6

Metals, ceramics, polymers and composites

- Are hydrides alloys or ceramics?
- Are glasses liquids?
- Are polymers glasses?
- Why are plastic bags difficult to degrade?

Traditionally, materials have been divided into three major groups – metals, ceramics and polymers. Metallic materials are made up of pure metals, for example, titanium, iron or copper, and a vast number of alloys, including the historically important alloys bronze, brass and steel. Ceramics bring to mind porcelain, silicon carbide, glass and synthetic gemstones such as ruby and zirconia. Polymers are mainly compounds of carbon and include the familiar materials poly(vinylchloride), polyethylene and nylon as well as important biological molecules such as DNA.

In addition to these major divisions, two others should be mentioned – composites and biomaterials. Composites are important materials that are combinations of compounds from more than one of the groups listed above. They are of importance because they have superior engineering properties to the separate compounds. For example, glass fibre (ceramic) reinforced epoxy resin (polymer) has mechanical properties superior to either of the separate components. One of the most important of composites is concrete, which is a composite of cement and stony material called aggregate.

Biomaterials are naturally occurring materials with important properties, such as wood, silk and bone. They are invariably composites, made of more than one material type. Because of the superior properties of many biomaterials, much effort is placed into trying to recreate these materials synthetically, as biomimetics.

At first sight, metals, ceramics and polymers have little in common. This is because of two main factors – the chemical bonding holding the atoms together and the microstructure of the solids themselves – that are quite different in representative examples of each material. However, the difference is illusory. Many ceramics can be considered as metals, for example the ceramic superconductors. Many polymers show electronic conductivity greater than metals and have use in lightweight batteries and electronic devices. The material in this and later chapters will allow these apparent anomalies to be understood.

6.1 Metals

Roughly speaking, about three quarters of the elements can be regarded as metallic, and metals form

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the largest group of materials in the periodic table. Because of the variation in the outer electron configuration that this implies, one might expect that a large variety of metallic structures would form and that the structures would vary in a predictable way across the periodic table. It is rather surprising, therefore, to find that the majority of metallic elements possess one of only three structures. This fact arises because the outer electrons of metals are distributed throughout the crystal structure and the core that remains is, to a very good approximation, spherical. The crystal structures of many metals can then be approximated to those described by sphere packing.

Alloys, materials made up of two or more metallic elements, show a much greater variety of structures. In this chapter two basic but important types of alloy structure are described. Substitutional alloys frequently have a structure similar to that of a simple metal, but with several metal atoms distributed over the atom positions. One metal atom type is said to substitute for the other. In interstitial alloys, one atom type fits into the structure between the 'parent' metal atoms. Both of these alloy types are of great importance.

6.1.1 The crystal structures of pure metals

Most pure metals adopt one of three crystal structures: A1, copper structure (cubic close-packed; Section 5.3.3); A2, tungsten structure (body-centred cubic; Section 5.3.4); or A3 magnesium structure (hexagonal close-packed; Section 5.3.5). The structures found at room temperature (25 °C) and atmospheric pressure are listed in Figure 6.1. The difference in energy between these structures is small, and changes in structure are commonly induced by changes in temperature and pressure. The different forms are called allotropes. Some changes induced by increased temperature are given in Table 6.1.

It is surprising, in view of the many structures that are derived from either the hexagonal (ABAB) or cubic (ABCABC) closest packing (see Section 5.4.1), that so few complex arrangements occur. Cobalt is one metal that shows this behaviour. Below about 435 °C the structure is a disordered random stacking of A, B and C planes of metal atoms. It can be transformed into the A3 structure by careful annealing at lower temperatures, and this transforms to the A1 structure above 435 °C.

Li A2 0.3509	Be A3 a 0.2286 c 0.3585											B	C
Na A2 0.4291	Mg A3 a 0.3209 c 0.5211											Al A1 0.4050	Si
K A2 0.5321	Ca A1 0.5588	Sc A3 a 0.3309 c 0.5268	Ti A3 a 0.2951 c 0.5686	V A2 0.3024	Cr A2 0.3885	Mn	Fe A2 0.2867	Co	Ni A1 0.3524	Cu A1 0.3615	Zn A3 a 0.2665 c 0.4947	Ga	Ge
Rb A2 0.5705	Sr A1 0.6084	Y A3 a 0.3648 c 0.5732	Zr A3 a 0.3232 c 0.5148	Nb A2 0.3300	Mo A2 0.3147	Tc A3 a 0.2738 c 0.4393	Ru A3 a 0.2706 c 0.4282	Rh A1 0.3803	Pd A1 0.3890	Ag A1 0.4086	Cd A3 a 0.2979 c 0.5620	In 0.1663	Sn
Cs A2 0.6141	Ba A2 0.5023	La	Hf A3 a 0.3195 c 0.5051	Ta A2 0.3303	W A2 0.3165	Re A3 a 0.2761 c 0.4458	Os A3 a 0.2734 c 0.4392	Ir A1 0.3839	Pt A1 0.3924	Au A1 0.4078	Hg	Tl A3 a 0.3457 c 0.5525	Pb A1 0.4950

Figure 6.1 The crystal structures of the metallic elements. Note: unit cell parameters are in nanometres. The figure given for cubic structures is a_0; A1 = copper (cubic close-packed) structure; A2 = tungsten (body-centred cubic) structure; A3 = magnesium (hexagonal close-packed) structure

Table 6.1 Allotropic structures of metals

Element	Room-temperature structure	High-temperature structure	Transition temperature/°C
Ca	A1	A2	445
Sr	A1	A2	527
Sc	A3	A2	1337
Ti	A3	A2	883
Zr	A3	A2	868
Hf	A3	A2	1742
Y	A3	A2	1481
Fe	A2	A1	912
Co	(A3)	A1	435

The metals lanthanum (La), praseodymium (Pr) and neodymium (Nd) adopt mixed closest packing that has an ABAC repeat. Samarium (Sm), has a packing repeat BABCAC.

To the right-hand side of Figure 6.1, the simple structures are no longer found. These elements were once called the semimetals. In them, the outer electrons are not completely lost to the structure, and the shapes of the electron orbitals begin to influence bonding. This first becomes noticeable in the anomalous metal, mercury (Hg). The structure can be thought of as the A1 structure compressed along one body diagonal, so that the crystal structure becomes rhombohedral. Similarly, indium has a slightly distorted A1 structure.

Stronger bonding effects are found within the carbon group. At normal temperatures and pressures, the bonding in carbon (graphite) is a mixture of sp^2 and weaker van der Waals bonding. At high pressures, graphite transforms to the diamond structure, in which the atoms are linked by sp^3 hybrid bonds arranged tetrahedrally. The diamond structure is adopted by silicon and germanium at normal temperatures and pressures. Tin is a borderline solid from the point of view of bonding effects. At temperatures below 13.2 °C, the allotrope α-tin (grey tin) is stable. This has the diamond structure built with sp^3 hybrid bonding. At temperatures above 13.2 °C the stable structure is β-tin (white tin). This is the normal metallic form of tin. Metallic tin is not stable at most normal temperatures. However, the transition from white to grey tin is slow, and the metallic form is stabilised by metallic impurities, so that tin is normally found in the metallic form. Although white tin is metallic, the structure is complex and not simply related to the A1, A2 or A3 structures, revealing the importance of bonding effects. With lead, the increased atomic size leads to extensive outer-electron delocalisation. The solid is metallic and the structure is the A1 type.

In the semimetals antimony, arsenic and bismuth, bonding effects are more pronounced, and the structures are not related to the simple structures of most metals. Bismuth, the heaviest, is the most 'metallic', and phosphorus, lying above antimony in the periodic table, is not even considered to be a semimetal.

6.1.2 Metallic radii

If we assume that the structures of metals are made up of touching spherical atoms, it is quite easy, knowing the structure type and the size of the unit cell, to work out metallic radii. The relationship between the cell edge, a_0, for cubic crystals – a_0 and c_0, for hexagonal crystals – and the radius of the component atoms, r, for the three common metallic structures is given below.

For the A1, copper structure [face-centred cubic (fcc)] the atoms are in contact along a cube face diagonal, so that

$$r = \frac{a_0}{2\sqrt{2}}$$

The separation d of the close-packed atom planes (along a cube body diagonal) is

$$d = \frac{a_0}{\sqrt{3}} = d_{111}$$

Each atom has 12 nearest neighbours.

For the A2, tungsten structure [body-centred cubic (bcc)] the atoms are in contact along a cube body diagonal, so that

$$r = \frac{\sqrt{3}\,a_0}{4}$$

Each atom has 8 nearest neighbours.

For the A3, magnesium structure [hexagonal close packed (hcp)] the atoms are in contact along the a axis, hence,

$$r = \frac{a_0}{2}$$

The separation of the close packed atom planes is $c_0/2$. The ratio of c_0/a_0 in an ideal close-packed structure is $\sqrt{8}/\sqrt{3} = (1.633)$. Each atom has 12 nearest neighbours.

As in the case of ionic radii, the radius determined experimentally is found to depend on the number of nearest neighbours – the coordination number – of the atom in question. Both the A1 (fcc) and A3 (hcp) structures have 12 nearest neighbours [i.e. a coordination number of 12 (CN12)], and the radius determined will be appropriate to that coordination. The A2 (bcc) structure has 8 nearest neighbours [i.e. a coordination number of 8 (CN8)], and it is necessary to convert the radii measured, r (CN8), directly into those appropriate to 12 coordination, r (CN12), in order to obtain a self-consistent set of values. The conversion can be made by using the empirical formula

$$r(\text{CN12}) = 1.032\, r\,(\text{CN8}) - 0.0006$$

where the radii are measured in nanometres. Figure 6.2 shows metallic radii for coordination number 12. The majority of the elements shown have the A1, A2 or A3 structure or close approximations to them. A few important elements, notably manganese (Mn), gallium (Ga) and tin (Sn), which have complex structures, are also included. The radii for these latter elements are derived from a comparison of the interatomic distances in many alloys with appropriate structures.

There are a number of trends to note. In the 'well-behaved' alkali metals and alkaline earth metals the radius of an atom increases smoothly as the atomic number increases. The d transition metals all have rather similar radii as one passes along the period, and these generally increase with atomic number going down a group. The same is true for the lanthanides and actinides.

6.1.3 Alloy solid solutions

Alloys are important because they often show superior properties to pure elements, especially mechanical properties. There are large numbers of alloys, many of which have unusual and complex structures. Here we will mention only two sorts of

Li 0.1562	Be 0.1128											B	C
Na 0.1911	Mg 0.1602											Al 0.1432	Si
K 0.2376	Ca 0.1974	Sc 0.1641	Ti 0.1462	V 0.1346	Cr 0.1282	Mn 0.1264	Fe 0.1274	Co 0.1252	Ni 0.1246	Cu 0.1278	Zn 0.1349	Ga 0.1411	Ge
Rb 0.2546	Sr 0.2151	Y 0.1801	Zr 0.1602	Nb 0.1468	Mo 0.1400	Tc 0.1360	Ru 0.1339	Rh 0.1345	Pd 0.1376	Ag 0.1445	Cd 0.1568	In 0.1663	Sn 0.1545
Cs 0.2731	Ba 0.2243	La 0.1877	Hf 0.1580	Ta 0.1467	W 0.1408	Re 0.1375	Os 0.1353	Ir 0.1357	Pt 0.1387	Au 0.1442	Hg	Tl 0.1716	Pb 0.1750

Figure 6.2 Metallic radii (nm) for metallic elements in 12 coordination

alloy – substitution and interstitial solid solutions – with structures closely related to the pure metals just discussed. Substitutional solid solutions have a structure identical to one of the metals involved – the parent structure – with the other alloy-forming atoms, or foreign atoms, simply occupying positions in the structure normally occupied by the parent atoms. Interstitial solid solutions are formed when very small atoms percolate the parent structure and sit in normally unoccupied interstitial positions. The foreign atoms in each of these examples can be regarded as being in solution in the matrix of the parent metal.

6.1.3.1 *Substitutional solid solutions*

The likelihood of a substitutional solid solution forming between two metals will depend on a variety of chemical and physical properties. A large number of alloy systems were investigated by Hume-Rothery, in the first part of the 20th century, with the aim of understanding the principles that controlled alloy formation. His findings with respect to substitutional solid solution formation are summarised in the empirical Hume-Rothery solubility rules. The likelihood of obtaining a solid solution between two metals is highest when:

1. the crystal structure of each element of the pair is identical;
2. the atomic sizes of the atoms do not differ by more than 15 %;
3. the elements do not differ greatly in electronegativity (otherwise they will form compounds with each other), implying that they should be near to each other in the periodic table;
4. the elements have the same valence, implying that they should lie in the same group of the periodic table.

Although formulated a century ago, these ‘rules’ remain of value for predicting substitutional alloy formation.

The rules predict, for example, that nickel–copper (Ni–Cu, see Section 4.2.2) and copper–gold (Cu–Au) should form extensive substitutional solid solutions. What they do not predict is the likelihood that the atoms in the solid solution will order. In such cases a new phase, an ordered solid solution, will form. This happens in many systems, especially when random substitutional solid solutions are annealed at lower temperatures. For example, a copper–gold alloy heated at temperatures between the melting point, (about 890 °C), and 410 °C, and then rapidly cooled, will have a random distribution of copper and gold atoms over the sites of the A1 (fcc) structure (Figure 6.3a). However, if the alloy is heated at a temperature of about 400 °C for some time, the atoms of copper and gold will order into a new arrangement. The ordering that occurs depends on the composition of the alloy, and two main patterns have been characterised: Cu_3Au and CuAu.

The structure of the copper-rich alloy phase, Cu_3Au, is shown in Figure 6.3(b). The gold atoms are located at the corners of the cubic unit cell and the copper atoms at the face centres. The ordered structure of the CuAu alloy, which contains equal numbers of atoms (Figure 6.3c) has alternating {1 0 0} planes composed of either copper or gold

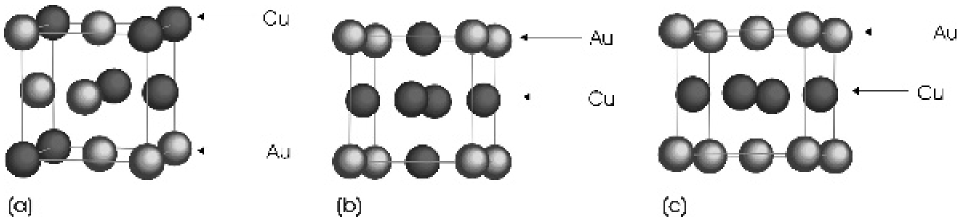

Figure 6.3 The cubic crystal structures of (a) disordered CuAu, (b) ordered Cu_3Au and (c) ordered CuAu I

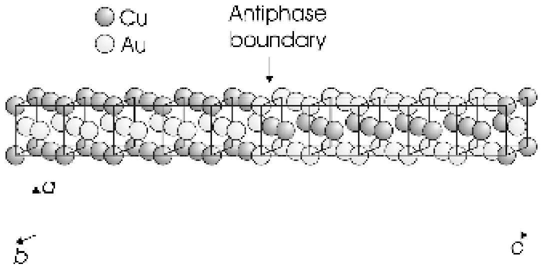

Figure 6.4 The ordered structure of CuAu II. The *c* axis is approximately 10 × the cubic unit cell *c* axis of CuAu I

atoms. This structure is called the CuAu I structure. Arrangements that are more complex also occur. For example, in the CuAu II structure (Figure 6.4) the structure 'slips' every five CuAu unit cells, to give an overall repeat along the *c* axis of approximately 10 times the cubic cell parameter. The plane of the displacement is an antiphase boundary. [Note that 'antiphase' means 'out of register', and the word 'phase' is used in a different sense from that in phase diagrams.]

Large numbers of ordered structures can be formed by appropriate annealing conditions, and these structures play a large part in determining the physical, especially mechanical, properties of the alloys. Annealing is therefore a very important process in the production of materials with specific properties.

6.1.3.2 Interstitial solid solutions

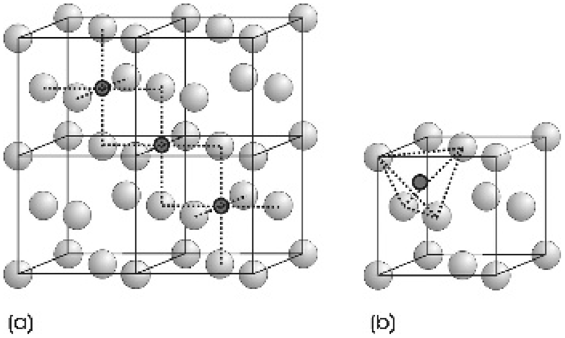

Figure 6.5 (a) Octahedral and (b) tetrahedral sites in the A1 structure. Four unit cells are drawn in part (a), and not all equivalent sites are marked

Just as atoms should ideally be of similar sizes to form extensive substitutional solid solutions, to form an interstitial solid solution the radius of the foreign atom should be less than about half of the atomic radius of the atoms of the parent structure. Traditionally, the interstitial alloys most studied are those of the transition metals with carbon and nitrogen, as the addition of these atoms to the crystal structure increases the hardness of the metal considerably. Steel remains the most important traditional interstitial alloy from a world perspective, consisting of carbon atoms distributed at random in interstitial sites within the A1 (fcc) structure of iron to form the phase austenite. More recently, hydrogen storage has become important and, today, interstitial alloys formed by incorporation of hydrogen into metals are of considerable interest.

The sites that are available for foreign atoms in interstitial alloys are of tetrahedral or octahedral geometry. The representation of the A1 (fcc) or A3 (hcp) structures as sphere packings (Section 5.4.1) shows that there are twice as many tetrahedral sites and the same number of octahedral sites present as metal atoms.

In a unit cell of the A1 structure, containing four metal atoms, the octahedral sites lie at the midpoints of each of the cell edges, with a further site at the cell centre (Figure 6.5a). Each site on a cell edge is shared by 4 cells, and there are 12 cell edges, hence each cell contains $\frac{1}{4} \times 12$ sites at the edges plus one at the cell centre, making four in total. The tetrahedral sites are found in each quarter of the unit cell, making 8 in all (Figure 6.5b). Two metal atoms are found per unit cell of the A3 structure and hence four tetrahedral sites and two octahedral sites per unit cell occur. In both of these structures, all of the tetrahedral sites and all of the octahedral sites have identical geometries (Figures 6.6a and 6.6b).

The A2 (bcc) structure also has 12 tetrahedral and 6 octahedral sites available. The octahedral sites lie

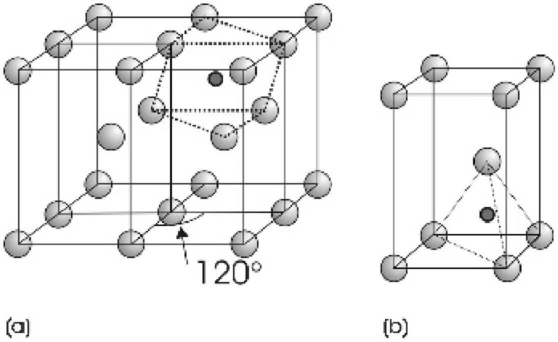

Figure 6.6 (a) Octahedral and (b) tetrahedral sites in the A3 structure. Four unit cells are drawn in part (a). Not all equivalent sites are marked

on all of the cube faces (Figure 6.7a), and the tetrahedral sites, also on the cube face, are slightly below them (Figure 6.7b). These octahedral and tetrahedral sites are of slightly different geometry from those in the A1 and A3 structures and, in addition, there are several different geometries found for the tetrahedral positions.

In all three structures the octahedral sites are larger and can accommodate carbon and nitrogen atoms. The tetrahedral sites are smaller, and only hydrogen commonly uses these positions.

The process by which these interstitial alloys form is similar in all systems. A reactive gas, typically hydrogen (H_2) for hydrides, methane (CH_4) for carbides, or ammonia (NH_3) for nitrides, decomposes on the metal surface. The atoms formed can then enter the structure, to occupy sites at random. The phases formed are often called α phases. Continued reaction leads to the formation of new structures, either by the ordering of the impurity atoms, as described for substitutional alloys (Section 6.1.3.1), or by more extensive structural rearrangements, as in cementite (Fe_3C).

Although the size of the foreign atoms is of importance, the sites that are occupied and the degree of occupancy of the available sites also depends critically on chemical interactions between the species. For example, in the α phase NbH_x only those tetrahedral sites with a particular geometry are occupied. The limiting composition of the α phase, approximately $NbH_{0.1}$, is achieved when only a fraction of these particular sites is filled. Chemical interactions then lead to the nucleation of the hydride NbH.

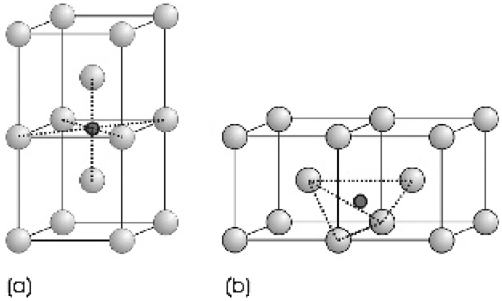

Figure 6.7 (a) Octahedral and (b) tetrahedral sites in the A2 structure. Two unit cells are drawn. Not all equivalent sites are marked

6.1.4 Metallic glasses

As mentioned in Section 3.2.3, metals can be made into a noncrystalline form by cooling at a rate of approximately 10^5–$10^6\ \mathrm{K\,s^{-1}}$. The first noncrystalline metallic material to be made in this way had a composition of $Au_{75}Si_{25}$. It was later confirmed that these rapidly cooled solids were glasses, with definite glass transition temperatures (see Section 6.3.1).

In order to make a metallic glass by rapid cooling it is necessary to disrupt the natural tendency of the liquid to crystallise. This can be achieved in a number of ways. First, a system having a deep eutectic point (see Section 4.2.3) is helpful, because then the liquid can cool significantly before solidification starts. Second, a system containing several metals, each of which crystallises in a different structure, will deter crystallisation. Last, mixtures of atoms with widely differing sizes crystallise less readily. This has led to a general formula for metallic glasses of $T_{70\text{–}90}(SM)_{0\text{–}15}(NM)_{10\text{–}30}$, where T is one or more transition metals, (SM) is one or more semimetals such as silicon (Si) or germanium (Ge), and (NM) is one or more nonmetals such as phosphorus (P) or carbon (C). These solids, which are usually produced in the form of ribbons, are used in transformer cores. A widely used magnetic material for this purpose is METGLAS®,[1] with a composition of $Fe_{40}Ni_{40}P_{14}B_6$. Other examples of transformer core materials include $Fe_{86}B_8C_6$ and $FeB_{11}Si_9$.

Studies of more complex systems have made it possible to fabricate glassy metals using much slower cooling rates, down to 10 K s^{-1}. This has opened the door to the production of glassy metals in bulk form compared to the ribbons normally produced by very rapid cooling. The same principles as mentioned above are used, but systems have tended to become more complex. For example, bulk glasses of interest in a variety of magnetic applications have formulae of which $Fe_{72}Al_5Ga_2P_{11}C_6B_4$ is typical. Another recently developed metallic glass, Vitreloy, which has superior mechanical properties, has a composition $Zr_{1.65}Ti_{0.55}Cu_{1.125}Ni_{0.9}B_{0.225}$. It is used, among other things, for golf-club heads.

6.1.5 The principal properties of metals

As with all materials, the observed properties arise via the interaction of bonding and microstructure. The typically metallic properties of good electrical and thermal conductivity are consequences of the metallic bond. The free electrons can move throughout the metal under the imposition of only a very low driving force, voltage or thermal energy, and the magnitude of the electrical conductivity in a metal is closely related to that of the thermal conductivity. The precise relationship is called the Wiedemann–Franz law, which states that the ratio of thermal conductivity to electrical conductivity is given as follows:

$$\frac{\text{thermal conductivity}}{\text{electrical conductivity}} = \frac{3Tk^2}{e^2}$$

where T is the temperature (in K), k is the Boltzmann constant and e is the charge on the electron.

The high reflectivity of metals is also due to the free electrons. When light photons strike the metal surface, those electrons near to the Fermi surface can absorb the photons, as plenty of empty energy states lie nearby. However, the electrons can just as easily fall back to the lower levels originally occupied, and the photons are re-emitted. A detailed explanation of reflectivity of a metal requires knowledge of the exact shape of the Fermi surface and the number of energy levels (density of states) at the Fermi surface.

When two dissimilar metals are joined, electrons will flow from the higher Fermi energy to the lower. This gives rise to thermoelectric effects and to the operation of thermocouples. Less directly, the Fermi energy is related to the extent to which metals corrode.

Alloying with other metals or nonmetals in small amounts will not change these physical attributes drastically but the foreign atoms generally impede electron transport. Alloys therefore tend to have poorer electrical conductivity than do pure metals. If a new phase forms, the Fermi surface and the density of states at the Fermi surface will change and the electrical conductivity will alter abruptly. For example, the incorporation of hydrogen within magnesium will initially produce an interstitial alloy with metallic properties but an inferior electronic conductivity. Additional hydrogen leads to the formation of the hydride MgH_2, which is transparent and nonmetallic.

An important mechanical property of a metal is that of ductility, meaning that a metal can be deformed easily without breaking and can retain the deformed shape indefinitely. Pure metals in particular are soft and easily drawn into wires or hammered into foils. This property can be attributed to the crystal structures of the metals, which consist of packing of more or less spherical atoms. These can readily roll over each other to produce the deformation. There are no strong localised bonds to be broken, and so the metallic bonding does not hinder the deformation. However, metallic bonding does occur and, generally, calculations show that a pure metal deforms more easily than the metallic bonds should permit. The conflict is resolved by recognition of the role that defects play in the

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(1) METGLAS is a registered tradename of AlliedSignal Inc.

crystals. Dislocations allow deformation to occur without the necessity of breaking significant numbers of metallic bonds at any moment.

Associated with the easy deformability of a metal is the fact that metals can easily be hardened. The explanation again lies with the dislocations present in the crystals. The trapping of these dislocations, called pinning, prevents easy deformation, and hence the metal becomes harder. At its simplest level, this can come about by the introduction of impurities and the formation of substitutional or interstitial alloys, a fact used empirically since the Bronze Age. However, more effective hardening comes about if precipitates form in the crystal. These, brought about by alloying and annealing, produce very hard metals. Steels, already far harder than pure iron, are hardened further by the incorporation of carbon or nitrogen followed by heat treatment that causes these elements to combine and form precipitates in the parent crystals. Alloy compositions that result in large amounts of second phase formation are hardest, as dislocation movement becomes completely impossible, with the consequence that the metal becomes brittle. Thus cast iron, which contains numerous precipitates of cementite and graphite, is very brittle, as are metals that contain large quantities of hydrogen.

In this short section, only the principal properties of metals and a simple appreciation of the origins of these properties are outlined. Far more detail will be found in Part 4, Chapters 10–15.

6.2 Ceramics

Ceramics are inorganic materials fabricated by a high-temperature chemical reaction. Most ceramics are oxides, but the term is also used for silicides, nitrides and oxynitrides, hydrides and other inorganic materials. Ceramics are regarded as chemically inert materials that are hard, brittle thermal and electronic insulators.

It is convenient to consider ceramics that are essentially silicates, called traditional ceramics, separately from all of the others. This latter group comprises engineering ceramics, with important mechanical properties, electroceramics, when electronic properties are emphasised, or glasses (noncrystalline ceramics). Traditional ceramics are used in utility applications such as brickwork and drainage pipes as well as for porcelain and other fine decorative ceramic objects. Engineering ceramics are used to extend the operating range available to metallic components. They are valued for high-temperature stability and for extreme hardness. Typical uses include: hard surface coatings on metallic components [titanium nitride (TiN), tungsten carbide (WC) and diamond]; inert high-temperature components (valves, cylinder liners, ceramic shielding and blankets, and furnace linings); high-speed cutting-tool inserts; and as abrasives [alumina (Al_2O_3), silicon carbide (SiC) and diamond]. Electroceramics are very-high-purity materials that possess unique electronic properties, varying from insulating to superconducting. Electroceramics form the active element in many gas sensors, temperature sensors, batteries and fuel cells. Ceramic magnets are widely used in motors. Ceramics are also important in fluorescent lighting and as components of computer displays.

6.2.1 Bonding and structure of silicate ceramics

The Earth's crust is composed very largely of silicates, as are the majority of semiprecious gemstones. Natural silicates are minerals that were formed from a complex molten magma and it is therefore not surprising that they are of variable composition. To each mineral is ascribed an 'ideal' composition – the composition that it would have if it were homogeneous. Isomorphous replacement, in which some cations are replaced by others of similar size, although not necessarily of the same charge, is common in minerals. Thus, the cations Na^+, Mg^{2+}, Ca^{2+}, Mn^{2+} and Fe^{3+} are readily interchangeable, as are the anions O^{2-}, F^- and OH^-. Aluminium, which is to the left of silicon in the periodic table, occupies a special role in silicate chemistry. Aluminium can replace silicon in silicates and does so in a random manner and to an indefinite extent. Isomorphous replacement produces substitutional defects in the crystal structure.

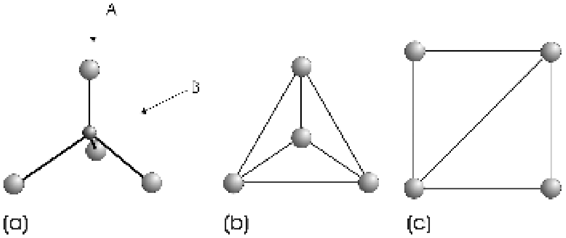

Figure 6.8 (a) Perspective view of a silicon – oxygen SiO_4 tetrahedron, (b) projection down A and (c) projection down B

The mineral hornblende provides an illustrative example of isomorphous replacement. The ideal composition of this silicate is $Ca_2Mg_2(Si_4O_{11})_2(OH)_2$. A typical analysis of a naturally occurring sample might well show that up to a quarter of the silicon is replaced by aluminium; most of the Mg^{2+} replaced by Fe^{2+}, together with smaller amounts of Fe^{3+}, Mn^{2+} and Ti^{4+}, and about a third of the Ca^{2+} replaced by a mixture of Na^+ and K^+.

Silicon is a small atom with an electronic structure [Ne] $3s^2$ $3p^2$. Silicon lies below carbon in the periodic table and, like carbon, makes use of sp^3 hybrid bonds, which are arranged tetrahedrally. In silicates, each silicon atom is usually linked to oxygen to form an $[SiO_4]$ tetrahedron (Figure 6.8 and Figure 5.29, page 139). The bonds are very strong, and silicon–oxygen tetrahedra are stable and vary very little in size. The Si–O distances are always close to 0.162 nm, and the O–O distances to 0.27 nm. In terms of an ionic model, the $[SiO_4]$ tetrahedral group has an overall charge of −4, and is written $[SiO_4]^{4-}$.

These tetrahedra form the basic structural unit in silicate chemistry, and the $[SiO_4]$ unit dominates silicate chemistry and physics. They are found as isolated units, or condensed to form $[SiO_4]$ chains, sheets or three-dimensional networks. In forming these $[SiO_4]$ structures, only the vertices of the tetrahedra are shared, never edges or faces.

As a first approximation, silicates can be divided into three groups.

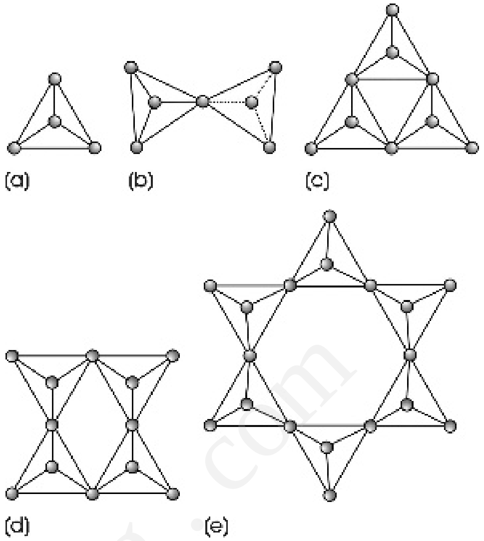

Figure 6.9 Corner-linked $[SiO_4]$ units found in ionic silicates: (a) isolated $[SiO_4]^{4-}$, (b) $[Si_2O_7]^{6-}$, (c) $[Si_3O_9]^{6-}$, (d) $[Si_4O_{12}]^{8-}$ and (e) $[Si_6O_{18}]^{12-}$

6.2.1.1 Three-dimensional silicates containing isolated silicate groups (ionic silicates)

These show little anisotropy of properties; that is, properties are the same in all crystallographic directions. There are a number of important divisions within this group, based on the geometry of the silicate groups. These are: isolated $[SiO_4]^{4-}$ units; pairs, $[Si_2O_7]^{6-}$; three-membered rings, $[SiO_9]^{6-}$; four-membered rings, $[Si_4O_{12}]^{8-}$; and six-membered rings, $[Si_6O_{18}]^{12-}$ (Figure 6.9).(2) Some examples of ionic silicates are listed in Table 6.2.

6.2.1.2 Silicates containing chains or sheets of silicate tetrahedra (extended anion silicates)

There are thousands of these compounds, many of which are valuable minerals. Even the simplest structure, a single chain of tetrahedra linked by corners,

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(2) The figures in this section are descriptive. In real structures the silicon–oxygen tetrahedra are often slightly distorted, and crystal structure studies should be consulted when precise detail is required.

Table 6.2 A summary of silicate structures

Structure	Formula	Mohs Hardness	Examples
Isolated silicate groups:			
Monomer	$[SiO_4]^{4-}$	8–5	Mg_2SiO_4, forserite, (*olivines*) $Ca_3Cr_2(SiO_4)_3$, uvarovite, (*garnets*)
Dimer	$[Si_2O_7]^{6-}$	5	$Sc_2Si_2O_7$, thortveitite
Three-ring	$[Si_3O_9]^{6-}$	7–4	$BaTi(Si_3O_9)$, benitoite
Four-ring	$[Si_4O_{12}]^{8-}$	7–4	$Ca_3Al_2(BO_3)(Si_4O_{12})(OH)$, axinite
Six-ring	$[Si_6O_{18}]^{12-}$	6–4	$Be_3Al_2(Si_6O_{18})$, beryl $NaMg_3Al_6(BO_3)_3(Si_6O_{18})(OH)_4$, tourmaline
Chains:			
Single	$[SiO_3]^{2-}$	7–4	$MgSiO_3$, enstatite, (*pyroxenes*)
Double	$[Si_4O_{11}]^{6-}$	5	$Ca_2Mg_5Si_8O_{22}(OH)_2$, tremolite, (*amphiboles*)
Sheets:			
Single silicate layer	$[Si_2O_5]^{2-}$	3–1	$Na_2Si_2O_5$
Double silicate layer	$[SiO_2]$	3–1	$CaAl_2Si_2O_8$ (half Si replaced by Al)
Single silicate plus single hydroxide layer	$[Si_2O_5]$ plus hydroxide	3–1	$Al_2(OH)_4Si_2O_5$, kaolinite, (*clays*) $Mg_3(OH)_4SiO_5$, chrysotile, (*clays*)
Single silicate plus double hydroxide layer	$[Si_4O_{10}]$ plus hydroxide	3–1	$Al_2(OH)_2Si_4O_{10}$, pyrophyllite, (*clays*) $Mg_3(OH)_2Si_4O_{10}$, talc, (*clays*)
Single silicate plus double hydroxide	$[Si,AlO_{10}]$	3–1	$KAl_2(OH)_2Si_3AlO_{10}$, muscovite, (*micas*) $KMg_3(OH)_2Si_3AlO_{10}$, phlogopite, (*micas*)
Networks:			
Silicate	$[SiO_2]$	8	SiO_2, quartz
Aluminosilicate	$[(Si,Al)_4O_8]$	7–5	$KAlSi_3O_8$, *feldspars*

can adopt several different configurations, one of which is drawn in Figure 6.10(a). The formula of the single chains is $[SiO_3]^{2-}$, leading to compounds of formula MSiO$_3$, the *pyroxenes*. Two single pyroxene chains can join by linking half of the free vertices to form a double chain, of formula $[Si_4O_{11}]^{6-}$ (Figure 6.10b). These double chains are found in the *amphiboles*, a group including several forms of asbestos. Linkage of the free vertices in the plane of Figure 6.10(b) leads to single silicate layers (Figures 6.11a and 6.11b), and linkage of the free vertices that lie above the plane of Figure 6.11(a) will form double silicate layers (Figure 6.11c).

These latter structures are rather rare in mineralogical terms, but silicate layers in which the free vertices link to a layer of magnesium or aluminium hydroxide octahedra to produce composite layers

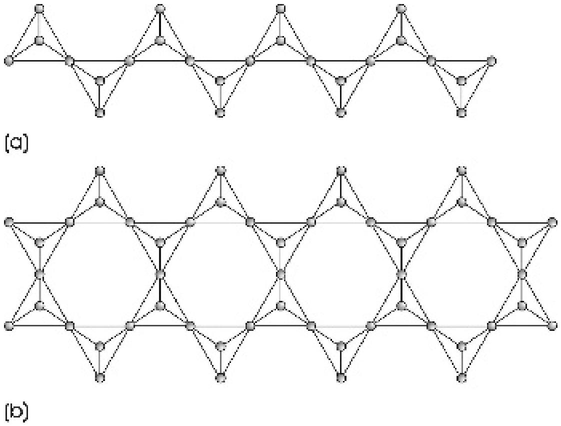


Figure 6.10 (a) Single-chain $[SiO_3]^{2-}$ strings, found in *pyroxenes* and (b) double-chain $[Si_4O_{11}]^{6-}$ strings found in *amphiboles*

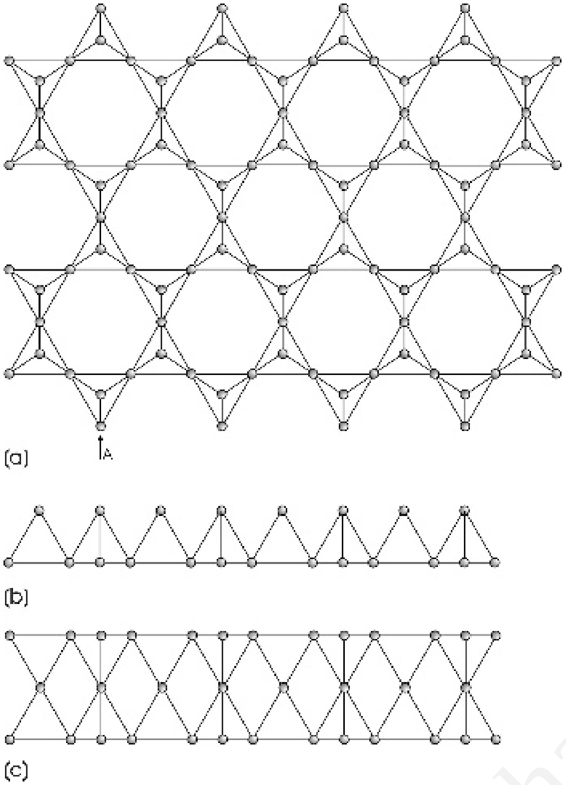


Figure 6.11 (a) A single sheet of corner-linked [SiO_4] tetrahedra, (b) the same sheet viewed along A and (c) double sheets formed by joining two layers of the type shown in part (a) by the free tetrahedral vertices, one over the other, viewed along A

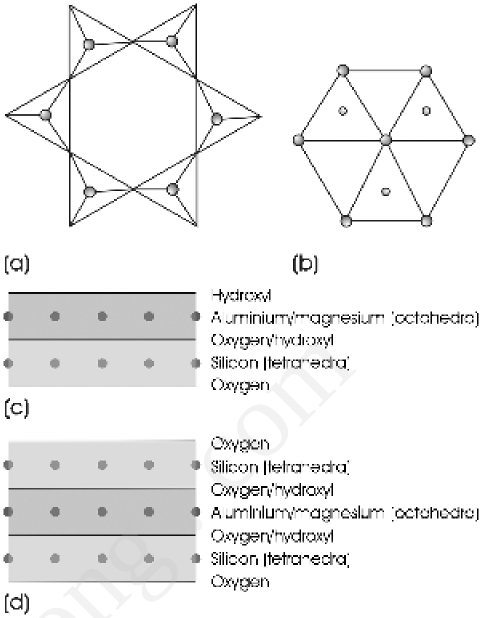
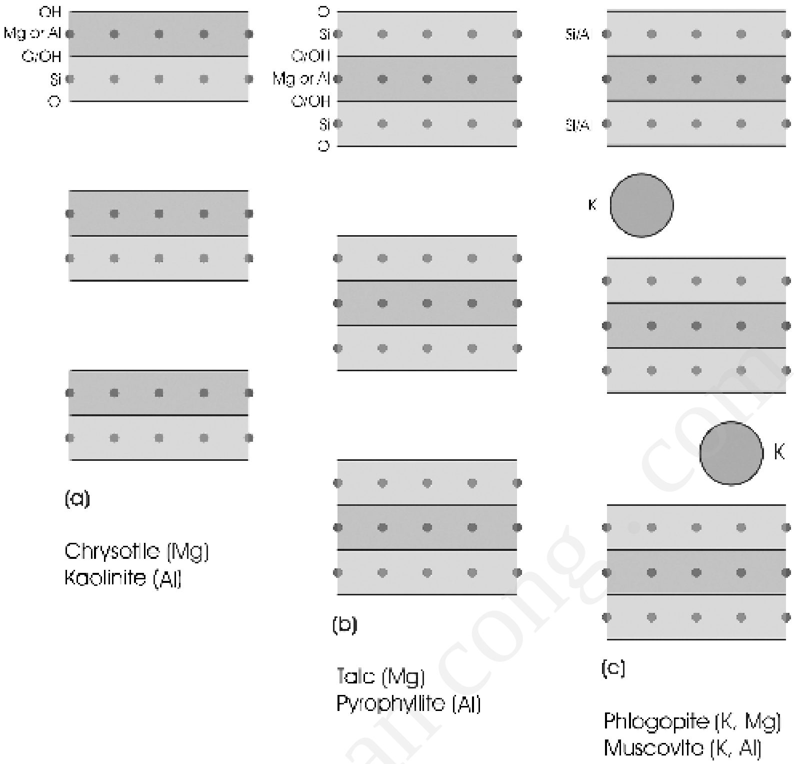


Figure 6.12 The structure of clays and related minerals: (a) a single layer of corner-linked [SiO_4] tetrahedra (the upper layer of apical oxygen atoms are drawn as spheres); (b) a basal close-packed layer of oxygen atoms in $Mg(OH)_2$ or $Al(OH)_3$ (large spheres) with cations in the octahedral sites above the layer (small spheres); (c) a composite layer formed by uniting a single silicate layer as in part (a) and a single hydroxide layer as in part (b); (d) a composite sandwich structure formed by uniting two silicate layers as in part (a), with a single hydroxide layer, as in part (b)

form an enormous group that includes many clays. These composite layers are possible because the positions of the oxygen atoms at the vertices of a silicate layer matches well the geometry of the close-packed array of oxygen atoms that occurs in the hydroxides $Mg(OH)_2$ and $Al(OH)_3$ (Figures 6.12a and 6.12b). In both of these structures, the cations are in octahedral sites (Figure 6.12b). The match between the oxygen arrays allows a single silicate layer to link to a single hydroxide layer (Figure 6.12c) or two silicate layers to sandwich a hydroxide layer (Figure 6.12d). The single silicate plus hydroxyl layer is found in clays such as kaolinite and in minerals such as chrysotile asbestos (Figure 6.13a). Double silicate sandwich layers enclosing a hydroxyl layer are found in minerals such as talc (Figure 6.13b). If aluminium replaces some of the silicon, the silicate layers take on a negative charge. This is counterbalanced by cations placed between the layers, to form the micas (Figure 6.13c).

6.2.1.3 Silicates with [SiO_4] tetrahedra linked by all vertices to form a three-dimensional covalent network

This type of network can adopt a number of different conformations, typified by the polymorphs of silica, SiO_2. The structure of the commonest of



(a)

Chrysotile (Mg)
Kaolinite (Al)

(b)

Talc (Mg)
Pyrophyllite (Al)

(c)

Phlogopite (K, Mg)
Muscovite (K, Al)

Figure 6.13 Structures of some clay and mica related minerals, formed from composite silicate–hydroxide layers

these polymorphs, quartz, is shown schematically in Figure 5.30 (page 139). When aluminium replaces some of the silicon, the framework takes on a negative charge, compensated for by the insertion of cations into the network. This produces the large group of minerals, the aluminosilcates, which includes the important *feldspars*, which make up many strong rocks, and the *zeolites* and *ultramarines*. All of these are of considerable industrial importance.

6.2.2 Bonding and structure of nonsilicate ceramics

Almost every inorganic oxide that does not contain silicon, as well as many carbides and nitrides, can be thought of, to some extent, as a nonsilicate ceramic. The bonding across this great variety of compounds varies widely, and no general bonding type predominates.

A large number of important ceramics adopt the *halite* (NaCl, B1) structure (Section 5.3.9). These include the oxides magnesium oxide (MgO) and nickel oxide (NiO) and many carbides and nitrides with a formula *MX*, such as titanium carbide (TiC) and titanium nitride (TiN). The oxides are often considered as ionic solids. The carbides and nitrides have metallic properties.

Alumina, Al_2O_3, is an oxide considered ionic in character. It is able to withstand high temperature and is used in laboratory furnaceware. A number of other important oxides, including Fe_2O_3 and Cr_2O_3, adopt the same (*corundum*) structure. The structure is most easily described as a hexagonal close-packed array of oxygen ions, with Al^{3+} ions distributed in an ordered fashion over two-thirds of the available octahedral sites (Figure 6.14). A number

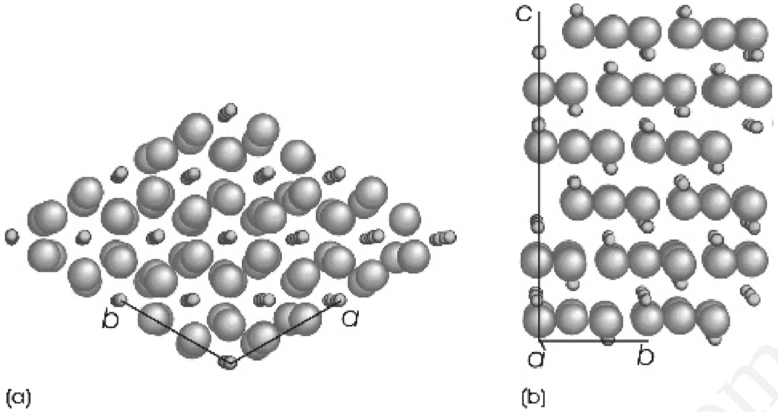


Figure 6.14 The structure of corundum, Al_2O_3: (a) projection down the [0 0 1] direction and (b) projection close to the [1 0 0] direction

of well-known gemstones consist of corundum doped with small amounts of transition metal impurities. Ruby is corundum containing about a half percent of Cr^{3+} substituted for Al^{3+}, and sapphire contains a small amount of Ti^{4+} and Fe^{2+} substituted for the Al^{3+}. Although the colour in these precious stones is due to the substitutional defects present, the exact hue exhibited is related to the unit cell parameter of the matrix.

Zirconia, ZrO_2, is an important ceramic because it is able to withstand high temperatures. At room temperature, the structure contains irregular polyhedra formed by seven oxygen ions surrounding each Zr^{4+} cation. The structure is monoclinic. At a temperature of about 1100 °C it becomes tetragonal, a change caused by the coordination polyhedra becoming more regular. At temperatures of about 2300 °C the structure becomes cubic and adopts the fluorite, CaF_2, structure (Figure 6.15). In this structure, each Zr^{4+} ion is surrounded by eight oxide ions at the corners of a cube. The structure can be visualised as an array of ZrO_8 cubes, each linked by all edges, in a three-dimensional checkerboard array. The monoclinic to tetragonal crystallographic transformation at approximately 1100 °C involves the crystals in a significant volume change. This causes cracking and weakness in ceramic components and makes it impossible to use zirconia in its pure state for high-temperature components. However, the cubic form can be stabilised by the

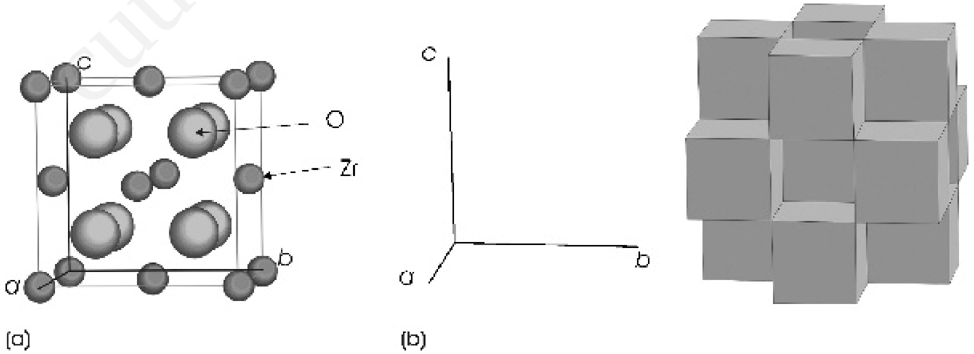


Figure 6.15 The cubic ZrO_2 (*fluorite*, CaF_2-type) structure. (a) a single unit cell and (b) the structure drawn as a stacking of (ZrO_8) cubes linked by edge sharing

addition of impurities such as calcia, CaO, in which Ca^{2+} ions substitute for Zr^{4+} ions in the structure (see Section 3.4.5). The resulting calcia-stabilised zirconia remains cubic from room temperature to the melting point, above 2300 °C, allowing it to be used for high-temperature applications.

The structures of a number of other important nonsilicate ceramics are discussed elsewhere, (Chapters 5, 8–14 and 16).

6.2.3 The preparation and processing of ceramics

Many of the characteristic properties of ceramics arise during manufacturing. Ceramic bodies are made by high-temperature firing (heating) routes that induce chemical reactions to take place, during which the final material is produced.

Traditional ceramics are mainly made from mixtures of clays, silica (often extracted as flint) and feldspars (especially $K_2Al_2Si_6O_{16}$ and $Na_2Al_2Si_6O_{16}$). Low-quality structural products such as bricks and pipes are made directly from the appropriate clay. Higher-quality ceramics such as porcelain are made from carefully controlled amounts of specific clay, flint and feldspar. The use of these three major components has led to the name triaxial whitewares for these materials.

Clay-based traditional ceramics are first formed into the shape desired by using traditional potters' techniques or automated processes. The resulting shapes are then heated to 1000 °C or higher. At these temperatures, the clays initially react to lose water and subsequently hydroxyl ions. The residues react to give a mixture of new phases, including glasses. Considerable shrinkage usually occurs during these reactions, and the production of an object with a precise size and shape remains a problem.

Engineering ceramics and electroceramics are usually pure single phases. Many are made by (a) milling the components to produce a fine powder; (b) pressing this into the desired shape; and (c) firing (heating to a high temperature). This third step is important for the production of the final shape in a useful form, and heating cycles are often complex. Initial heating is usually at a low temperature, 100–400 °C, to remove water and to burn off binder (an organic material used to cement the dry grains together). At a later stage of processing, the material is heated to a final temperature, in excess of 1000 °C, to sinter the particles and allow any chemical reactions to occur (see Section 8.4). In this final stage, some components may melt and in some cases (i.e. porcelain) one of the products is a glass. This is called vitrification.

Hard ceramic surface coatings on metallic components can be made by heating the metal in an appropriate gaseous atmosphere. Reaction takes place at the metal surface and atoms from the gaseous component diffuse into the surface layer. Thus, if titanium is heated in nitrogen gas a layer of titanium nitride (TiN) will form on the surface as a hard layer.

6.2.4 The principal properties of ceramics

The principal properties of ceramics arise from a combination of chemical bonding and the atomic defects and microstructure resulting from the fabrication techniques described above.

The bonding, whether described as ionic or covalent, is strong, which ensures that the solids are chemically inert and often stable to high temperatures (refractory). Refractory ceramics are widely used in furnaces and other high-temperature equipment. In addition, in aerospace applications refractory components are used both externally, to protect the outside of re-entry modules, and internally, in rocket motors.

The lack of free electrons endows basic ceramics with poor thermal and electronic conductivity. The chemical flexibility of ceramics, however, allows them to be selectively doped with other ions. In particular, doping with transition metal or lanthanide ions generates a wide variety of colours and can radically alter electronic and magnetic properties. Thus, insulators can be transformed into superconductors. How this comes about is described in Part 4, Chapters 10–15.

Ceramics do not deform very easily at ordinary temperatures, as strong chemical bonds must be broken and, unlike metals, dislocation movement is severely hampered. Generally, stress results in brittle fracture, especially under impact (see Section 10.1.7). However, in large part, the brittle nature of ceramics arises not from the bonding or dislocation density but in the microstructure. Surface flaws cause many ceramics to fail catastrophically when flexed, and pores in the structure, resulting from the chemical reactions that take place during high-temperature fabrication, are another source of weakness. Although ceramics have a rather low tensile strength and readily fracture when stretched they are much stronger when compressed. This property, coupled with the strong bonding, makes ceramics hard, and they are used as abrasives, cutting tools and hard coatings. Mechanical failure under compression also occurs because of structural defects, including voids and pores, large grains and foreign inclusions, rather than by bond breaking.

6.3 Glass

Most glasses are oxides, but specialised glasses such as metallic glasses, are becoming increasingly important. Glass is usually understood to mean a hard, transparent, fairly strong, corrosion-resistant material, in which the main component is silica, SiO_2. These silicate glasses are the only glasses discussed in this Chapter. There are a number of naturally occurring silicate glasses, including obsidian (a volcanic rock which is black as a result of iron oxide impurities), pumice (a glassy froth), flint and opal. These all show the typical glass properties of hardness and brittleness.

Silicate glass production marks an early stage in civilisation. Faience was made by the Egyptians thousands of years ago. This material was made from moulded sand coated with 'natron', a residue of minerals left after flooding of the River Nile, consisting mainly of calcium carbonate ($CaCO_3$), sodium carbonate (Na_2CO_3), common salt (NaCl) and copper oxide (CuO). The object was heated to about 1000 °C, at which point the alkali coating reacted to form a glassy exterior with a blue colour imparted by the copper oxide.

Improvements in glass technology were carefully guarded secrets of medieval guilds, and it is only relatively recently that high-quality transparent glass has been readily available. Great advances in the manufacture of silica glass of high transparency were brought about with the development of optical fibre based communication systems towards the end of the 20th century.

Some widely used silicate glasses are listed in Table 6.3.

6.3.1 *Bonding and structure of silicate glasses*

There is no one structure of glass any more than there is one structure of a crystal, and almost any solid can be produced in a glassy state if the melt is cooled sufficiently quickly. To some extent, glass can be thought of a product of kinetics, and the

Table 6.3 Some silicate glasses

Name	Typical composition	Important property	Principal uses
Soda glass	15 % Na_2O: 85 % SiO_2	Cheap	Window glazing
Soda-lime glass	72 % SiO_2: 14 % Na_2O: 14 % CaO	Cheap	Window glazing
Borosilicate (Pyrex®)	80 % SiO_2: 13 % B_2O_3: 7 % Na_2O	Low coefficient of expansion	Cooking ware, laboratory ware
Crown glass	9 % Na_2O: 11 % K_2O: 5 % CaO: 75 % SiO_2	Low refractive index	Optical components
Flint glass	45 % PbO: 55 % SiO_2	High refractive index	Optical components, 'crystal' glass
Lead glass	Up to 80 % PbO: SiO_2	Absorbs radiation	Radiation shielding
Silica	100 % SiO_2	Very low coefficient of thermal expansion	Optical components, laboratory ware, optical fibre

structure of a glass may depend on the rate at which the liquid is cooled.

The main structural unit in silicate glasses is the [SiO_4] group (Figure 6.8). The covalent bonds between the central silicon atom and the oxygen atoms are very strong, and the liquid and the solid states of silica and silicates contain large numbers of [SiO_4] tetrahedra. These tetrahedra link to one another by sharing corner oxygen atoms to form discrete or interpenetrating chains and rings. In the solid these are locked in place whereas in the liquid they are continually changing orientation.

To form a crystalline solid, a liquid must first form crystal nuclei. In the case of metals, this is extremely easy, as the spherical atoms can quickly pack into arrays. In the case of silicates, the entangled chains are difficult to rearrange into an ordered crystalline array. This process often needs bonds to be broken as well as a rearrangement of tetrahedra. Because of this, nucleation is very slow, and cooling the melt at even slow rates can result in the formation of a glass. The structure of a silicate glass was thus envisaged by Zachariasen, in 1932, as an irregular intertwining of chains of corner-linked [SiO_4] tetrahedra to form a loose random network (Figure 6.16).

A silicate glass can also be thought of as a liquid that has been cooled to below the crystallisation point without crystallisation occurring. This state is referred to as supercooling, and glass is often described as a supercooled liquid. However, it is important to keep in mind that glass is *not* a liquid but a solid with a structure that does not show any long-range order. This status of glass is revealed by the behaviour on heating, because glasses do not have a sharp melting point. Instead, they continually soften from a state which can be confidently defined as solid to a state which can be defined as a viscous liquid. In place of a melting point, glasses can be characterised by a glass transition temperature, T_g. The glass transition temperature is determined by plotting the specific volume (the volume per unit mass) of the glass as a function of temperature (Figure 6.17). Both the high-temperature and low-temperature regions of such a plot are usually linear. The value of T_g is given by the intersection of the extrapolated high-temperature and low-temperature lines. Above the glass transition temperature, the material can be considered a liquid whereas below the glass transition temperature it is considered a solid. The glass transition temperature is not a fixed material property but varies with the cooling rate. Nevertheless, it is a useful material parameter and gives guidance concerning the softening and working temperature of a particular glass.

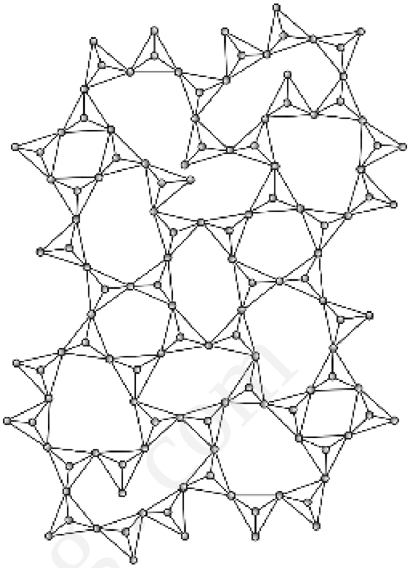


Figure 6.16 The random network structure of corner-linked [SiO_4] tetrahedra in a silicate glass

The random network model works well for silicate glasses. It is based on the idea that the cations forming the network are linked to three or four oxygen atoms to form a strong polyhedron, and each oxygen atom is linked to one cation or, at most, two cations. This is equivalent to noting that polyhedra share some corners with neighbouring polyhedra. Small ions, which adopt triangular or tetrahedral metal–oxygen coordination polyhedra, should therefore take part in glass formation. These ions, typically B^{3+}, Ge^{4+}, Al^{3+}, Be^{2+} and P^{5+}, are known as *network formers*. Large cations, which tend to disrupt the ability of the [SiO_4] tetrahedra to crystallise in regular arrays, also enhance glass formation. These ions, known as *network modifiers*, are typified by K^+, Na^+, Mg^{2+} or Ca^{2+}. Other cations, those with higher valence

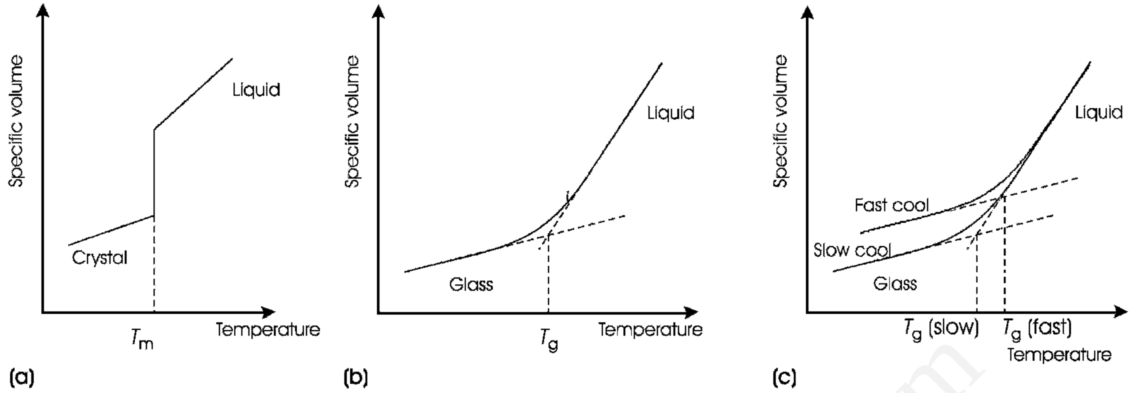


Figure 6.17 Specific volume versus temperature curves: (a) a crystalline solid with a melting point T_m; (b) a glass, with a glass transition temperature T_g; and (c) the effects of cooling rate on glass transition temperature

and a coordination typically of 6, are called *intermediates*. Typical examples are Ti^{4+}, Cu^{2+} and Zn^{2+}. Although intermediate ions alter the properties of a glass (e.g. by adding colour) they do not have a direct role to play in glass formation. Note that these three divisions are not mutually exclusive and some ions fall into more than one category. For example, Al^{3+} is regarded both as a network former, when in triangular or tetrahedral positions, and as an intermediate, when in octahedral coordination.

6.3.2 Glass deformation

One of the most curious properties of glass, and one that differentiates glass from metals and crystalline ceramics, is the fact that it can be deformed readily in a semimolten state by traditional techniques such as glass blowing. This is because glasses behave as very viscous liquids at moderate temperatures. This state can be manipulated into the desired shape, which is retained in solid form on cooling.

The viscosity of a glass is an important physical parameter, as it defines the temperature regimes over which the glass can be worked. For example, the working range of a glass is the range of viscosities over which normal processing takes place, usually between viscosity values of 10^3 Pa s and $10^{6.6}$ Pa s. The important viscosity ranges for glass manipulation are given in Table 6.4, together with the approximate temperature at which these values are reached for an ordinary soda-lime glass.

Table 6.4 Glass viscosity

Glass condition	η/Pa s	Comment	Temperature/°C for soda-lime glass
Melting temperature	10	Glass becomes fluid and a homogeneous melt is achievable	1450
Working point	10^3	Glass is easily deformed but retains its shape	1000
Softening point	$10^{6.6}$	Glass deforms under its own weight	700
Annealing point	10^{12}	Residual stress in a thin plate can be removed in 15–20 minutes	550
Strain point	$10^{13.5}$	Fracture–plastic deformation boundary (see Section 10.1.10)	500

Note: η = viscosity. All figures given in this table are approximate.

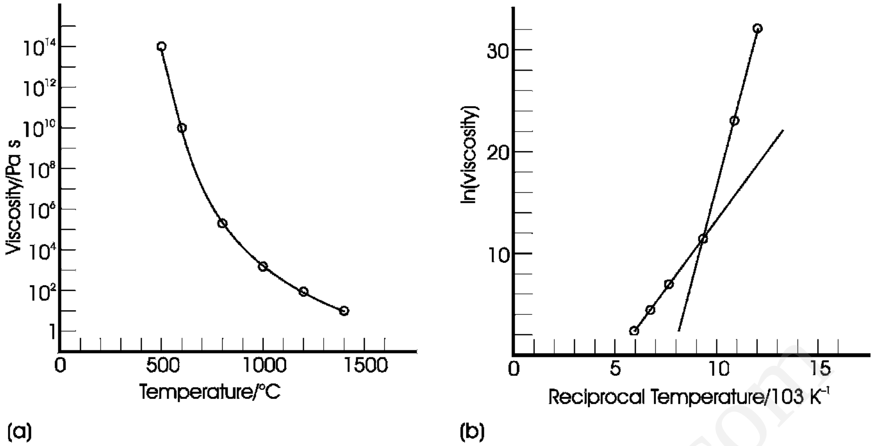


Figure 6.18 (a) Viscosity versus temperature for a typical soda-lime glass and (b) plot of ln (viscosity) versus reciprocal temperature for the same glass

[The temperature at which any glass reaches the requisite viscosity depends on its composition.] The variation of viscosity with temperature for a soda-lime glass is plotted in Figure 6.18(a).

Because of the practical importance of viscosity, there have been several attempts to define the relationship between viscosity and temperature by a mathematical equation. The simplest of these is an Arrhenius equation:

$$\eta = \eta_0 e^{E/RT} \qquad (6.1)$$

where η is the viscosity (Pa s), η_0 is a constant, E is the energy for viscous flow, often called the activation energy, R is the gas constant and T the temperature (in kelvin). This equation well describes activated processes, such as diffusion (see Section 7.4). In such processes, the reaction or transformation is possible only when the reactants or participants overcome an energy barrier, the activation energy. Arrhenius behaviour is confirmed by a plot of ln η versus $1/T$:

$$\ln \eta = \ln \eta_0 + \frac{E}{RT} \qquad (6.2)$$

The plot should be linear with a slope of E/R. Materials that conform to Equation (6.2) are said to exhibit Arrhenian behaviour. This is not generally found to occur for glasses. The data in Figure 6.18(a) is plotted in this form in Figure 6.18(b). It is seen that the low-temperature and high-temperature parts of the graph are good fits to Equation (6.2), but the two slopes are quite different. At high temperatures, the slope is lower than at low temperatures. Such behaviour is typical of glasses and is referred to as non-Arrhenian behaviour.

Several other equations have been suggested to overcome the shortcomings of the Arrhenius equation. The most widely used is the Vogel–Fulcher–Tamman equation (also called the Vogel–Fulrath equation):

$$\eta = A \exp\left(\frac{B}{T - T_0}\right)$$

where A, B and T_0 are empirical constants, and T is the temperature (in kelvin). This leads to the relation;

$$\ln \eta = \ln A + \frac{B}{T - T_0}$$

It has been found that liquids that readily form glasses exhibit non-Arrhenian behaviour whereas those that do not readily form glasses show Arrhenian behaviour. Melts that are Arrhenian are classified as strong whereas those that are non-Arrhenian are classified as fragile. The fragility of a liquid, its fragility index, can be related to the structure of the liquid and gives guidance on the ease of glass formation in a system (for more information on this development, see the Further Reading section at the end of this chapter).

6.3.3 Strengthened glass

Glass is strong in compression but notoriously weak in tension. Freshly drawn glass fibres, for example, are stronger than steel, but, in particular, attack of the surface by water vapour in the atmosphere causes the strength of the fibre to fall dramatically. This weakness is usually attributed to small flaws in the glass surface, called Griffiths flaws (see Section 10.1.7). Under tension the flaws generate cracks, which open, allowing the material to fracture. The various mechanisms for strengthening glass are ways to prevent the cracks from propagating through the solid.

Tempered glass is about four times stronger than ordinary glass, and, when it fractures, it breaks into small, blunt pieces rather than jagged shards. The glass is strengthened by rapidly cooling the hot surface with air jets. Initially, the glass is cut to shape, and surface flaws and rough edges removed by grinding and polishing. The glass is then heated to 620 °C. High-pressure jets of air, in a predetermined array, rapidly cool the surface in several seconds. During this quenching process, the outside of the glass sheet becomes rigid, as the outside temperature drops below the glass transition temperature. The inside, though, is still above this temperature as it cools more slowly than the outside. As the inside cools, it tends to shrink away from the solid outer surfaces. This results in the centre of the sheet being in tension, whereas the outside of the sheets are being pulled in and so are in compression. These opposing tensile and compressive stresses are the strengthening mechanism. As glass usually fails because of the generation of surface cracks, a surface under a compressive force is much harder to break. Carefully controlled patterns of stresses are generated, dependent on the final use of the material.

Chemical strengthening aims to mimic the tension and compression distribution just described by using chemical means. The methods used are successful but tend to be more expensive than air cooling and are used only in applications in which cost is a secondary consideration. The principal of the method is selectively to replace some of the metal ions in the glass to achieve tension or compression. For example, if a soda-lime glass is placed in a bath of molten potassium nitrate (KNO_3) the Na^+ in the glass surface is replaced by the larger K^+. This causes a surface compressive stress and an interior tensile stress, and the glass is strengthened. This process is used to produce aircraft glazing and lenses. Similarly, if the Na^+ is replaced by Li^+, which is smaller, the surface is under tension and the centre under compression. This process is used in the fabrication of glass for use as laser material.

6.3.4 Glass ceramics

A glass ceramic is a solid that is largely crystalline, made by the crystallisation or devitrification of a glass object of the desired shape. Glass ceramics are therefore composite materials that consist of crystals and some glass. They combine the ease of production of glass with much enhanced thermal and mechanical properties. In this section, the microstructures of some glass ceramics are described, and the way in which the superior properties are achieved is outlined.

The transformation of the initial glass object into a largely crystalline object of the same shape and size is carried out by a thermal treatment. This induces the precipitation of crystal nuclei, the growth of crystals on the nuclei and the development of an almost fully crystalline final product (Figure 6.19). It is important that each of these steps is carefully controlled if the desired glass ceramic is to result. In addition, the crystallisation must occur in a glass that is viscous enough not to sag or distort during the transformation, so the viscosity must also be closely controlled. As nucleation, crystal growth

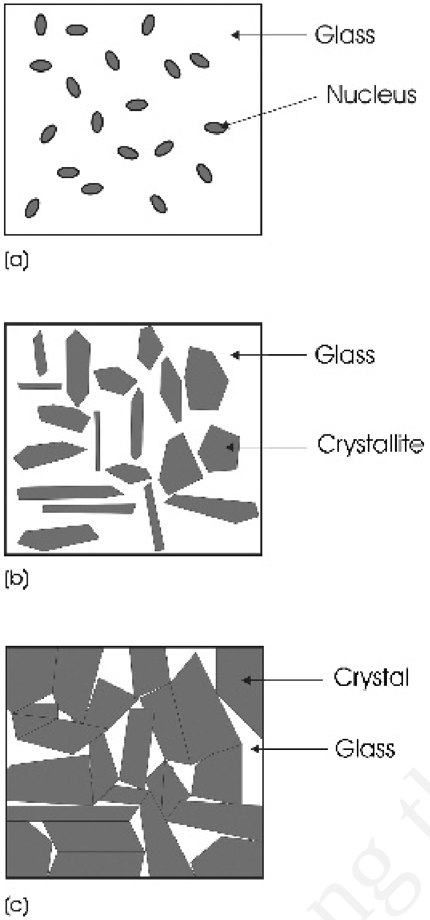


Figure 6.19 Nucleation (part a) and growth (parts b and c) in a glass ceramic

and viscosity are all temperature-sensitive the correct conditions to give a satisfactory product must be achieved by a precise juggling of the chemical components used.

Good mechanical properties are achieved because the solid consists of a mass of interlocking crystals. Any surface flaws cannot easily propagate through the solid, as the passage of a crack is blocked by crystals in its path. Good thermal properties are achieved by ensuring that the crystals that form have very low coefficients of expansion, thus making the material resistant to thermal shock (see Sections 15.1.6–15.1.8). The optical properties of the solid can also be manipulated. If the crystals are kept to a dimension below that of the wavelength of light, the solid will be transparent to visible light. If the crystal dimensions are larger, the solid can be, for instance, opaque to visible light but transparent to microwaves or radar waves. Crystallites of a modest size that are well dispersed in a glass residue give a translucent solid, typified by porcelain.

The two most important factors in glass ceramic production are the composition of the melt and the microstructure of the final product. These are interrelated, of course. The composition controls the ability of the substance to form a glass with the correct viscosity and workability, as the starting solid is completely glassy in nature. Composition also controls what nuclei can form in the glass and the types of crystal that can grow. Most crystals have a definite crystal habit, and this factor greatly influences the microstructure of the final solid.

The simplest glass ceramics, from a microstructural viewpoint, are the transparent ultrafine-grained materials. These consist essentially of the high-temperature form of quartz (Figure 5.30, page 139). The preparation of these materials starts with a silica melt that also contains some zirconia (ZrO_2), titania (TiO_2), alumina (Al_2O_3) and magnesia (MgO). The melt is formed into the desired shape and then heat treated, with the viscosity remaining at a value great enough to prevent sag or deformation. At this temperature, $ZrTiO_4$ crystals are the first to nucleate and, on these, crystals of the high-temperature form of quartz, stable between 573 °C and 870 °C, grow. The presence of the aluminium in the melt means that the quartz is not pure SiO_2, but some aluminium substitutes for silicon in the crystals. In order to maintain charge neutrality, some Mg^{2+} is also incorporated into the quartz, and this stabilises the structure to room temperature. The final solid is a mass of crystals less than 60 nm in size, together with some residual glass, which cements them together. The small crystal size means that the solid is transparent, and the very low thermal expansion of quartz means that the material is resistant to thermal shock. The many small grains in the structure prevent crack growth, so that the ceramic is also strong.

Other compositions and heat treatments result in glass ceramics with different microstructures. The amount of glass present and the type of crystalline phase present will have a profound effect on the resultant properties. For example, in materials used as rocket nose cones, the structure contains mainly cordierite ($Mg_2Al_2Si_5O_{18}$), an aluminosilicate with a very low thermal expansion coefficient. The residual glass is in the form of isolated volumes, so that flow is not easy when the material is heated. Machinable glass ceramics can also be prepared by suitable control of chemistry and crystallisation. These materials contain a crystalline phase consisting of interlocking plates of mica, with a composition approximating to fluorphlogopite ($KMg_3AlSi_3O_{10}F_2$). The presence of the interlocking plates prevents the solid from splintering when it is cut. These are used for precision ceramic components that can be manufactured only via a machining stage.

6.4 Polymers

Polymers are long chain-like giant molecules (macromolecules) made by the linkage of large numbers of small repeating molecules called monomers. Short chain lengths formed in the course of synthesis or degradation of polymers are called oligomers. The majority of polymers, and the only ones considered here, are compounds of carbon. Polymers are very widespread and can be synthetic (e.g. nylon) or natural (e.g. rubber). They form vital components of living organisms, and the most important molecule, DNA, is a polymer of amino acids. Colloquially, polymers are often called plastics. More precisely, plastics are sometimes defined as polymers that can be easily formed at low temperatures, and sometimes as a pure polymer together with a nonpolymeric additive, which may be solid, liquid or gas.

There are two main divisions of polymeric materials: thermoplastic and thermosetting. Thermoplastic materials can be formed repeatedly; that is, they can be melted and reformed a number of times. Thermosetting materials can be formed only once; they cannot be remelted. They are usually strong, and are typified by resins. A further group of polymers merits mention: elastomers. Elastomers can be deformed a considerable amount and return to their original size rapidly when the force is removed.

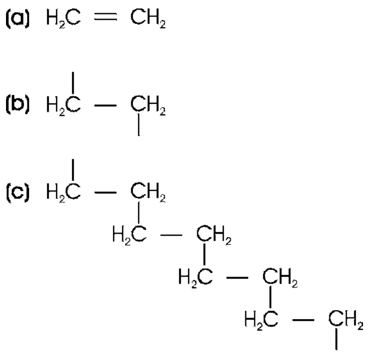
The properties of polymers depend both on the details of the carbon chain of the polymer molecule and on the way in which these chains fit together. The chain form can be linear, branched or cross-linked, and a great variety of chemical groups can be linked to the chain backbone. The chains can be carefully packed to form crystals, or they can be tangled in amorphous regions. Amorphous polymers tend not to have a sharp melting point, but soften gradually. These materials are characterised by a glass transition temperature, T_g, (Section 6.3.1), and in a pure state are often transparent.

Although polymers are associated with electrically insulating behaviour, the increasing ability to control both the fabrication and the constitution of polymers has led to the development of polymers that show metallic conductivity superior to that of copper (see Section 13.2.8) and to polymers that can conduct ions well enough to serve as polymer electrolytes in batteries and fuel cells (see Sections 9.2.5 and 9.3.7).

In this section, polymers will be discussed largely from a structural and microstructural point of view. Several typical and differing polymers are used as examples: polyethylene (polythene), nylon and epoxy resins. In addition, elastomers are described, as they differ in a fundamental way from other materials.

6.4.1 The chemical structure of some polymers

Polymers were once grouped mainly in terms of the overall chemistry of the polymerisation reaction. Molecules that simply added together were called addition polymers, and those that joined and at the same time eliminated one or more small molecules were called condensation polymers. These designations, which derived from organic chemistry, have now largely been replaced by groupings that reflect the mechanism of the polymerisation rather than the overall chemical reaction. [Section S2.1 gives a synopsis of relevant organic chemistry terminology.]



Scheme 6.1 The polymerisation of ethene (ethylene): (a) a single monomer molecule, (b) double bond opening and (c) monomer linkage to form the polymer chain

In this section the older common names, rather than the systematic names, are frequently used for organic compounds, as they have largely been retained in polymer names.

In order to link a large number of molecules, or monomers, together it is necessary for each end of the molecules to be made chemically reactive. Generally, this involves breaking chemical bonds to yield two reactive half-bonds. The simplest starting point for a discussion of this process is the monomer molecule ethene (ethylene):

$$CH_2{=}CH_2$$

Schematically, the monomer ethene can be linked to other ethene monomers if the double bond is opened and the resulting broken bonds are linked together, in an addition reaction (Scheme 6.1). The chemical formula of the resulting polymer, called polyethylene or polythene, is:

$$[CH_2{-}CH_2]_n$$

where n takes a value of several thousand. [Note that the industrial preparation of polyethylene (and of all the polymers described here) is quite different from the scheme illustrated. Very skilled chemistry has been employed to achieve the precise properties that polymers now display.] The polymer chain is constructed from (CH_2) units. In these, the carbon atoms are bonded to two hydrogen atoms and two carbon atoms using strong sp^3 hybrid bonds (Figure 6.20). The carbon–carbon bonds are free to rotate, which allows the polymer chain to coil into ordered or disordered regions. Note that polyethylene, like all polymers, does not have a definite chemical formula. The number of (CH_2) units in the chain is influenced by preparation conditions. Polymers with low average values of n have different physical properties from those in which n is larger (see below).

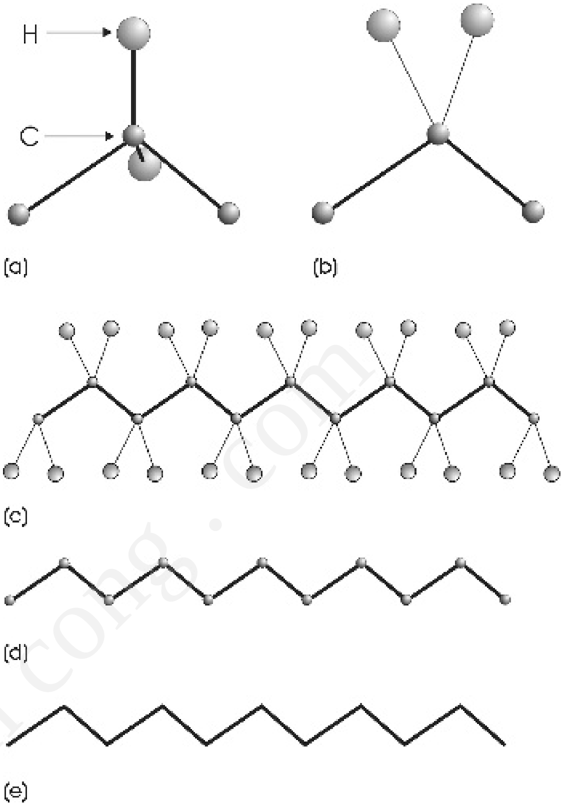


Figure 6.20 (a, b) The structure of the CH_2 unit in a polymer chain, in two orientations (the four bonds arising at the carbon atom are arranged tetrahedrally), (c) a chain of linked CH_2 units in a polymer chain and (d, e) representations of the chains with H atoms omitted

Other related polymers are formed by replacing one or more of the hydrogen atoms in the monomer ethene with a chemical group of atoms, represented by X. Hence the formula of the monomer becomes $CH_2{=}CHX$ when one hydrogen is replaced. The

Table 6.5 Addition polymers

Monomer	Polymer	Names	Uses
$CH_2{=}CH_2$ (ethene, ethylene)	$(CH_2{-}CH_2)_n$	Polyethylene, polythene, PE	Squeeze bottles, food bags, dishes, insulation, coatings
$CH_2{=}CHCl$ (vinyl chloride)	$(CH_2{-}CHCl)_n$	Poly(vinylchloride), PVC	Pipes, floor covering, insulation, adhesives, films, credit cards
$CH_2{=}CCl_2$ (vinylidene chloride)	$(CH_2{-}CCl_2)_n$	Poly(vinylidene chloride)	Food wraps, fibres, cling film
$CH_2{=}CHCH_3$ (propylene)	$[CH_2{-}CH\,(CH_3)]_n$	Polypropylene, PP	Pipes, valves, carpets
$CH_2{=}CHC_6H_5$ (styrene)	$[CH_2{-}CH\,(C_6H_5)]_n$	Polystyrene, PS	Jugs, cups, packaging, styrofoam, appliance parts
$CH_2{=}CHCN$ (acrylonitrile)	$[CH_2{-}CH\,(CN)]_n$	Polyacrylonitrile, PAN, Orlon®, Acrilan®	Fabrics, carpets, high-impact plastics
$CH_2{=}CHCOOCH_3$ (vinyl acetate)	$[CH_2{-}CH\,(CH_3\,COO)]_n$	Poly(vinyl acetate), PVA	Wood adhesives, paper coatings, latex paints
$CF_2{=}CF_2$ (tetrafluoroethene)	$(CF_2{-}CF_2)_n$	Polytetrafluoroethylene, PTFE, Teflon	Nonstick coating, electrical insulation, bearings
$CH_2{=}C(CH_3)COOCH_3$ (methyl methacrylate)	$[CH_2{-}C(CH_3)\,COOCH_3]_n$	Poly(methyl methacrylate) Perspex®, Lucite®, Plexiglas®	Substitute glass, acrylic paints, pipes
$CH_2{=}CH{-}CH{=}CH_2$ (1,3-butadiene)	$(CH_2{-}CH{-}CH{-}CH_2)_n$	Polybutadiene, buna rubber	Tyres, hoses, pond liners

principle of polymerisation remains precisely the same, however, although the details are modified by the size and location of the side-group *X*. Some examples of these polymers are given in Table 6.5.

A typical condensation reaction can take place between an acid group, $-COOH$, and a hydroxyl group, $-OH$, to form a larger molecule and to 'split out' water:

$$R{-}COOH + R'{-}OH \rightarrow R{-}COO{-}R' + H_2O \qquad [6.1]$$

where R and R′ represent different carbon chains. In molecules with only one acid or hydroxyl group, as written in Reaction [6.1], the reaction stops after the first step. In order to create a polymer, the monomers of condensation polymers need *two* reactive functional groups on each monomer.

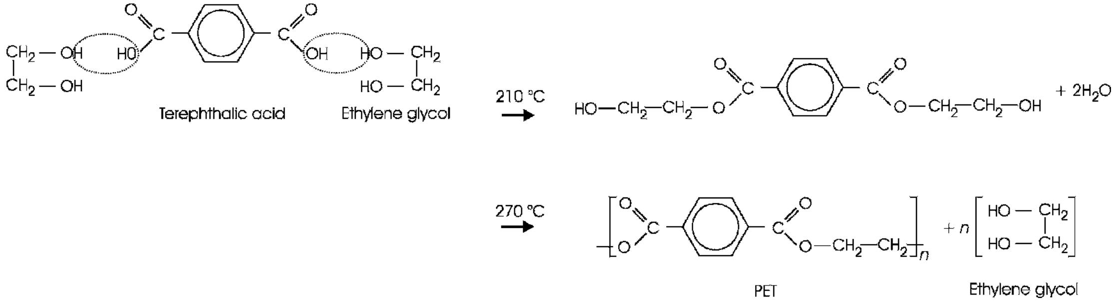
The polyesters, which generally start from terephthalic acid and the alcohol ethylene glycol, are an important group of polymers made in this way. The reaction is between acid groups and hydroxyl groups (Scheme 6.2). The product, a polyester called poly(ethylene terephthalate), or PET, is widely used to make shatter-proof bottles.

A second group of polymers that form in a similar way are the thermoplastic polyamides, better known as nylons. The principal reaction is between an acid group, $-COOH$, and an amide group, $-NH_2$:

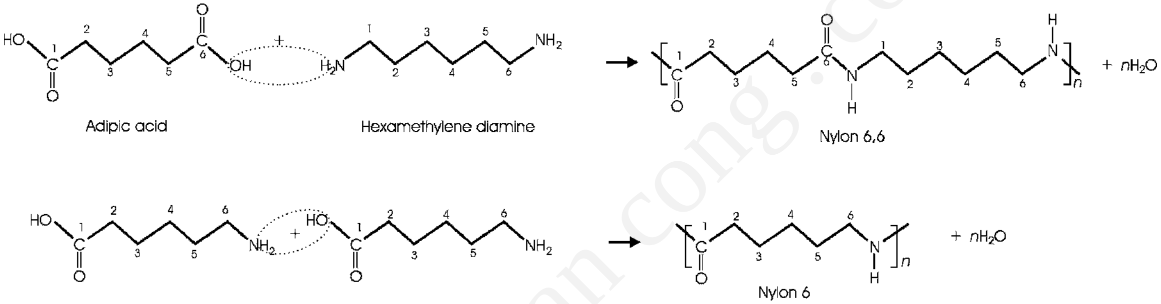
$$R{-}COOH + R'{-}NH_2 \rightarrow R{-}CONH{-}R' + H_2O$$

where R and R′ represent different carbon chains. Once again, in order to form a polymer, each monomer must have a reactive group at each end of the molecule. The schematic structure and the reaction scheme for the formation the commonest type of nylon, called nylon 6,6, is drawn in Scheme 6.3(a). In this scheme, the carbon skeleton of the polymer chain is drawn as a zigzag (see Figure 6.20) and the carbon atoms are numbered. The name, nylon 6,6, indicates that there are six carbon atoms in each section of the repeat unit of the polymer.

Amino acids are molecules with an acid group at one end and an amide group at the other, separated



Scheme 6.2 The production of the polyester poly(ethylene terephthalate), PET. The linking of the terephthalic acid and ethylene glycol molecules occurs at 210 °C, and polymerisation and regeneration of ethylene glycol at 270 °C

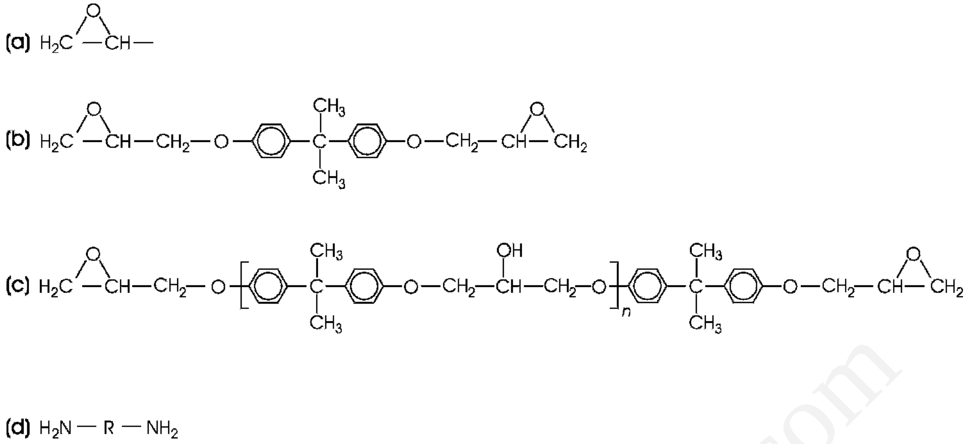


Scheme 6.3 (a) The formation of nylon 6,6; (b) the formation of nylon 6. The figures give the number of carbon atoms in the polymer chain between nitrogen atoms

by a carbon chain, HOOC—R—NH_2. These molecules can also polymerise by linking head to tail, to generate a nylon. The amino acid analogue of nylon 6,6 is nylon 6 (Scheme 6.3b). [Note that nylon 6 is not actually made from the amino acid shown, but from a molecule called ε-caprolactam.]

Nylon 6,6 is an example of an even–even nylon, sometimes just abbreviated to ‘even’. It is easy to envision other even–even polymers, such as nylon 4,4. Similarly, it is possible to think of odd–odd, or just ‘odd’, nylons, such as nylon 5,5. Although these nylons have very similar chemical properties they differ in important electrical aspects, and the nature of the chain determines whether these plastics can be used to make piezoelectric components (see Section 11.2.3).

A rather similar chemical reaction produces widely used thermosetting polymers typified by epoxy resins. In this group of materials, instead of a reactive double bond a reactive group, the epoxide group (Scheme 6.4), is opened and used to link monomers. Epoxy resin adhesives normally come as two-part mixes. The resin component contains small and medium-sized molecules with an epoxy group at each end, called diepoxy molecules (Schemes 6.4b and 6.4c). The resin is set by adding a cross-linking agent, or ‘catalyst’. This material is a diamine (Scheme 6.4d). These join the epoxy-containing molecules together to form a strong cross-linked network. Once the network has been formed it is very difficult to disrupt, and epoxy resins are typical thermoset polymers. Note that there is no reaction product on polymerisation, which means that only a small dimensional change occurs as the precursors harden. This is of importance in applications where shrinkage or expansion would create difficulties, as in the original application of these materials, for dental fillings.

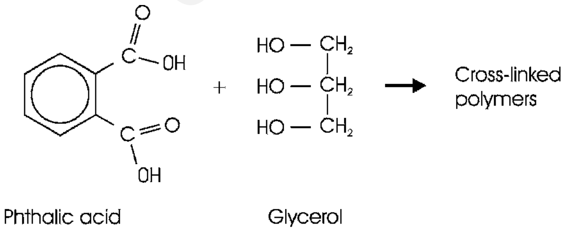


Scheme 6.4 The structure of molecules in epoxy resins: (a) the epoxy group; (b) a small diepoxy molecule; (c) a small polymer molecule (with n up to about 25), found in the resin part of a two-part epoxy adhesive mix; and (d) a diamine linking group ('catalyst') in which R represents a short chain of CH_2 groups

All cross-linked polymers tend to be difficult to disrupt, and they can be regarded as one giant molecule. This makes them of use when durability is needed. Many of the polymers mentioned above can be modified so as to form extensive cross-linking by increasing the number of reactive groups on the monomers. For example, the polyester formed by phthalic acid and glycerol (Scheme 6.5) can cross-link to form a polymer that is used in bake-on car paints.

6.4.2 Microstructures of polymers

Although the chemical makeup of polymers influences properties, by far the most important aspect, from this point of view, is that of the microstructure. The microstructure of polymers can be considered to derive from that of a long chain of strongly linked carbon atoms. The most important aspects of polymer microstructure that need to be considered are chain length, chain branching, chain side-groups (which contribute to chain stiffness) and the strength of cross-links between chains. The degree of crystallinity of the polymer, which depends on the factors just listed, is also of considerable importance. In fact, the strength of most thermoplastic polymers depends on the degree of crystallinity of the material. In this section, these basic microstructural features are described. The way in which these are achieved during manufacture is covered in Section 6.4.3, and properties are discussed in terms of microstructure in Section 6.4.5.



Scheme 6.5 Reaction of molecules with several active groups can give rise to cross-linked polymers: the reaction of phthalic acid and glycerol

6.4.2.1 Molar mass

Polymers consist of long chains of varying length that cannot be characterised by a constant molar mass. Indeed, cross-linked polymers can be thought of as a single molecule, so that the molar mass is the total mass of the object. However, it is helpful to have a measure of the degree of polymerisation or the distribution of chain lengths in a polymer, and

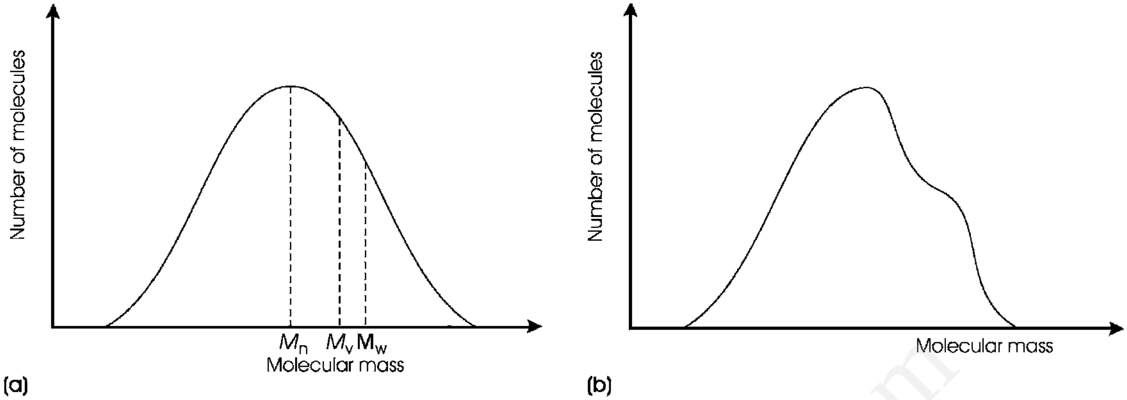


Figure 6.21 (a) Idealised distribution of molecular mass of a polymer (M_n = number average molecular mass; M_v = viscosity molecular mass; M_w = weight average molecular mass); (b) example of a real mass distribution, more complex than the simple distribution in part (a)

this is given in terms of an average molar mass. Ideally, the distribution of chain lengths in a sample of a polymer will take on the shape of a bell-shaped curve. As the chain length is reflected in the mass of the molecule, this information is often given as a graph of the number of molecules against the molar mass (Figure 6.21a). Generally, the distribution departs from a simple bell shape (Figure 6.21b) and the form of the curve is often characteristic of a particular reaction mechanism.

In order to quantify the chain length, the molar mass (or molecular weight) must be defined statistically. The number average molar mass, M_n, is given by:

$$M_n = \sum_i x_i M_i$$

$$x_i = n_i \left[\sum_i n_i \right]^{-1}$$

where x_i is the fraction of the total number of chains within the chosen molar mass range, and n_i is the number of molecules with a molar mass M_i. The number average molar mass corresponds to the peak in a bell-shaped distribution curve. An alternative measure, the weight average molar mass, M_w, takes into account the fact that most of the mass of the sample resides in bigger molecules:

$$M_w = \sum_i w_i M_i$$

$$w_i = n_i M_i \left[\sum_i n_i M_i \right]^{-1}$$

where w_i is the mass fraction of each type of molecule present within the chosen molar mass range. The molar mass can also be determined experimentally. A method frequently used is to measure the viscosity of a solution containing the polymer. A greater viscosity indicates longer chains and a higher molar mass. The molar mass determined in this way, M_v, lies between M_n and M_w (Figure 6.21a).

The degree of polymerisation, N, is the number of monomer units in an average chain. It is given by the molar mass divided by the mass of the monomer, m. The value obtained depends on which of the various molar mass values are chosen:

$$N_n = \frac{M_n}{m}$$

$$N_w = \frac{M_w}{m}$$

$$N_v = \frac{M_v}{m}$$

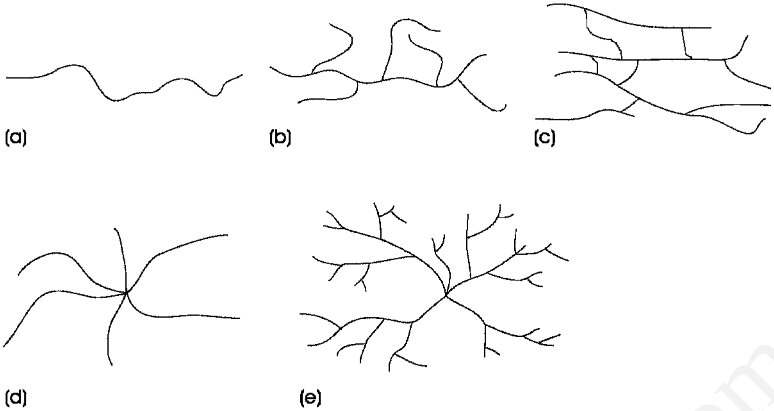


Figure 6.22 Polymer chain geometries: (a) linear; (b) branched; (c) cross-linked; (d) star; (e) dendrimer

6.4.2.2 Chain structure

Polymerisation involves the breaking and reforming of large numbers of chemical bonds. This energetic process results in a number of different molecular structures. Frequently, chains are not simply linear but also have side-branches, which can also cross-link molecules. Growth of several chains can also start from a small nucleation centre, and the resulting chains can branch to give a dendritic structure (Figure 6.22). Each of these molecular geometries imparts different physical properties to the resultant polymer.

Polyethylene (polythene) is a long-chain polymer 10^4 ethene (ethylene) units or more long. If these chains are relatively short and highly branched, the material has a low density, a low refractive index and is very flexible but weak. It is referred to as low-density polyethylene (LDPE). High-density polyethylene (HDPE) consists of linear molecules and has a molecular weight of between 200 000 and 500 000. It is much stronger than LDPE. Ultrahigh-molecular-weight polyethylene (UHMWPE), with a molecular weight of the order of 5 000 000, is stronger still. The mechanical properties of polyethylene are influenced further by the degree of crystallisation that occurs. On cooling slowly from the melt, some chains can order into crystalline regions 10–20 nm thick. These crystalline regions are of high density and of high refractive index. Most polyethylene is a mixture of crystalline and amorphous regions, which is why it appears milky.

6.4.2.3 Crystal structure

Straight chains rarely occur in polymers. More often, as in solid polyethylene and many similar polymers, the chains fold back on themselves with a characteristic fold length (Figure 6.23a). The folded chains aggregate into blocks that have a regular structure similar to a crystal. This unit of microstructure is called a lamella (Figure 6.23b). The lamellae are not usually made from a single folded chain but are formed by a variety of neighbouring chains (Figure 6.23c). The parts of the chains not incorporated into the lamellae then link one lamella to another in the partly crystalline material. During crystallisation of the melt, lamellae form in three dimensions, from a nucleation site, to form a spherulite. This feature consists of a set of spokes, called lamellar fibrils, radiating out from a common centre into the amorphous interspoke regions. A two-dimensional cross-section of such a region is sketched in Figure 6.24.

The degree to which a polymer can crystallise depends on the details of the chain. For example, the amide group is a polar unit and forms hydrogen bonds with the carboxyl oxygen in nylons (Scheme 6.13, p. 186). These intermolecular forces hold the

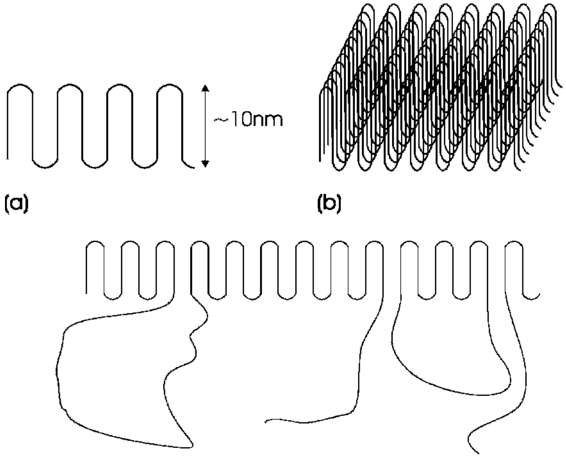


Figure 6.23 (a) The structure of polymer chains in polyethylene fold back on themselves approximately every 10 nm; (b) folded chains aggregate to form a lamella; (c) lamellae can contain more than one polymer chain, or a chain folded back into the arrangement

chains together, which produces a highly crystalline polymer with excellent strength.

The degree of crystallinity of a polymer can be determined if the density of polymer crystals and purely amorphous material is known. The reasoning is exactly the same as used in Vegard's law, for the determination of the lattice parameter of a solid solution (see Section 5.2.2). The fraction of crystalline polymer, x_c, is:

$$x_c = \frac{\rho_s - \rho_a}{\rho_c - \rho_a}$$

where ρ_s is the density of the sample, ρ_c is the density of the crystals, and ρ_a is the density of completely amorphous polymer.

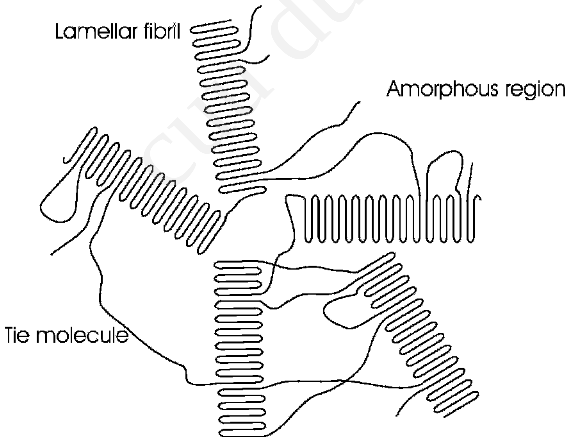


Figure 6.24 Schematic structure of a spherulite in a polymer such as polyethylene

6.4.2.4 Tacticity

The disposition of side-groups on a polymer chain has a great influence on properties, especially the flexibility of the chain, thus changing the melting point of the polymer, and the ability of the chains to pack together, changing strength and optical properties. Three different arrangements have been characterised: isotactic polymers have the side-groups all on one side of the chain (Figures 6.25a and 6.25b), syndiotactic polymers have the side-groups alternating (Figure 6.25c), and atactic polymers have a random arrangement of side-groups (Figure 6.25d). For example, atactic polypropylene is largely amorphous and weak. The stereoregular material syndiotactic polypropylene is crystalline, transparent and hard, whereas isotactic polypropylene crystallises and readily forms fibres. Polystyrene is similar. The atactic material is amorphous whereas syndiotactic polystyrene is crystalline. Poly(methyl methacrylate), used as a replacement for glass, is almost completely amorphous.

6.4.2.5 Cross-linking

The degree of cross-linking between chains changes properties dramatically. Weak cross-links tend to soften materials, whereas extensive cross-linking turns the material into a hard resin. Most thermoplastics, such the epoxy resins, are heavily cross-linked into a hard mass. Cross-linking is the key to elastomeric properties and is considered again below, in Section 6.4.4.

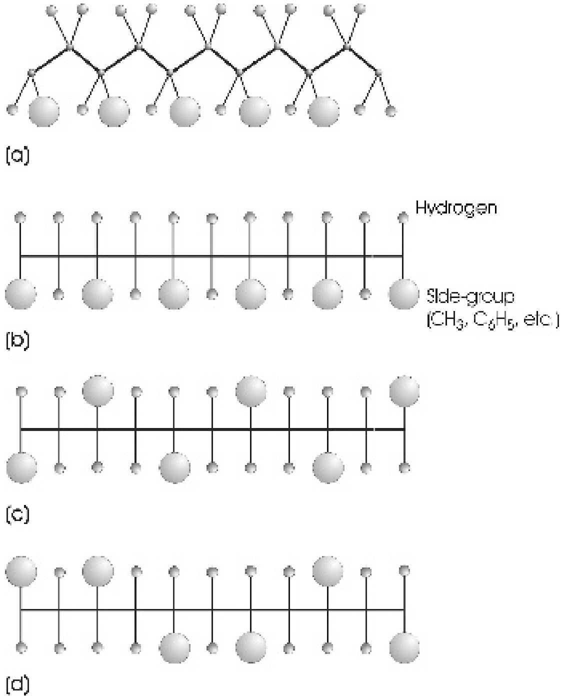


Figure 6.25 (a) Perspective view of an isotactic polymer chain; (b) a projection of part (a) from above to give a schematic plan of an isotactic polymer chain; (c) a syndiotactic polymer chain, depicted as per the polymer in part (b); (d) an atactic polymer chain, depicted as per the polymer in part (b)

6.4.2.6 Copolymers

Besides these different chain geometries, polymer properties are considerably changed by the polymerisation of two different monomers together. These materials are called copolymers and have different names according to the arrangement of the monomers (Figure 6.26). The physical and chemical properties of these materials can be regarded as a combination of the properties of the two polymers in the 'mixture'. For example, pure atactic polystyrene is transparent and brittle. Polybutadiene (synthetic rubber) is resilient but soft. High-impact polystyrene, a graft copolymer of these two materials, is durable, strong and transparent.

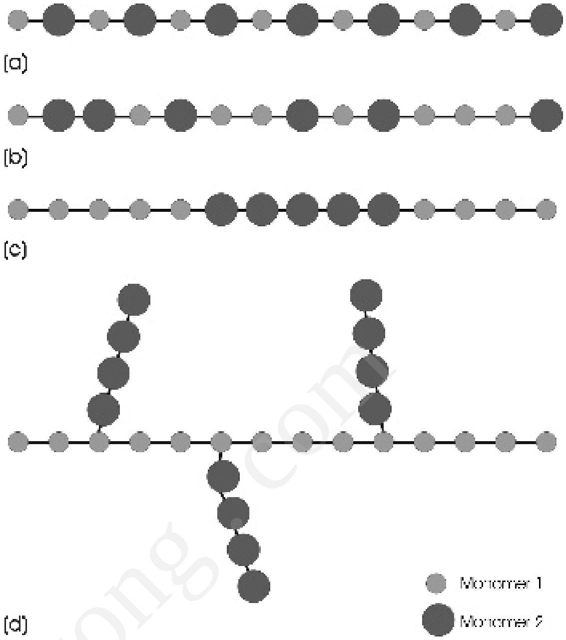
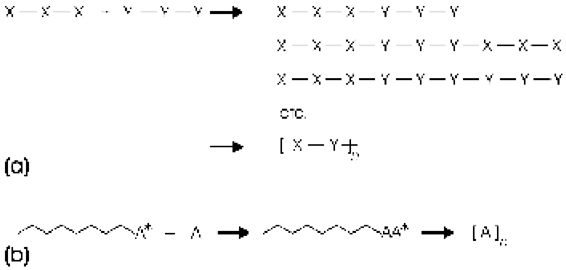


Figure 6.26 Schematic polymer geometry: (a) an alternating copolymer; (b) a random copolymer; (c) a block copolymer; and (d) a graft copolymer

6.4.3 Production of polymers

Because the properties of polymers depend so critically on microstructure, the manufacture of polymers is a highly skilled undertaking. Much of the evolution in the properties of plastics can be attributed to improvements in preparation methods.

The division of polymers into two categories – addition polymers and condensation polymers – is not very useful when formation reactions are concerned. Here the emphasis is better placed on the growth mechanism. There are two principal growth mechanisms – step growth and chain growth. In step growth, growing chains can link together to form longer chains (Scheme 6.6a). In chain growth, monomers are added, one by one, to the growing end of the chain, and different chains do not link together (Scheme 6.6b). Nylons, for example, are condensation polymers that form by a step-growth mechanism. In addition, monomer molecules or chains can link head to tail (the most common



Scheme 6.6 (a) Step-growth polymerisation. Short chains can link to give a variety of sequences. (b) Chain-growth polymerisation involves the addition of new molecules to one end of a growing chain. A^* represents a free radical or similar active centre where addition of new material can occur

way), head to head, or tail to tail. Random linkage can also occur, so increasing the complexity of the reaction.

6.4.3.1 Initiation

To form a polymer, the initial monomers must be activated in some way to start the reaction, a step called initiation. This can be accomplished by heat or high-energy radiation such as ultraviolet light. These processes, which are not reproducible enough for industrial production, contribute to the degradation of polymers in use. Industrially, the initiation stage is achieved by mixing a wide variety of active molecules with the monomers.

6.4.3.2 Propagation

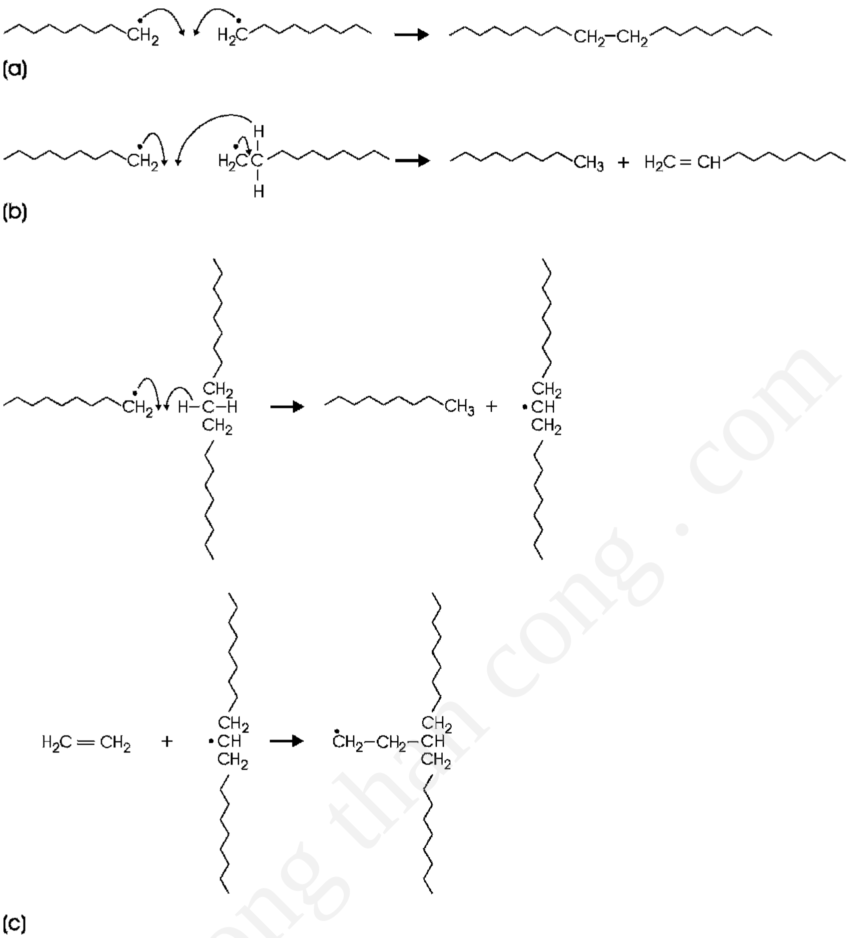
The production of the polymer chains by linkage of the monomers, the second stage of the reaction, is called propagation. The mechanisms of propagation are complex and not all of the reaction steps are fully understood for all reactions. Nevertheless, the propagation stage is of key importance in the production of special polymers and, for this, catalysts are usually employed. In several cases, catalysts not only increase the rate of reaction but also ensure that the addition of the monomers to the growing polymer chain takes place in a constrained way. That is, the reacting molecules approach the growing chain in only one direction. This leads to the production of polymers with a single tacticity, such as isotactic polystyrene. Ziegler–Natta and metallocene catalysts fall into this group and are used to prepare polymers with controlled structures. The production of polypropylene using a metallocene catalyst is described in Sub-section 6.4.3.4.

6.4.3.3 Termination

Growing polymer chains must ultimately stop growing. This is brought about by the process of termination. Chain termination can come about in two ways. The simplest is for two growing chains to meet and join. In such cases, the reactive end of the chain is usually a free radical, which is a molecule or a fragment of a molecule that has an unpaired electron. The unpaired electrons, which are extremely reactive, unite to form a pair bond joining the chains (Scheme 6.7a). A second mechanism, called disproportionation, allows one growing chain to take a hydrogen atom from another chain. The resultant is that one chain terminates with a $—CH_3$ group and one in a double bond (Scheme 6.7b). Further reaction at this double bond can continue to lengthen the chain. The hydrogen can also be extracted from the middle of a chain. This will terminate one chain in a $—CH_3$ group and create a free radical in the interior of the chain. This reactive region can act as a centre for new chain growth (described in Sub-section 6.4.3.5), and continued polymerisation will produce a branch (Scheme 6.7c). This is a very common occurrence in polyethylene polymerisation and results in the highly branched low-density polythene (LDPE) described in Sub-section 6.4.2.2. In order to make much stronger nonbranched high-density polythene, different preparation methods need to be used.

6.4.3.4 Metallocene catalysis

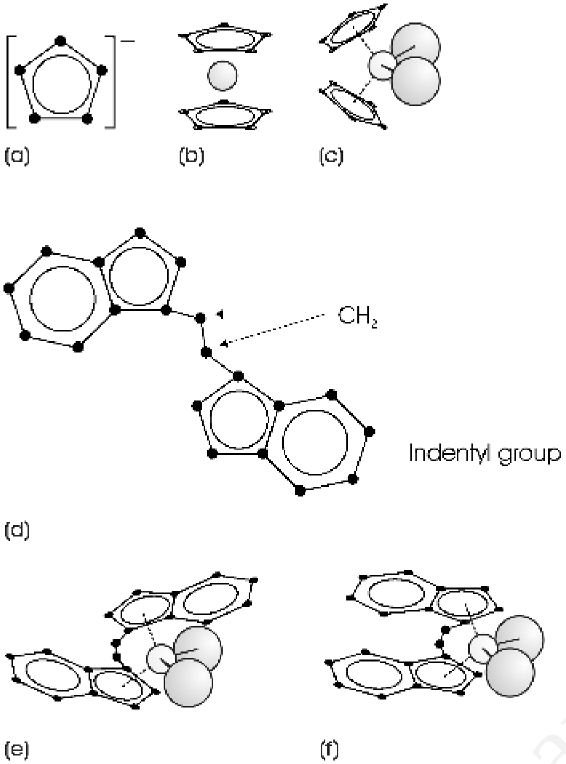
Metallocenes are derived from the cyclopentadiene anion, $(C_5H_5)^-$, shown in Scheme 6.8(a). These are stable units, in which a delocalised orbital, similar



Scheme 6.7 (a) Chain termination as a result of two chains meeting; (b) chain termination as a result of disproportionation; and (c) disproportionation, leading to branching

to that in benzene, lies above and below the plane of the pentagon of carbon atoms. This orbital allows strong chemical bonds to form with metal cations, and the first metalocene investigated, ferrocene, contained Fe^{2+} sandwiched between the anions (Scheme 6.8b). At present, catalysts for polymer production are derived from a molecule called zirconocene, containing Zr^{4+} cations (Scheme 6.8c). In order to produce polymers with a precise structure, the components surrounding the Zr^{4+} ion are carefully modified. A change in the cyclopentadiene anions alters the geometry of the approach of monomers to the cation. The point where the polymer chain grows is controlled by replacement of the Cl^- ions with methyl (CH_3) groups, as the methyl group acts as the point of attachment of successive monomer molecules.

In the molecule used to produce polypropylene, a complex structure called an indentyl group (a benzene ring linked to a cyclodiene), replaces each of the cyclopentadiene groups. The indentyl groups are actually linked by a short chain of two CH_2 groups (Scheme 6.8d). When these are opposed (Scheme 6.8e) the incoming monomers are guided into a position where only isotactic polypropylene can form. In molecules in which the bulky groups are



Scheme 6.8 (a) The cyclopentadiene anion, $[C_5H_5]^-$ (only the carbon atom framework is shown; the delocalised π molecular orbitals above and below the plane of the carbon atoms are represented by the circle). (b) The structure of a molecule of ferrocene, in which the Fe^{2+} cation is sandwiched between two $[C_5H_5]^-$ anions. (c) The structure of a molecule of zirconocene; the cation Zr^{4+} is bonded to two $[C_5H_5]^-$ anions and two Cl^- anions. (d) Two identyl groups linked by two CH_2 groups (the hydrogen atoms are omitted from this representation). (e) The molecular geometry required to produce isotactic polypropylene. (f) The molecular geometry required to produce atactic polypropylene

on the same side of the Zr^{4+} cation (Scheme 6.8f) the approach of the monomers is variable, and atactic polypropylene is produced.

6.4.3.5 *Free-radical polymerisation*

Free-radical polymerisation combines initiation and propagation into one process. This method is used to produce low-density branched polyethylene, poly(methyl methacrylate) and poly(vinyl acetate). Taking ethene (ethylene) as an example, the gas is pressurised to 100 atm. at 100 °C, and a small amount of an unstable initiator molecule, typically an organic peroxide or azide, is added (Schemes 6.9a and 6.9b). These decompose to form free radicals, which are molecules or molecular fragments that have an unpaired electron present. Because of this, they are extremely reactive chemically.

Free radicals are reactive enough to attack double bonds, thus initiating polymerisation (Scheme 6.9c). The reaction is able to satisfy the bonding requirements of the initial free radical but creates a new free radical in the process, which can attack another ethene molecule in turn, leading to continued chain growth (Schemes 6.9d and 6.9e). The reactions can be written as follows:

$$R^{\bullet} + CH_2{=}CHX \rightarrow R{-}CH_2{-}CHX^{\bullet},$$

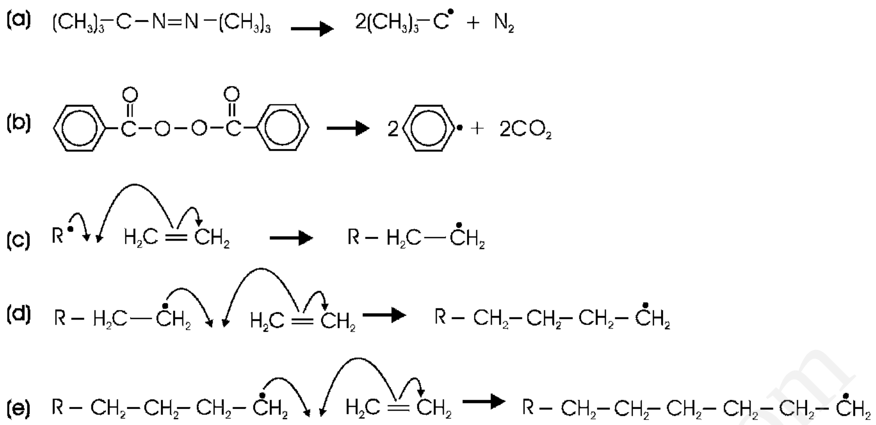
$$R{-}CH_2{-}CHX^{\bullet} + CH_2{=}CHX \rightarrow R{-}CH_2{-}CHX{-}CH_2{-}CHX^{\bullet}$$

where $R^{\bullet}$ represents an organic free radical. Free-radical polymerisation can occur with many, but not all, ethene derivatives. Because there are no constraints on how the chain grows, the polymers are atactic.

6.4.4 *Elastomers*

Elastomers are materials that behave like rubber. They can be stretched to many times their original length and, when the force is released, they spring back to their original size and shape.

Elastomers are a subgroup of amorphous thermoplastics. The distinction depends on the glass transition temperature, T_g, of the polymer. Normal thermoplastics have a glass transition temperature well above room temperature and behave as hard, brittle solids. Those with a glass transition temperature below room temperature are soft and can be deformed easily at room temperature. These are elastomers. If an elastomer is cooled to well



Scheme 6.9 (a, b) The generation of free radicals, which contain an unpaired electron on one atom (marked •), by bond breaking in an azide (part a) and a peroxide (part b). (c) Reactions of a free radical, $R^\bullet$, with ethene (ethylene) to extend the polymer chain. (d, e). Continued reaction and chain growth

below its glass transition temperature it will become hard and brittle. For example, a piece of rubber tubing dipped in liquid nitrogen becomes brittle and can easily be shattered with a hammer blow.

In its normal form, the microstructure of an elastomer is a mess of jumbled coiled polymer chains (Figure 6.27a). On being stretched, the chains tend to partly align parallel to one another (Figure 6.27b). The stretched state is thermodynamically less stable than the coiled state, and the material will revert to the coiled state when the deforming stress is removed. The entropy of the coiled state is greater than that of the stretched state and provides the driving force for the material to return to the coiled configuration. However, entropy alone does not control the key ‘snap-back’ property of elastomers. This is provided by cross-linking *a few* of the elastomer molecules using other molecules (Figure 6.27). When the elastomer is now stretched, some of the bonds in the cross-links are stretched, and these spring back rapidly when the tension is released.

The best-known elastomer is natural rubber, polyisoprene (Scheme 6.10). Isoprene (Scheme 6.10a) is a liquid at room temperature, which polymerises readily to give the elastomer polyisoprene (Scheme 6.10b). The polymerisation produces two main geometrical isomers (see Section S2.1.) Natural rubber is the all-*cis* form of polyisoprene (Scheme 6.10c), in which the methyl (–CH_3) groups and hydrogen (H) atoms are on the same side of the carbon–carbon double bond. Rubber latex, a milky liquid, is a suspension of rubber in water. It is found in many plants (e.g. in dandelions) as well as rubber

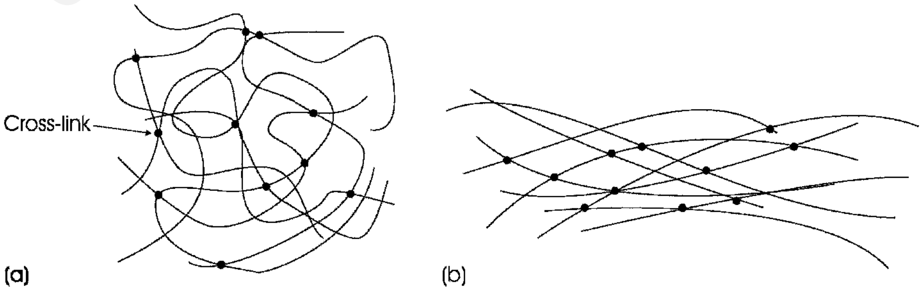
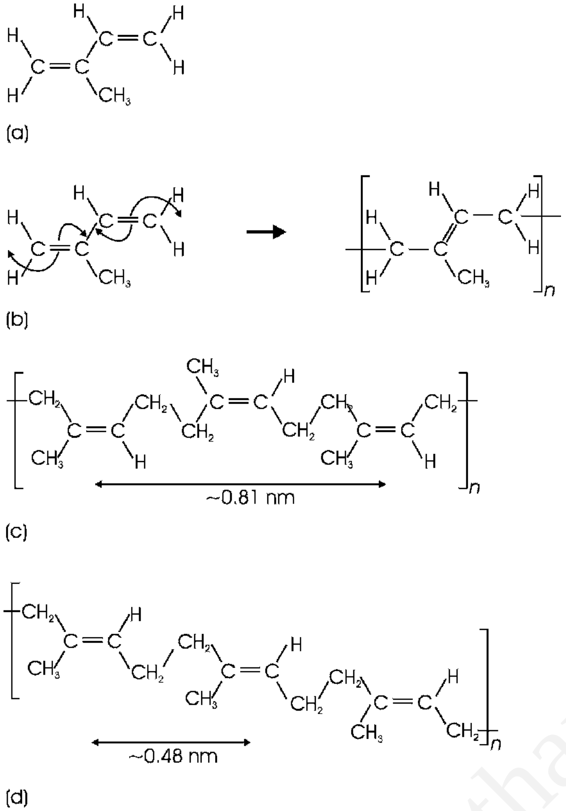
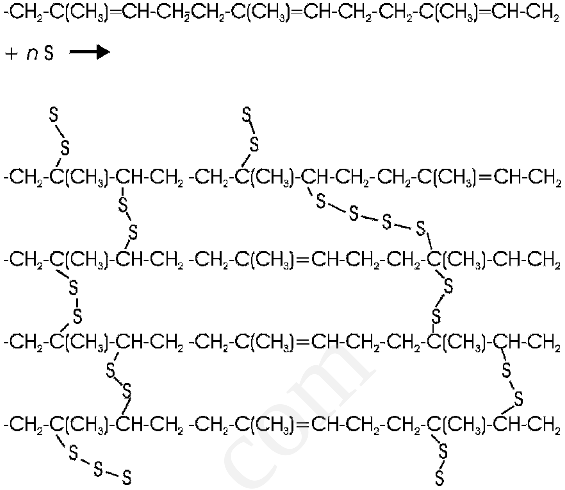


Figure 6.27 An elastomer in (a) an unstretched and (b) a stretched state



Scheme 6.10 (a) The structure of an isoprene molecule. (b) Bond redistribution and subsequent polymerisation to form poly(isoprene). (c) The structure of natural rubber, all-*cis*-poly(isoprene). (d) The structure of gutta-percha, all-*trans*-poly(isoprene)

trees. The rubber in latex can be coagulated by the addition of acetic acid, to give a soft, easily oxidised material called crepe or gum rubber. In its natural state rubber, like most amorphous thermoplastics, is sticky at a temperature above T_g and does not posses the typical elastomer properties of snap when stretched. The all-*trans* form, called gutta-percha (Scheme 6.10d) is also found in nature. It is harder and finds use in golf balls and dentistry.



Scheme 6.11 The formation of sulphur cross-links between rubber molecules, produced during vulcanisation

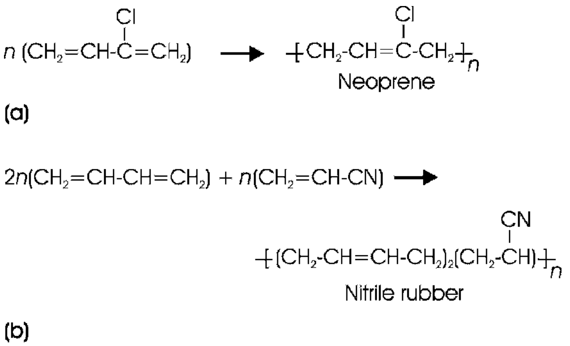
The practice of cross-linking the polyisoprene chains in natural rubber to form a usable elastomer was discovered by Goodyear, in 1839. He heated natural rubber latex with sulphur, a process called vulcanisation. This transforms the sticky runny natural latex into a product in which the elastic properties are retained yet the stickiness is lost. The cross-linking (Scheme 6.11) utilises the remaining double bonds in the elastomer chains. These are opened by the cross-linking molecules to form the ties.

Cross-linking makes the polymer more rigid. For a soft rubber, 1–2 % of sulphur is added. If this process is carried too far, the whole mass of polymer turns into a solid block. Hard rubbers contain up to 35 % sulphur and, in essence, are transformed into thermosetting polymers similar to epoxy resins by this extensive cross-linking.

A large family of artificial rubbers related to natural rubber is now produced. One of the earliest examples was obtained by the polymerisation of butadiene in the presence of sodium (Na), to give buna (*Bu*tadiene + *Na*) rubber. Two other widely used rubbers are neoprene (Scheme 6.12a), a rubber resistant to organic solvents, and nitrile rubber (Scheme 6.12b), which is a copolymer of butadiene ($CH_2{=}CH{-}CH{=}CH_2$) and propenenitrile ($CH_2{=}CH{-}CN$).

6.4.5 The principal properties of polymers

Polymers consist mainly of carbon and hydrogen, and one of the principal properties of this group of



$$n\,(\mathrm{CH_2{=}CH{-}\overset{Cl}{C}{=}CH_2}) \longrightarrow \left[\mathrm{CH_2{-}CH{=}\overset{Cl}{C}{-}CH_2}\right]_n$$

$$2n(\mathrm{CH_2{=}CH{-}CH{=}CH_2}) + n(\mathrm{CH_2{=}CH{-}CN}) \longrightarrow \left[(\mathrm{CH_2{-}CH{=}CH{-}CH_2})_2(\mathrm{CH_2{-}\overset{CN}{C}H})\right]_n$$

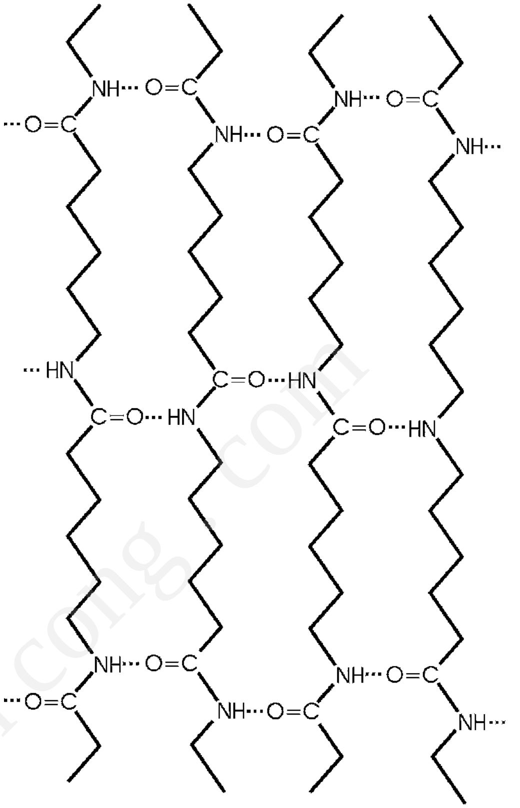
Scheme 6.12 (a) The structural formula of neoprene, prepared from a chlorinated hydrocarbon precursor. (b) The structural formula of nitrile rubber, a copolymer of butadiene and a hydrocarbon containing a nitrile (cyanide, —CN) group

materials is that they are low-density solids. This is enhanced by the fact that the polymer chains often do not pack together very closely, although the crystalline regions in polymers are denser than the overall solid.

Many properties of polymers depend on the functional groups that occur on the chains. Nylon fibres gain strength from >NH···O=C< hydrogen bonding (Scheme 6.13). This also allows them to absorb water and adds to the comfortable feel of these materials when used in clothing. The —NH— group in the polymers can pick up charge from the water to give $-\mathrm{NH_2^+}-$. This is noticeable as electrostatic charge buildup on carpets and clothing.

Other properties of polymers can be varied widely by making changes to processing and additives. As we have seen, introducing a small number of cross-links into a thermoplastic elastomer can change it from a sticky substance to a useful rubber. Similarly, although polymers are inherently insulators, doping can turn them into good conductors of electricity, as explained in Section 13.2.8. Moreover, they can be made into electronic and ionic conductors, allowing these materials to be used as electrolytes and current collectors in lightweight batteries.

The behaviour of polymers under stress is very variable and depends on the polymer structure and microstructure. Thermoplastic polymers are brittle at low temperatures and are easily deformed and plastic at higher temperatures. This is because the polymer chains are not linked to each other. In the brittle state, cracks can easily pass right through the solid, between the chains. At higher temperatures, the molecules can easily slip past each other. Crystalline regions in thermoplastics oppose these tendencies and add appreciably to the strength of the solid. Cross-linking, characteristic of thermosetting polymers, prevents molecular movement and results in solids that combine good mechanical strength with chemical stability.



Scheme 6.13 Hydrogen bonding between chains of nylon 6. The hydrogen bonds (broken lines) between H and O draw the chains together and give a nylon fabric enhanced properties

One of the principal properties shown by polymers relates to this aspect of chemical stability. Polymers do not degrade rapidly and present an eyesore in many parts of the world. The ease of degradation of a polymer rapidly decreases as the degree of cross-linking of the polymer chains increases, as the many large dumps of used tyres indicate. The heart of the problem is that the carbon–carbon backbone of polymers is extremely resistant to chemical attack as the bonds are so strong. The same is true of the carbon–hydrogen bonds that make up much of the rest of the molecules. In order to make a polymer more degradable, weak links must be introduced into the chain. To some extent, double bonds are more susceptible to attack than are single bonds, and elastomers with only one double bond are less likely to be attacked and degraded than are those rubbers with two double bonds available. Degradability can be enhanced by the introduction of deliberate points of attack into the polymer. For example, inclusion of oxygen atoms, or hydroxyl or acid groups, allow for water penetration and aid bacterial attack.

6.5 Composite materials

Composites are solids made up of more than one material, designed to have enhanced properties compared with the separate materials themselves.

Composites are widely used in nature. For example, wood is composed of strong flexible cellulose plus stiff lignin, and bone consists of strong soft collagen (a protein) plus apatite (a brittle hard ceramic). Composites are also are widely used for advanced engineering applications, from use in aircraft, to use in high-technology leisure items such as skis and sails. One of the earliest applications of a composite was the Macintosh raincoat. The fabric for this garment consisted of a sandwich of natural rubber between two sheets of a woven natural polymer, cotton.

Man-made composites fall into three broad classes, depending on whether the main part of the composite, the matrix, is a polymer, a metal or a ceramic. Often, but not always, the composite combines materials from two classes, as in glass-fibre-reinforced plastics. However, the most widely used composite material, concrete, is a ceramic – ceramic composite. The most important classes of artificial composite are described below. The mechanical properties of composites are discussed in Section 10.4. Biological composites are very varied and will not be considered here.

6.5.1 *Fibre-reinforced plastics*

The main polymers (plastics) used as matrices in polymer composites are thermosetting resins, especially polyester and epoxy resins. Polyester resins are relatively inexpensive but tend to shrink during curing and tend to absorb water. Epoxy resins are more expensive but do not shrink on curing and are fairly resistant to water penetration. In principle, any highly cross-linked polymer will form a matrix. The resins are reinforced by filling with fibreglass, carbon fibre or strong polymer fibres such Kevlar®, an aramid fibre.

The purpose of the matrix is to hold the fibres together in the desired orientation. Fibres alone tend to be brittle and, although they have good tensile strength, they cannot sustain compression readily. The purpose of the fibres is to add strength. The resultant strength depends on the type of fibre utilised and geometrical factors. These include the amount of fibre added and the length of the fibres (Figure 6.28), as well as the bonding between the matrix and the fibre inserts. The orientation of the fibres is also important. Composites are strong in

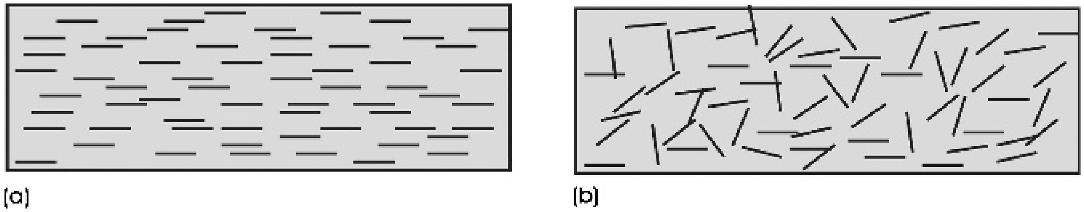


Figure 6.28 (a) Aligned fibre-reinforced composite; (b) random fibre-reinforced composite

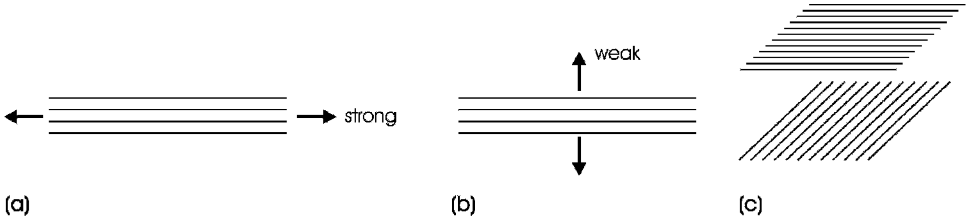


Figure 6.29 Reinforcing fibres tend to be strong in tension (part a) but are weak when subjected to a transverse force (part b); laminates in which the fibres are aligned in differing orientations offset this disadvantage (part c)

the direction of alignment and weaker normal to this direction. To overcome this, the orientation of successive layers of fibres is often changed to form a laminate (Figure 6.29).

6.5.2 Metal–matrix composites

Metals are frequently reinforced with continuous fibres to give improvements to strength. The fibres used are ceramic [e.g. silicon carbide (SiC) or alumina (Al_2O_3)] or metallic [e.g. boron (B) or tungsten (W)]. Fibres of these materials are difficult to fabricate and, unless superior performance is vital, it is easier to make composites by using small particles of a hard material such as alumina or silicon carbide. These ceramics are usually mixed with the molten alloy, which is then formed into the intended shape. Among the most widespread of metal–particle composites are the cemented carbide materials used as cutting tools for machining steel. The first of these was made from a matrix of the metal cobalt, containing hard tungsten carbide particles. Interestingly, this was the first combination tried by the producer and, although many other metal–metal carbide combinations were tried later, the cobalt–tungsten carbide composite remains the best for most purposes.

6.5.3 Ceramic-matrix composites

Ceramic-matrix composites are utilised to overcome the inherent brittleness of ceramics. The reinforcement consists of fibres or particles. The materials used include silicon carbide and alumina. The toughening comes about because the fibres or particles deflect or bridge cracks in the matrix. Naturally occurring ceramic–ceramic composites include granite and marble. These are imitated in concrete, discussed below.

Although glass in composite materials is associated mostly with the strengthening component in the form of fibres, laminated glass is a widely used composite. This material consists of a thin plastic film sandwiched between two or more sheets of glass. The purpose of the polymer is to prevent the glass splintering on impact. It is widely used as bullet-proof glass.

6.5.4 Cement and concrete

Concrete is a composite material made from cement paste and aggregate (a coarse, stony material). The composition of concrete varies widely and depends on the intended application but always contains cement, water and aggregate. The mixture of cement, water and sand is called mortar, whereas cement and water alone constitute cement paste.

Early forms of cement, which were composed mainly of calcium hydroxide [$Ca(OH)_2$] partly transformed to calcium carbonate ($CaCO_3$) predate Roman times. The material was made from limestone, [impure calcium carbonate ($CaCO_3$)] heated or 'burned' to give quicklime or burnt lime, calcium oxide (CaO).

$$CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(g)$$

Quicklime reacts with water to release considerable heat, a process called slaking, to give slaked lime, calcium hydroxide [$Ca(OH)_2$]:

$$CaO\,(s) + H_2O\,(l) \rightarrow Ca(OH)_2\,(s).$$

Table 6.6 Constituents of Portland cement

Chemical name	Mineral name	Chemical formula	Shorthand notation	Typical composition/wt%
Tricalcium silicate	Alite	Ca_3SiO_5	C_3S	40–65
Dicalcium silicate	Belite	Ca_2SiO_4	C_2S	10–20
Tricalcium aluminate		$Ca_3Al_2O_6$	C_3A	10
Tetracalcium aluminoferrite		$Ca_4Al_2Fe_2O_{10}$	C_4AF	10
Calcium sulphate dihydrate	Gypsum	$CaSO_4 \cdot 2H_2O$	CSH_2	2–5

The slaked lime was mixed to a paste with water and used to cement sand or stone. The paste slowly reacted with carbon dioxide in the air to give calcium carbonate again:

$$Ca(OH)_2\,(s) + CO_2\,(g) \rightarrow CaCO_3\,(s) + H_2O\,(l).$$

The Romans improved the process by adding volcanic ash to the limestone, to produce a far more durable cement, which is still seen today.

6.5.4.1 *Portland cement*

Portland cement, invented in 1892 by Joseph Aspdin of Leeds, was so called because it resembled expensive Portland stone (at least to the eye of the inventor). It is made from about 80 % limestone and about 20 % clay. It was widely adopted because it possessed superior qualities to the older quicklime-based material, including the especially important property of being able to harden in damp conditions. This latter property was especially valuable at a time when tunnel construction was widespread, including amongst other projects, the London underground system.

To make cement powder, the raw materials are ground with water to form a slurry. This is heated in a kiln at gradually increasing temperatures, initially to drive off water and then to decompose the calcium carbonate:

$$CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(g).$$

As the temperature increases, other reactions take place, and the reaction products partly melt and sinter, to produce 'clinker'. In the final stage of manufacture, the cooled clinker is ground, and about 2–5 % gypsum, calcium sulphate hydrate ($CaSO_4 \cdot 2H_2O$) is added to produce cement powder.

Portland cement powder contains five major constituents. These are complex minerals and are known by their chemical names, mineral names and by a shorthand notation, listed in Table 6.6. There are also traces of other impurities in ordinary cement powder, which may have a large effect on the final strength and durability of the concrete. The composition of typical Portland cement is included in Table 6.6.

6.5.4.2 *Hardening of cement*

Cement hardens when the constituents react with water to produce an interlocking array of hydrated silicate crystals. The main reactions are rather indeterminate, because of the variable quantities of water and cement powder involved and because the reactions that take place are extremely complex. Broadly, the sequence of reactions that take place are (Figure 6.30):

- reaction of alite and water;
- reaction of belite and water;
- reaction of aluminate and water;
- reaction of ferrite and water;
- reaction of gypsum with aluminate and water.

Reaction of alite and water

$$\begin{aligned} &\text{alite} + \text{water} \rightarrow \text{calcium hydroxide} \\ &\qquad\qquad + \text{calcium silicate hydrate} \\ &Ca_3SiO_4 + H_2O \rightarrow Ca(OH)_2 + (CaO)_x(SiO_2)_y \cdot aq \end{aligned}$$

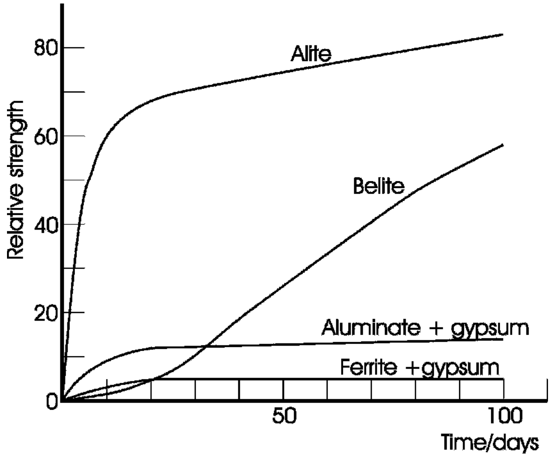


Figure 6.30 The approximate relative strengths of the components of Portland cement after hydration as a function of time elapsed

This chemical equation is not balanced because, in practice, x varies between the approximate limits of 1.8–2.2, y varies around a mean value of 1.0 and 'aq' means that water is also combined in the material in an indeterminate amount. The idealised composition of the calcium silicate hydrate phase is $Ca_2SiO_4 \cdot aq$. The reaction is rapid and continues for up to approximately 20 days. Considerable heat is evolved – in the order of 500 J per gram of powder – and care must be taken to remove this heat when forming large masses of concrete into structures. The reaction gives a high-strength product.

Reaction of belite and water

$$\begin{aligned} \text{belite} + \text{water} &\rightarrow \text{calcium hydroxide} \\ &\quad + \text{calcium silicate hydrate} \\ Ca_2SiO_5 + H_2O &\rightarrow Ca(OH)_2 \\ &\quad + (CaO)_x(SiO_2)_y \cdot aq \end{aligned}$$

The reaction, like that of alite, is imprecise, and the chemical equation is not balanced. Belite reacts slowly, taking about a year to harden and is responsible for the long-term strength of concrete. The heat liberated, approximately 250 J per gram of powder, is not as great as that liberated in the reaction of alite and, because the reaction is slower, does not have such immediate consequences during construction.

Reaction of aluminate and water

$$\begin{aligned} &\text{aluminate} + \text{water} \rightarrow \text{calcium aluminate hydrate} \\ &Ca_3Al_2O_6 + 6H_2O \rightarrow Ca_3Al_2O_6 \cdot 6H_2O \end{aligned}$$

This is a very rapid reaction and is completed in minutes. It is also a very energetic reaction, with about 900 J per gram released during the hydration. The product is of very low strength and is attacked by sulphate, a common impurity in many soils and rocks.

Reaction of ferrite and water Ferrite and water react very slowly. Moderate amounts of heat are evolved – about 300 J per gram. The product is not attacked by sulphate and is beneficial mainly to the strength of the cement. However, the main importance of ferrite is cosmetic, as it influences the colour of the product.

Reaction of gypsum with aluminate and water

$$\begin{aligned} &\text{gypsum} + \text{aluminate} + \text{water} \rightarrow \text{etringite} \\ &Ca_3Al_2O_6 + 3CaSO_4 \cdot 2H_2O + 30\,H_2O \\ &\rightarrow Ca_6Al_2S_3O_{18} \cdot 32H_2O \end{aligned}$$

Gypsum is important as it reacts with aluminate to give etringite – calcium aluminium sulphate hydrate, $Ca_6Al_2S_3O_{18} \cdot 32H_2O$ – on the surface of the aluminate grains. This slows the reaction of aluminate with water and allows the wet cement paste to be worked for longer.

6.5.4.3 Heat of hydration

The hydration of cement involves a number of exothermic reactions which liberate a great deal of heat and, when building substantial concrete structures, this must be removed to prevent cracking or other deterioration of the structure. The evolution of heat takes place over a period, and the rate of heat evolution is as important as the total amount of heat given out. Several empirical relationships between the composition of the cement, the heat of hydration and the time elapsed have been developed. These take the typical form:

$$\text{heat of hydration} = A\,x_{\mathrm{C_3S}} + B\,x_{\mathrm{C_2S}} + C\,x_{\mathrm{C_3A}} + D\,x_{\mathrm{C_4AF}}$$

where x_i is the weight fraction of constituent i (see Table 6.6), and A, B, C and D are empirical constants that vary over time, reflecting the changes in the composition of the cement as it hardens; the heat of hydration is measured in joules per gram of cement. For example, the heats of hydration after three days, $H(3\,\mathrm{d})$, and after a year, $H(1\,\mathrm{yr})$, are given as follows:

$$H(3\,\mathrm{d}) = 240x_{\mathrm{C_3S}} + 50x_{\mathrm{C_2S}} + 880x_{\mathrm{C_3A}} + 290x_{\mathrm{C_4AF}}$$

$$H(1\,\mathrm{yr}) = 490x_{\mathrm{C_3S}} + 225x_{\mathrm{C_2S}} + 1160x_{\mathrm{C_3A}} + 375x_{\mathrm{C_4AF}}$$

6.5.4.4 Microstructures of cement and concrete

The microstructures that form as the paste reacts with water are important in controlling the final strength of the concrete. Initially, water reacts to give a silicate gel. This material is amorphous and produces a glutinous coating on the powder particles, holding the particles together and causing a certain amount of swelling to occur. The gel slowly crystallises, to give a mass of interpenetrating needles and plates. Gypsum reacts slowly to form hexagonal needle-like prisms of the silicate ettringite – hydrated calcium aluminium sulphate hydroxide, $Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$ – which further interlock the mass. In addition, the material contains free water, at least in the early stages of reaction, and pores. The details of these reactions still remain to be completely worked out for all the constituents present.

The microstructure of concrete is further complicated by the presence of the aggregate. Although this is often supposed to be inert chemically it can also react with the other constituents and with water, particularly if this contains acidic or alkaline impurities.

Answers to introductory questions

Are hydrides alloys or ceramics?

Hydrides are composed of metals (elements or alloys) and hydrogen. The answer to the question will depend on the composition of the hydride. Broadly speaking, when only small amount of hydrogen is present, it occupies interstitial positions in the metallic crystal structure and the material behaves as a metal. With more hydrogen, the electrons dispersed throughout the metallic crystal begin to localise, resulting in a more brittle solid, although the electronic properties remain metallic. Eventually, chemical compounds form. These tend to resemble ceramics in that the electrons in the solid are localised and the materials are insulators. MgH_2, for example, is transparent and resembles an insulating ceramic such as MgO.

Are glasses liquids?

Glasses are not liquids; they are obviously solids. However, the structure of a glass is similar to the structure of the liquid phase that exists at high temperatures. Glasses are called supercooled liquids because they do not crystallise on cooling from this state. The liquid structure is frozen in and for kinetic reasons does not rearrange into a crystal.

Are polymers glasses?

Polymers are not glasses, as glasses are defined as inorganic materials formed by a high-temperature process. Polymers are (mostly) carbon compounds and are made by low-temperature routes from organic precursors, derived mainly from oil. Structurally, however, polymers often resemble glasses. Polymers that are largely amorphous in structure show a glass transition temperature. The glass transition temperature in a polymer gives an idea of how easily the polymer chains slip past each other. It is easily changed by adding small molecules, called plasticisers, to the polymer mix.

Why are plastic bags difficult to degrade?

Plastic bags are made of polymers that are formed from chains of carbon atoms linked mainly by strong sp^3 hybrid bonds. The majority of the other bonds in the molecules are the equally strong bonds between carbon and hydrogen, which are also mainly sp^3 hybrid bonds. These strong bonds resist chemical attack by water, oxygen and bacteria, the major forces for degradation in the natural world. They do slowly degrade when exposed to high-energy radiation, such as the ultraviolet radiation present in sunlight, but the process is slow and often affects the pigments in the plastic before having an effect on the polymer chains, so that although the bag appears to degrade, the polymer remains mostly intact. Plastic bags and other polymers can be made to degrade more rapidly by introducing weak links into the carbon–carbon chains similar to those found in naturally occurring polymers such as proteins.

Further reading

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Problems and exercises

Quick quiz

1 An allotrope of a metallic element is:
   (a) A high-temperature form
   (b) A form with a different crystal structure
   (c) A compound of the element

2 An interstitial alloy is an alloy in which:
   (a) Impurity atoms occupy normally empty sites in the crystal structure
   (b) Impurity atoms replace atoms in normally filled sites in the crystal structure
   (c) Impurity atoms alloy and form a new crystal structure

3 In the A1, copper structure, face-centred cubic: the atoms are in contact along:
   (a) A cube body diagonal
   (b) A cube face diagonal
   (c) A cube edge

4 Ordered alloy structures such as Cu_3Au are formed by:
   (a) Rapidly cooling the alloy
   (b) Slowly cooling the alloy
   (c) Annealling the alloy

5 Steel is an alloy of iron and carbon in which the carbon occupies:
   (a) Substitutional sites
   (b) Interstitial sites
   (c) Substitutional and interstitial sites

6 In each unit cell of the A1 (face-centred cubic) structure there are:
   (a) 4 octahedral sites
   (b) 8 octahedral sites
   (c) 12 octahedral sites

7 In each unit cell of the A2 (body-centred cubic) structure there are:
   (a) 4 tetrahedral sites
   (b) 6 tetrahedral sites
   (c) 8 tetrahedral sites

8 The tetrahedral sites in interstitial alloys can be occupied by:
  - (a) Hydrogen
  - (b) Nitrogen
  - (c) Both hydrogen and nitrogen

9 The inclusion of semimetals in a mixture:
  - (a) Hinders the formation of metallic glasses
  - (b) Aids the formation of metallic glasses
  - (c) Has no effect on the formation of metallic glasses

10 Crystallisation of metals is hindered by:
  - (a) The addition of glass to the melt
  - (b) The addition of other metals to the melt
  - (c) The addition of nonmetallic elements to the melt

11 The high electrical conductivity and reflectivity of metals is attributed to:
  - (a) The nature of the metallic bond
  - (b) The crystal structure of metals
  - (c) The defects present in metals

12 The ductility of metals is attributed to:
  - (a) The metallic bond
  - (b) Impurities in metals
  - (c) The crystal structure of metals

13 Metals can be hardened by:
  - (a) Adding impurities
  - (b) Removing impurities
  - (c) Removing defects

14 Silicon carbide is regarded as:
  - (a) An electroceramic
  - (b) An engineering ceramic
  - (c) A glass

15 Isomorphous replacement in silicate ceramics creates:
  - (a) Substitutional defects
  - (b) Interstitial defects
  - (c) No defects

16 Silicates are stable because of strong bonds between:
  - (a) Oxygen and oxygen
  - (b) Metal atoms and silicon
  - (c) Silicon and oxygen

17 Ionic silicates contain isolated:
  - (a) Silicate groups
  - (b) Silicate chains
  - (c) Silicate sheets

18 Clays are silicates containing:
  - (a) Chains of [SiO_4] plus hydroxyl
  - (b) Networks of [SiO_4] plus hydroxyl
  - (c) Sheets of [SiO_4] plus hydroxyl

19 Ruby is a gemstone consisting of aluminium oxide containing small amounts of:
  - (a) Titanium impurity
  - (b) Chromium impurity
  - (c) Titanium and iron impurities

20 The ceramic zirconia, ZrO_2,
  - (a) Adopts the *fluorite* structure
  - (b) Adopts the *corundum* structure
  - (c) Adopts several structures, depending on temperature

21 The formation of a glass during ceramic production is called:
  - (a) Vitrification
  - (b) Sintering
  - (c) Glass – ceramic formation

22 A refractory ceramic is one that is:
  - (a) Difficult to process
  - (b) Particularly hard
  - (c) Able to withstand high temperatures

23 Pyrex® glass is also known as:
  - (a) Flint glass
  - (b) Borosilicate glass
  - (c) Soda-lime glass

24 The glass transition temperature marks the point at which:
  - (a) A glass transforms from a solid to a viscous liquid

(b) The glass can be moulded and blown

(c) The glass becomes stable

25 In glass technology, small ions such as those of phosphorus (P) and boron (B) are known as:
(a) Network modifiers
(b) Network formers
(c) Intermediates

26 A glass ceramic is:
(a) A glass processed at high temperatures
(b) A transparent ceramic
(c) A ceramic containing crystals and glass

27 Polymers are:
(a) Small molecules that can join together
(b) Very large molecules made of small units
(c) Molecules also called oligomers

28 Thermosetting plastics:
(a) Can be reformed repeatedly
(b) Can be formed only once
(c) Set at high temperatures

29 Polystyrene is an example of:
(a) An addition polymer
(b) A condensation polymer
(c) An elastomer

30 The formula of the monomer of poly(acrylonitrile) is
(a) $CH_2{=}CH_2\ CN$
(b) $CH_3{-}CH{=}CN$
(c) $CH_2{=}CH\ CN$

31 Nylon 6, 6 is an example of:
(a) An addition polymer
(b) A condensation polymer
(c) An elastomer

32 Nylons are:
(a) Polyamides
(b) Polyesters
(c) Polycarbonates

33 The molar mass of a specific polymer:
(a) Is a fixed number
(b) Varies between narrow limits
(c) Varies between wide limits

34 The molecular mass of a monomer:
(a) Is a fixed number
(b) Varies between narrow limits
(c) Varies between wide limits

35 A lamella is:
(a) A spherulite in a polymer
(b) A chain in a polymer
(c) A crystalline region in a polymer

36 A polymer in which the side-groups lie on alternate sides of the polymer chain backbone is:
(a) Isotactic
(b) Syndiotactic
(c) Atactic

37 Copolymers are formed from:
(a) Two different monomers
(b) Two different polymers
(c) Mixed polymers

38 The growth of polymer chains by the joining of existing chains is called:
(a) Chain growth
(b) Step growth
(c) Link growth

39 The ‘snap-back’ property of elastomers is due to:
(a) A few weak cross-links between chains
(b) A few strong cross-links between chains
(c) Large numbers of cross-links between chains

40 A solid made by combining several different types of material is called:
(a) A combination material
(b) A consolidation material
(c) A composite material

41 Ceramic matrix composites are designed to overcome:
(a) The weight of ceramics
(b) The brittle nature of ceramics
(c) The inertness of ceramics

42 The initial hardening of Portland cement is attributed to:
   (a) Alite
   (b) Belite
   (c) Gypsum

43 The main source of heat when Portland cement hardens is due to the reaction of:
   (a) Tricalcium silicate
   (b) Dicalcium silicate
   (c) Tricalcium aluminate

44 The long-term hardening of Portland cement is attributed to the presence of:
   (a) Tricalcium silicate
   (b) Dicalcium silicate
   (c) Tricalcium aluminate

45 Which of the following is *not* used to make Portland cement:
   (a) Clay
   (b) Limestone
   (c) Portland stone

Calculations and questions

6.1 The radius of a gold atom is 0.144 nm. Gold adopts the A1 structure. Estimate the unit cell parameter of gold crystals.

6.2 The radius of a lead atom is 0.175 nm. Lead adopts the A1 structure. Estimate the unit cell parameter of lead crystals.

6.3 The radius of a palladium atom is 0.138 nm. Palladium adopts the A1 structure. Estimate the unit cell parameter of palladium crystals.

6.4 The radius of an iridium atom is 0.136 nm. Iridium adopts the A1 structure. Estimate the unit cell parameter of iridium crystals.

6.5 Nickel adopts the A1 structure, with a lattice parameter of 0.3524 nm. Estimate the metallic radius of nickel in this structure.

6.6 Rhodium adopts the A1 structure, with a lattice parameter of 0.3803 nm. Estimate the metallic radius of rhodium in this structure.

6.7 The radius of a barium atom is 0.224 nm. Barium adopts the A2 structure. Estimate the unit cell parameter of barium crystals.

6.8 The radius of a niobium atom is 0.147 nm. Niobium adopts the A2 structure. Estimate the unit cell parameter of niobium crystals.

6.9 Vanadium adopts the A2 structure, with a lattice parameter of 0.3024 nm. Estimate the metallic radius of vanadium in this structure.

6.10 Potassium adopts the A2 structure, with a lattice parameter of 0.5321 nm. Estimate the metallic radius of potassium in this structure.

6.11 At room temperature, iron adopts the A2 structure with a lattice parameter of 0.28665 nm.
   (a) Estimate the metallic radius of iron in this structure.
   (b) Ignoring thermal expansion, estimate the lattice parameter of the high-temperature A1 structure that exists above 912 °C.

6.12 At room temperature, calcium adopts the A1 structure with a lattice parameter of 0.5588 nm.
   (a) Estimate the metallic radius of calcium in this structure.
   (b) Ignoring thermal expansion, estimate the lattice parameter of the high-temperature A2 structure that exists above 445 °C.

6.13 At room temperature, strontium adopts the A1 structure. The metallic radius of strontium in this structure is 0.215 nm.
   (a) Estimate the lattice parameter of the A1 structure of strontium.
   (b) Ignoring thermal expansion, estimate the lattice parameter of the high-temperature A2 structure that exists above 527 °C.

6.14 The metallic radius of magnesium, which adopts the A3 structure, is 0.160 nm. Estimate the value of the lattice parameters a_0 and c_0 (ideal).

6.15 The metallic radius of rhenium, which adopts the A3 structure, is 0.138 nm. Estimate the value of the lattice parameters a_0 and c_0 (ideal).

6.16 The a_0 lattice parameter of titanium, which adopts the A3 structure, is 0.2951 nm. Estimate the radius r of titanium in this structure and the ideal value of the parameter c_0.

6.17 The a_0 lattice parameter of beryllium, which adopts the A3 structure, is 0.2286 nm. Estimate the radius r of beryllium in this structure and the ideal value of the parameter c_0.

6.18 At room temperature, hafnium adopts the A3 structure, with lattice parameters $a_0 = 0.3195$ nm, and $c_0 = 0.5051$ nm.

(a) Estimate the metallic radius of hafnium in this structure.

(b) Ignoring thermal expansion, estimate the lattice parameter of the high-temperature A2 structure that exists above 1742 °C.

6.19 At room temperature, yttrium adopts the A3 structure, with lattice parameters $a_0 = 0.3648$ nm, and $c_0 = 0.5732$ nm.

(a) Estimate the metallic radius of yttrium in this structure.

(b) Ignoring thermal expansion, estimate the lattice parameter of the high-temperature A2 structure that exists above 1481 °C.

6.20 The rapidly cooled form of the alloy CuAu has the A1 structure, in which the metals atoms are distributed at random over the available sites. The unit cell parameter is 0.436 nm. Estimate the density of the alloy.

6.21 Cartridge brass is a composition in the phase range of the alloy α-brass, which is made up with 30 wt% zinc and 70 wt% copper. The alloy has the A1 structure, in which the metal atoms are disordered over the available sites. The density is 8470 kg m^{-3}. Estimate the lattice parameter of the alloy.

6.22 Which of the following metals would be expected to form the most extensive substitutional solid solution with nickel, A1 structure, metallic radius 0.1246 nm, electronegativity 1.8?

(a) Cobalt, A3 structure, metallic radius 0.125 nm, electronegativity 1.7.

(b) Chromium, A2 structure, metallic radius 0.128 nm, electronegativity 1.4.

(c) Platinum, A1 structure, metallic radius 0.139 nm, electronegativity 2.1.

(d) Silver, A1 structure, metallic radius 0.145 nm, electronegativity 1.8.

6.23 Which of the following metals would be expected to form the most extensive substitutional solid solution with copper, A1 structure, metallic radius 0.1278 nm, electronegativity 1.8?

(a) Aluminium, A1 structure, metallic radius 0.143 nm, electronegativity 1.5.

(b) Palladium, A1 structure, metallic radius 0.138 nm, electronegativity 2.0.

(c) Vanadium, A2 structure, metallic radius 0.135 nm, electronegativity 1.4.

(d) Titanium, A3 structure, metallic radius 0.146 nm, electronegativity 1.6.

6.24 Ceramics for use in technical applications are often divided into the groups 'traditional', 'engineering', 'electroceramics' and 'glass'. Define each of these categories and give a typical use for a material from each group. [Note: answer is not provided at the end of this book.]

6.25 Why does the refractory zirconia, ZrO_2, not find more high-temperature uses when pure? Explain how the problem is overcome by doping. [Note: answer is not provided at the end of this book.]

6.26 It is necessary to identify some plate-shaped crystals that have appeared in a glass melt. X-ray diffraction shows that they are single phase and of a structure related to muscovite mica, talc or pyrophyllite. the chemical analysis gives an empirical formula of $KF \cdot AlF \cdot BaO \cdot MgO \cdot Al_2O_3 \cdot 5MgSiO_3$. Suggest substitutions that could have been made in the muscovite mica, talc and pyrophyllite structures to produce the crystals. [Note: answer is not provided at the end of this book.]

6.27 The mineral pyrophyllite, $Al_2(OH)_2Si_4O_{10}$, has a Mohs hardness of 1; muscovite mica, $KAl_2(OH)_2Si_3AlO_{10}$, has a Mohs hardness of 2.5; and the mica margite, $CaAl_2(OH)_2Si_2Al_2O_{10}$, has a Mohs hardness of 5. Explain this in terms of the structure and bonding in these compounds. [Note: answer is not provided at the end of this book.]

6.28 The viscosity of a soda-lime glass is given in Table 6.7. Estimate the glass transition temperature.

Table 6.7 Soda-lime: viscosity, with temperature; for Question 6.28

Viscosity/dPa s	Temperature/°C
5×10^{14}	450
5×10^{7}	700
1×10^{4}	1050
1×10^{2}	1450

6.29 Calculate the viscosity at (a) 940 °C and (b) 1400 °C of a high-silica glass for which η_0 is 3.5×10^{-5} Pa s and the activation energy, E, is 382 kJ mol^{-1}.

6.30 The viscosity parameters for a clear float glass are: softening point, 720 °C; annealing point, 535 °C; strain point, 504 °C. Estimate the activation energy for the viscosity.

6.31 The viscosity parameters for a glass are: softening point, 677 °C; annealing point, 532 °C; strain point, 493 °C. Estimate the activation energy for the viscosity.

6.32 The viscosity parameters for a borosilicate glass are: softening point, 794 °C; annealing point, 574 °C; strain point, 530 °C. Estimate the activation energy for viscosity.

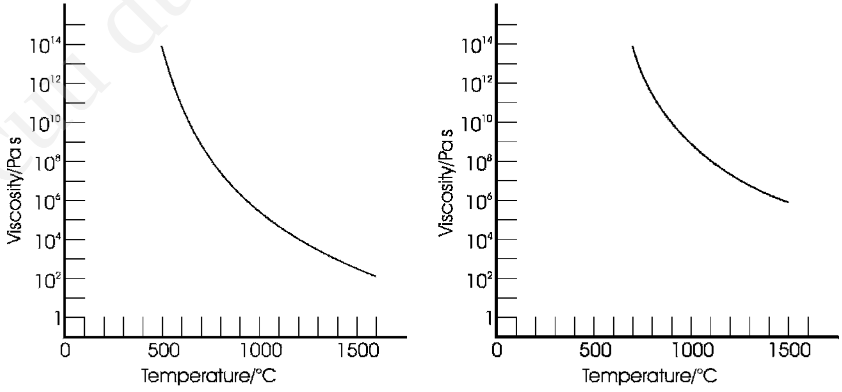
6.33 The viscosity of a borosilicate glass is drawn in Figure 6.31(a). Estimate the activation energy of the viscosity and comment on the form of the Arrhenius plot.

6.34 The viscosity of a high-silica glass is drawn in Figure 6.31(b). Estimate the activation energy of the viscosity and comment on the form of the Arrhenius plot.

6.35 Write the reaction equation for the reaction of two monomer molecules of styrene to produce a dimer. [Note: equation is not shown in the answers at the end of this book.]

(a) What weight of monomer is needed to produce 100 kg of polymer?

(b) How many monomer molecules is this?



(a) (b)

Figure 6.31 Plot of viscosity against temperature for (a) a borosilicate glass, for Question 6.33, and (b) a high-silica glass, for Question 6.34

(c) The number average molar mass of the polymer is 250 000 g mol^{-1}. What is the degree of polymerisation?

6.36 Write the reaction equation for the reaction of two monomer molecules of methyl methacrylate to produce a dimer. [Note: equation is not shown in the answers at the end of this book.]

(a) What weight of monomer is needed to produce 100 kg of polymer?

(b) How many monomer molecules is this?

(c) The number average molar mass of the polymer is 200 000 g mol^{-1}. What is the degree of polymerisation?

6.37 Nitrile rubber is a copolymer of butadiene, ($CH_2{=}CH{-}CH{=}CH_2$) and acrylonitrile (propenenitrile), ($CH_2{=}CH{-}CN$). Write the reaction equation between these two molecules to produce a dimer. [Note: equation is not shown in the answers at the end of this book.]

(a) What masses of the reactants are needed to give 100 kg of polymer?

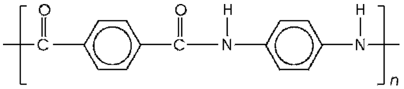
(b) How many molecules of each reactant is this?

6.38 PET is a polymer of terephthalic acid and ethylene glycol (see Scheme 6.2). Write the hypothetical reaction equation between these two molecules to produce a dimer. [Note: equation is not shown in the answers at the end of this book.]

(a) What masses of the reactants are needed to give 100 kg of polymer?

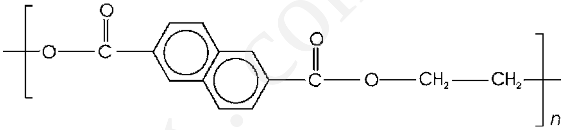
(b) How many molecules of each reactant is this?

6.39 The structural formula of the aramid polymer Kevlar®, used in bullet-proof vests, is shown in Scheme 6.14. Write the formulae of the two monomers used. [Note: the full version of Scheme 6.14 is shown at in the answers, at the end of this book.]



Scheme 6.14 Kevlar®

6.40 The structural formula of the polycarbonate PEN [poly(ethylene naphthalate)], used in recyclable jars and bottles, is shown in Scheme 6.15. Write the formulae of the two monomers used. [Note: the full version of Scheme 6.15 is shown in the answers, at the end of this book.]



Scheme 6.15 Poly(ethylene naphthalate) (PEN)

6.41 Compute (a) the number-average molar mass and (b) the degree of polymerisation for polypropylene from the data given in Table 6.8.

Table 6.8 Polypropylene: data for Question 6.41

Molar mass/ g mol^{-1} Range	Mean in range	Fraction of molecules in range
5 000–10,000	7 500	0.01
10 000–15 000	12 500	0.09
15 000–20 000	17 500	0.17
20 000–25 000	22 500	0.18
25 000–30 000	27 500	0.20
30 000–35 000	32 500	0.17
35 000–40 000	37 500	0.09
40 000–45 000	42 500	0.06
45 000–50 000	47 500	0.03

6.42 Compute (a) the weight-average molar mass and (b) the degree of polymerisation for polypropylene from the data in Table 6.9.

6.43 The density of polyethylene crystals is 998 kg m^{-3}, and the unit cell has dimensions

Table 6.9 Polypropylene: data for Queston 6.42

Molar mass/g mol^{-1}		Weight fraction of molecules
Range	Mean in range	in range
5 000–10 000	7 500	0.01
10 000–15 000	12 500	0.07
15 000–20 000	17 500	0.16
20 000–25 000	22 500	0.20
25 000–30 000	27 500	0.23
30 000–35 000	32 500	0.18
35 000–40 000	37 500	0.08
40 000–45 000	42 500	0.05
45 000–50 000	47 500	0.02

$a = 0.741$ nm, $b = 0.494$ nm, and $c = 0.255$ nm.

(a) How many CH_2 units are there in a unit cell?

(b) How many 'monomer' ($CH_2—CH_2$) units are there?

6.44 The density of amorphous polythene is approximately 810 kg m^{-3}. Estimate the crystallinity of: low-density polyethylene, density 920 kg m^{-3}; medium-density polyethylene, density 933 kg m^{-3}; and high-density polyethylene, density 950 kg m^{-3}. [Note: the density of crystalline polyethylene is given in Question 6.43.]

6.45 Calculate the heats of hydration after three days, $H(3\text{ d})$, and one year, $H(1\text{ yr})$, for the following Portland cement compositions, (wt%):

(a) 50 % C_3S; 25 % C_2S; 12 % C_3A; 8 % C_4AF;

(b) 45 % C_3S; 30 % C_2S; 7 % C_3A; 12 % C_4AF;

(c) 60 % C_3S; 15 % C_2S; 10 % C_3A; 8 % C_4AF.