Chapter 1

Introduction

1.1 Introduction and synopsis

The word 'cell' derives from the Latin *cella*: a small compartment, an enclosed space. Our interest is in clusters of cells – to the Romans, *cellarium*, to us (less elegantly) *cellular solids*. By this we mean an assembly of cells with solid edges or faces, packed together so that they fill space. Such materials are common in nature: wood, cork, sponge and coral are examples (cellulose is from the Latin diminutive *cellula*: full of little cells).

Man has made use of these natural cellular materials for centuries: the pyramids of Egypt have yielded wooden artefacts at least 5000 years old, and cork was used for bungs in wine bottles in Roman times (Horace, 27 BC). More recently man has made his own cellular solids. At the simplest level there are the honeycomb-like materials, made up of parallel, prismatic cells, which are used for lightweight structural components. More familiar are the polymeric foams used in everything from disposable coffee cups to the crash padding of an aircraft cockpit. Techniques now exist for foaming not only polymers, but metals, ceramics and glasses as well. These newer foams are increasingly used structurally – for insulation, as cushioning, and in systems for absorbing the kinetic energy from impacts. Their uses exploit the unique combination of properties offered by cellular solids, properties which, ultimately, derive from the cellular structure.

This book brings together the understanding of the structure and properties of cellular solids, and of the ways their properties can be exploited in engineering

design. They are an important class of engineering material, yet a curiously neglected one. Economically speaking, they are far more important than are fibre-composites, for example, but the literature on them is, by comparison, tiny – most undergraduate texts do not even mention them. They are produced and used on an enormous scale; if we include wood, the economics of the business is comparable with that of the aluminium or glass industry, yet they are less researched, less well understood and less adequately documented than almost any other class of material.

In this chapter we introduce briefly the structure of cellular materials, ways of making them, their properties and the applications for which they are used. We conclude the chapter with an outline of the remainder of the book and a brief description of the sources of literature on cellular materials.

1.2 What is a cellular solid?

A cellular solid is one made up of an interconnected network of solid struts or plates which form the edges and faces of cells. Three typical structures are shown in Fig. 1.1. The simplest (Fig. 1.1(a)) is a two-dimensional array of polygons which pack to fill a plane area like the hexagonal cells of the bee; and for this reason we call such two-dimensional cellular materials *honeycombs*. More commonly, the cells are polyhedra which pack in three dimensions to fill space; we can such three-dimensional cellular materials *foams*. If the solid of which the foam is made is contained in the cell edges only (so that the cells connect through open faces), the foam is said to be open-celled (Fig. 1.1(b)). If the faces are solid too, so that each cell is sealed off from its neighbours, it is said to be closed-celled (Fig. 1.1(c)); and of course, some foams are partly open and partly closed. The geometry and characterization of cells is an interesting subject in its own right, and one which has led to ingenious analysis; we deal with it in more depth in Chapter 2.

The single most important feature of a cellular solid is its *relative density*, ρ^*/ρ_s; that is, the density of the cellular material, ρ^*, divided by that of the solid from which the cell walls are made, ρ_s. Special ultra-low-density foams can be made with a relative density as low as 0.001. Polymeric foams used for cushioning, packaging and insulation have relative densities which are usually between 0.05 and 0.2; cork is about 0.14; and most softwoods are between 0.15 and 0.40. As the relative density increases, the cell walls thicken and the pore space shrinks; above about 0.3 there is a transition from a cellular structure to one which is better thought of as a solid containing isolated pores (Fig. 1.2). In this book we are concerned with the true cellular solids, and thus with relative densities of less than 0.3.

1.3 Making cellular solids

Almost any material can be foamed. Polymers, of course, are the most common. But metals, ceramics, glasses, and even composites, can be fabricated into cells. Pictures of a wide range of cellular materials are shown in Chapter 2. Here we briefly summarize the ways of making them.

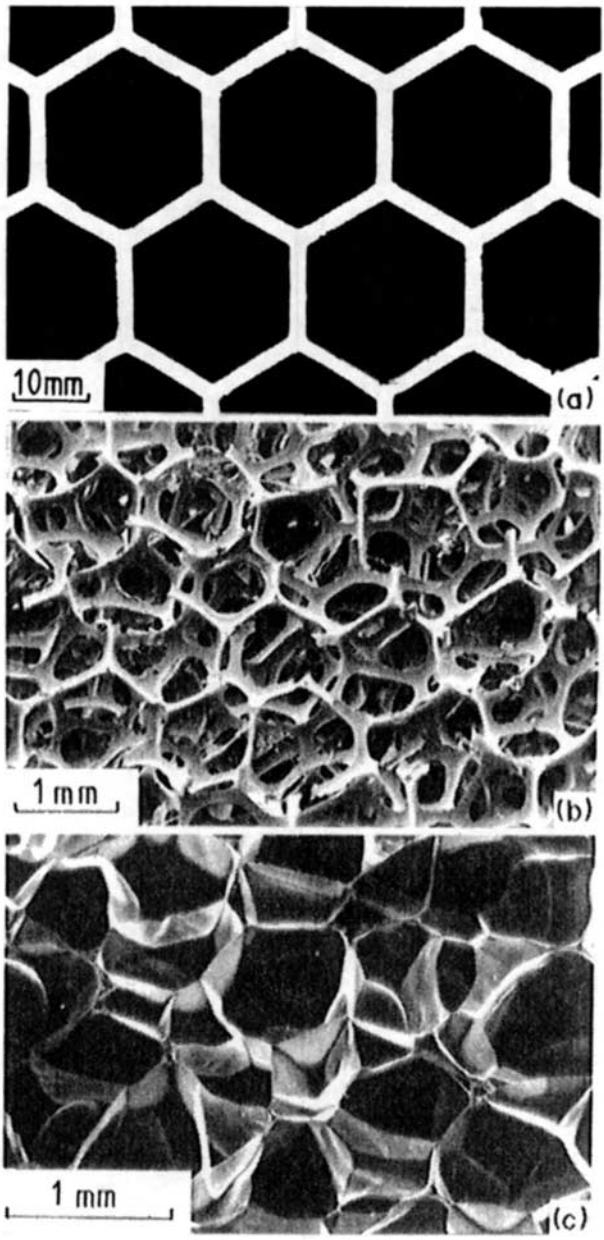

Figure 1.1 Examples of cellular solids: (a) a two-dimensional honeycomb: (b) a three-dimensional foam with open cells: (c) a three-dimensional foam with closed cells.

(a) Honeycombs

Structures like the honeycomb shown in Fig. 1.1(a) can be made in at least four ways. The most obvious is to press sheet material into a half-hexagonal profile and glue the corrugated sheets together. More commonly, glue is laid in parallel strips on flat sheets, and the sheets are stacked so that the glue bonds them together along the strips. The stack of sheets is pulled apart ('expanded') to give a honeycomb. Paper–resin honeycombs are made like this; the paper is glued and expanded, and then dipped into the resin to protect and stiffen it. Honeycombs can also be cast into a mould; the silicone rubber honeycomb shown in the figure was made by casting. And, increasingly, honeycombs are made by extrusion; the ceramic honeycombs used to support exhaust catalysts in automobiles are made in this way.

(b) Foams

Different techniques are used for foaming different types of solids. Polymers are foamed by introducing gas bubbles into the liquid monomer or hot polymer, allowing the bubbles to grow and stabilize, and then solidifying the whole thing by cross-linking or cooling (Suh and Skochdopole, 1980). The gas is introduced either by mechanical stirring or by mixing a blowing agent into the polymer. *Physical blowing agents* are inert gases such as carbon dioxide or nitrogen; they are forced into solution in the hot polymer at high pressure and expanded into bub-

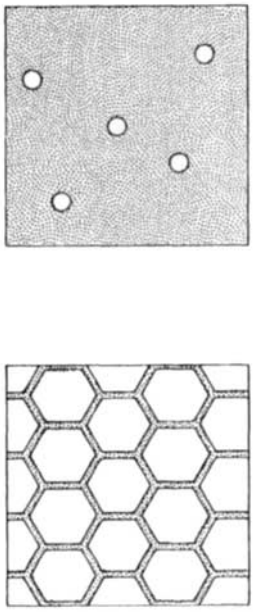

Figure 1.2 Comparison between a cellular solid and a solid with isolated pores.

bles by reducing the pressure. Alternatively, low melting point liquids such as chlorofluoro-carbons or methylene chloride are mixed into the polymer and volatilize on heating to form vapour bubbles. Microcellular foams, with cell sizes on the order of 10μ, can be made by saturating, under pressure and at room temperature, a polymer with an inert gas and then relieving the pressure and heating the supersaturated polymer to the glass transition temperature, causing cell nucleation and growth to occur. *Chemical blowing agents* are additives which either decompose on heating, or which combine together when mixed to release gas; sodicarbonamide is an example. Each process can produce open- or closed-cell foams; the final structure depends on the rheology and surface tension of the fluids in the melt. Closed-cell foams then sometimes undergo a further process called reticulation, in which the faces of the cells are ruptured to give an open-cell foam. Finally, low-density microcellular polymer foams and aerogels with relative densities as low as 0.002 and cell sizes as small as 0.1μ can be made by a variety of phase separation methods: one is to precipitate the polymer as a low-density gel in a fluid and then remove the fluid by evaporation (LeMay *et al.*, 1990).

Metallic foams can be made using either *liquid or solid state processing* (Shapovalov, 1994 and Davies and Zhen, 1983). Powdered metal and powdered titanium hydride or zirconium hydride can be mixed, compacted and then heated to the melting point of the metal to evolve hydrogen as a gas and form the foam. Mechanical agitation of a mixture of liquid aluminium and silicon carbide particles forms a froth which can be cooled to give aluminium foam. Liquid metals can also be infiltrated around granules which are then removed: for instance, carbon beads can be burned off or salt granules can be leached out. Metals can be coated onto an open-cell polymer foam substrate using electroless deposition, electrochemical deposition or chemical vapor deposition. Metal foams can also be made by a eutectic transformation: the metal is melted in an atmosphere of hydrogen and then cooled through the eutectic point, yielding the gas as a separate phase within the metal. Solid state processes usually use powder metallurgy. In the powder sintering method, the powdered metal is mixed with a spacing agent which decomposes or evaporates during sintering. Alternatively, a slurry of metal powder mixed with a foaming agent in an organic vehicle can be mechanically agitated to form a foam which is then heated to give the porous metal. Metal foams can also be formed by coating an organic sponge with a slurry of powdered metal, drying the slurry and firing to remove the organic sponge. In one of the most remarkable processes, single crystal silicon can be made porous by anodization: a silicon wafer is immersed in a solution of hydrofluoric acid, ethanol and water and subjected to a current for a brief time (Bellet and Dolino, 1994). The anodizing process tunnels, giving an interconnected network of pores with a cell size of 10 nm and a relative density as low as 0.1; yet the material remains a single crystal.

Glass foams are made by methods which parallel those for polymers; principally, by the use of blowing agents (often, H_2S). Carbon foams can be made by graphitizing polymeric foams in a carefully controlled environment. Ceramic foams are made by infiltrating a polymer foam with a slip (a fine slurry of ceramic in water or some other fluid); when the aggregate is fired the slip bonds to give an image of the original foam which, of course, burns off. Ceramic foams can also be made by chemical vapour deposition onto a substrate of reticulated carbon foam. Cement foams can be made by mixing a slurry of cement with a preformed aqueous foam made by mixing compressed air with an aqueous solution of suitable foaming agents. Microcellular silica foams, with cell sizes less than 100 nm and densities as low as $4\,kg/m^3$, have been made by the sol–gel polymerization of tetraalkoxy silanes.

Cellular solids can also be made by bonding together previously expanded spheres or granules. Polystyrene is sometimes moulded in this way. Glass and metal foams can be made by sintering hollow spheres together. Syntactic foams are made by mixing hollow spheres, usually made of glass, with a binder such as an epoxy resin. And fibres can be bonded to give low-density mats (like felt) which have much in common with other types of cellular solids.

Finally, it is worth mentioning that many foodstuffs are foams. Some, like meringue, are made by mechanical beating. Others, like breads, use a biological blowing agent (yeast). Still others, like cornflakes, rely on a physical blowing agent (steam). And nature has devised her own ways of making foams either as part of the growth process of a single organism (as in bone, woods, cork and leaves) or as the product of a community of organisms (like coral, or sponge, or the nests of certain insects).

1.4 Properties of cellular solids

Foaming dramatically extends the range of properties available to the engineer. Cellular solids have physical, mechanical and thermal properties which are measured by the same methods as those used for fully dense solids. Figure 1.3 shows the range of four of these properties: the density, the thermal conductivity, the Young's modulus, and the compressive strength. The bar with dotted shading shows the range of the property spanned by conventional solids; the solid bar shows the extension of this range made possible by foaming. This enormous extension of properties creates applications for foams which cannot easily be filled by fully dense solids, and offers potential for engineering ingenuity. The low densities permit the design of light, stiff components such as sandwich panels and large portable structures, and of flotation of all sorts. The low thermal conductivity allows cheap, reliable thermal insulation that can be bettered only by expensive vacuum-based methods. The low stiffness makes foams ideal for a

wide range of cushioning applications; elastomeric foams, for instance, are the standard materials for seating. The low strengths and large compressive strains make foams attractive for energy-absorbing applications; there is an immense market for cellular solids for the protection of everything from computers to canisters of hazardous wastes. The next section discusses applications of foams in a little more detail. The reader might bear Fig. 1.3 in mind while reading it.

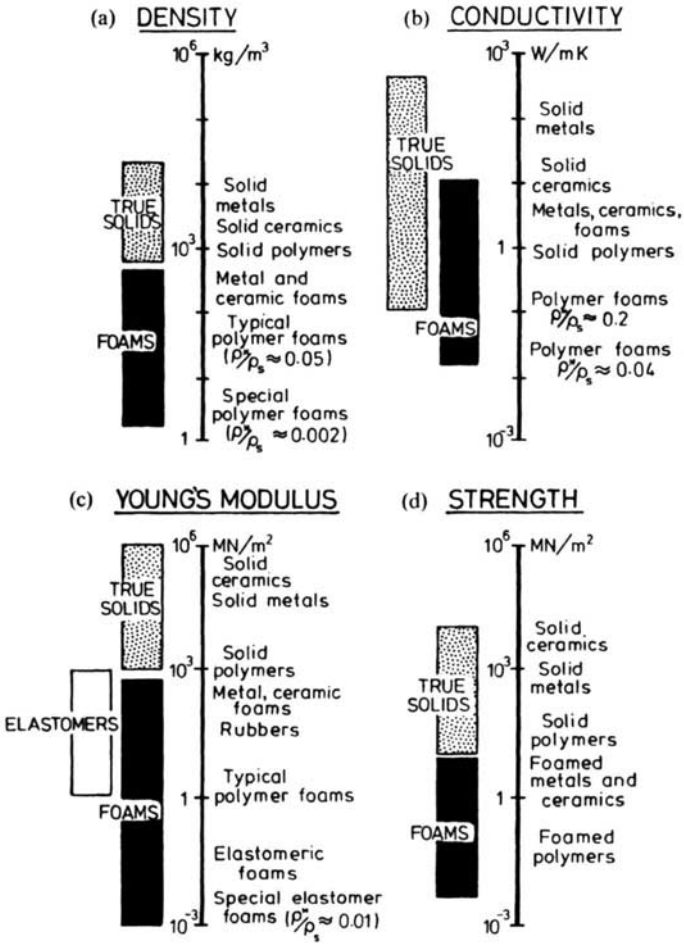

Figure 1.3 The range of properties available to the engineer through foaming: (a) density; (b) thermal conductivity (c) Young's modulus; (d) compressive strength.

1.5 Applications of cellular solids

The four diagrams of Fig. 1.3 relate directly to four major areas of application of cellular materials: thermal insulation, packaging, structural use, and buoyancy. Between them they account for most of the foams produced today, so we shall start with those. But there are other, smaller areas of application which are important, and growing; we will return to some of these at the end of the section.

(a) Thermal insulation

The largest single application for polymeric and glass foams is as thermal insulation. Products as humble as disposable coffee cups, and as elaborate as the insulation of the booster rockets for the space shuttle, exploit the low thermal conductivity of foams. Modern buildings, transport systems (refrigerated trucks and railway cars), and even ships (particularly those designed to carry liquid natural gas) all take advantage of the low thermal conductivity of expanded plastic foams. When fire hazard is a major consideration (as in some buildings), or when a very long life is envisaged (as in pipes and roofs) glass foams can be used instead. A particular advantage of foams for ultra-low-temperature research is their low thermal mass, reducing the amount of refrigerant needed to cool the insulation itself. The same is true, at higher temperatures, in the design of kilns and furnaces: a large part of the energy dissipated in the kiln is used to raise the temperature of the structure to its operating level; the lower the thermal mass, the greater the efficiency. The thermal mass of a foam is proportional to its relative density, so it is only a small percentage of that of the solid from which it is made. Thermal properties of foams are discussed in more detail in Chapter 7.

(b) Packaging

The second major use of man-made cellular solids is in packaging (Kiessling, 1961). An effective package must absorb the energy of impacts or of forces generated by deceleration without subjecting the contents to damaging stresses. Foams are particularly well suited for this. Figure 1.3 shows that the strength of a foam can be adjusted over a wide range by controlling its relative density. In addition, foams can undergo large compressive strains (0.7 or more) at almost constant stress, so that large amounts of energy can be absorbed without generating high stresses.

We leave the details of package design and energy absorption to Chapter 8. Here we note that foams also offer a number of secondary advantages as packaging materials. The low density means that the package is light, reducing handling and shipping costs. The low cost per unit volume and ease of moulding

means that an article of curious shape can be completely embedded in a foam package, protecting it cheaply. Currently, the foams most widely used in packaging are polystyrene, polyurethane and polyethylene (Suh and Skochdopole, 1980).

(c) Structural

Many natural structural materials are cellular solids: wood, cancellous bone, and coral all support large static and cyclic loads, for long periods of time. The structural use of natural cellular materials by man is as old as history itself. Wood is still the world's most widely used structural material. The understanding of the way in which its properties depend on the density and on the direction of loading (Chapter 10) can lead to improved design with wood. Interest in the mechanics of cancellous bone (Chapter 11) stems from the need to understand bone diseases and attempts to devise materials to replace damaged bone. And, increasingly, man-made foams and honeycombs are used in applications in which they perform a truly structural function.

The most obvious example is their use in sandwich panels. The innovative design of the deHavilland Mosquito (a World War II bomber) used panels made from thin plywood skins bonded to balsa wood cores (Hoff, 1951); in later designs the balsa wood was replaced by a cellulose acetate foam. Today, sandwich panels in modern aircraft use glass or carbon-fibre composite skins separated by aluminium or paper–resin honeycombs, or by rigid polymer foams, giving a panel with enormous specific bending stiffness and strength. The same technology has spread to other applications where weight is critical: space vehicles, skis, racing yachts and portable buildings. Sandwich panels are found in nature, too: the skull is made up of two layers of dense, compact bone separated by a lightweight core of spongy, cancellous bone; some types of leaves are structured around the sandwich principle; and the cuttle bone of the cuttle fish is an elaborate multi-layer sandwich panel. The mechanics and design of sandwich panels are discussed in Chapter 9.

(d) Buoyancy

Cellular materials found one of their earliest markets in marine buoyancy. Pliny (AD 77) describes the use of cork for fishing floats. Today, closed-cell plastic foams are extensively used as supports for floating structures and as flotation in boats. Foams are much more damage-tolerant than flotation bags or chambers; because of their closed cells they retain their buoyancy even when extensively damaged; they are unaffected by extended immersion in water; and they do not rust or corrode. Flotation is commonly made from foamed polystyrene, polyethylene, polyvinyl chloride or silicones, all of which can be foamed easily to

give closed cells and have outstanding resistance to water and to common pollutants. Buoyancy foams are conveniently characterized by the buoyancy factor, B, which is used to calculate the volume of foam required in a given application. It is defined by

$$B = \frac{\rho_{\text{water}} - \rho_{\text{foam}}}{\rho_{\text{water}}}.$$

Taking the density of water as 1000 kg/m^3 and that of a typical flotation foam as 40 kg/m^3 gives a typical buoyancy factor of 0.96. In modern sailboat design, cellular materials have been used as the core of a sandwich structure forming the deck and hull of the boat, providing structural rigidity as well as buoyancy.

(e) Other applications

Foams and honeycombs are used as *filters* at many different levels. High-quality metal castings must be free of inclusions: pouring the metal through an open-cell ceramic foam is the best way to filter them out. Foam pads can be used as cheap, disposable air filters. Most exciting is the development of the molecular filters used in membrane technology for separation of one sort of molecule from others in solution. The membrane itself is a rather special open-cell foam.

Foam sheets can be used as *carriers* for inks, dyes and lubricants, and even for enzymes for chemical processing. The cells are saturated with the dye or chemical, which either leaches slowly out (giving a controlled rate of release) or is expelled when the sheet is pressed or struck. Carriers of catalysts are important, too. Ceramic foams or honeycombs, lightly coated with platinum, are currently used as car exhaust catalysts; and the same ceramic foams can be used to carry the nickel and other catalysts used in hydrogenation and other energy-related applications.

Foams have special advantages as *water-repellent membranes* which still allow free passage of air. Open-cell polytetrafluoroethylene (PTFE) is used as a microporous, hydrophobic barrier in high-quality sporting and leisurewear, providing a fabric which breathes, yet excludes water. A similar material is used as *artificial skin*, providing protection to burn victims, while still allowing free access of air.

The special mechanical properties of foams, mentioned already, lead to a number of special uses. Their compressibility makes them unsurpassed as stoppers for bottles (Chapter 12), and the same property is exploited in bulletin boards and other functions requiring insertion and removal of pins or nails. Their slightly rough surface gives them a *high coefficient of friction*, so they are used as non-slip surfaces for trays, tables or floors. Their *high damping capacity* means that they absorb sound well, and they are used to line ceilings and walls