sides of a vinyl polymer chain. Example: syndiotactic polypropylene.

Stereospecific catalyst: a catalyst that creates mostly a specific type of stereoisomer during polymerization. Example: the Ziegler catalyst used to polymerize propylene to mainly the isotactic polypropylene isomer.

Sec. 10.5

Injection molding: a molding process whereby a heat-softened plastic material is forced by a screw-drive cylinder into a relatively cool mold cavity that gives the plastic the desired shape.

Extrusion: the forcing of softened plastic material through an orifice, producing a continuous product. Example: plastic pipe is extruded.

Blow molding: a method of fabricating plastics in which a hollow tube (parison) is forced into the

shape of a mold cavity by internal air pressure.

Compression molding: a thermoset molding process in which a molding compound (which is usually heated) is first placed in a molding cavity. Then the mold is closed and heat and pressure are applied until the material is cured.

Transfer molding: a thermoset molding process in which the molding compound is first softened by heat in a transfer chamber and then is forced under high pressure into one or more mold cavities for final curing.

Thermoforming: a process in which sheets or films of polymers are converted into useable products through the application of heat and pressure.

Sec. 10.6

Plasticizers: chemical agents added to plastic compounds to improve flow and processibility and to reduce brittleness. Example: plasticized polyvinyl chloride.

Filler: a low-cost inert substance added to plastics to make them less costly. Fillers may also improve some physical properties such as tensile strength, impact strength, hardness, wear resistance, etc.

Heat stabilizer: a chemical that prevents the reaction between chemicals.

Pigment: particles added to a material to develop color.

10.11 PROBLEMS

Answers to problems marked with an asterisk are given at the end of the book.

Knowledge and Comprehension Problems

- 10.1 Define and differentiate polymers, plastics, and elastomers.
- 10.2 (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?
- 10.3 What is a pendant atom or group of atoms?
- 10.4 (a) What type of bonding exists within the molecular chains of thermoplastics? (b) What type of bonding exists between the molecular chains of thermoplastics?
- 10.5 (a) Define thermosetting plastics. (b) Describe the atomic structural arrangement of thermosetting plastics.
- 10.6 Define the following terms: chain polymerization, monomer, and polymer.
- 10.7 Describe the bonding structure within an ethylene molecule by using (a) the electron-dot notation and (b) straight-line notation for the bonding electrons.
- 10.8 (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.
- 10.9 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?
- 10.10 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 notation and (b) straight-line notation for the bonding electrons.

- 10.11 (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.
- 10.12 What is the functionality of a monomer? Distinguish between a bifunctional and trifunctional monomer.
- *10.13 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.
- *10.14 Write structural formulas for the mers of the following vinylidene polymers (a) polyvinylidene chloride and (b) polymethyl methacrylate
- 10.15 Distinguish between a homopolymer and a copolymer.
- 10.16 Illustrate the following types of copolymers by using filled and open circles for their mers. (a) random, (b) alternating, (c) block, and (d) graft
- 10.17 Define stepwise polymerization of linear polymers. What by-products are commonly produced by stepwise polymerization?
- 10.18 What are three basic raw materials used to produce the basic chemicals needed for the polymerization of plastic materials?
- 10.19 Describe and illustrate the following polymerization processes (a) bulk, (b) solution, (c) suspension, and (d) emulsion
- 10.20 Describe the Unipol process for producing low-density polyethylene. What are the advantages of this process?
- 10.21 (a) Define the glass transition temperature T_g for a thermoplastic. (b) What are the measured T_g values for (i) polyethylene, (ii) polyvinyl chloride, and (iii) polymethyl methacrylate? Are the T_g values constants?
- 10.22 Describe and illustrate the fringed-micelle and folded-chain models for the structure of partly crystalline thermoplastics.
- 10.23 Describe the spherulitic structure found in some partly crystalline thermoplastics.
- 10.24 (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
- 10.25 What is a stereospecific catalyst? How did the development of a stereospecific catalyst for the polymerization of polypropylene affect the usefulness of commercial polypropylene?
- 10.26 In general, how does the processing of thermoplastics into the desired shape differ from the processing of thermosetting plastics?
- 10.27 (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?
- 10.28 Describe the extrusion process for processing thermoplastics.
- 10.29 Describe the blow-molding and thermoforming processes for forming thermoplastics
- 10.30 (a) Describe the compression-molding process for thermosetting plastics (b) What

- are some of the advantages and disadvantages of the compression-molding process?
- 10.31** (a) Describe the transfer-molding process for thermosetting plastics. (b) What are some of the advantages of the transfer-molding process?
- 10.32** 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?
- 10.33** Define an engineering thermoplastic. Why is this definition arbitrary?
- 10.34** What is the structural formula for the amide linkage in thermoplastics? What is the general name for polyamide thermoplastics?
- 10.35** (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?
- 10.36** What is the basic repeating chemical structural unit for polycarbonates? What is the carbonate linkage? What are the common trade names for polycarbonate?
- 10.37** What is the basic repeating chemical structural unit for the polyphenylene oxide-based resins? What are the trade names for these resins?
- 10.38** 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?
- 10.39** What are the two most important engineering thermoplastic polyesters? What are their repeating chemical structural units?
- 10.40** What is the chemical structure of the ester linkage?
- 10.41** What is the repeating chemical structural unit for polysulfone?
- 10.42** (a) 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?
- 10.43** (a) What is the chemical structure of polyetherimide? (b) What is its trade name?
- 10.44** (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?
- 10.45** (a) What are the major processing methods used for thermosets? (b) What are the two major ingredients of thermosetting molding compounds?
- 10.46** What are elastomers? What are some elastomeric materials?
- 10.47** From what tree is most natural rubber obtained? What countries have large plantations of these trees?
- 10.48** What is natural rubber latex? Briefly describe how natural rubber is produced in the bulk form.
- 10.49** What is natural rubber mainly made of? What other components are present in natural rubber?
- 10.50** To what structural arrangement is the coiling of the natural rubber polymer chains attributed? What is steric hindrance?
- 10.51** What are chemical structural isomers?
- 10.52** What is gutta-percha? What is the repeating chemical structural unit for gutta-percha?
- 10.53** What does the *trans*- prefix in the name *trans*-1,4 polyisoprene refer to?

- 10.54** 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.
- 10.55** What materials are used in the compounding of rubber, and what is the function of each?
- 10.56** What is styrene-butadiene rubber (SBR)? What weight percent of it is styrene? What are the repeating chemical structural units for SBR?
- 10.57** What are the silicones? What is the general repeating chemical structural unit for the silicones?
- 10.58** 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?
- 10.59** Describe the general deformation behavior of a thermoplastic plastic above and below its glass transition temperature.
- 10.60** What deformation mechanisms are involved during the elastic and plastic deformation of thermoplastics?
- 10.61** What is viscoelastic behavior of plastic materials?
- 10.62** Define the creep modulus of a plastic material.
- 10.63** What is a craze in a glassy thermoplastic?
- 10.64** Describe the structure of a craze in a thermoplastic.
- 10.65** Describe the molecular structure changes that occur during the ductile fracturing of a thermoplastic.

Application and Analysis Problems

- *10.66** A high-molecular-weight polyethylene has an average molecular weight of 410,000 g/mol. What is its average degree of polymerization?
- 10.67** If a type of polyethylene has an average degree of polymerization of 10,000, what is its average molecular weight?
- 10.68** 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).
- 10.69** 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).
- *10.70** 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

- 10.71** A copolymer consists of 70 wt % polystyrene and 30 wt % polyacrylonitrile. Calculate the mole fraction of each component in this material.
- 10.72** 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.
- *10.73** 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.
- 10.74** How much sulfur must be added to 70 g of butadiene rubber to cross-link 3.0 percent of the mers? (Assume all the sulfur is used to cross-link the mers and that only one sulfur atom is involved in each cross-linking bond.)
- 10.75** 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?
- *10.76** How much sulfur must be added to cross-link 10 percent of the cross-link sites in 90 g of polyisoprene rubber?
- 10.77** How many kilograms of sulfur are needed to cross-link 15 percent of the cross-link sites in 200 kg of polyisoprene rubber?
- 10.78** If 3 kg of sulfur is added to 300 kg of butadiene rubber, what fraction of the cross-links are joined?
- 10.79** 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.)
- 10.80** What weight percent sulfur must be added to polybutadiene to cross-link 20 percent of the possible cross-link sites?
- *10.81** 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.)
- 10.82** If 15 percent of the cross-link sites in isoprene rubber are to be bonded, what weight percent sulfur must the rubber contain?
- *10.83** A stress of 9.0 MPa is applied to an elastomeric material at a constant stress at 20°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?
- 10.84** 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?
- 10.85** 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.
- 10.86** 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?
- *10.87** 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?

- 10.88** What is the difference between a saturated and an unsaturated carbon-containing molecule?
- 10.89** 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 notation and (b) straight-line notation for the bonding electrons.
- 10.90** Write a general chemical reaction for the chain polymerization of ethylene monomer into the linear polymer polyethylene.
- *10.91** 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.
- 10.92** Write an equation for the reaction of an organic free radical (RO) with an ethylene molecule to form a new, longer-chain free radical.
- 10.93** Write a reaction for the free radical $R-CH_2-CH_2\cdot$ with an ethylene molecule to extend the free radical. What type of reaction is this?
- 10.94** (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?
- 10.95** Write a general reaction for the polymerization of a vinyl-type polymer.
- 10.96** Write a general reaction for the polymerization of a vinylidene polymer.
- 10.97** Write a general polymerization reaction for the formation of a vinyl chloride and vinyl acetate copolymer.
- 10.98** 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?
- 10.99** Write the reaction for the stepwise polymerization of two phenol molecules with one of formaldehyde to produce a phenol formaldehyde molecule.
- 10.100** (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.
- 10.101** How does the molecular-chain structure differ for the following types of polyethylene: (a) low-density, (b) high-density, and (c) linear-low-density?
- 10.102** How does chain branching affect the following properties of polyethylene: (a) amount of crystallinity, (b) strength, and (c) elongation?
- 10.103** (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?
- 10.104** (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?
- 10.105** (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?

- 10.106** 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?
- 10.107** Write a chemical reaction for one molecule of adipic acid and one molecule of hexamethylene diamine to form an amide linkage.
- 10.108** Write the reaction for the polymerization of nylon 6 from ϵ -caprolactam.
- 10.109** Illustrate the bonding between polymer chains of nylon 6,6. Why is this bonding particularly strong? (See Fig. 10.35.)
- 10.110** What part of the polycarbonate structure makes the molecule stiff? What part of the polycarbonate molecule provides molecular flexibility?
- 10.111** What part of the structure of polyphenylene oxide provides its relatively high strength? What part of its structure provides its molecular flexibility?
- 10.112** What part of the structure of the acetals provides high strength?
- 10.113** What part of the structure of the thermoplastic polyesters provides rigidity? What part provides molecular mobility?
- 10.114** What part of the polysulfone structure provides its high strength? What part provides chain flexibility and impact strength? What part provides high-oxidation stability?
- 10.115** What part of the structure of PPS provides its rigidity and strength? What part provides its high resistance to chemicals?
- 10.116** What is the function of the ether linkage in polyetherimide?
- 10.117** 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?
- 10.118** 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?
- 10.119** Why are large percentages of fillers used in phenolic molding compounds? What types of fillers are used and for what purposes?
- 10.120** Write the structural formula for the epoxide group and the repeating unit of a commercial epoxy resin.
- 10.121** What are two types of reaction sites that are active in the cross-linking of commercial epoxy resins?
- 10.122** Write the reaction for the cross-linking of two epoxy molecules with ethylene diamine.
- 10.123** What makes an unsaturated polyester resin "unsaturated"?
- 10.124** How are linear unsaturated polyesters cross-linked? Write a structural formula chemical reaction to illustrate the cross-linking of an unsaturated polyester.
- 10.125** 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?
- 10.126** Why does the *trans* isomer lead to a higher degree of crystallinity than the *cis* isomer for polyisoprene?
- 10.127** 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?
- 10.128** How can oxygen atoms cross-link the rubber molecules? How can the cross-linking of rubber molecules by oxygen atoms be retarded?
- 10.129** Can SBR be vulcanized? Explain.

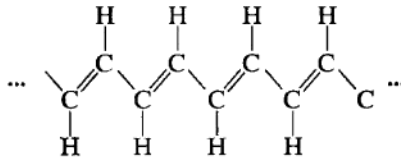
- 10.130** What is the composition of nitrile rubbers? What effect does the nitrile group have on the main carbon chain in nitrile rubber?
- 10.131** Write the repeating chemical structural unit for polychloroprene. What common name is given to polychloroprene rubber? How does the presence of the chlorine atom in polychloroprene affect some of its properties?
- 10.132** How are polychloroprene elastomeric materials vulcanized?
- 10.133** How can a silicone rubber be cross-linked at room temperature?
- 10.134** How does the average molecular mass of a thermoplastic affect its strength?
- 10.135** How does the amount of crystallinity within a thermoplastic material affect (a) its strength, (b) its tensile modulus of elasticity, and (c) its density?
- 10.136** Explain why low-density polyethylene is weaker than high-density polyethylene.
- 10.137** Explain why bulky side groups strengthen thermoplastics.
- 10.138** Explain how highly polar atoms bonded to the main carbon chain strengthen thermoplastics. Give examples.
- 10.139** Explain how oxygen atoms covalently bonded in the main carbon chain strengthen thermoplastics. Give an example.
- 10.140** Explain how phenylene rings covalently bonded in the main carbon chain strengthen thermoplastics. Give an example.
- 10.141** Explain why thermosetting plastics have in general high strengths and low ductilities.
- 10.142** How do the prices of engineering thermoplastics compare with those of the commodity plastics such as polyethylene, polyvinyl chloride, and polypropylene?
- 10.143** How do the densities and tensile strengths of engineering thermoplastics compare with those of polyethylene and polyvinyl chloride?
- 10.144** How does increasing the temperature of thermoplastics affect their strength? What changes in bonding structure occur as thermoplastics are heated?
- 10.145** Why do cured thermoset plastics not become viscous and flow at elevated temperatures?
- 10.146** How do increases in stress and temperature affect the creep resistance of thermoplastics?
- 10.147** (a) What are the fluoroplastics? (b) What are the repeating chemical structural units for polytetrafluoroethylene and polychlorotrifluoroethylene? (c) What are some of the important properties and applications of polytetrafluoroethylene?
- 10.148** How can the creep modulus of a thermoplastic be increased?
- 10.149** How can the extra energy required to fracture glassy thermoplastics, as compared to inorganic glasses, be explained?
- 10.150** How is it possible for a polymer chain such as a polyethylene to keep growing spontaneously during polymerization?
- 10.151** During the solidification of thermoplastics, how does the specific volume versus temperature plots differ for noncrystalline and partly crystalline thermoplastics?
- 10.152** (a) What are some of the properties that make polyethylene such an industrially important plastic material? (b) What are some its industrial applications?
- 10.153** (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?
- 10.154** (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?
- 10.155** (a) How is the processibility of PVC improved to produce rigid PVC? (b) What are some of the applications for plasticized PVC?
- 10.156** (a) What are SAN resins? (b) What desirable properties do SAN thermoplastics have? (c) What are some of the applications for SAN thermoplastics?
- 10.157** (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?
- 10.158** (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?
- 10.159** What properties do nylons have that make them useful for engineering applications? What is an important undesirable property of nylon?
- 10.160** What are some of the engineering applications for nylons?
- 10.161** What are some engineering applications for polycarbonates?
- 10.162** What are some of the properties of polycarbonates that make them useful engineering thermoplastics?
- 10.163** What are some of the engineering applications for polyphenylene oxide resins?
- 10.164** What are some of the properties that make polyphenylene oxide resins important engineering thermoplastics?
- 10.165** What are some of the properties of acetals that make them important engineering thermoplastics?
- 10.166** What outstanding property advantage do the acetals have over nylons?
- 10.167** What are some of the engineering applications for acetals?
- 10.168** What types of materials have acetals commonly replaced?
- 10.169** What are some of the properties of thermoplastic polyesters that make them important engineering thermoplastics?
- 10.170** What are some engineering applications for PBT thermoplastics?
- 10.171** What are some of the properties of polysulfone that are important for engineering designs?
- 10.172** What are some of the engineering applications for polysulfone?
- 10.173** What properties make PPS a useful engineering thermoplastic?
- 10.174** What are some engineering applications for PPS?
- 10.175** What special properties does polyetherimide have for (a) electrical engineering designs and (b) mechanical engineering designs?
- 10.176** What are some applications for polyetherimide?
- 10.177** Why are polymer alloys of great importance for engineering applications?
- 10.178** What are the major advantages of phenolic plastics for industrial applications?
- 10.179** What are some of the applications for phenolic compounds?
- 10.180** What are some of the advantages of epoxy thermoset resins? What are some of their applications?
- 10.181** How are most unsaturated polyesters reinforced?
- 10.182** What are some applications for reinforced polyesters?
- 10.183** What are some applications for nitrile rubbers?
- 10.184** What are some engineering applications for neoprene rubbers?

- 10.185** What are some of the engineering applications for silicone rubber?
- 10.186** What are some of the advantages and disadvantages of SBR? Natural rubber?

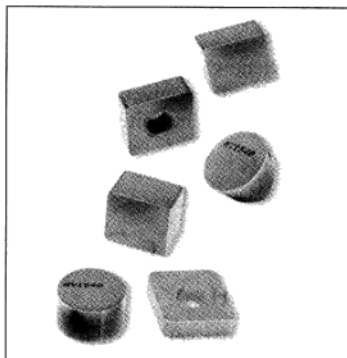
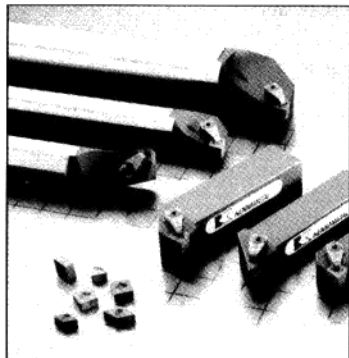
Synthesis and Evaluation Problems

- 10.187** Using Fig. 10.47, (a) 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.
- 10.188** 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.



- 10.189** Suggest a way of making a standard polymer self-lubricating.
- 10.190** 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?
- 10.191** 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.
- 10.192** (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.
- 10.193** Explain why is PMMA a good material to use for glazing of boats. What is the purpose of glazing on a boat?
- 10.194** 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?
- 10.195** Investigate the role of polymers in the ophthalmic lens manufacturing industry. Which polymers are used and what characteristics do they have?
- 10.196** 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?
- 10.197** 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?

Ceramics



(Courtesy of Kennametal.)

Due to their desirable characteristics such as high hardness, wear resistance, chemical stability, high-temperature strength, and low coefficient of thermal expansion, advanced ceramics are being selected as the preferred material for many applications. These include but are not limited to mineral processing, seals, valves, heat exchangers, metal-forming dies, adiabatic diesel engines, gas turbines, medical products, and cutting tools.

Ceramic cutting tools have many advantages over their conventional metal counterparts, including chemical stability, higher resistance to wear, higher hot hardness, and superior heat dispersal during the chip removal process. Some examples of ceramic materials that are used to manufacture cutting tools are metal oxide composites (70% Al_2O_3 –30% TiC), silicon-aluminum-oxynitride (sialons), and cubic boron nitride. These tools are manufactured through powder metallurgy processes in which ceramic particles are densified into a final shape through compaction and sintering. The chapter-opening images are examples of various types of metal removal products made from advanced ceramics.¹ ■

¹"Ceramics Engineered Materials Handbook," vol. 1, ASM International.

LEARNING OBJECTIVES

By the end of this chapter, students will be able to . . .

1. Define and classify ceramic materials including traditional and engineering ceramics.
2. Describe various ceramic crystal structures.
3. Describe carbon and its allotropes.
4. Describe various processing methods for ceramics.
5. Describe the mechanical properties of ceramics and the corresponding mechanisms of deformation, toughening, and failure of ceramics.
6. Describe thermal properties of ceramics.
7. Describe various types of ceramic glasses, glass transition temperature, forming methods, and structure of glass.
8. Describe various ceramic coatings and applications.

11.1 INTRODUCTION

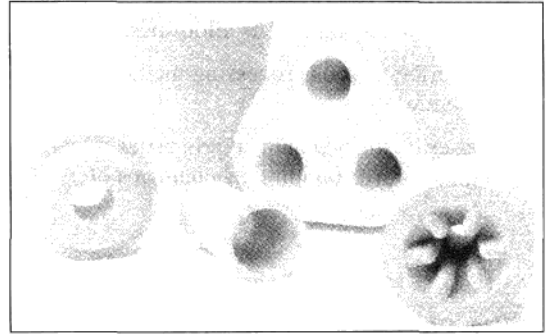
Ceramic materials are inorganic, nonmetallic materials that consist of metallic and nonmetallic elements bonded together primarily by ionic and/or covalent bonds. The chemical compositions of ceramic materials vary considerably, from simple compounds to mixtures of many complex phases bonded together.

The properties of ceramic materials also vary greatly due to differences in bonding. In general, ceramic materials are typically hard and brittle with low toughness and ductility. Ceramics are usually good electrical and thermal insulators because of the absence of conduction electrons. Ceramic materials normally have relatively high melting temperatures and high chemical stability in many hostile environments because of the stability of their strong bonds. Because of these properties, ceramic materials are indispensable for many engineering designs. Two examples of the strategic importance of ceramic materials in new high technology are shown in Fig. 11.1.

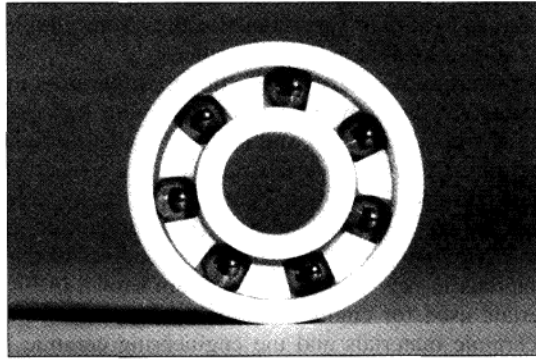
In general, ceramic materials used for engineering applications can be divided into two groups: traditional ceramic materials and the engineering ceramic materials. Typically, traditional ceramics are made from three basic components: clay, silica (flint), and feldspar. Examples of traditional ceramics are glasses, bricks, and tiles used in the construction industries and electrical porcelain in the electrical industry. The engineering ceramics, in contrast, typically consist of pure or nearly pure compounds such as aluminum oxide (Al_2O_3), silicon carbide (SiC), and silicon nitride (Si_3N_4). Examples of the use of the engineering ceramics in high technology are silicon carbide in the high-temperature areas of the experimental AGT-100 automotive gas turbine engine and aluminum oxide in the support base for integrated circuit chips in a thermal-conduction module.



(a)



(b)



(c)

Figure 11.1

(a) Zircoa (zirconium dioxide) crucibles are used in melting superalloys. (b) Zircoa coarse-grained product line includes nozzles, crucibles, burner blocks, setter plates, and disks.

((a) and (b) after *American Ceramic Bulletin*, Sept., 2001. Photo Courtesy of Zircoa, Inc.)

(c) High-performance Ceratec ball bearing and races are made from titanium and carbon nitride feedstocks through powder metal technology.

(© David A. Tietz/Editorial Image, LLC.)

In this chapter, we shall first examine some simple ceramic crystal structures and then look at some of the more complicated silicate ceramic structures. Then we shall explore some of the methods for processing ceramic materials, and following that, study some of the mechanical and thermal properties of ceramic materials. We shall examine some aspects of the structure and properties of glasses, ceramic coatings and surface engineering, and the use of ceramics in biomedical applications. Finally, we shall explore nanotechnology and ceramics.

11.2 SIMPLE CERAMIC CRYSTAL STRUCTURES

11.2.1 Ionic and Covalent Bonding in Simple Ceramic Compounds

Let us first consider some simple ceramic crystal structures. Some ceramic compounds with relatively simple crystal structures are listed in Table 11.1 with their melting points.

In the ceramic compounds listed, the atomic bonding is a mixture of ionic and covalent types. Approximate values for the percentages of ionic and covalent character for the bonds between the atoms in these compounds can be obtained by considering the electronegativity differences between the different types of atoms in the compounds and by using Pauling's equation for percent ionic character (Eq. 2.10). Table 11.2 shows that the percent ionic or covalent character varies considerably in simple ceramic compounds. The amount of ionic or covalent bonding between the

Table 11.1 Some simple ceramic compounds with their melting points

Ceramic compound	Formula	Melting point (°C)	Ceramic compound	Formula	Melting point (°C)
Hafnium carbide	HfC	4150	Boron carbide	B ₄ C ₃	2450
Titanium carbide	TiC	3120	Aluminum oxide	Al ₂ O ₃	2050
Tungsten carbide	WC	2850	Silicon dioxide†	SiO ₂	1715
Magnesium oxide	MgO	2798	Silicon nitride	Si ₃ N ₄	1700
Zirconium dioxide	ZrO ₂ *	2750	Titanium dioxide	TiO ₂	1605
Silicon carbide	SiC	2500			

*Is believed to have a monoclinic fluorite (distorted) crystal structure when melted.

†Cristobalite.

Table 11.2 Percent ionic and covalent bonding in some ceramic compounds

Ceramic compound	Bonding atoms	Electronegativity difference	% ionic character	% covalent character
Zirconium dioxide, ZrO ₂	Zr-O	2.3	73	27
Magnesium oxide, MgO	Mg-O	2.2	69	31
Aluminum oxide, Al ₂ O ₃	Al-O	2.0	63	37
Silicon dioxide, SiO ₂	Si-O	1.7	51	49
Silicon nitride, Si ₃ N ₄	Si-N	1.3	34.5	65.5
Silicon carbide, SiC	Si-C	0.7	11	89

atoms of these compounds is important since it determines to some extent what type of crystal structure will form in the bulk ceramic compound.

11.2.2 Simple Ionic Arrangements Found in Ionically Bonded Solids

In ionic (ceramic) solids, the packing of the ions is determined primarily by the following factors:

1. The relative size of the ions in the ionic solid (assume the ions to be hard spheres with definite radii)
2. The need to balance electrostatic charges to maintain electrical neutrality in the ionic solid

When ionic bonding between atoms takes place in the solid state, the energies of the atoms are lowered by the formation of the ions and their bonding into an ionic solid. Ionic solids tend to have their ions packed together as densely as possible to lower the overall energy of the solid as much as possible. The limitations to dense packing are the relative sizes of the ions and the necessity for maintaining charge neutrality.

Size Limitations for the Dense Packing of Ions in an Ionic Solid Ionic solids consist of cations and anions. In ionic bonding, some atoms lose their outer electrons to become *cations* and others gain outer electrons to become *anions*. Thus, cations are normally smaller than the anions they bond with. The number of anions that surround a central cation in an ionic solid is called the **coordination number (CN)** and corresponds to the number of nearest neighbors surrounding a central cation. For stability, as many anions as possible surround a central cation. However, the anions must make contact with the central cation, and charge neutrality must be maintained.

Figure 11.2 shows two stable configurations for the coordination of anions around a central cation in an ionic solid. If the anions do not touch the central cation, the structure becomes unstable because the central cation can “rattle around in its cage of anions” (third diagram, Fig. 11.2). The ratio of the radius of the central cation

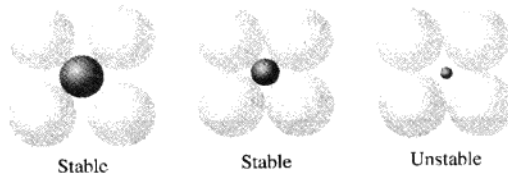
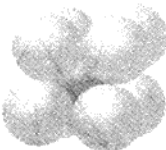





Figure 11.2
Stable and unstable coordination configurations for ionic solids.

(From W.D. Kingery, H.K. Bowen, and D.R. Uhlmann, "Introduction to Ceramics," 2d ed., Wiley, 1976. Reprinted with permission of John Wiley & Sons, Inc.)

Disposition of ions about central ion	CN	Range of cation radius ratio to anion radius	
Corners of cube	8	≥ 0.732	
Corners of octahedron	6	≥ 0.414	
Corners of tetrahedron	4	≥ 0.225	
Corners of triangle	3	≥ 0.155	

CN = Coordination number

Figure 11.3

Radius ratios for coordination numbers of 8, 6, 4, and 3 anions surrounding a central cation in ionic solids.

(From W.D. Kingery, H.K. Bowen, and D.R. Uhlmann, "Introduction to Ceramics," 2d ed., Wiley, 1976. Reprinted with permission of John Wiley & Sons, Inc.)

to that of the surrounding anions is called the **radius ratio**, $r_{\text{cation}}/r_{\text{anion}}$. The radius ratio when the anions just touch each other and contact the central cation is called the **critical (minimum) radius ratio**. Allowable radius ratios for ionic solids with coordination numbers of 3, 4, 6, and 8 are listed in Fig. 11.3 along with illustrations showing the coordinations.

Calculate the critical (minimum) radius ratio r/R for the triangular coordination (CN = 3) of three anions of radii R surrounding a central cation of radius r in an ionic solid.

**EXAMPLE
PROBLEM 11.1**

■ **Solution**

Figure EP11.1a shows three large anions of radii R surrounding and just touching a central cation of radius r . Triangle ABC is an equilateral triangle (each angle = 60°), and line

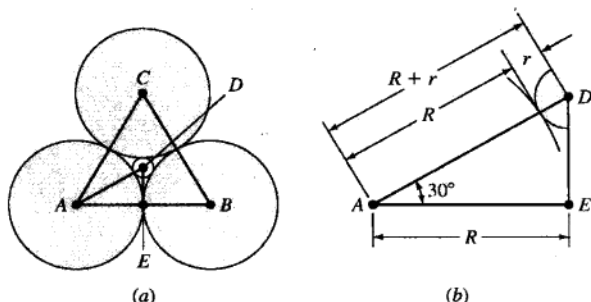
**Figure EP11.1**

Diagram for triangular coordination.

AD bisects angle CAB . Thus, angle $DAE = 30^\circ$. To find the relationship between R and r , triangle ADE is constructed as shown in Fig. EP11.1b. Thus,

$$\begin{aligned}
 AD &= R + r \\
 \cos 30^\circ &= \frac{AE}{AD} = \frac{R}{R + r} = 0.866 \\
 R &= 0.866(R + r) = 0.866R + 0.866r \\
 0.866r &= R - 0.866R = R(0.134) \\
 \frac{r}{R} &= 0.155 \blacktriangleleft
 \end{aligned}$$

**EXAMPLE
PROBLEM 11.2**

Predict the coordination number for the ionic solids CsCl and NaCl . Use the following ionic radii for the prediction:

$$\text{Cs}^+ = 0.170 \text{ nm} \quad \text{Na}^+ = 0.102 \text{ nm} \quad \text{Cl}^- = 0.181 \text{ nm}$$

■ Solution

The radius ratio for CsCl is

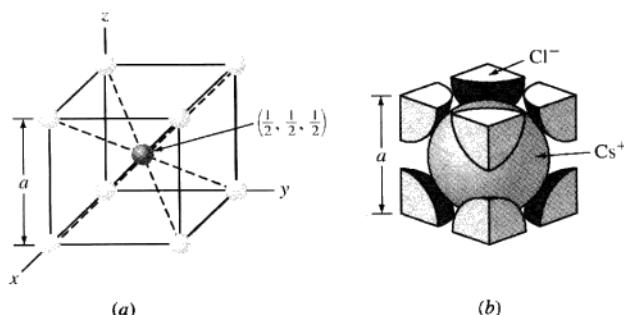
$$\frac{r(\text{Cs}^+)}{R(\text{Cl}^-)} = \frac{0.170 \text{ nm}}{0.181 \text{ nm}} = 0.94$$

Since this ratio is greater than 0.732, CsCl should show cubic coordination ($\text{CN} = 8$), which it does.

The radius ratio for NaCl is

$$\frac{r(\text{Na}^+)}{R(\text{Cl}^-)} = \frac{0.102 \text{ nm}}{0.181 \text{ nm}} = 0.56$$

Since this ratio is greater than 0.414 but less than 0.732, NaCl should show octahedral coordination ($\text{CN} = 6$), which it does.

**Figure 11.4**

Cesium chloride (CsCl) crystal structure unit cell. (a) Ion-site unit cell. (b) Hard-sphere unit cell. In this crystal structure, eight chloride ions surround a central cation in cubic coordination (CN = 8). In this unit cell, there is one Cs^+ and one Cl^- ion.



11.2.3 Cesium Chloride (CsCl) Crystal Structure

The chemical formula for solid cesium chloride is CsCl , and since this structure is principally ionically bonded, there are equal numbers of Cs^+ and Cl^- ions. Because the radius ratio for CsCl is 0.94 (see Example Problem 11.2), cesium chloride has cubic coordination (CN = 8), as shown in Fig. 11.4. Thus, eight chloride ions surround a central cesium cation at the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ position in the CsCl unit cell. Ionic compounds that also have the CsCl crystal structure are CsBr, TlCl, and TlBr. The intermetallic compounds AgMg, LiMg, AlNi, and $\beta\text{-Cu-Zn}$ also have this structure. The CsCl structure is not of much importance for ceramic materials but does illustrate how higher radius ratios lead to higher coordination numbers in ionic crystal structures.

Calculate the ionic packing factor for CsCl. Ionic radii are $\text{Cs}^+ = 0.170 \text{ nm}$ and $\text{Cl}^- = 0.181 \text{ nm}$.

EXAMPLE PROBLEM 11.3

■ Solution

The ions touch each other across the cube diagonal of the CsCl unit cell, as shown in Fig. EP11.3. Let $r = \text{Cs}^+$ ion and $R = \text{Cl}^-$ ion. Thus

$$\begin{aligned}\sqrt{3}a &= 2r + 2R \\ &= 2(0.170 \text{ nm} + 0.181 \text{ nm}) \\ a &= 0.405 \text{ nm}\end{aligned}$$

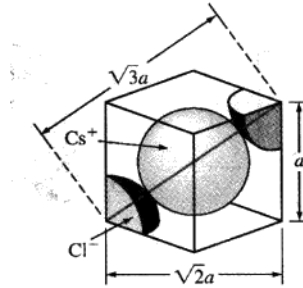


Figure EP11.3

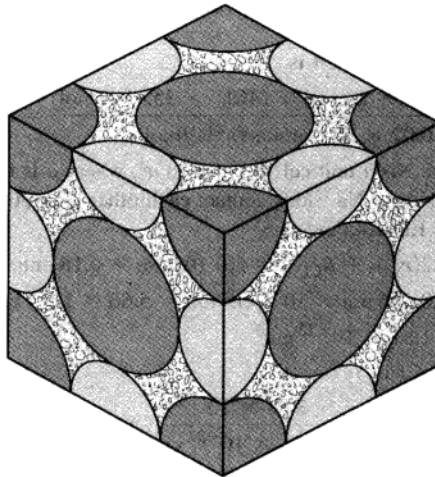
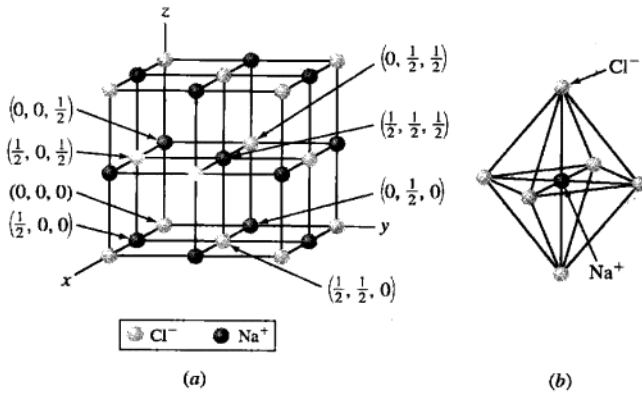
$$\begin{aligned}
 \text{CsCl ionic packing factor} &= \frac{\frac{4}{3}\pi r^3(1 \text{ Cs}^+ \text{ ion}) + \frac{4}{3}\pi R^3(1 \text{ Cl}^- \text{ ion})}{a^3} \\
 &= \frac{\frac{4}{3}\pi(0.170 \text{ nm})^3 + \frac{4}{3}\pi(0.181 \text{ nm})^3}{(0.405 \text{ nm})^3} \\
 &= 0.68 \blacktriangleleft
 \end{aligned}$$

11.2.4 Sodium Chloride (NaCl) Crystal Structure

The sodium chloride or rock salt crystal structure is highly ionically bonded and has the chemical formula NaCl. Thus, there are an equal number of Na^+ and Cl^- ions to maintain charge neutrality. Figure 11.5a shows a lattice-site NaCl unit cell and Fig. 2.18b a hard-sphere model of the NaCl unit cell. Figure 11.5a has negative Cl^- anions occupying regular FCC atom lattice sites and positive Na^+ cations occupying the interstitial sites between the FCC atom sites. The centers of the Na^+ and Cl^- ions occupy the following lattice positions, which are indicated in Fig. 11.5a:

$$\begin{array}{ll}
 \text{Na}^+: & (\frac{1}{2}, 0, 0) \quad (0, \frac{1}{2}, 0) \quad (0, 0, \frac{1}{2}) \quad (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \\
 \text{Cl}^-: & (0, 0, 0) \quad (\frac{1}{2}, \frac{1}{2}, 0) \quad (\frac{1}{2}, 0, \frac{1}{2}) \quad (0, \frac{1}{2}, \frac{1}{2})
 \end{array}$$

Since each central Na^+ cation is surrounded by six Cl^- anions, the structure has octahedral coordination (that is, $\text{CN} = 6$), as shown in Fig. 11.5b. This type of coordination is predicted from the radius ratio calculation of $r_{\text{Na}^+}/R_{\text{Cl}^-} = 0.102 \text{ nm}/0.181 \text{ nm} = 0.56$, which is greater than 0.414 but less than 0.732. Other examples of ceramic compounds that have the NaCl structure include MgO, CaO, NiO, and FeO.



Sodium Chloride Crystal Structure
NaCl

(Light color) sodium ions—(0.102 nm radius) $\frac{r_{\text{Na}^+}}{R_{\text{Cl}^-}} = 0.56$
(Dark color) chloride ions—(0.181 nm radius)

(c)

Figure 11.5

(a) NaCl lattice-point unit cell indicating positions of the Na^+ (radii = 0.102 nm) and Cl^- (radii = 0.181 nm) ions. (b) Octahedron showing octahedral coordination of six Cl^- anions around a central Na^+ cation. (c) NaCl unit cell truncated.

**EXAMPLE
PROBLEM 11.4**

Calculate the density of NaCl from a knowledge of its crystal structure (Fig. 11.5a), the ionic radii of Na^+ and Cl^- ions, and the atomic masses of Na and Cl. The ionic radius of Na^+ = 0.102 nm and that of Cl^- = 0.181 nm. The atomic mass of Na = 22.99 g/mol and that of Cl = 35.45 g/mol.

■ Solution

As shown in Fig. 11.5a, the Cl^- ions in the NaCl unit cell form an FCC-type atom lattice, and the Na^+ ions occupy the interstitial spaces between the Cl^- ions. There is the equivalent of one Cl^- ion at the corners of the NaCl unit cell since $8 \text{ corners} \times \frac{1}{8} \text{ ion} = 1 \text{ ion}$, and there is the equivalent of three Cl^- ions at the faces of the NaCl unit cell since $6 \text{ faces} \times \frac{1}{2} \text{ ion} = 3 \text{ Cl}^- \text{ ions}$, making a total of four Cl^- ions per NaCl unit cell. To maintain charge neutrality in the NaCl unit cell, there must also be the equivalent of four Na^+ ions per unit cell. Thus, there are four Na^+Cl^- ion pairs in the NaCl unit cell.

To calculate the density of the NaCl unit cell, we shall first determine the mass of one NaCl unit cell and then its volume. Knowing these two quantities, we can calculate the density m/V .

The mass of a NaCl unit cell is

$$= \frac{(4\text{Na}^+ \times 22.99 \text{ g/mol}) + (4\text{Cl}^- \times 35.45 \text{ g/mol})}{6.02 \times 10^{23} \text{ atoms (ions)/mol}} = 3.88 \times 10^{-22} \text{ g}$$

The volume of the NaCl unit cell is equal to a^3 , where a is the lattice constant of the NaCl unit cell. The Cl^- and Na^+ ions contact each other along the cube edges of the unit cell, as shown in Fig. EP11.4, and thus

$$a = 2(r_{\text{Na}^+} + R_{\text{Cl}^-}) = 2(0.102 \text{ nm} + 0.181 \text{ nm}) = 0.566 \text{ nm}$$

$$= 0.566 \text{ nm} \times 10^{-7} \text{ cm/nm} = 5.66 \times 10^{-8} \text{ cm}$$

$$V = a^3 = 1.81 \times 10^{-22} \text{ cm}^3$$

The density of NaCl is

$$\rho = \frac{m}{V} = \frac{3.88 \times 10^{-22} \text{ g}}{1.81 \times 10^{-22} \text{ cm}^3} = 2.14 \frac{\text{g}}{\text{cm}^3} \blacktriangleleft$$

The handbook value for the density of NaCl is 2.16 g/cm^3 .

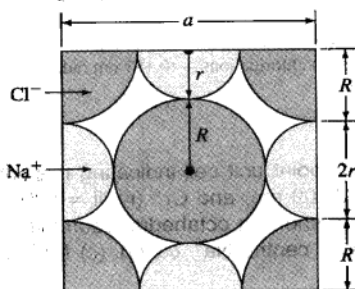


Figure EP11.4

Cube face of NaCl unit cell. Ions contact along the cube edge, and thus $a = 2r + 2R = 2(r + R)$.

Calculate the linear density of Ca^{2+} and O^{2-} ions in ions per nanometer in the $[110]$ direction of CaO , which has the NaCl structure. (Ionic radii: $\text{Ca}^{2+} = 0.106 \text{ nm}$ and $\text{O}^{2-} = 0.132 \text{ nm}$.)

**EXAMPLE
PROBLEM 11.5**

■ **Solution**

From Fig. 11.5 and Fig. EP11.5, we see that the $[110]$ direction passes through two O^{2-} ion diameters in traversing from $(0, 0, 0)$ to $(1, 1, 0)$ ion positions. The length of the $[110]$ distance across the base face of a unit cube is $\sqrt{2}a$, where a is the length of a side of the cube, or lattice constant. From EP11.4 of the cube face of the NaCl unit cell, we see that $a = 2r + 2R$. Thus, for CaO ,

$$\begin{aligned} a &= 2(r_{\text{Ca}^{2+}} + R_{\text{O}^{2-}}) \\ &= 2(0.106 \text{ nm} + 0.132 \text{ nm}) = 0.476 \text{ nm} \end{aligned}$$

The linear density of the O^{2-} ions in the $[110]$ direction is

$$\rho_L = \frac{2\text{O}^{2-}}{\sqrt{2}a} = \frac{2\text{O}^{2-}}{\sqrt{2}(0.476 \text{ nm})} = 2.97\text{O}^{2-}/\text{nm} \blacktriangleleft$$

The linear density of Ca^{2+} ions in the $[110]$ direction is also $2.97 \text{ Ca}^{2+}/\text{nm}$ if we shift the origin of the $[110]$ direction from $(0, 0, 0)$ to $(0, \frac{1}{2}, 0)$. Thus, the solution to the problem is that there are $2.97(\text{Ca}^{2+} \text{ or } \text{O}^{2-})/\text{nm}$ in the $[110]$ direction.

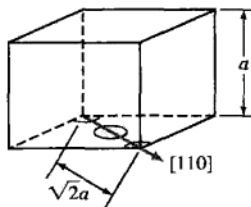


Figure EP11.5

Calculate the planar density of Ca^{2+} and O^{2-} ions in ions per square nanometer on the (111) plane of CaO , which has the NaCl structure. (Ionic radii: $\text{Ca}^{2+} = 0.106 \text{ nm}$ and $\text{O}^{2-} = 0.132 \text{ nm}$.)

**EXAMPLE
PROBLEM 11.6**

■ **Solution**

If we consider the anions (O^{2-} ions) to be located at the FCC positions of a cubic unit cell as shown for the Cl^- ions of Fig. 11.5 and Fig. EP11.6, then the (111) plane contains the equivalent of two anions. [$3 \times 60^\circ = 180^\circ = \frac{1}{2}$ anion + $(3 \times \frac{1}{2})$ anions at each mid-point of the sides of the (111) planar triangle of Fig. EP11.6 = a total of 2 anions within the (111) triangle.] The lattice constant for the unit cell $a = 2(r + R) = 2(0.106 \text{ nm} + 0.132 \text{ nm}) = 0.476 \text{ nm}$. The planar area $A = \frac{1}{2}bh$, where $h = \frac{\sqrt{3}}{2}a^2$.

Thus,

$$A = \left(\frac{1}{2}\sqrt{2}a\right)\left(\sqrt{\frac{3}{2}}a\right) = \frac{\sqrt{3}}{2}a^2 = \frac{\sqrt{3}}{2}(0.476 \text{ nm})^2 = 0.196 \text{ nm}^2$$

The planar density for the O^{2-} anions is

$$\frac{2(\text{O}^{2-} \text{ ions})}{0.196 \text{ nm}^2} = 10.2 \text{ O}^{2-} \text{ ions/nm}^2 \blacktriangleleft$$

The planar density for the Ca^{2+} cations is the same if we consider the Ca^{2+} to be located at the FCC lattice points of the unit cell, and thus

$$\rho_{\text{planar}}(\text{CaO}) = 10.2(\text{Ca}^{2+} \text{ or } \text{O}^{2-})/\text{nm}^2 \blacktriangleleft$$

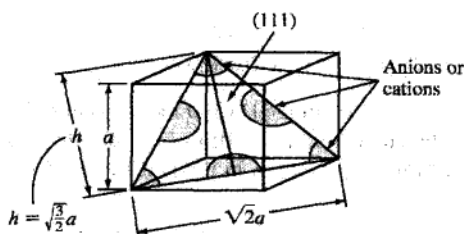
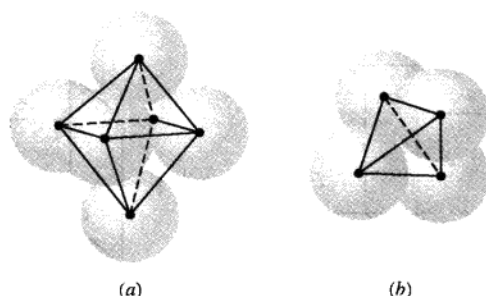


Figure EP11.6

11.2.5 Interstitial Sites in FCC and HCP Crystal Lattices

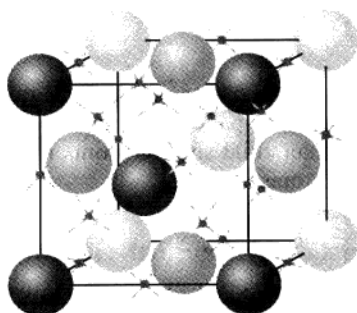
There are empty spaces or voids among the atoms or ions that are packed into a crystal-structure lattice. These voids are *interstitial sites* in which atoms or ions other than those of the parent lattice can be fitted in. In the FCC and HCP crystal structures, which are close-packed structures, there are two types of interstitial sites: **octahedral** and **tetrahedral**. In the octahedral site, there are six nearest atoms or ions equidistant from the center of the void, as shown in Fig. 11.6a. This site is called *octahedral* because the atoms or ions surrounding the center of the site form an eight-sided octahedron. In the tetrahedral site there are four nearest atoms or ions equidistant from the center of the tetrahedral site, as shown in Fig. 11.6b. A regular tetrahedron is formed when the centers of the four atoms surrounding the void are joined.

In the FCC crystal-structure lattice, the octahedral interstitial sites are located at the center of the unit cell and at the cube edges, as indicated in Fig. 11.7. There are the equivalent of four octahedral interstitial sites per FCC unit cell. Since there are

**Figure 11.6**

Interstitial sites in FCC and HCP crystal-structure lattices. (a) Octahedral interstitial site formed at the center where six atoms contact each other. (b) Tetrahedral interstitial site formed at the center where four atoms contact each other.

(From W.D. Kingery, H.K. Bowen, and D.R. Uhlmann, "Introduction to Ceramics," 2d ed., Wiley, 1976. Reprinted with permission of John Wiley & Sons, Inc.)

**Figure 11.7**

Location of octahedral and tetrahedral interstitial void sites in an FCC ionic crystal-structure unit cell. The octahedral sites are located at the center of the unit cell and at the centers of the cube edges. Since there are 12 cube edges, one-fourth of a void is located within the cube at each edge. Thus, there is the equivalent of $12 \times \frac{1}{4} = 3$ voids within the FCC unit cell at the cube edges. Therefore, there is the equivalent of four octahedral voids per FCC unit cell (one at the center and the equivalent of three at the cube edges). The tetrahedral voids are located at the $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ -type sites, which are indicated by points with tetrahedrally directed rays. Thus, there are a total of eight tetrahedral void sites located within the FCC unit cell.

(From W.D. Kingery, "Introduction to Ceramics," Wiley, 1960, p. 104. Reprinted with permission of John Wiley & Sons, Inc.)

four atoms per FCC unit cell, there is one octahedral interstitial site per atom in the FCC lattice. Figure 11.8a indicates the lattice positions for octahedral interstitial sites in an FCC unit cell.

The tetrahedral sites in the FCC lattice are located at the $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ -type positions, as indicated in Figs. 11.7 and 11.8b. In the FCC unit cell, there are eight tetrahedral

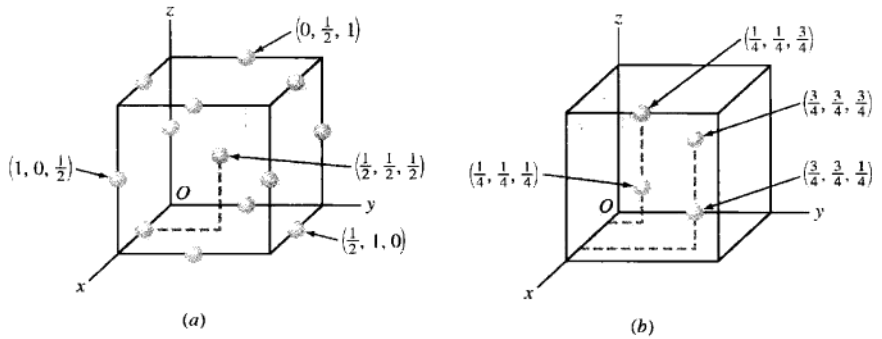


Figure 11.8

Location of interstitial sites in the FCC atom unit cell. (a) The octahedral sites in the FCC unit cell are located at the center of the unit cell and at the centers of the cube edges. (b) The tetrahedral sites in the FCC unit cell are located at the unit-cell positions indicated. Only representative positions are located in the figure.

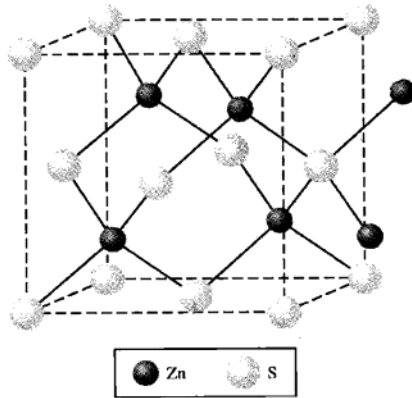
sites per unit cell or *two* per atom of the parent FCC unit cell. In the HCP crystal structure, because of similar close packing to the FCC structure, there is also the same number of octahedral interstitial sites as atoms in the HCP unit cell and twice as many tetrahedral sites as atoms.

11.2.6 Zinc Blende (ZnS) Crystal Structure

The zinc blende structure has the chemical formula ZnS and the unit cell shown in Fig. 11.9, which has the equivalent of four zinc and four sulfur atoms. One type of atom (either S or Zn) occupies the lattice points of an FCC unit cell, and the other type (either S or Zn) occupies half the tetrahedral interstitial sites of the FCC unit cell. In the ZnS crystal-structure unit cell shown in Fig. 11.9, sulfur atoms occupy the FCC unit-cell atom positions, as indicated by the lighter circles, and Zn atoms occupy half the tetrahedral interstitial positions of the FCC unit cell, as indicated by the darker circles. The position coordinates of the S and Zn atoms in the ZnS crystal structure can thus be indicated as

S atoms:	$(0, 0, 0)$	$(\frac{1}{2}, \frac{1}{2}, 0)$	$(\frac{1}{2}, 0, \frac{1}{2})$	$(0, \frac{1}{2}, \frac{1}{2})$
Zn atoms:	$(\frac{3}{4}, \frac{1}{4}, \frac{1}{4})$	$(\frac{1}{4}, \frac{1}{4}, \frac{3}{4})$	$(\frac{1}{4}, \frac{3}{4}, \frac{1}{4})$	$(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$

According to Pauling's equation (Eq. 2.12), the Zn-S bond has 87 percent covalent character, and so the ZnS crystal structure must be essentially covalently bonded. As a result, the ZnS structure is tetrahedrally covalently bonded and the Zn and S atoms have a coordination number of 4. Many semiconducting compounds such as CdS, InAs, InSb, and ZnSe have the zinc blende crystal structure.

**Figure 11.9**

Zinc blende (ZnS) crystal structure. In this unit cell the sulfur atoms occupy the FCC atom unit-cell sites (equivalent of four atoms). The zinc atoms occupy half the tetrahedral interstitial sites (four atoms). Each Zn or S atom has a coordination number of 4 and is tetrahedrally covalently bonded to other atoms.

(From W.D. Kingery, H.K. Bowen, and D.R. Uhlmann, "Introduction to Ceramics," 2d ed., Wiley, 1976. Reprinted with permission of John Wiley & Sons, Inc.)



Calculate the density of zinc blende (ZnS). Assume the structure to consist of ions and that the ionic radius of $\text{Zn}^{2+} = 0.060 \text{ nm}$ and that of $\text{S}^{2-} = 0.174 \text{ nm}$.

**EXAMPLE
PROBLEM 11.7**

■ **Solution**

$$\text{Density} = \frac{\text{mass of unit cell}}{\text{volume of unit cell}}$$

There are four zinc ions and four sulfur ions per unit cell. Thus,

$$\begin{aligned} \text{Mass of unit cell} &= \frac{(4\text{Zn}^{2+} \times 65.37 \text{ g/mol}) + (4\text{S}^{2-} \times 32.06 \text{ g/mol})}{6.02 \times 10^{23} \text{ atoms/mol}} \\ &= 6.47 \times 10^{-22} \text{ g} \end{aligned}$$

$$\text{Volume of unit cell} = a^3$$

From Fig. EP11.7,

$$\frac{\sqrt{3}}{4}a = r_{\text{Zn}^{2+}} + R_{\text{S}^{2-}} = 0.060 \text{ nm} + 0.174 \text{ nm} = 0.234 \text{ nm}$$

$$a = 5.40 \times 10^{-8} \text{ cm}$$

$$a^3 = 1.57 \times 10^{-22} \text{ cm}^3$$

Thus,

$$\text{Density} = \frac{\text{mass}}{\text{volume}} = \frac{6.47 \times 10^{-22} \text{ g}}{1.57 \times 10^{-22} \text{ cm}^3} = 4.12 \text{ g/cm}^3 \blacktriangleleft$$

The handbook value for the density of ZnS (cubic) is 4.10 g/cm^3 .

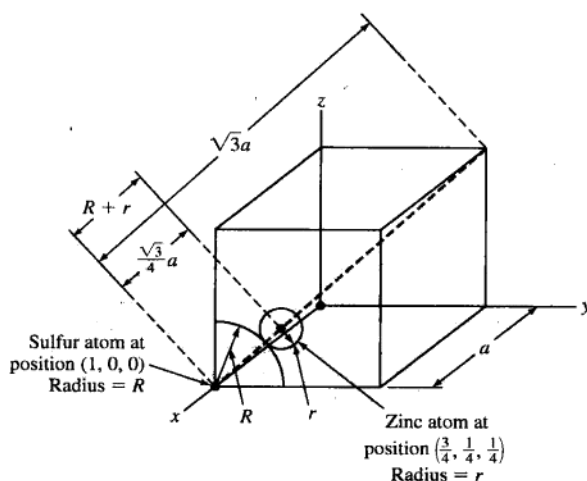


Figure EP11.7

Zinc blende structure showing the relationship between the lattice constant a of the unit cell and the radii of the sulfur and zinc atoms (ions):

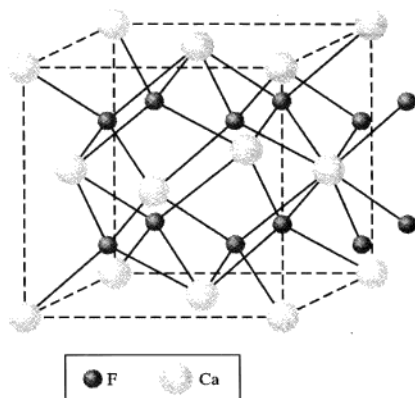
$$\frac{\sqrt{3}}{4}a = r_{\text{Zn}^{2+}} + R_{\text{S}^{2-}}$$

or

$$a = \frac{4}{\sqrt{3}}(r + R)$$

11.2.7 Calcium Fluoride (CaF_2) Crystal Structure

The calcium fluoride structure has the chemical formula CaF_2 and the unit cell shown in Fig. 11.10. In this unit cell, the Ca^{2+} ions occupy the FCC lattice sites, while the F^- ions are located at the eight tetrahedral sites. The four remaining octahedral sites in the FCC lattice remain vacant. Thus, there are four Ca^{2+} ions and eight F^- ions per unit cell. Examples of compounds that have this structure are UO_2 , BaF_2 , AuAl_2 , and PbMg_2 . The compound ZrO_2 has a distorted (monoclinic) CaF_2 structure. The large number of unoccupied octahedral interstitial sites in UO_2 allows this material to be used as a nuclear fuel since fission products can be accommodated in these vacant positions.

**Figure 11.10**

Calcium fluoride (CaF_2) crystal structure (also called *fluorite structure*). In this unit cell, the Ca^{2+} ions are located at the FCC unit-cell sites (four ions). Eight fluoride ions occupy all the tetrahedral interstitial sites.

(From W.D. Kingery, H.K. Bowen, and D.R. Uhlmann, "Introduction to Ceramics," 2d ed., Wiley, 1976. Reprinted with permission of John Wiley & Sons, Inc.)



Calculate the density of UO_2 (uranium oxide), which has the calcium fluoride, CaF_2 , structure. (Ionic radii: $\text{U}^{4+} = 0.105 \text{ nm}$ and $\text{O}^{2-} = 0.132 \text{ nm}$.)

EXAMPLE PROBLEM 11.8

■ Solution

$$\text{Density} = \frac{\text{mass/unit cell}}{\text{volume/unit cell}}$$

There are four uranium ions and eight oxide ions per unit cell (CaF_2 type). Thus,

$$\begin{aligned} \text{Mass of a unit cell} &= \frac{(4\text{U}^{4+} \times 238 \text{ g/mol}) + (8\text{O}^{2-} \times 16 \text{ g/mol})}{6.02 \times 10^{23} \text{ ions/mol}} \\ &= 1.794 \times 10^{-21} \text{ g} \end{aligned}$$

$$\text{Volume of a unit cell} = a^3$$

From Fig. EP11.7,

$$\frac{\sqrt{3}}{4}a = r_{\text{U}^{4+}} + r_{\text{O}^{2-}}$$

$$a = \frac{4}{\sqrt{3}}(0.105 \text{ nm} + 0.132 \text{ nm}) = 0.5473 \text{ nm} = 0.5473 \times 10^{-7} \text{ cm}$$

$$a^3 = (0.5473 \times 10^{-7} \text{ cm})^3 = 0.164 \times 10^{-21} \text{ cm}^3$$

$$\text{Density} = \frac{\text{mass}}{\text{volume}} = \frac{1.79 \times 10^{-21} \text{ g}}{0.164 \times 10^{-21} \text{ cm}^3} = 10.9 \text{ g/cm}^3 \blacktriangleleft$$

The handbook value for the density of UO_2 is 10.96 g/cm^3 .

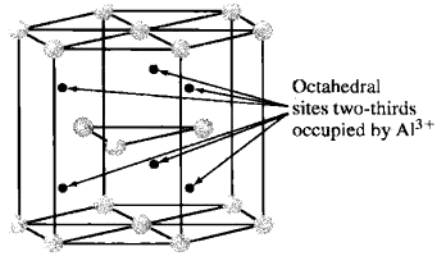


Figure 11.11

Corundum (Al_2O_3) crystal structure. Oxygen ions (O^{2-}) occupy the HCP unit-cell sites. Aluminum ions (Al^{3+}) occupy only two-thirds of the octahedral interstitial sites to maintain electrical neutrality.

11.2.8 Antifluorite Crystal Structure

The antifluorite structure consists of an FCC unit cell with anions (for example, O^{2-} ions) occupying the FCC lattice points. Cations (for example, Li^+) occupy the eight tetrahedral sites in the FCC lattice. Examples of compounds with this structure are Li_2O , Na_2O , K_2O , and Mg_2Si .

11.2.9 Corundum (Al_2O_3) Crystal Structure

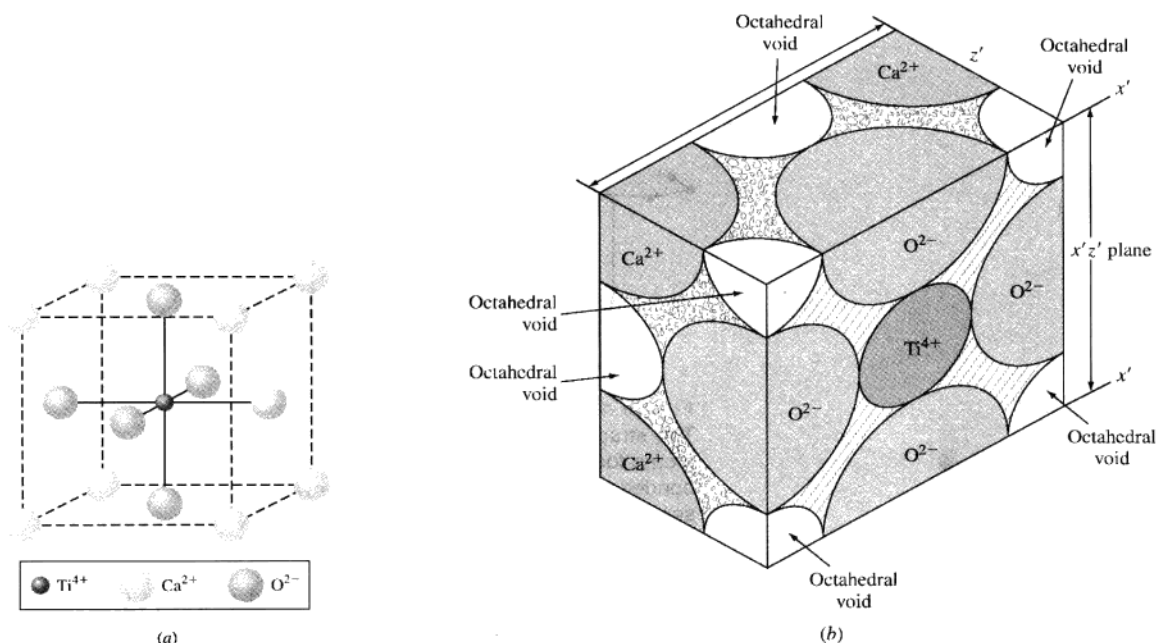
In the corundum (Al_2O_3) structure, the oxygen ions are located at the lattice sites of a hexagonal close-packed unit cell, as shown in Fig. 11.11. In the HCP crystal structure, as in the FCC, structure there are as many octahedral interstitial sites as there are atoms in the unit cell. However, since aluminum has a valence of $+3$ and oxygen a valence of -2 , there can be only *two* Al^{3+} ions for every three O^{2-} ions to maintain electrical neutrality. Thus, the aluminum ions can only occupy two-thirds of the octahedral sites of the HCP Al_2O_3 lattice, which leads to some distortion of this structure.

11.2.10 Spinel (MgAl_2O_4) Crystal Structure

A number of oxides have the MgAl_2O_4 or spinel structure, which has the general formula AB_2O_4 , where A is a metal ion with a $+2$ valence and B is a metal ion with a $+3$ valence. In the spinel structure, the oxygen ions form an FCC lattice, and the A and B ions occupy tetrahedral and octahedral interstitial sites, depending on the particular type of spinel. Compounds with the spinel structure are widely used for nonmetallic magnetic materials for electronic applications and will be studied in more detail in Chap. 16 on magnetic materials.

11.2.11 Perovskite (CaTiO_3) Crystal Structure

In the perovskite (CaTiO_3) structure, the Ca^{2+} and O^{2-} ions form an FCC unit cell with the Ca^{2+} ions at the corners of the unit cell and the O^{2-} ions in the centers of

**Figure 11.12**

Perovskite (CaTiO_3) crystal structure. (a) Calcium ions occupy FCC unit-cell corners, and oxygen ions occupy FCC unit-cell face-centered sites. The titanium ion occupies the octahedral interstitial site at the center of the cube.

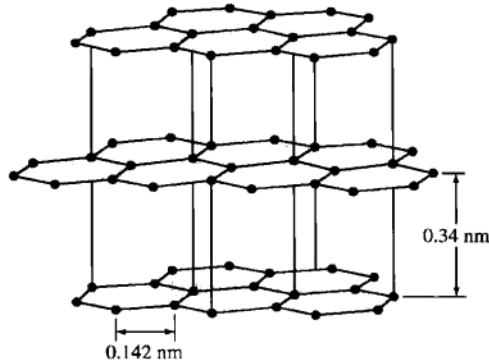
(From W.D. Kingery, H.K. Bowen, and D.R. Uhlmann, "Introduction to Ceramics," 2d ed., Wiley, 1976. Reprinted with permission of John Wiley & Sons, Inc.)

(b) Midsection of perovskite (CaTiO_3) crystal structure (truncated).

the faces of the unit cell (Fig. 11.12). The highly charged Ti^{4+} ion is located at the octahedral interstitial site at the center of the unit cell and is coordinated to six O^{2-} ions. BaTiO_3 has the perovskite structure above 120°C , but below this temperature its structure is slightly changed. Other compounds having this structure are SrTiO_3 , CaZrO_3 , SrZrO_3 , LaAlO_3 , and many others. This structure is important for piezoelectric materials (see Sec. 14.8).

11.2.12 Carbon and Its Allotropes

Carbon has many allotropes, i.e., it can exist in many crystalline forms. These allotropes have different crystal structures and have substantially different properties. Carbon and its polymorphs do not directly belong to any of the conventional classes of materials, but since graphite is sometimes considered a ceramic material, the discussion of its structure as well as some of its polymorphs are included in this section. In this section, the structure and properties of graphite, diamond, buckyball, and buckytube—all of which are allotropes of carbon—will be discussed.

**Figure 11.13**

The structure of crystalline graphite. Carbon atoms form layers of strongly covalently bonded hexagonal arrays. There are weak secondary bonds between the layers.



MatVis

Graphite The word **graphite** is based on the Greek word *graphein* (meaning to write). Graphite is formed because of trigonal sp^2 bonding of carbon atoms. Recalling the discussion of hybridized sp^3 orbitals (Chap. 2), sp^2 hybrid orbitals form only when one of the 2s electrons is promoted with two 2p electrons to form three sp^2 orbitals. The remaining electron forms an unhybridized free p orbital. The three sp^2 orbitals are in the same plane, making equal angles of 120 degrees with each other. The orbital due to the delocalized nonhybridized p electron is directed perpendicular to the plane of the three sp^2 hybrid orbitals. Accordingly, graphite has a layered structure in which the carbon atoms in the layers are strongly bonded (through sp^2 orbitals) in hexagonal arrays as shown in Fig. 11.13. The layers are bonded together by weak secondary bonds and can slide past each other easily. The free electron can easily travel from one side of the layer to the other but do not easily travel from one layer to another. Thus, graphite is *anisotropic* (i.e., its properties are dependent on direction). It has a low density of 2.26 g/cm^3 , is a good thermal conductor in the basal plane of graphite but not perpendicular to the plane, and is a good electrical conductor (again only on the basal plane and not perpendicular to it). Graphite can be made to form long fibers for composite materials and can also be used as a lubricant.

Diamond The structure of diamond is explained in detail in Chap. 2. It has a cubic structure (Fig. 2.23) that is based on covalently bonded sp^3 hybrid orbitals. Its properties are significantly different from graphite. Unlike graphite, it is isotropic and has a higher density of about 3.51 g/cm^3 . Diamond is the stiffest, hardest, and least compressible material made by nature. It has very high thermal conductivity (similar to graphite) but minimal thermal conductivity values (essentially an excellent insulator). Impurities such as nitrogen, however, affect its properties adversely. Natural diamond

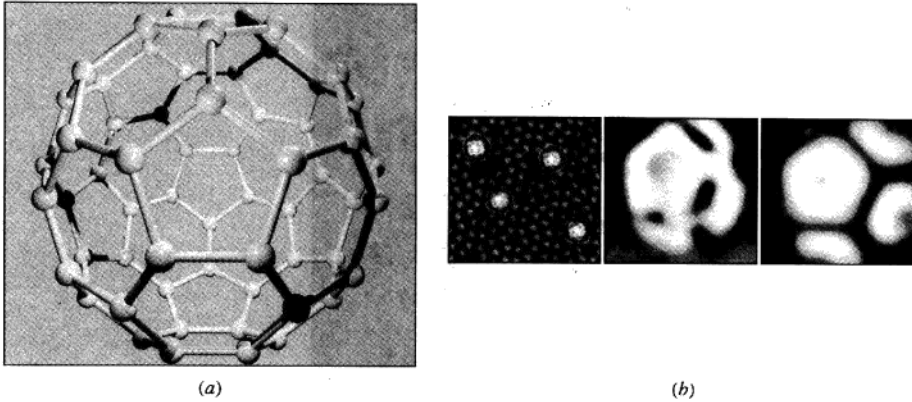


Figure 11.14

(a) A schematic of the C_{60} molecule. (b) A series of STM images showing the C_{60} molecule (the left and center images are actual STM images and the right image is a simulated image).

((a) © Tim Evans/Photo Researchers, Inc. (b) Omicron NanoTechnology GmbH.)

is extremely expensive and has mostly gem value. However, synthetic (man-made) diamonds have comparable hardness, are cheaper, and are used as cutting tools, coatings, and abrasives.

Buckminster Fullerenes (Buckyball) In 1985 scientists discovered the presence of clusters of carbon atoms in a molecular range of C_{30} to C_{100} . In 1990 other scientists were able to synthesize this molecular form of carbon in the laboratory. The new structure has a form similar to the geodesic truss structures developed by the world-renowned architect Buckminster Fuller. As a result, the new polymorph was named a *fullerene* or a **buckyball**. The buckyball looks very similar to a soccer ball that is made of 12 pentagons and 20 hexagons. At each junction point a carbon atom is covalently bonded to three other carbon atoms as shown schematically in Fig. 11.14a. The STM image of part of the C_{60} molecule is presented in Fig. 11.14b. The structure consists of a total of 60 carbon atoms; the resulting molecule is therefore C_{60} . Since 1990 other forms of this molecule such as C_{70} , C_{76} , and C_{78} have also been identified. These various forms are collectively called *fullerenes*. The diameter of the C_{60} fullerene is 0.710 nm and is therefore classified as a *nanocluster*. The aggregate form of C_{60} has an FCC structure with a C_{60} molecule at each FCC lattice point. The molecules in the FCC structure are bonded by van der Waals forces. Thus, the aggregate C_{60} and graphite have similar lubrication applications. Fullerenes are being studied for possible applications in the electronic industries and in fuel cells, lubricants, and superconductors.

Carbon Nanotubes Another recently identified carbon polymorph is the highly interesting carbon nanotube. Consider rolling a single graphite atomic layer (a

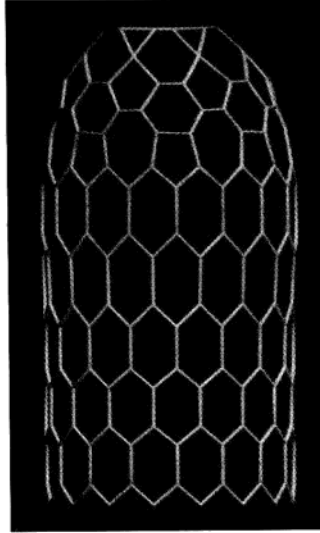


Figure 11.15

A schematic of the nanotube showing hexagonal patterns on the tube and pentagonal patterns on the end cap.

(Eisenstadt, M., "Introduction to Mechanical Properties of Materials: An Ecological Approach," 1st ed., © 1971. Reprinted by permission of Pearson Education, Inc., Upper Saddle River, NJ.)

graphene) with the conventional hexagonal structure into a tube making sure that the edge hexagons meet perfectly. Then by closing the ends of the tube using two hemi-fullerenes, made up of only pentagons, one obtains the structure of a carbon nanotube (Fig. 11.15). Although nanotubes of various diameters may be synthesized, the most frequently encountered diameter is 1.4 nm. The length of a nanotube can be in the micrometer or even millimeter range (a very important feature). The nanotubes can be synthesized in a *single-wall nanotube* (SWNT) or *multiwall nanotube* (MWNT) form. These nanotubes are believed to have a tensile strength 20 times that of the strongest steels. Some measurements actually show a tensile strength of 45 Gpa in the length direction of the tube. The elastic modulus of these nanotubes has been estimated at a level of 1.3 Tpa ($T = \text{Tera} = 10^{12}$). For comparison, the strongest commercially available carbon based fiber has a strength of 7 Gpa and the highest elastic modulus available is close to 800 Gpa. In addition, carbon nanotubes have low density, high heat conductivity, and high electron conductivity. Even more importantly, one can form structures such as ropes, fibers, and thin films by aligning a large number of these tubes. The combination of these characteristics and properties has convinced many scientists that carbon nanotubes will be involved in many

of the technological breakthroughs in this century. Some of the early applications are as STM tips because of their stiffness and slenderness, field emitters in flat panel displays (or any device requiring an electron producing cathode), chemical sensors, and fiber material for composites.

11.3 SILICATE STRUCTURES

Many ceramic materials contain silicate structures, which consist of silicon and oxygen atoms (ions) bonded together in various arrangements. Also, a large number of naturally occurring minerals such as clays, feldspars, and micas are silicates since silicon and oxygen are the two most abundant elements in the earth's crust. Many silicates are useful for engineering materials because of their low cost, availability, and special properties. Silicate structures are particularly important for the engineering construction materials glass, portland cement, and brick. Many important electrical insulative materials also are made with silicates.

11.3.1 Basic Structural Unit of the Silicate Structures

The basic building block of the silicates is the silicate (SiO_4^{4-}) tetrahedron (Fig. 11.16). The Si—O bond in the SiO_4^{4-} structure is about 50 percent covalent and 50 percent ionic according to calculations from Pauling's equation (Eq. 2.10). The tetrahedral coordination of SiO_4^{4-} satisfies the directionality requirement of covalent bonding and the radius ratio requirement of ionic bonding. The radius ratio of the Si—O bond is 0.29, which is in the tetrahedral coordination range for stable-ion close packing. Because of the small, highly charged Si^{4+} ion, strong bonding forces are created within the SiO_4^{4-} tetrahedrons, and as a result the SiO_4^{4-} units are normally joined corner to corner and rarely edge to edge.

11.3.2 Island, Chain, and Ring Structures of Silicates

Since each oxygen of the silicate tetrahedron has one electron available for bonding, many different types of silicate structures can be produced. Island silicate structures are produced when positive ions bond with oxygens of the SiO_4^{4-} tetrahedra. For example, Fe^{2+} and Mg^{2+} ions combine with SiO_4^{4-} to form olivine, which has the basic chemical formula $(\text{Mg,Fe})_2\text{SiO}_4$.

If two corners of each SiO_4^{4-} tetrahedron are bonded with the corners of other tetrahedra, a chain (Fig. 11.17a) or ring structure with the unit chemical formula of SiO_3^{2-} results. The mineral enstatite (MgSiO_3) has a chain silicate structure, and the mineral beryl [$\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$] has a ring silicate structure.

11.3.3 Sheet Structures of Silicates

Silicate sheet structures form when three corners in the same plane of a silicate tetrahedron are bonded to the corners of three other silicate tetrahedra, as shown in Fig. 11.17b. This structure has the unit chemical formula of $\text{Si}_2\text{O}_5^{2-}$. These silicate sheets can bond with other types of structural sheets because there is still one unbonded oxygen on each silicate tetrahedron (Fig. 11.17b). For example, the

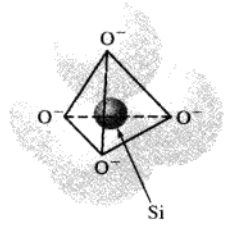


Figure 11.16
The atom (ion) bonding arrangement of the SiO_4^{4-} tetrahedron. In this structure four oxygen atoms surround a central silicon atom. Each oxygen atom has an extra electron, and thus a net negative charge, for bonding with another atom. (Eisenstadt, M., "Introduction to Mechanical Properties of Materials: An Ecological Approach," 1st ed., © 1971. Reprinted by permission of Pearson Education, Inc., Upper Saddle River, NJ.)

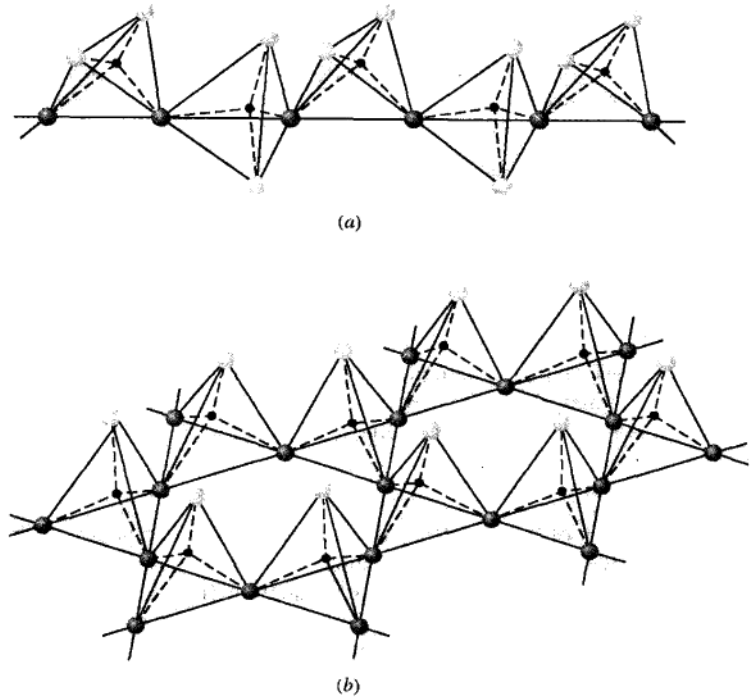


Figure 11.17

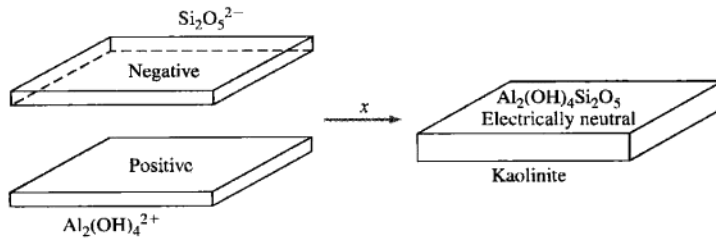
(a) Silicate chain structure. Two of the four oxygen atoms of the SiO_4^{4-} tetrahedra are bonded to other tetrahedra to form silicate chains.

(b) Silicate sheet structure. Three of the four oxygen atoms of the SiO_4^{4-} tetrahedra are bonded to other tetrahedra to form silicate sheets. The unbonded oxygen atoms are shown as lighter spheres.

(After M. Eisenstadt, "Mechanical Properties of Materials," Macmillan, 1971, p. 82.)

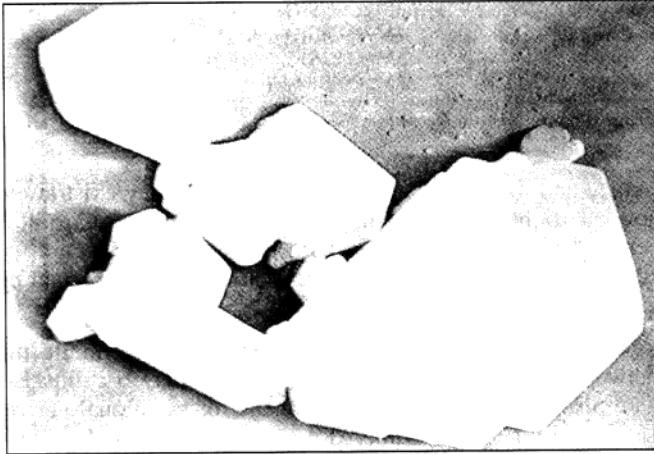
negatively charged silicate sheet can bond with a positively charged sheet of $\text{Al}_2(\text{OH})_4^{2+}$ to form a composite sheet of kaolinite, as shown schematically in Fig. 11.18. The mineral kaolinite consists (in its pure form) of very small, flat plates roughly hexagonal in shape, with their average size being about $0.7 \mu\text{m}$ in diameter and $0.05 \mu\text{m}$ thick (Fig. 11.19). The crystal plates are made of a series (up to about 50) of parallel sheets bonded together by weak secondary bonds. Many high-grade clays consist mainly of the mineral kaolinite.

Another example of a sheet silicate is the mineral talc, in which a sheet of $\text{Mg}_3(\text{OH})_2^{4+}$ bonds with two outer-layer $\text{Si}_2\text{O}_5^{2-}$ sheets (one on each side) to form a composite sheet with the unit chemical formula $\text{Mg}_3(\text{OH})_2(\text{Si}_2\text{O}_5)_2$. The composite talc sheets are bonded together by weak secondary bonds, and thus this structural arrangement allows the talc sheets to slide over each other easily.

**Figure 11.18**

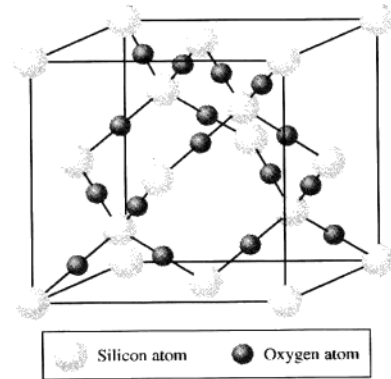
Schematic diagram of the formation of kaolinite from sheets of $\text{Al}_2(\text{OH})_4^{2+}$ and $\text{Si}_2\text{O}_5^{2-}$. All the primary bonds of the atoms in the kaolinite sheet are satisfied.

(From W.D. Kingery, H.K. Bowen, and D.R. Uhlmann, "Introduction to Ceramics," 2d ed., Wiley, 1976. Reprinted with permission of John Wiley & Sons, Inc.)

**Figure 11.19**

Kaolinite crystals as observed with the electron microscope (replica technique).

(F.H. Norton, "Elements of Ceramics," 2nd Edition, © 1974. Reprinted by permission of Pearson Education Inc., Upper Saddle River, NJ.)

**Figure 11.20**

Structure of high cristobalite, which is a form of silica (SiO_2). Note that each silicon atom is surrounded by four oxygen atoms and that each oxygen atom forms part of two SiO_4 tetrahedra.

(Reprinted from "Treatise in Materials Science and Technology," vol. 9, J.S. Reed and R.B. Runk, "Ceramic Fabrication Processes," p. 74, Copyright 1976, with permission from Elsevier.)

11.3.4 Silicate Networks

Silica When all four corners of the SiO_4^{4-} tetrahedra share oxygen atoms, an SiO_2 network called *silica* is produced (Fig. 11.20). Crystalline silica exists in several polymorphic forms that correspond to different ways in which the silicate tetrahedra are arranged with all corners shared. There are three basic silica structures: *quartz*, *tridymite*, and *cristobalite*, and each of these has two or three modifications. The

Table 11.3 Ideal silicate mineral compositions

Silica:	
Quartz	Common crystalline phases of SiO ₂
Tridymite	
Cristobalite	
Alumina silicate:	
Kaolinite (china clay)	Al ₂ O ₃ · 2SiO ₂ · 2H ₂ O
Pyrophyllite	Al ₂ O ₃ · 4SiO ₂ · H ₂ O
Metakaolinite	Al ₂ O ₃ · 2SiO ₂
Sillimanite	Al ₂ O ₃ · SiO ₂
Mullite	3Al ₂ O ₃ · 2SiO ₂
Alkali alumina silicate:	
Potash feldspar	K ₂ O · Al ₂ O ₃ · 6SiO ₂
Soda feldspar	Na ₂ O · Al ₂ O ₃ · 6SiO ₂
(Muscovite) mica	K ₂ O · 3Al ₂ O ₃ · 6SiO ₂ · 2H ₂ O
Montmorillonite	Na ₂ O · 2MgO · 5Al ₂ O ₃ · 24SiO ₂ · (6 + n)H ₂ O
Leucite	K ₂ O · Al ₂ O ₃ · 4SiO ₂
Magnesium silicate:	
Cordierite	2MgO · 5SiO ₂ · 2Al ₂ O ₃
Steatite	3MgO · 4SiO ₂
Talc	3MgO · 4SiO ₂ · H ₂ O
Chrysotile (asbestos)	3MgO · 2SiO ₂ · 2H ₂ O
Forsterite	2MgO · SiO ₂

Source: O.H. Wyatt and D. Dew-Hughes, "Metals, Ceramics and Polymers," Cambridge, 1974.

most stable forms of silica and the temperature ranges in which they exist at atmospheric pressure are low quartz below 573°C, high quartz between 573°C to 867°C, high tridymite between 867°C and 1470°C, and high cristobalite between 1470°C and 1710°C (Fig. 11.20). Above 1710°C silica is liquid. Silica is an important component of many traditional ceramics and many different types of glasses.

Feldspars There are many naturally occurring silicates that have infinite three-dimensional silicate networks. Among the industrially important network silicates are the feldspars, which are also among the main components of traditional ceramics. In the feldspar silicate structural network, some Al³⁺ ions replace some Si⁴⁺ ions to form a network with a net negative charge. This negative charge is balanced with large ions of alkali and alkaline earth ions such as Na⁺, K⁺, Ca²⁺, and Ba²⁺, which fit into interstitial positions. Table 11.3 summarizes the ideal compositions of some silicate minerals.

11.4 PROCESSING OF CERAMICS

Most traditional and engineering ceramic products are manufactured by compacting powders or particles into shapes that are subsequently heated to a high enough temperature to bond the particles together. The basic steps in the processing of ceramics by the agglomeration of particles are (1) material preparation, (2) forming or casting, and (3) thermal treatment by drying (which is usually not required) and **firing** by heating the ceramic shape to a high enough temperature to bond the particles together.

11.4.1 Materials Preparation

Most ceramic products are made by the agglomeration of particles.² The raw materials for these products vary, depending on the required properties of the finished ceramic part. The particles and other ingredients such as binders and lubricants may be blended wet or dry. For ceramic products that do not have very “critical” properties such as common bricks, sewer pipe, and other clay products, the blending of the ingredients with water is common practice. For some other ceramic products, the raw materials are ground dry along with binders and other additives. Sometimes wet and dry processing of raw materials are combined. For example, to produce one type of high-alumina (Al_2O_3) insulator, the particulate raw materials are milled with water along with a wax binder to form a slurry that is subsequently spray-dried to form small, spherical pellets (Fig. 11.21).

11.4.2 Forming

Ceramic products made by agglomerating particles may be formed by a variety of methods in the dry, plastic, or liquid conditions. Cold-forming processes are predominant in

²The production of glass products and the casting of concrete are two major exceptions.

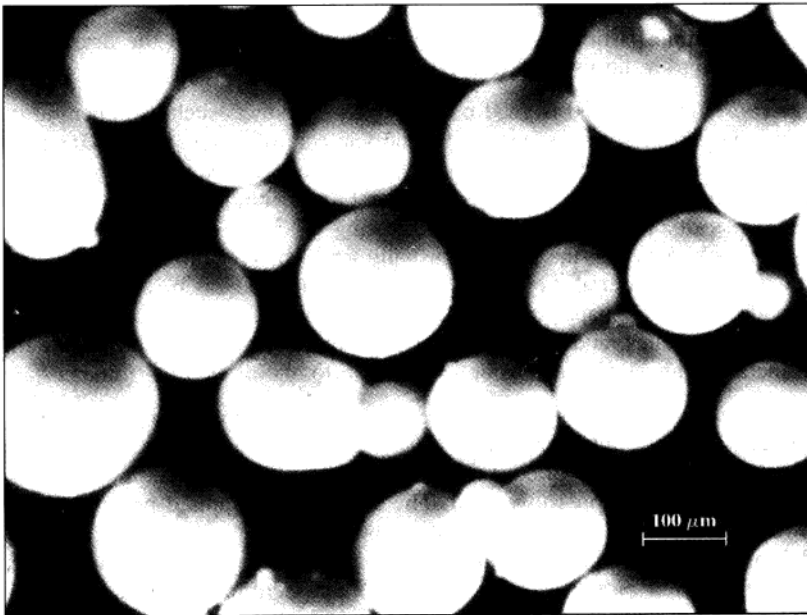


Figure 11.21

Spray-dried pellets of high-alumina ceramic body.

(After J.S. Owens et al., *American Ceramic Society Bulletin*, 56:437(1977).)

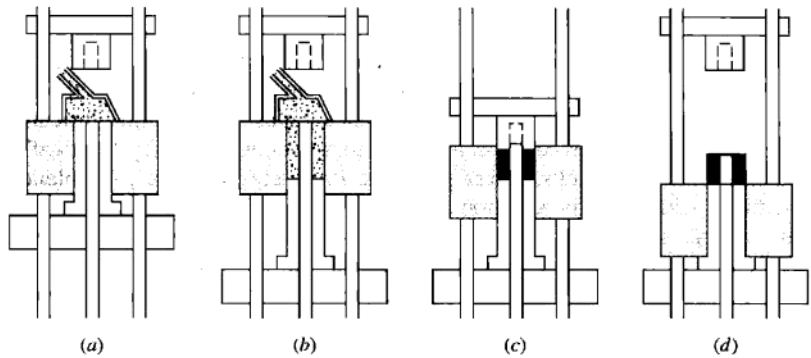


Figure 11.22

Dry pressing of ceramic particles: (a) and (b) filling, (c) pressing, and (d) ejection.

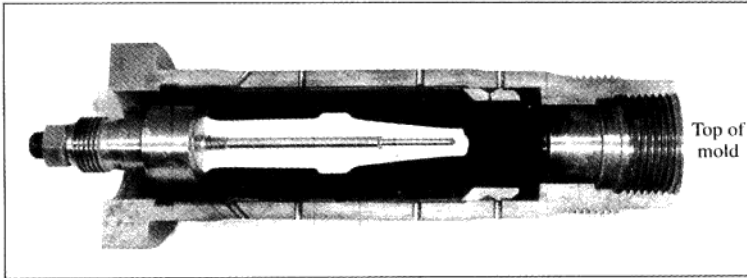
(After J.S. Reed and R.B. Runk, "Ceramic Fabrication Processes," vol. 9: "Treatise in Materials Science and Technology," Academic, 1976, p. 74.)

the ceramic industry, but hot-forming processes are also used to some extent. Pressing, slip casting, and extrusion are commonly used ceramic forming methods.

Pressing Ceramic particulate raw materials can be pressed in the dry, plastic, or wet condition into a die to form shaped products.

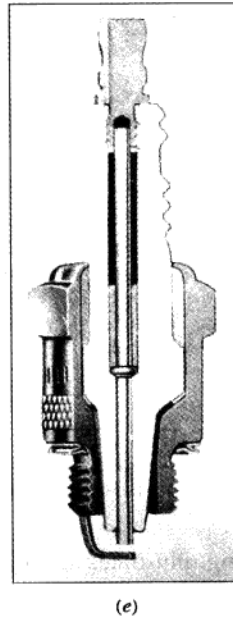
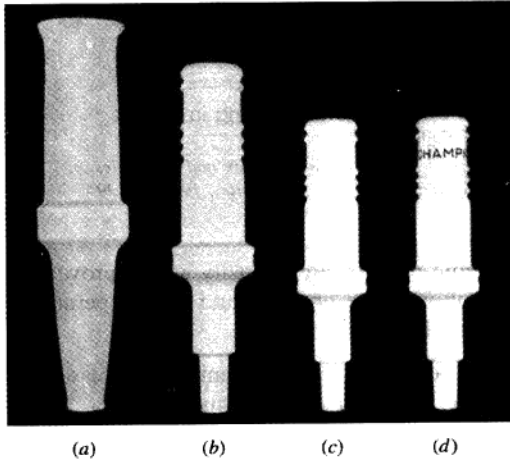
Dry Pressing This method is used commonly for products such as structural refractories (high-heat-resistant materials) and electronic ceramic components. **Dry pressing** may be defined as the simultaneous uniaxial compaction and shaping of a granular powder along with small amounts of water and/or organic binder in a die. Figure 11.22 shows a series of operations for the dry pressing of ceramic powders into a simple shape. After cold pressing, the parts are usually fired (sintered) to achieve the required strength and microstructural properties. Dry pressing is used extensively because it can form a wide variety of shapes rapidly with uniformity and close tolerances. For example, aluminas, titanates, and ferrites can be dry-pressed into sizes from a few mils to several inches in linear dimensions at a rate of up to about 5000 per minute.

Isostatic Pressing In this process, the ceramic powder is loaded into a flexible (usually rubber), airtight container (called a *bag*) that is inside a chamber of hydraulic fluid to which pressure is applied. Figure 11.23 shows a cross section of a spark plug insulator in an isostatic pressing mold. The force of the applied pressure compacts the powder uniformly in all directions, with the final product taking the shape of the flexible container. After cold isostatic pressing, the part must be fired (sintered) to achieve the required properties and microstructure. Ceramic parts manufactured by isostatic pressing include refractories, bricks and shapes, spark plug insulators, radomes, carbide tools, crucibles, and bearings. Figure 11.24 shows the stages for the manufacturing of a spark plug insulator by isostatic pressing.

**Figure 11.23**

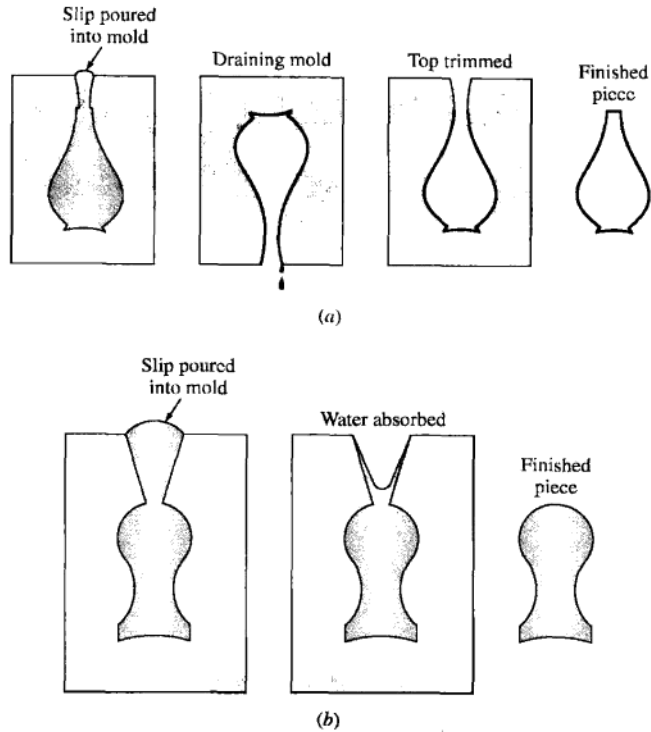
Cross section of insulator blank in isostatic pressing mold. Spray-dried nearly spherical pellets (Fig. 11.21) are fed by gravity into top of mold and compressed by isostatic pressure, normally in the 3000 to 6000 psi range. The hydraulic fluid enters the side of the mold through the holes shown in the cross section.

(Courtesy of Champion Spark-Plug Co.)

**Figure 11.24**

Stages of spark plug insulator manufacture by the isostatic processing method. (a) Pressed blank. (b) Turned (ground) insulator. (c) Fired insulator. (d) Glazed and decorated finished insulator. (e) Cross section of assembled automotive spark plug showing position of insulator.

(Courtesy of Champion Spark-Plug Co.)

**Figure 11.25**

Slip casting of ceramic shapes. (a) Drain casting in porous plaster of paris mold. (b) Solid casting.

(From J.H. Brophy, R.M. Rose and J. Wulff, "The Structure and Properties of Materials," vol. II: "Thermodynamics of Structure," Wiley, 1964, p. 139.)

Hot Pressing In this process ceramic parts of high density and improved mechanical properties are produced by combining the pressing and firing operations. Both uniaxial and isostatic methods are used.

Slip Casting Ceramic shapes can be cast by using a unique process called **slip casting**, illustrated in Fig. 11.25. The main steps in slip casting are:

1. Preparation of a powdered ceramic material and a liquid (usually clay and water) into a stable suspension called a *slip*.
2. Pouring the slip into a porous mold that is usually made of plaster of paris and allowing the liquid portion of the slip to be partially absorbed by the mold. As the liquid is removed from the slip, a layer of semihard material is formed against the mold surface.

3. When a sufficient wall thickness has been formed, the casting process is interrupted and the excess slip is poured out of the cavity (Fig. 11.25a). This is known as *drain casting*. Alternatively, a solid shape may be made by allowing the casting to continue until the whole mold cavity is filled, as illustrated in Fig. 11.25b. This type of slip casting is called *solid casting*.
4. The material in the mold is allowed to dry to provide adequate strength for handling and the subsequent removal of the part from the mold.
5. Finally, the cast part is fired to attain the required microstructure and properties.

Slip casting is advantageous for forming thin-walled and complex shapes of uniform thickness. Slip casting is especially economical for development parts and short production runs. Several new variations of the slip-casting process are pressure and vacuum casting, in which the slip is shaped under pressure or vacuum.

Extrusion Single cross sections and hollow shapes of ceramic materials can be produced by extruding these materials in the plastic state through a forming die. This method is commonly used to produce, for example, refractory brick, sewer pipe, hollow tile, technical ceramics, and electrical insulators. The means most commonly used is the vacuum-auger-type extrusion machine in which the plastic ceramic material (e.g., clay and water) is forced through a hard steel or alloy die by a motor-driven auger (Fig. 11.26). Special technical ceramics are frequently produced using a piston extrusion under high pressure so that close tolerances can be attained.

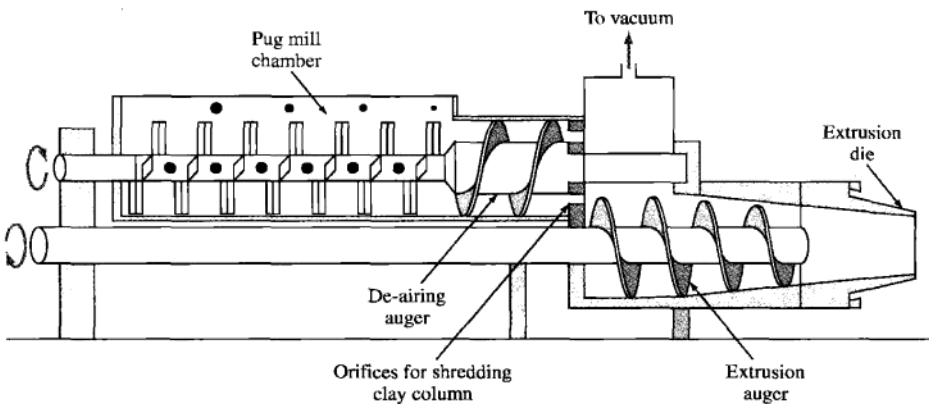


Figure 11.26
Cross section of combination mixing mill (pug mill) for ceramic materials and vacuum-auger extrusion machine.

(After W.D. Kingery, "Introduction to Ceramics," Wiley, 1960.)

11.4.3 Thermal Treatments

Thermal treatment is an essential step in the manufacturing of most ceramic products. In this subsection, we shall consider the following thermal treatments: drying, sintering, and vitrification.

Drying and Binder Removal The purpose of drying ceramics is to remove water from the plastic ceramic body before it is fired at higher temperatures. Generally, drying to remove water is carried out at or below 100°C and can take as long as 24 h for a large ceramic part. The bulk of organic binders can be removed from ceramic parts by heating in the range of 200°C to 300°C, although some hydrocarbon residues may require heating to much higher temperatures.

Sintering The process by which small particles of a material are bonded together by solid-state diffusion is called **sintering**. In ceramic manufacturing, this thermal treatment results in the transformation of a porous compact into a dense, coherent product. Sintering is commonly used to produce ceramic shapes made of, for example, alumina, beryllia, ferrites, and titanates.

In the sintering process, particles are coalesced by solid-state diffusion at very high temperatures but below the melting point of the compound being sintered. For example, the alumina spark plug insulator shown in Fig. 11.24a is sintered at 1600°C (the melting point of alumina is 2050°C). In sintering, atomic diffusion takes place between the contacting surfaces of the particles so that they become chemically bonded together (Fig. 11.27). As the process proceeds, larger particles are formed at the expense of the smaller ones, as illustrated in the

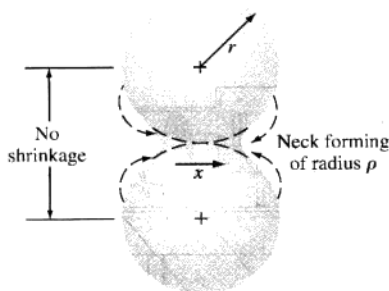
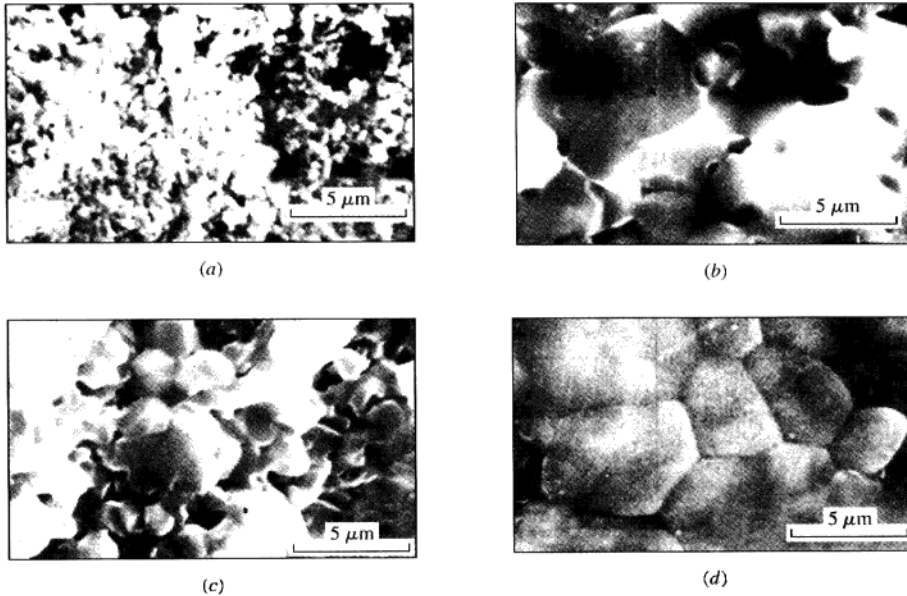


Figure 11.27

Formation of a neck during the sintering of two fine particles. Atomic diffusion takes place at the contacting surfaces and enlarges the contact area to form a neck.

(From B. Wong and J.A. Pask, *J. Am. Ceram. Soc.*, **62**:141 (1979). Reprinted by permission of Blackwell Publishing.)

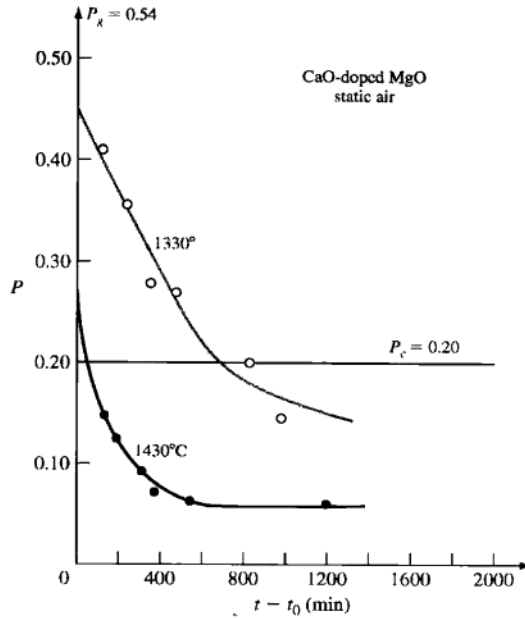
**Figure 11.28**

Scanning electron micrographs of fractured surfaces of MgO compacts (compressed powders) sintered at 1430°C in static air for (a) 30 min (fractional porosity = 0.39); (b) 303 min (f.p. = 0.14); (c) 1110 min (f.p. = 0.09); as-annealed surface of (c) is shown in (d).

[After B. Wong and J.A. Pask, *Journal of American Ceramics Society*, **62**:141(1997).]

sintering of MgO compacts shown in Fig. 11.28a, b, and c. As the particles get larger with the time of sintering, the porosity of the compacts decreases (Fig. 11.29). Finally, at the end of the process, an “equilibrium grain size” is attained (Fig. 11.28d). The driving force for the process is the lowering of the energy of the system. The high surface energy associated with the original individual small particles is replaced by the lower overall energy of the grain-boundary surfaces of the sintered product.

Vitrification Some ceramic products such as porcelain, structural clay products, and some electronic components contain a glass phase. This glass phase serves as a reaction medium by which diffusion can take place at a lower temperature than in the rest of the ceramic solid material. During the firing of these types of ceramic materials, a process called **vitrification** takes place whereby the glass phase liquefies and fills the pore spaces in the material. This liquid glass phase may also react with some of the remaining solid refractory material. Upon cooling, the liquid phase solidifies to form a vitreous or glassy matrix that bonds the unmelted particles together.

**Figure 11.29**

Porosity versus time for MgO compacts doped with 0.2 wt % CaO and sintered in static air at 1330°C and 1430°C. Note that the higher sintering temperature produces a more rapid decrease in porosity and a lower porosity level.

[After B. Wong and J.A. Pask, *J. Am. Ceram. Soc.*, 62:141(1979).]

11.5 TRADITIONAL AND ENGINEERING CERAMICS

11.5.1 Traditional Ceramics

Traditional ceramics are made from three basic components: *clay*, *silica* (flint), and *feldspar*. Clay consists mainly of hydrated aluminum silicates ($\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$) with small amounts of other oxides such as TiO_2 , Fe_2O_3 , MgO , CaO , Na_2O , and K_2O . Table 11.4 lists the chemical compositions of several industrial clays.

The clay in traditional ceramics provides workability of the material before firing hardens it and constitutes the major body material. The silica (SiO_2), also called *flint* or quartz, has a high melting temperature and is the refractory component of traditional ceramics. Potash (potassium) feldspar, which has the basic composition $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$, has a low melting temperature and makes a glass when the ceramic mix is fired. It bonds the refractory components together.

Table 11.4 Chemical compositions of some clays

Type of clay	Weight percentages of major oxides									Ignition loss
	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O	H ₂ O	
Kaolin	37.4	45.5	1.68	1.30	0.004	0.03	0.011	0.005	13.9	
Tenn ball clay	30.9	54.0	0.74	1.50	0.14	0.20	0.45	0.72	...	11.4
Ky. ball clay	32.0	51.7	0.90	1.52	0.21	0.19	0.38	0.89	...	12.3

Source: P.W. Lee, "Ceramics," Reinhold, 1961.

Table 11.5 Some triaxial whiteware chemical compositions

Type body	China clay	Ball clay	Feldspar	Flint	Other
Hard porcelain	40	10	25	25	
Electrical insulation ware	27	14	26	33	
Vitreous sanitary ware	30	20	34	18	
Electrical insulation	23	25	34	18	
Vitreous tile	26	30	32	12	
Semivitreous whiteware	23	30	25	21	
Bone china	25	...	15	22	38 bone ash
Hotel china	31	10	22	35	2 CaCO ₃
Dental porcelain	5	...	95		

Source: W.D. Kingery, H.K. Bowen, and D.R. Uhlmann, "Introduction to Ceramics," 2d ed., Wiley, 1976, p. 532.

Structural clay products such as building brick, sewer pipe, drain tile, roofing tile, and floor tile are made of natural clay, which contains all three basic components. Whiteware products such as electrical porcelain, dinner china, and sanitary ware are made from components of clay, silica, and feldspar for which the composition is controlled. Table 11.5 lists the chemical compositions of some triaxial whitewares. The term *triaxial* is used since there are three major materials in their composition.

Typical composition ranges for different types of whitewares are illustrated in the silica-leucite-mullite ternary phase diagram of Fig. 11.30. The composition ranges of some whitewares are indicated by the circled areas.

The changes that occur in the structure of triaxial bodies during firing are not completely understood due to their complexity. Table 11.6 is an approximate summary of what probably occurs during the firing of a whiteware body.

Figure 11.31 is an electron micrograph of the microstructure of an electrical insulator porcelain. As observed in this micrograph, the structure is very heterogeneous. Large quartz grains are surrounded by a solution rim of high-silica glass. Mullite needles that cross feldspar relicts and fine mullite-glass mixtures are present.

Triaxial porcelains are satisfactory as insulators for 60-cycle use, but at high frequencies dielectric losses become too high. The considerable amounts of alkalis derived from the feldspar used as a flux increase the electrical conductivity and dielectric losses of triaxial porcelains.

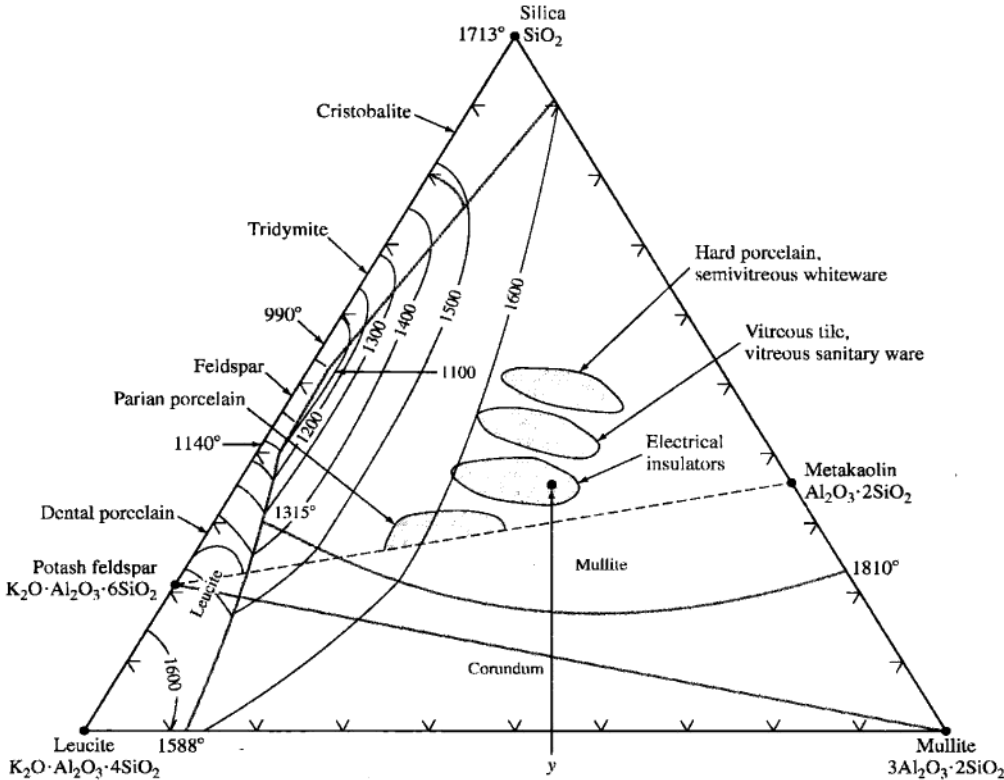


Figure 11.30
Areas of triaxial whiteware compositions shown on the silica-leucite-mullite phase-equilibrium diagram.
(After W.D. Kingery, H.K. Bowen, and D.R. Uhlmann, "Introduction to Ceramics," 2d ed., Wiley, 1976, p. 533.)

Table 11.6 Life history of a triaxial body

Temperature (°C)	Reactions
Up to 100	Loss of moisture
100–200	Removal of absorbed water
450	Dehydroxylation
500	Oxidation of organic matter
573	Quartz inversion to high form. Little overall volume damage
980	Spinel forms from clay. Start of shrinkage
1000	Primary mullite forms
1050–1100	Glass forms from feldspar, mullite grows, shrinkage continues
1200	More glass, mullite grows, pores closing, some quartz solution
1250	60% glass, 21% mullite, 19% quartz, pores at minimum

Source: F. Norton, "Elements of Ceramics," 2d ed., Addison-Wesley, 1974, p. 140.

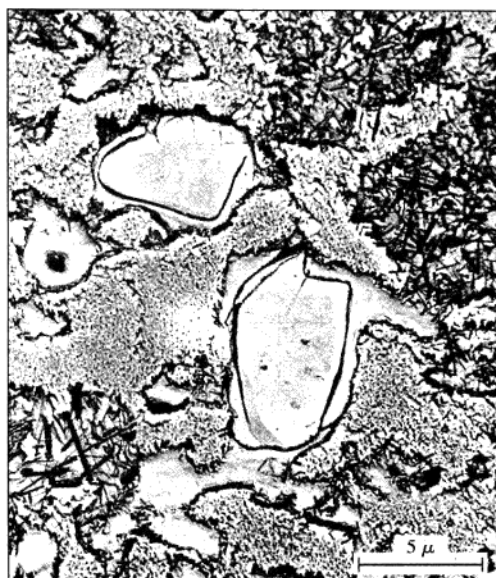


Figure 11.31

Electron micrograph of an electrical insulator porcelain (etched 10 s, 0°C, 40% HF, silica replica).

(After S.T. Lundin as shown in W.D. Kingery, H.K. Bowen, and D.R. Uhlmann, "Introduction to Ceramics," 2d ed., Wiley, 1976, p. 539.)

11.5.2 Engineering Ceramics

In contrast to the traditional ceramics, which are mainly based on clay, engineering or technical ceramics are mainly pure compounds or nearly pure compounds of chiefly oxides, carbides, or nitrides. Some of the important engineering ceramics are alumina (Al_2O_3), silicon nitride (Si_3N_4), silicon carbide (SiC), and zirconia (ZrO_2) combined with some other refractory oxides. The melting temperatures of some of the engineering ceramics are listed in Table 11.1, and the mechanical properties of some of these materials are given in Table 11.7. A brief description of a few of the properties, processes, and applications of some of the important engineering ceramics follows.

Alumina (Al_2O_3) Alumina was originally developed for refractory tubing and high-purity crucibles for high-temperature use and now has wide application. A classic example of the application of alumina is in spark plug insulator material (Fig. 11.24). Aluminum oxide is commonly doped with magnesium oxide, cold-pressed, and sintered, producing the type of microstructure shown in Fig. 11.32. Note the uniformity of the alumina grain structure as compared to the microstructure of the electrical porcelain of Fig. 11.31. Alumina is used commonly for high-quality electrical applications where low dielectric loss and high resistivity are needed.

Table 11.7 Mechanical properties of selected engineering ceramic materials

Material	Density (g/cm ³)	Compressive strength		Tensile strength		Flexural strength		Fracture toughness	
		MPa	ksi	MPa	ksi	MPa	ksi	MPa√m	ksi√m
Al ₂ O ₃ (99%)	3.85	2585	375	207	30	345	50	4	3.63
Si ₃ N ₄ (hot-pressed)	3.19	3450	500	690	100	6.6	5.99
Si ₃ N ₄ (reaction-bonded)	2.8	770	112	255	37	3.6	3.27
SiC (sintered)	3.1	3860	560	170	25	550	80	4	3.63
ZrO ₂ , 9% MgO (partially stabilized)	5.5	1860	270	690	100	8+	7.26+

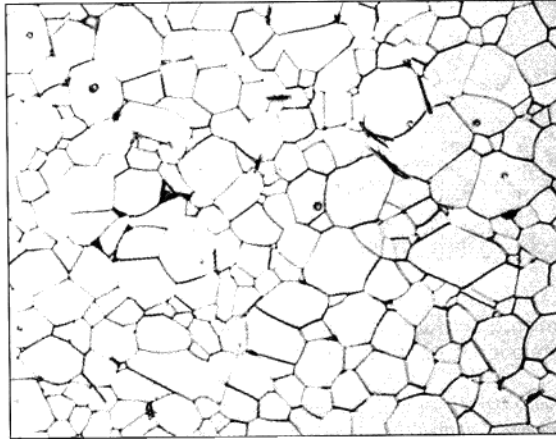


Figure 11.32
Microstructure of sintered, powdered aluminum oxide doped with magnesium oxide. The sintering temperature was 1700°C. The microstructure is nearly pore-free, with only a few pores within the grains. (Magnification 500×.)
(Courtesy of C. Greskovich and K.W. Lay.)

Silicon Nitride (Si₃N₄) Of all the engineering ceramics, silicon nitride has probably the most useful combination of engineering properties. Si₃N₄ dissociates significantly at temperatures above 1800°C and so cannot be directly sintered. Si₃N₄ can be processed by reaction bonding in which a compact of silicon powder is nitrided in a flow of nitrogen gas. This process produces a microporous Si₃N₄ with moderate strength (Table 11.7). Higher-strength nonporous Si₃N₄ is made by hot-pressing with 1% to 5% MgO. Si₃N₄ is being explored for use for parts of advanced engines (Fig. 1.9a).

Silicon Carbide (SiC) Silicon carbide is a hard, refractory carbide with outstanding resistance to oxidation at high temperatures. Although a nonoxide, SiC at high temperatures forms a skin of SiO₂ that protects the main body of material. SiC can

be sintered at 2100°C with 0.5% to 1% B as a sintered aid. SiC is commonly used as a fibrous reinforcement for metal-matrix and ceramic-matrix composite materials.

Zirconia (ZrO_2) Pure zirconia is polymorphic and transforms from the tetragonal to monoclinic structure at about 1170°C with an accompanying volume expansion and so is subject to cracking. However, by combining ZrO_2 with other refractory oxides such as CaO, MgO, and Y_2O_3 , the cubic structure can be stabilized at room temperature and has found some applications. By combining ZrO_2 with 9% MgO and using special heat treatments, a partially stabilized zirconia (PSZ) can be produced with especially high fracture toughness, which has led to new ceramic applications. (See Sec. 11.6 on the fracture toughness of ceramics for more details.)

11.6 MECHANICAL PROPERTIES OF CERAMICS

11.6.1 General

As a class of materials, ceramics are relatively brittle. The observed tensile strength of ceramic materials varies greatly, ranging from very low values of less than 100 psi (0.69 MPa) to about 10^6 psi (7×10^3 MPa) for whiskers of ceramics such as Al_2O_3 prepared under carefully controlled conditions. However, as a class of materials, few ceramics have tensile strengths above 25,000 psi (172 MPa). Ceramic materials also have a large difference between their tensile and compressive strengths, with the compressive strengths usually being about 5 to 10 times higher than the tensile strengths, as indicated in Table 11.7 for the 99 percent Al_2O_3 ceramic material. Also, many ceramic materials are hard and have low impact resistance due to their ionic-covalent bindings. However, there are many exceptions to these generalizations. For example, plasticized clay is a ceramic material that is soft and easily deformable due to weak secondary bonding forces between layers of strongly ionic-covalently bonded atoms.

11.6.2 Mechanisms for the Deformation of Ceramic Materials

The lack of plasticity in crystalline ceramics is due to their ionic and covalent chemical bonds. In metals, plastic flow takes place mainly by the movement of line faults (dislocations) in the crystal structure over special crystal slip planes (see Sec. 6.5). In metals, dislocations move under relatively low stresses due to the nondirectional nature of the metallic bond and because all atoms involved in the bonding have an equally distributed negative charge at their surfaces. That is, there are no positive or negatively charged ions involved in the metallic bonding process.

In covalent crystals and covalently bonded ceramics, the bonding between atoms is specific and directional, involving the exchange of electron charge between pairs of electrons. Thus, when covalent crystals are stressed to a sufficient extent, they exhibit brittle fracture due to a separation of electron-pair bonds without their subsequent reformation. Covalently bonded ceramics, therefore, are brittle in both the single-crystal and polycrystalline states.

The deformation of primarily ionically bonded ceramics is different. Single crystals of ionically bonded solids such as magnesium oxide and sodium chloride show considerable plastic deformation under compressive stresses at room temperature. Polycrystalline ionically bonded ceramics, however, are brittle, with cracks forming at the grain boundaries.

Let us briefly examine some conditions under which an ionic crystal can be deformed, as illustrated in Fig. 11.33. The slip of one plane of ions over another involves ions of different charge coming into contact, and thus attractive and repulsion forces may be produced. Most ionically bonded crystals having the NaCl-type structure slip on the $\{110\}$ - $\{1\bar{1}0\}$ systems because slip on the $\{110\}$ family of planes involves only ions of unlike charge, and hence the slip planes remain attracted to each other by coulombic forces during the slip process. Slip of the $\{110\}$ type is indicated by the line AA' of Fig. 11.33. On the other hand, slip on the $\{100\}$ family of planes is rarely observed because ions of the same charge come into contact, which will tend to separate the planes of ions slipping over each other. This $\{100\}$ -type slip is indicated by the line BB' of Fig. 11.33. Many ceramic materials in the single-crystal form show considerable plasticity. However, in polycrystalline ceramics, adjacent grains must change shape during deformation. Since there are limited slip systems in ionically bonded solids, cracking occurs at the grain boundaries and subsequent brittle fracture occurs. Since most industrially important ceramics are polycrystalline, most ceramic materials tend to be brittle.

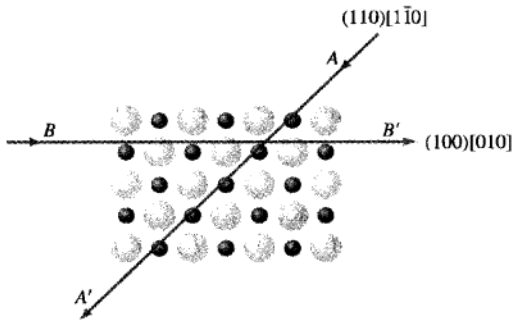
11.6.3 Factors Affecting the Strength of Ceramic Materials

The mechanical failure of ceramic materials occurs mainly from structural defects. The principal sources of fracture in ceramic polycrystals include surface cracks produced during surface finishing, voids (porosity), inclusions, and large grains produced during processing.³

Pores in brittle ceramic materials are regions where stress concentrates, and when the stress at a pore reaches a critical value, a crack forms and propagates since there are no large, energy-absorbing processes in these materials such as those that operate in ductile metals during deformation. Thus, once cracks start to propagate, they continue to grow until fracture occurs. Pores are also detrimental to the strength of ceramic materials because they decrease the cross-sectional area over which a load is applied and hence lower the stress a material can support. Thus, the size and volume fraction of pores in ceramic materials are important factors affecting their strength. Figure 11.34 shows how an increasing volume fraction of pores decreases the transverse tensile strength of alumina.

Flaws in processed ceramics may also be critical in determining the fracture strength of a ceramic material. A large flaw may be the major factor affecting the strength of a ceramic. In fully dense ceramic materials in which there are no large pores, the flaw size is usually related to the grain size. For porosity-free ceramics, the strength of a pure ceramic material is a function of its grain size, with finer-grain-size ceramics

³A. G. Evans, *J. Am. Ceram. Soc.*, **65**:127(1982).

**Figure 11.33**

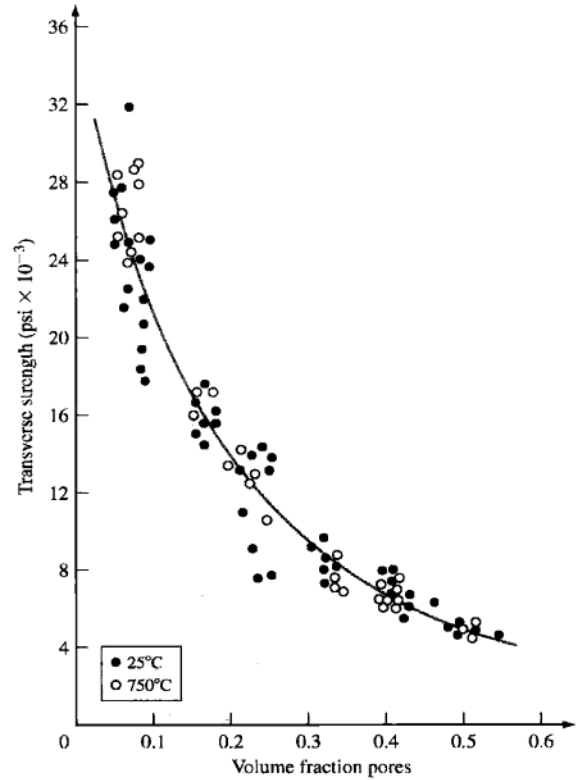
Top view of NaCl crystal structure indicating (a) slip on the (110) plane and in the [110] direction (line AA') and (b) slip on the (100) plane in the [010] direction (line BB').

having smaller-size flaws at their grain boundaries and hence being stronger than large-grain-size ones.

The strength of a polycrystalline ceramic material is thus determined by many factors that include chemical composition, microstructure, and surface condition as major factors. Temperature and environment also are important as well as the type of stress and how it is applied. However, the failure of most ceramic materials at room temperature usually originates at the largest flaw.

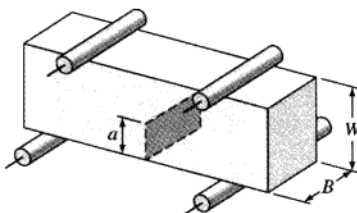
11.6.4 Toughness of Ceramic Materials

Ceramic materials, because of their combination of covalent-ionic bonding, have inherently low toughness. A great amount of research has been carried out in the past years to improve the toughness of ceramic materials. By the use of processes

**Figure 11.34**

The effect of porosity on the transverse strength of pure alumina.

[After R.L. Coble and W.D. Kingery, *J. Am. Ceram. Soc.*, 39:377(1956).]

**Figure 11.35**

Setup for four-point beam fracture-toughness test of a ceramic material using a single-edge notch.

such as hot pressing ceramics with additives and reaction bonding, engineering ceramics with improved toughness have been produced (Table 11.7).

Fracture-toughness tests can be made on ceramic specimens to determine K_{IC} values in a manner similar to the fracture-toughness testing of metals (see Sec. 7.3). K_{IC} values for ceramic materials are usually obtained by using a four-point bend test with a single-edge or chevron-notched beam specimen (Fig. 11.35). The fracture-toughness equation,

$$K_{IC} = Y\sigma_f\sqrt{\pi a} \quad (11.1)$$

which relates fracture-toughness K_{IC} values to the fracture stress and the largest flaw size can also be used for ceramic materials. In Eq. 11.1, K_{IC} is measured in $\text{MPa}\sqrt{\text{m}}$ ($\text{ksi}\sqrt{\text{in.}}$), the fracture stress σ_f in MPa (ksi), and a (half the size of the largest internal flaw) in meters (inches). Y is a dimensionless constant equal to about 1. Example Problem 11.9 shows how this equation can be used to determine the largest-size flaw that a particular engineering ceramic of a known fracture toughness and strength can tolerate without fracture.

EXAMPLE PROBLEM 11.9

A reaction-bonded silicon nitride ceramic has a strength of 300 MPa and a fracture toughness of $3.6 \text{ MPa}\sqrt{\text{m}}$. What is the largest-size internal crack that this material can support without fracturing? Use $Y = 1$ in the fracture-toughness equation.

■ Solution

$$\sigma_f = 300 \text{ MPa} \quad K_{IC} = 3.6 \text{ MPa}\sqrt{\text{m}} \quad a = ? \quad Y = 1$$

$$K_{IC} = Y\sigma_f\sqrt{\pi a}$$

or

$$a = \frac{K_{IC}^2}{\pi\sigma_f^2} = \frac{(3.6 \text{ MPa}\sqrt{\text{m}})^2}{\pi(300 \text{ MPa})^2}$$

$$= 4.58 \times 10^{-5} \text{ m} = 45.8 \mu\text{m}$$

Thus, the largest internal crack $= 2a = 2(45.8 \mu\text{m}) = 91.6 \mu\text{m}$. ◀

11.6.5 Transformation Toughening of Partially Stabilized Zirconia (PSZ)

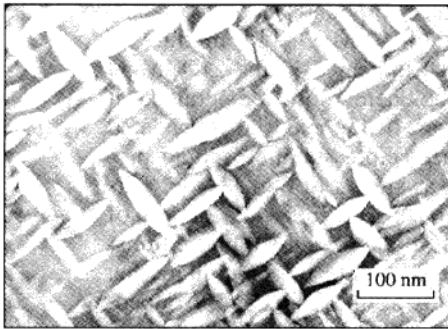
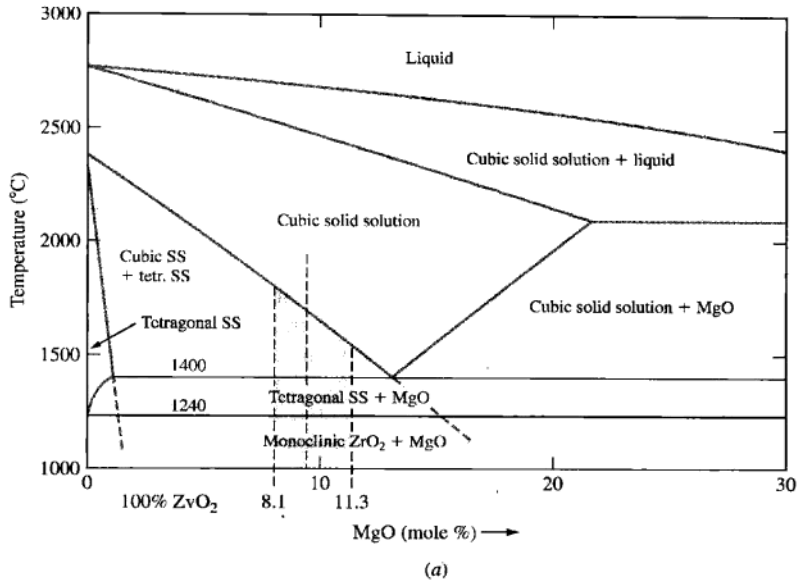
Recently it has been discovered that phase transformations in zirconia combined with some other refractory oxides (that is, CaO, MgO, or Y_2O_3) can produce ceramic materials with exceptionally high fracture toughness. Let us now look into the mechanisms that produce transformation toughening in a ZrO_2 -9 mol % MgO ceramic material. Pure zirconia, ZrO_2 , exists in three different crystal structures: *monoclinic* from room temperature to 1170°C, *tetragonal* from 1170°C to 2370°C, and *cubic* (the fluorite structure of Fig. 11.10) above 2370°C.

The transformation of pure ZrO_2 from the tetragonal to monoclinic structure is martensitic and cannot be suppressed by rapid cooling. Also, this transformation is accompanied by a volume increase of about 9 percent, and so it is impossible to fabricate articles from pure zirconia. However, by the addition of about 10 mol % of other refractory oxides such as CaO, MgO, or Y_2O_3 , the cubic form of zirconia is stabilized so that it can exist at room temperature in the metastable state, and articles can be fabricated from this material. Cubic ZrO_2 combined with stabilizing oxides so that it retains the cubic structure at room temperature is referred to as *fully stabilized zirconia*.

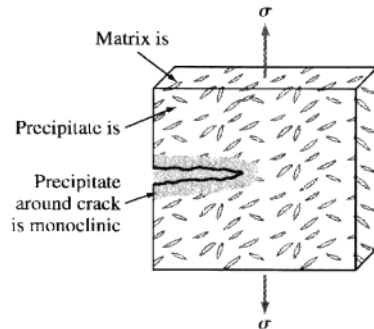
Recent developments have produced zirconia-refractory oxide ceramic materials with enhanced toughness and strength by taking advantage of their phase transformations. One of the more important zirconia compound ceramics is partially stabilized zirconia (PSZ), which contains 9 mol % MgO. If a mixture of ZrO_2 -9 mol % MgO is sintered at about 1800°C, as indicated in the ZrO_2 -MgO phase diagram of Fig. 11.36a, and then rapidly cooled to room temperature, it will be in the all-metastable cubic structure. However, if this material is reheated to 1400°C and held for a sufficient time, a fine metastable submicroscopic precipitate with the tetragonal structure is precipitated, as shown in Fig. 11.36b. This material is known as *partially stabilized zirconia* (PSZ). Under the action of stresses that cause small cracks in the ceramic material, the tetragonal phase transforms to the monoclinic phase, causing a volume expansion of the precipitate that retards the crack propagation by a kind of crack-closing mechanism. By impeding the advances of cracks, the ceramic is "toughened" (Fig. 11.36c). Partially stabilized zirconia has a fracture toughness of $8+ \text{ MPa } \sqrt{\text{m}}$, which is higher than the fracture toughness of all the other engineering ceramic materials listed in Table 11.7.

11.6.6 Fatigue Failure of Ceramics

Fatigue failure in metals occurs under repeated cyclic stresses due to the nucleation and growth of cracks within a work-hardened area of a specimen. Because of the ionic-covalent bonding of the atoms in a ceramic material, there is an absence of plasticity in ceramics during cyclic stressing. As a result, fatigue fracture in ceramics is rare. Recently, results of stable fatigue-crack growth at room temperature under compression-compression stress cycling in notched plates of polycrystalline alumina have been reported. A straight fatigue crack was produced after 79,000 compression



(b)



(c)

Figure 11.36

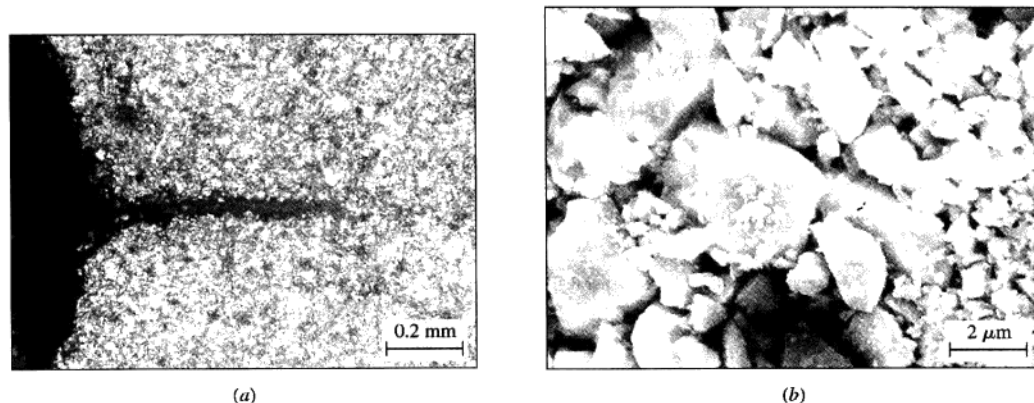
(a) Phase diagram of high- ZrO_2 part of the ZrO_2 - MgO binary phase diagram. The shaded area represents the region used for combining MgO with ZrO_2 to produce partially stabilized zirconia.

(After A.H. Heuer, "Advances in Ceramics," vol. 3, "Science and Technology of Zirconia," American Ceramic Society, 1981.)

(b) Transmission electron micrograph of optimally aged MgO -partially stabilized ZrO_2 showing the tetragonal oblate spheroid precipitate. Upon the application of sufficient stress, these particles transform to the monoclinic phase with a volume expansion.

(Courtesy of A.H. Heuer.)

(c) Schematic diagram illustrating the transformation of the tetragonal precipitate to the monoclinic phase around a crack in a partially stabilized ZrO_2 -9 mol % MgO ceramic specimen.

**Figure 11.37**

Fatigue cracking of polycrystalline alumina under cyclic compression. (a) Optical micrograph showing fatigue crack (the compression axis is vertical). (b) Scanning electron fractograph of the fatigue area of the same specimen where the intergranular mode of failure is evident.

[After S. Suresh and J.R. Brockenbrough, *Acta Metall.* 36:1455 (1988).]

cycles (Fig. 11.37a). Microcrack propagation along grain boundaries led to final intergranular fatigue failure (Fig. 11.37b). Much research is being carried out to make tougher ceramics that can support cyclic stresses for applications such as turbine rotors.

11.6.7 Ceramic Abrasive Materials

The high hardness of some ceramic materials makes them useful as abrasive materials for cutting, grinding, and polishing other materials of lower hardness. Fused alumina (aluminum oxide) and silicon carbide are two of the most commonly used manufactured ceramic abrasives. Abrasive products such as sheets and wheels are made by bonding individual ceramic particles together. Bonding materials include fired ceramics, organic resins, and rubbers. The ceramic particles must be hard with sharp cutting edges. Also, the abrasive product must have a certain amount of porosity to provide channels for air or liquid to flow through in the structure. Aluminum oxide grains are tougher than silicon carbide ones but are not as hard, and so silicon carbide is normally used for the harder materials.

By combining zirconium oxide with aluminum oxide, improved abrasives were developed⁴ with higher strength, hardness, and sharpness than aluminum oxide alone. One of these ceramic alloys contains 25 percent ZrO_2 and 75 percent Al_2O_3 and another 40 percent ZrO_2 and 60 percent Al_2O_3 . Another important ceramic abrasive

⁴ ZrO_2 - Al_2O_3 ceramic abrasive alloys were developed by the Norton Co. in the 1960s.

is cubic boron nitride, which has the trade name Borazon.⁵ This material is almost as hard as diamond but has better heat stability than diamond.

11.7 THERMAL PROPERTIES OF CERAMICS

In general, most ceramic materials have low thermal conductivities due to their strong ionic-covalent bonding and are good thermal insulators. Figure 11.38 compares the thermal conductivities of many ceramic materials as a function of temperature. Because of

⁵Borazon, a product of the General Electric Co., was developed in the 1950s.

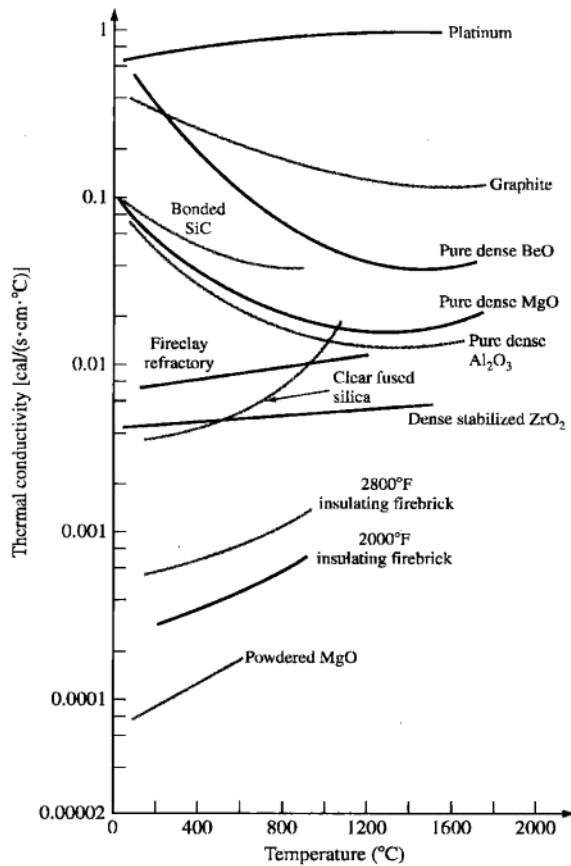


Figure 11.38
Thermal conductivity (logarithmic scale) of ceramic materials over a wide temperature range.
(Courtesy of NASA.)

Table 11.8 Compositions and applications for some refractory brick materials

	Composition (wt %)			
	SiO ₂	Al ₂ O ₃	MgO	Other
<i>Acidic types:</i>				
Silica brick	95–99			
Superduty fireclay brick	53	42		
High-duty fireclay brick	51–54	37–41		
High-alumina brick	0–50	45–99+		
<i>Basic types:</i>				
Magnesite	0.5–5		91–98	0.6–4 CaO
Magnesite-chrome	2–7	6–13	50–82	18–24 Cr ₂ O ₃
Dolomite (burned)			38–50	38–58 CaO
<i>Special types:</i>				
Zircon	32			66 ZrO ₂
Silicon carbide	6	2		91 SiC
<i>Applications for some refractories:</i>				
<i>Superduty fireclay bricks:</i> linings for aluminum-melting furnaces, rotary kilns, blast furnaces, and hot-metal transfer ladles				
<i>High-duty fireclay brick:</i> linings for cement and lime kilns, blast furnaces, and incinerators				
<i>High-alumina brick:</i> boiler furnaces, spent-acid regenerating furnaces, phosphate furnaces, glass-tank refiner walls, carbon black furnaces, continuous-casting tundish linings, coal gasification reactor linings, and petroleum coke kilns				
<i>Silica brick:</i> chemical reactor linings, glass tank parts, ceramic kilns, and coke ovens				
<i>Magnesite brick:</i> basic-oxygen-process furnace linings for steelmaking				
<i>Zircon brick:</i> glass-tank bottom paving and continuous-casting nozzles				

Source: *Harbison-Walker Handbook of Refractory Practice*, Harbison-Walker Refractories, Pittsburgh, 1980.

their high heat resistance, ceramic materials are used as **refractories**, which are materials that resist the action of hot environments, both liquid and gaseous. Refractories are used extensively by the metals, chemical, ceramic, and glass industries.

11.7.1 Ceramic Refractory Materials

Many pure ceramic compounds with high melting points such as aluminum oxide and magnesium oxide could be used as industrial refractory materials, but they are expensive and difficult to form into shapes. Therefore, most industrial refractories are made of mixtures of ceramic compounds. Table 11.8 lists the compositions of some refractory brick compositions and gives some of their applications.

Important properties of ceramic refractory materials are low- and high-temperature strengths, bulk density, and porosity. Most ceramic refractories have bulk densities that range from 2.1 to 3.3 g/cm³ (132 to 206 lb/ft³). Dense refractories with low porosity have higher resistance to corrosion and erosion and to penetration by liquids and gases. However, for insulating refractories, a high amount of porosity is desirable. Insulating refractories are mostly used as backing for brick or refractory material of higher density and refractoriness.

Industrial ceramic refractory materials are commonly divided into acidic and basic types. Acidic refractories are based mainly on SiO₂ and Al₂O₃ and basic ones on MgO, CaO, and Cr₂O₃. Table 11.8 lists the compositions of many types of industrial refractories and gives some of their applications.

11.7.2 Acidic Refractories

Silica refractories have high refractoriness, high mechanical strength, and rigidity at temperatures almost to their melting points.

Fireclays are based on a mixture of plastic fireclay, flint clay, and clay (coarse-particle) grog. In the unfired (green) condition, these refractories consist of a mixture of particles varying from coarse to extremely fine. After firing, the fine particles form a ceramic bond between the larger particles.

High-alumina refractories contain from 50 to 99 percent alumina and have higher fusion temperatures than fireclay bricks. They can be used for more severe furnace conditions and at higher temperatures than fireclay bricks but are more expensive.

11.7.3 Basic Refractories

Basic refractories consist mainly of magnesia (MgO), lime (CaO), chrome ore, or mixtures of two or more of these materials. As a group, basic refractories have high bulk densities, high melting temperatures, and good resistance to chemical attack by basic slags and oxides but are more expensive. Basic refractories containing a high percentage (92 to 95 percent) of magnesia are used extensively for linings in the basic-oxygen steelmaking process.

11.7.4 Ceramic Tile Insulation for the Space Shuttle Orbiter

The development of the thermal protection system for the space shuttle orbiter is an excellent example of modern materials technology applied to engineering design. So that the space shuttle orbiter could be used for at least 100 missions, new insulative ceramic tile materials were developed.

About 70 percent of the orbiter's external surface is protected from heat by approximately 24,000 individual ceramic tiles made from a silica-fiber compound. Figure 11.39 shows the microstructure of the *high-temperature reusable-surface insulation* (HRSI) tile material, and Fig. 11.40 indicates the surface area where it is attached to the body of the orbiter. This material has a density of only 4 kg/ft³ (9 lb/ft³) and can withstand temperatures as high as 1260°C (2300°F). The effectiveness of this insulative material is indicated by the ability of a technician to hold a piece of the ceramic tile only about 10 s after it has been removed from a furnace at 1260°C (2300°F).

11.8 GLASSES

Glasses have special properties not found in other engineering materials. The combination of transparency and hardness at room temperature along with sufficient strength and excellent corrosion resistance to most normal environments make glasses indispensable for many engineering applications such as construction and vehicle glazing. In the electrical industry, glass is essential for various types of lamps because of its insulative properties and ability to provide a vacuum-tight enclosure. In the electronics industry, electron tubes also require the vacuum-tight enclosure



Figure 11.39
Microstructure of LI900 high-temperature reusable-surface insulation (ceramic tile material used for space shuttle); structure consists of 99.7% pure silica fibers. (Magnification 1200 \times .)
(Courtesy of Lockheed Martin Missiles and Space Co.)

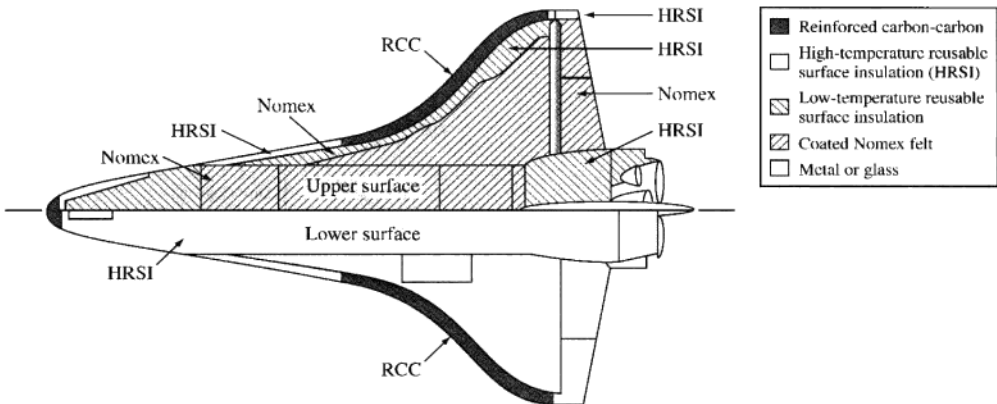


Figure 11.40
Space shuttle thermal protection systems.
(Courtesy of Corning Incorporated.)

provided by glass along with its insulative properties for lead-in connectors. The high chemical resistance of glass makes it useful for laboratory apparatus and for corrosion-resistant liners for pipes and reaction vessels in the chemical industry.

11.8.1 Definition of a Glass

A glass is a ceramic material in that it is made from inorganic materials at high temperatures. However, it is distinguished from other ceramics in that its constituents are heated to fusion and then cooled to a rigid state without crystallization. Thus, a **glass** can be defined as *an inorganic product of fusion that has cooled to a rigid condition without crystallization*. A characteristic of a glass is that it has a noncrystalline or amorphous structure. The molecules in a glass are not arranged in a regular repetitive long-range order as exists in a crystalline solid. In a glass, the molecules change their orientation in a random manner throughout the solid material.

11.8.2 Glass Transition Temperature

The solidification behavior of a glass is different from that of a crystalline solid, as illustrated in Fig. 11.41, which is a plot of specific volume (reciprocal of density) versus temperature for these two types of materials. A liquid that forms a crystalline solid upon solidifying (i.e., a pure metal) will normally crystallize at its melting point with a significant decrease in specific volume, as indicated by path *ABC* in Fig. 11.41. In contrast, a liquid that forms a glass upon cooling does not crystallize but follows a path like *AD* in Fig. 11.41. Liquid of this type becomes more viscous as its temperature is

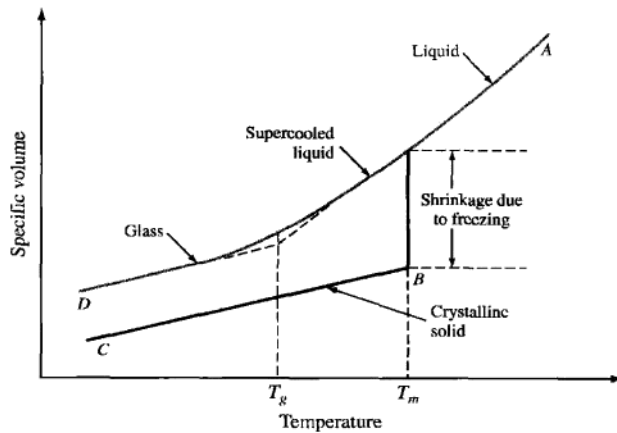


Figure 11.41

Solidification of crystalline and glassy (amorphous) materials showing changes in specific volume. T_g is the glass transition temperature of the glassy material. T_m is the melting temperature of the crystalline material.

(From O.H. Wyatt and D. Dew-Hughes, "Metals, Ceramics, and Polymers," Cambridge University Press, 1974, p. 263. Reprinted with the permission of Cambridge University Press.)

lowered and transforms from a rubbery, soft plastic state to a rigid, brittle glassy state in a narrow temperature range where the slope of the specific volume versus temperature curve is markedly decreased. The point of intersection of the two slopes of this curve define a transformation point called the **glass transition temperature** T_g . This point is structure-sensitive, with faster cooling rates producing higher values of T_g .

11.8.3 Structure of Glasses

Glass-Forming Oxides Most inorganic glasses are based on the **glass-forming oxide** silica, SiO_2 . The fundamental subunit in silica-based glasses is the SiO_4^{4-} tetrahedron in which a silicon (Si^{4+}) atom (ion) in the tetrahedron is covalently ionically bonded to four oxygen atoms (ions), as shown in Fig. 11.42a. In crystalline silica, for example, cristobalite, the Si—O tetrahedra are joined corner to corner in a regular arrangement, producing long-range order as idealized in Fig. 11.42b. In a simple silica glass, the tetrahedra are joined corner to corner to form a *loose network* with no long-range order (Fig. 11.42c).

Boron oxide, B_2O_3 , is also a glass-forming oxide and by itself forms subunits that are flat triangles with the boron atom slightly out of the plane of the oxygen atoms. However, in borosilicate glasses that have additions of alkali and alkaline earth oxides, BO_3^{3-} triangles can be converted to BO_4^{4-} tetrahedra, with the alkali or alkaline earth cations providing the necessary electroneutrality. Boron oxide is an important addition to many types of commercial glasses such as borosilicate and aluminoborosilicate glasses.

Glass-Modifying Oxides Oxides that break up the glass network are known as **network modifiers**. Alkali oxides such as Na_2O and K_2O and alkaline earth oxides such as CaO and MgO are added to silica glass to lower its viscosity so that it can be worked and formed more easily. The oxygen atoms from these oxides enter the silica network at points joining the tetrahedra and break up the network, producing

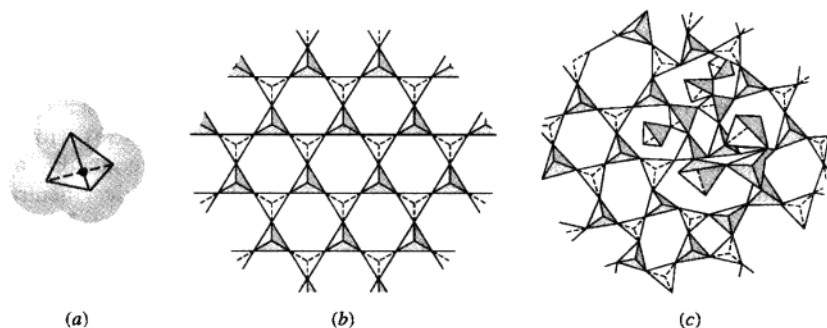
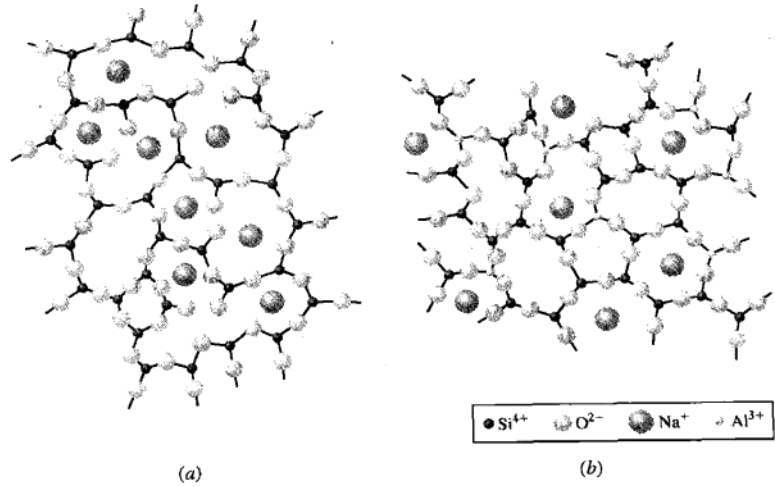


Figure 11.42

Schematic representation of (a) a silicon-oxygen tetrahedron, (b) ideal crystalline silica (cristobalite) in which the tetrahedra have long-range order, and (c) a simple silica glass in which the tetrahedra have no long-range order.

(From O.H. Wyatt and D. Dew-Hughes, "Metals, Ceramics, and Polymers," Cambridge University Press, 1974, p. 259. Reprinted with the permission of Cambridge University Press.)

**Figure 11.43**

(a) Network-modified glass (soda-lime glass); note that the metallic (Na^{+}) ions do not form part of the network. (b) Intermediate-oxide glass (alumina-silica) glass; note that the small metallic (Al^{3+}) ions form part of the network.

(After O.H. Wyatt and D. Dew-Hughes, "Metals, Ceramics, and Polymers," Cambridge, 1974, p. 263.)

oxygen atoms with an unshared electron (Fig. 11.43a). The Na^{+} and K^{+} ions from the Na_2O and K_2O do not enter the network but remain as metal ions ionically bonded in the interstices of the network. By filling some of the interstices, these ions promote crystallization of the glass.

Intermediate Oxides in Glasses Some oxides cannot form a glass network by themselves but can join into an existing network. These oxides are known as **intermediate oxides**. For example, aluminum oxide, Al_2O_3 , can enter the silica network as AlO_4^{4-} tetrahedra, replacing some of the SiO_4^{4-} groups (Fig. 11.43b). However, since the valence of Al is +3 instead of the necessary +4 for the tetrahedra, alkali cations must supply the necessary other electrons to produce electrical neutrality. Intermediate oxides are added to silica glass to obtain special properties. For example, aluminosilicate glasses can withstand higher temperatures than common glass. Lead oxide is another intermediate oxide that is added to some silica glasses. Depending on the composition of the glass, intermediate oxides may sometimes act as network modifiers as well as taking part in the network of the glass.

11.8.4 Compositions of Glasses

The compositions of some important types of glasses are listed in Table 11.9 along with some remarks about their special properties and applications. Fused silica glass,

Table 11.9 Compositions of some glasses

Glass	SiO ₂	Na ₂ O	K ₂ O	CaO	B ₂ O ₃	Al ₂ O ₃	Other	Remarks
1. (Fused) silica	99.5+							Difficult to melt and fabricate but usable to 1000°C. Very low expansion and high thermal shock resistance.
2. 96% silica	96.3	<0.2	<0.2		2.9	0.4		Fabricate from relatively soft borosilicate glass; heat to separate SiO ₂ and B ₂ O ₃ phases; acid leach B ₂ O ₃ phase; heat to consolidate pores.
3. Soda-lime: plate glass	71–73	12–14		10–12		0.5–1.5	MgO, 1–4	Easily fabricated. Widely used in slightly varying grades for windows, containers, and electric bulbs.
4. Lead silicate: electrical	63	7.6	6	0.3	0.2	0.6	PbO, 21 MgO, 0.2	Readily melted and fabricated with good electrical properties.
5. High-lead	35		7.2				PbO, 58	High lead absorbs X-rays; high refractive used in achromatic lenses.
6. Borosilicate: low expansion	80.5	3.8	0.4		12.9	2.2		Decorative crystal glass. Low expansion, good thermal shock resistance, and chemical stability. Widely used in chemical industry.
7. Low electrical loss	70.0		0.5		28.0	1.1	PbO, 1.2	Low dielectric loss.
8. Aluminoborosilicate: standard apparatus	74.7	6.4	0.5	0.9	9.6	5.6	B ₂ O, 2.2	Increased alumina, lower boric oxide improves chemical durability.
9. Low alkali (E-glass)	54.5	0.5		22	8.5	14.5		Widely used for fibers in glass resin composites.
10. Aluminosilicate	57	1.0		5.5	4	20.5	MgO, 12	High-temperature strength, low expansion.
11. Glass-ceramic	40–70					10–35	MgO, 10–30 TiO ₂ , 7–15	Crystalline ceramic made by devitrifying glass. Easy fabrication (as glass), good properties. Various glasses and catalysts.

Source: O.H. Wyatt and D. Dew-Hughes, *Metals, Ceramics, and Polymers*, Cambridge, 1974, p. 261.

which is the most important single-component glass, has a high spectral transmission and is not subject to radiation damage, which causes browning of other glasses. It is therefore the ideal glass for space vehicle windows, wind tunnel windows, and optical systems in spectrophotometric devices. However, silica glass is difficult to process and expensive.

Soda-Lime Glass The most commonly produced glass is soda-lime glass, which accounts for about 90 percent of all the glass produced. In this glass, the basic composition is 71 to 73 percent SiO_2 , 12 to 14 percent Na_2O , and 10 to 12 percent CaO . The Na_2O and CaO decrease the softening point of this glass from 1600°C to about 730°C so that the soda-lime glass is easier to form. An addition of 1 to 4 percent MgO is used to prevent devitrification, and an addition of 0.5 to 1.5 percent Al_2O_3 is used to increase durability. Soda-lime glass is used for flat glass, containers, pressed and blown ware, and lighting products where high chemical durability and heat resistance are not needed.

Borosilicate Glasses The replacement of alkali oxides by boric oxide in the silica glassy network produces a lower-expansion glass. When B_2O_3 enters the silica network, it weakens its structure and considerably lowers the softening point of the silica glass. The weakening effect is attributed to the presence of planar three-coordinate borons. Borosilicate glass (Pyrex glass) is used for laboratory equipment, piping, ovenware, and sealed-beam headlights.

Lead Glasses Lead oxide is usually a modifier in the silica network but can also act as a network former. Lead glasses with high lead oxide contents are low melting and are useful for solder-sealing glasses. High-lead glasses are also used for shielding from high-energy radiation, and they find application for radiation windows, fluorescent lamp envelopes, and television bulbs. Because of their high refractive indexes, lead glasses are used for some optical glasses and for decorative-purpose glasses.

11.8.5 Viscous Deformation of Glasses

A glass behaves as a viscous (supercooled) liquid above its glass transition temperature. Under stress, groups of silicate atoms (ions) can slide past each other, allowing permanent deformation of the glass. Interatomic bonding forces resist deformation above the glass transition temperature but cannot prevent viscous flow of the glass if the applied stress is sufficiently high. As the temperature of the glass is progressively increased above its glass transition temperature, the viscosity of the glass decreases and viscous flow becomes easier. The effect of temperature on the viscosity of a glass follows an Arrhenius-type equation except that the sign of the exponential term is positive instead of negative as is usually the case (i.e., for diffusivity, the Arrhenius-type equation is $D = D_0 e^{(-Q/RT)}$). The equation relating viscosity to temperature for viscous flow in a glass is

$$\eta^* = \eta_0 e^{+Q/RT} \quad (11.2)$$

where η = viscosity of the glass, P or $\text{Pa} \cdot \text{s}$;⁶ η_0 = preexponential constant, P or $\text{Pa} \cdot \text{s}$; Q = molar activation energy for viscous flow; R = universal molar gas

⁶ η = Greek letter eta, pronounced "eight-ah."

⁶1 P (poise) = 1 dyne \cdot s/cm²; 1 Pa \cdot s (pascal-second) = 1 N \cdot s/m²; 1 P = 0.1 Pa \cdot s.

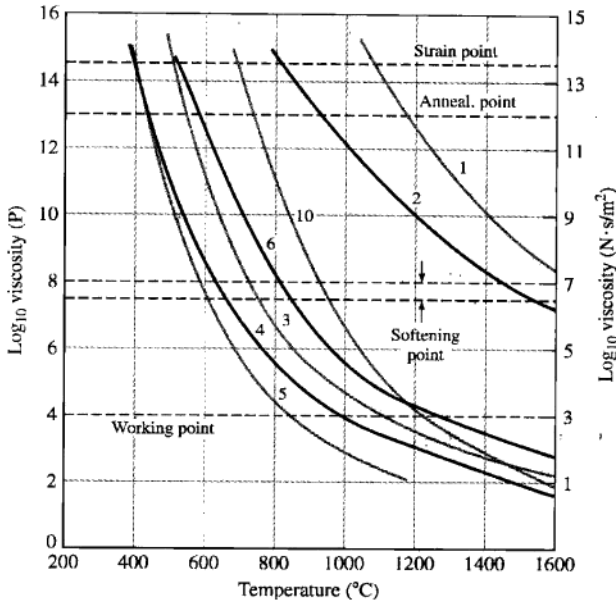


Figure 11.44

Effect of temperature on the viscosities of various types of glasses. Numbers on curves refer to compositions in Table 10.11.

(After O.H. Wyatt and D. Dew-Hughes, "Metals, Ceramics, and Polymers," Cambridge, 1974, p. 259.)

constant; and T = absolute temperature. Example Problem 11.10 shows how a value for the activation energy for viscous flow in a glass can be determined from this equation using viscosity-temperature data.

The effect of temperature on the viscosity of some commercial types of glasses is shown in Fig. 11.44. For the comparison of glasses, several viscosity reference points are used, indicated by horizontal lines in Fig. 11.44. These are working, softening, annealing, and strain points. Their definitions are:

1. **Working point:** viscosity = 10^4 poises ($10^3 \text{ Pa} \cdot \text{s}$). At this temperature, glass fabrication operations can be carried out.
2. **Softening point:** viscosity = 10^8 poises ($10^7 \text{ Pa} \cdot \text{s}$). At this temperature, the glass will flow at an appreciable rate under its own weight. However, this point cannot be defined by a precise viscosity because it depends on the density and surface tension of the glass.
3. **Annealing point:** viscosity = 10^{13} poises ($10^{12} \text{ Pa} \cdot \text{s}$). Internal stresses can be relieved at this temperature.

4. **Strain point:** viscosity = $10^{14.5}$ poises ($10^{13.5}$ Pa · s). Below this temperature the glass is rigid, and stress relaxation occurs only at a slow rate. The interval between the annealing and strain points is commonly considered the annealing range of a glass.

Glasses are usually melted at a temperature that corresponds to a viscosity of about 10^2 poises (10 Pa · s). During forming, the viscosities of glasses are compared qualitatively. A *hard glass* has a high softening point, whereas a *soft glass* has a lower softening point. A *long glass* has a large temperature difference between its softening and strain points. That is, the long glass solidifies slower than a *short glass* as the temperature is decreased.

EXAMPLE PROBLEM 11.10

A 96 percent silica glass has a viscosity of 10^{13} P at its annealing point of 940°C and a viscosity of 10^8 P at its softening point of 1470°C . Calculate the activation energy in kilojoules per mole for the viscous flow of this glass in this temperature range.

■ Solution

$$\text{Annealing point of glass} = T_{ap} = 940^\circ\text{C} + 273 = 1213 \text{ K} \quad \eta_{ap} = 10^{13} \text{ P}$$

$$\text{Softening point of glass} = T_{sp} = 1470^\circ\text{C} + 273 = 1743 \text{ K} \quad \eta_{sp} = 10^8 \text{ P}$$

$$R = \text{gas constant} = 8.314 \text{ J/(mol} \cdot \text{K)} \quad Q = ? \text{ J/mol}$$

Using Eq. 11.2, $\eta = \eta_0 e^{Q/RT}$,

$$\frac{\eta_{ap}}{\eta_{sp}} = \frac{\eta_0 e^{Q/RT_{ap}}}{\eta_0 e^{Q/RT_{sp}}} \quad \text{or} \quad \frac{\eta_{ap}}{\eta_{sp}} = \exp \left[\frac{Q}{R} \left(\frac{1}{T_{ap}} - \frac{1}{T_{sp}} \right) \right] = \frac{10^{13} \text{ P}}{10^8 \text{ P}} = 10^5$$

$$10^5 = \exp \left[\frac{Q}{8.314} \left(\frac{1}{1213 \text{ K}} - \frac{1}{1743 \text{ K}} \right) \right]$$

$$\ln 10^5 = \frac{Q}{8.314} (8.244 \times 10^{-4} - 5.737 \times 10^{-4}) = \frac{Q}{8.314} (2.507 \times 10^{-4})$$

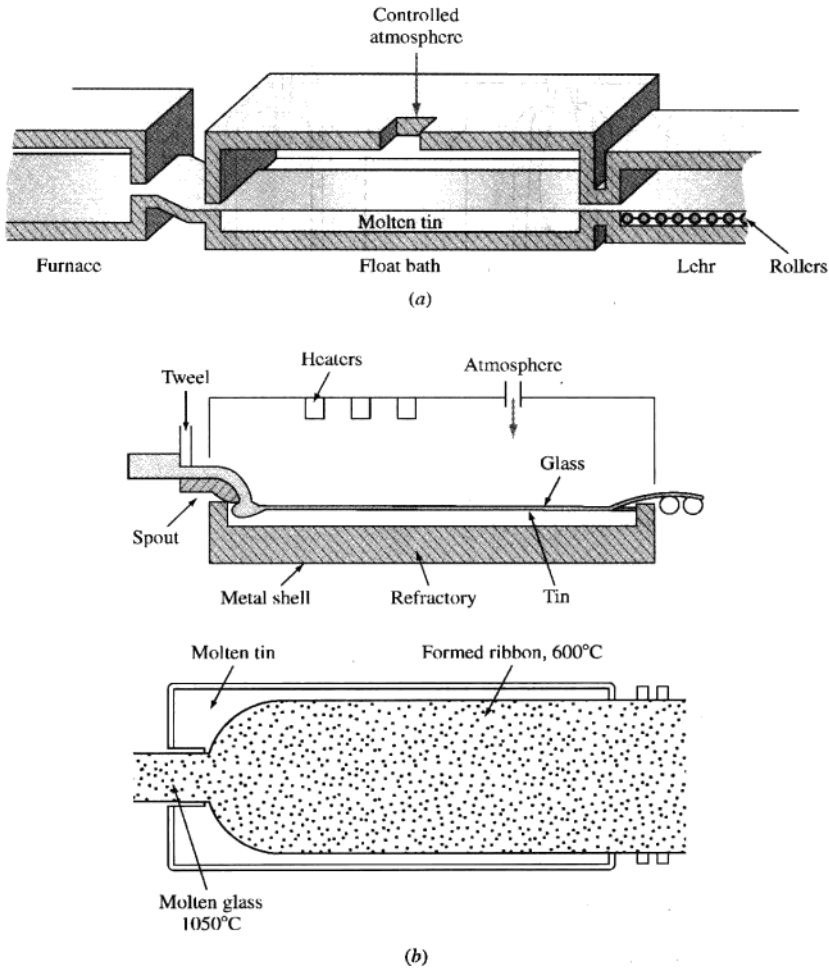
$$11.51 = Q(3.01 \times 10^{-5})$$

$$Q = 3.82 \times 10^5 \text{ J/mol} = 382 \text{ kJ/mol} \blacktriangleleft$$

11.8.6 Forming Methods for Glasses

Glass products are made by first heating the glass to a high temperature to produce a viscous liquid and then molding, drawing, or rolling it into a desired shape.

Forming Sheet and Plate Glass About 85 percent of the flat glass produced in the United States is made by the **float-glass** process in which a ribbon of glass moves out of the melting furnace and floats on the surface of a bath of molten tin (Fig. 11.45). The glass ribbon is cooled while moving across the molten tin and while under a chemically controlled atmosphere (Fig. 11.45). When its surfaces are

**Figure 11.45**

(a) Diagram of the float-glass process.

(After D.C. Boyd and D.A. Thompson, "Glass," vol. II: "Kirk-Othmer Encyclopedia of Chemical Technology," 3rd ed., Wiley, 1980, p. 862.)

(b) Side and top schematic views of the float-glass process.

sufficiently hard, the glass sheet is removed from the furnace without being marked by rollers and passed through a long annealing furnace called a *lehr*, where residual stresses are removed.

Blowing, Pressing, and Casting of Glass Deep items such as bottles, jars, and light bulb envelopes are usually formed by blowing air to force molten glass into

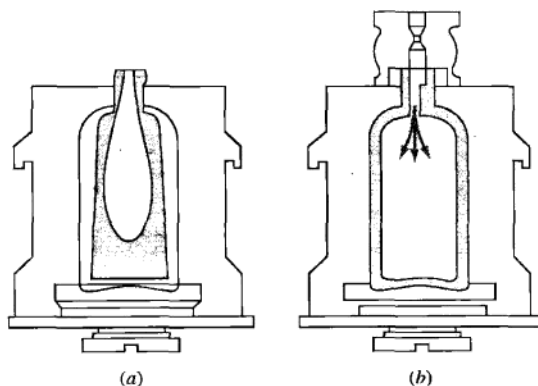


Figure 11.46

(a) Reheat and (b) final blow stages of a glass blowing machine process.

(From p. 270 in E.B. Shand, "Engineering Glass," vol. 6: *Modern Materials*, Academic, 1968.)

molds (Fig. 11.46). Flat items such as optical and sealed-beam lenses are made by pressing a plunger into a mold containing molten glass.

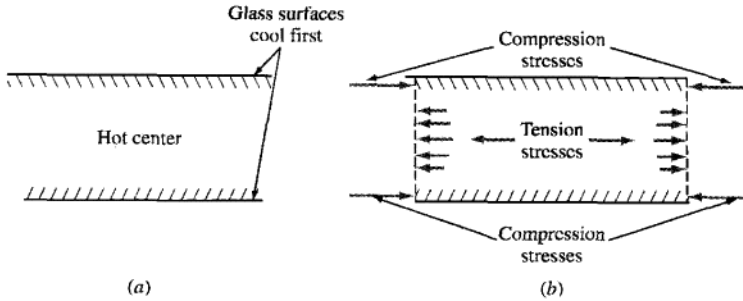
Many articles can be made by casting the glass into an open mold. A large borosilicate glass telescope mirror 6 m in diameter was made by casting the glass. Funnel-shaped items such as television tubes are formed by centrifugal casting. Gobs of molten glass from a feeder are dropped onto a spinning mold that causes the glass to flow upward to form a glass wall of approximately uniform thickness.

11.8.7 Tempered Glass

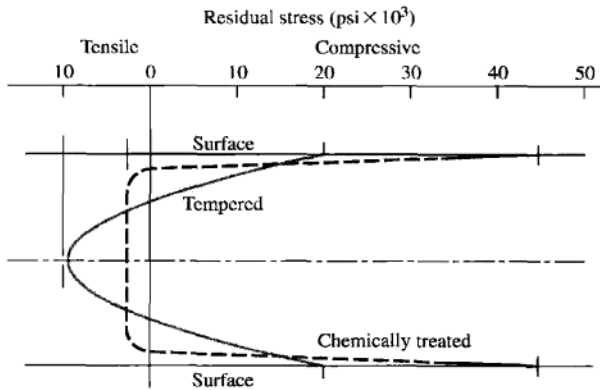
This type of glass is strengthened by rapid air cooling of the surface of the glass after it has been heated to near its softening point. The surface of the glass cools first and contracts, while the interior is warm and readjusts to the dimensional change with little stress (Fig. 11.47a). When the interior cools and contracts, the surfaces are rigid, and so tensile stresses are created in the interior of the glass and compressive stresses on the surfaces (Figs. 11.47b and 11.48). This "tempering" treatment increases the strength of the glass because applied tensile stresses must surpass the compressive stresses on the surface before fracture occurs. Tempered glass has a higher resistance to impact than annealed glass and is about four times stronger than annealed glass. Auto side windows and safety glass for doors are items that are thermally tempered.

11.8.8 Chemically Strengthened Glass

The strength of glass can be increased by special chemical treatments. For example, if a sodium aluminosilicate glass is immersed in a bath of potassium nitrate at a

**Figure 11.47**

Cross section of tempered glass (a) after surface has cooled from high temperature near glass-softening temperature and (b) after center has cooled.

**Figure 11.48**

Distribution of residual stresses across the sections of glass **thermally tempered** and **chemically strengthened**.

(After E.B. Shand, "Engineering Glass," vol. 6: "Modern Materials," Academic, 1968, p. 270.)

temperature about 50°C below its stress point ($\sim 500^\circ\text{C}$) for 6 to 10 h, the smaller sodium ions near the surface of the glass are replaced by larger potassium ions. The introduction of the larger potassium ions into the surface of the glass produces compressive stresses at the surface and corresponding tensile stresses at its center. This chemical tempering process can be used on thinner cross sections than can thermal tempering since the compressive layer is much thinner, as shown in Fig. 11.48. Chemically strengthened glass is used for supersonic aircraft glazing and ophthalmic lenses.

11.9 CERAMIC COATINGS AND SURFACE ENGINEERING

The surface of a component is susceptible to mechanical (friction and wear), chemical (corrosion), electrical (conductivity or insulation), optical (reflectivity), and thermal (high-temperature damage) interactions. As a result, any designer in any engineering field must consider the quality and protection of the surface of any component as a major design criterion, i.e., surface engineering. One possible method of protecting the surface of a component is through the application of coatings. Coating materials may be metallic such as in the chromium plating of an automobile trim, polymeric such as paints resisting corrosion, and also ceramic. Various ceramic materials are used as coatings for applications in which high-temperature environments exist or premature wear is of concern. Ceramic coatings offer physical characteristics to the substrate material that it does not inherently possess. These coatings can transform the surface of a substrate to a chemically inert, abrasion resistant, low friction, and easy-to-clean surface over a range of temperatures. They can also offer electrical resistance and prevent hydrogen diffusion (a major source of damage in many metals). Examples of ceramic coating materials include glasses, oxides, carbides, silicides, borides, and nitrides.

11.9.1 Silicate Glasses

Silicate glass coatings have extensive industrial applications. A glass coating applied to (1) a ceramic substrate is called a **glaze**, (2) a metal surface is called a **porcelain enamel**, and (3) a glass substrate is called **glass enamel**. These coatings are used mostly for aesthetic reasons, but they also provide protections against environmental elements, largely by decreasing their permeability. Specific applications include engine exhaust ducts, space heaters, and radiators. These coatings are applied using spraying or dipping techniques. The surface of a component to be glazed or enameled must be clean (free of particles and oil) and sharp corners must be rounded to assure proper coating adhesion (i.e., avoid peeling).

11.9.2 Oxides and Carbides

Oxide coatings provide protection against oxidation and damage at elevated temperatures while carbide coatings (because of their hardness) are used in applications in which wear and seal are important. For example, zirconia (ZrO_2) is applied as a coating to an engine's moving parts. The zirconia protects the metallic substrate (Al or Fe alloys) against high temperature damage. The coating is generally applied using flame or thermal spraying technique. In this technique, the ceramic particles (oxide or carbide) are heated and propelled onto the substrate surface. The microstructure of the coating, which has a thickness of approximately 100 microns, is shown in Fig. 11.49. The coating protection of the roller in paper-processing industries is important because of the highly acidic or basic nature of the pulp. Ceramics are the only materials that offer resistance to abrasion and corrosion in such harsh environments. However, any cracks in the brittle coating layer that reaches the substrate will grow from those points, eventually resulting in the failure of the component.