POLYMER CONVERSION

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PREFACE

This book is concerned primarily with the conversion of polymeric materials into useful articles. The subject is an immense one, and parts of it have been treated separately and exhaustively by many specialist writers. My aim has been to provide a rather simplified view of the whole sequence of operations starting with the raw materials, dealing in turn with the various processing stages and ending with the finished product.

We shall not concern ourselves with the pilot or industrial scale manufacture of polymers, since the techniques used are often highly complex and specific to individual materials. We are, however, concerned with the nature of polymers and their plan in the spectrum of materials, since by appreciating these things we are able to handle them in the most appropriate ways and for the most suitable applications. These points are also brought out again in the chapters on composite materials, and designing with plastics, which have been included in the text.

Also, since in most of the major conversion processes the polymer is subjected to various combinations of heat and pressure, a chapter on the rheological behaviour of polymeric materials is included.

After this we deal with the techniques used for the preparation of the polymer for the processing stages.

Processing itself is split up into what I have called the primary conversion processes, which involve the direct conversion of the powder or granules into shaped—but not necessarily finished—articles. This is followed by a consideration of the secondary conversion processes where a product—for example, a sheet—is further converted.

Obviously, this is only one of the many ways in which the matter could e treated, but it does have the merit of making it possible to emphasise wo important considerations which run throughout the whole of the ubject. They are the following:

(a) Although we have discussed different processes and parts of proesses separately, the various stages of the conversion process are strongly terdependent and what happens at each stage will have a profound ffect not only on subsequent stages, but also on the finished product.

(b) The processes themselves cannot either be considered in isolation since the choice of process will be influenced by such factors as:

(i) the material used;
(ii) the type of product;
(iii) the application;
(iv) the number of articles required.

It is for these reasons that chapters have been included on designi with plastics, plastics in combination with other materials, and sections the layout of conversion plant.

I have provided only a very brief guide for further reading, since, a mentioned earlier, detailed information is best obtained by consulting the many specialist publications.

A large number of firms and individuals have been kind enough to provide illustrations and data, and where appropriate these have been acknowledged in the text. In addition it is a pleasure to place on record the help and information given by many friends and former colleagues.

Finally, I should like to express my gratitude to the publishers for their understanding and forbearance when this book had to compete, at times unsuccessfully, with many other tasks. A number of my colleagues have made helpful suggestions, and I am particularly indebted to Miss Alma West who has not only typed the work but has also provided much editorial help.

W. A. HOLMES-WALKER

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CHAPTER 1

POLYMERS AS MATERIALS

1.1 INTRODUCTION

Although this book is concerned primarily with polymers, it must at once be made clear that polymers are only a part of the whole spectrum of materials. It is obvious, therefore, that in order to be able to derive the maximum benefit from using polymeric materials it is absolutely vital that their place in the spectrum is thoroughly understood. This is particularly important since not only do the different classes of materials behave in strikingly similar ways, although usually under different time/temperature/pressure ranges, but processes originally designed for one material are being used or adapted for others. An example of this is the use of metal forging techniques in the solid phase forming of polymers.

Once this is done it is logical for us to take a closer look at polymers themselves and try to establish some of the factors which control their properties.

1.2 STRUCTURE/PROPERTY RELATIONSHIPS IN MATERIALS

All materials are made up from assemblies of atoms, and there are two principal factors which control the properties of the material. These are:

(a) the nature and variety of atoms;
(b) the arrangement of the atoms in space.

The importance of the nature of the atom in determining material properties is strikingly demonstrated by considering the two elements, carbon and nitrogen. These atoms are next-door neighbours in the periodic classification of the elements and their properties are shown in Table 1.1. We shall return to this theme later, but in the meantime we must consider briefly some other facets of atomic structure. This is such a complex subject with so many variations that there are dangers in attempting to over-simplify. However, it is possible to observe a reasonably satisfactory connecting thread extending from relatively simple materials to those of considerable complexity.

TABLE 1.1

Element	*Atomic number*	*Density at 20°C (g cm^{-3})*	*Melting point (°C)*	*Boiling point (°C)*
C Graphite	6	2·25	3700[a]	4830
C Diamond	6	3·2	—	—
N Nitrogen	7	0·001 25	−210	−196

[a] Sublimes.

1.3 METALS

It is convenient to start with metals, not only because they are the most familiar engineering materials, but also since an appreciation of the fundamentals of their structure/property relationships will make it easier for us to understand polymeric behaviour.

Most metals consist of relatively simple, close-packed assemblies of atoms and it is possible for specific properties to be created in a number of ways.

1.3.1 The presence of imperfections in the crystal lattice

Engineering metals and alloys owe their unique combination of strength and ductility to their ability to slip. Practically all crystalline solids can slip, however—even diamond and sapphire when the temperature is high enough or when there is a sufficiently large hydrostatic pressure to prevent fracture. Some geological processes, for example, are brought about by the plastic deformation of normally brittle minerals under high pressures at great depths below the Earth's surface.

Where a fault or dislocation exists in the crystal there is a net increase in energy which renders it unstable. Under an applied stress this dislocation is able to travel through the material producing slip and thus deformation occurs relatively easily. The reduction in strength compared with that of the perfect crystal is often very striking in pure metals, and Fig. 1.1 shows how the strength disappears as soon as dislocations are made in a copper whisker.

The calculated strength of metals should be about $E/20$ whereas it can be seen from Fig. 1.1 that once dislocations have been created the stress has fallen to about $E/2000$. The initial yield stress, incidentally, in the case of a dislocation-free copper whisker ($E/200$) is of the same order as the tensile strength which can be obtained for copper by extreme cold-working at room temperature.

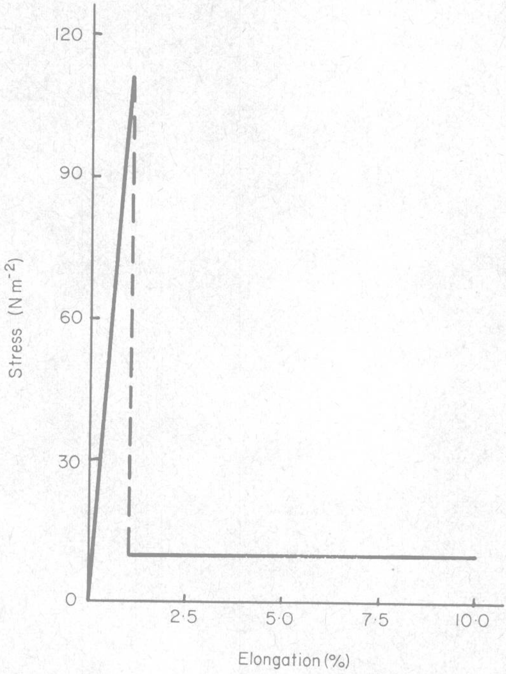

FIG. 1.1. Stress–strain curve of a copper whisker.

The creation of imperfections by the addition of foreign atoms generally serves to strengthen the material. The solute atom decreases the stress around a dislocation; as a result the dislocation is more stable and requires a greater stress to move it. Thus solid solution metals always have higher strengths than do pure metals (Fig. 1.2).

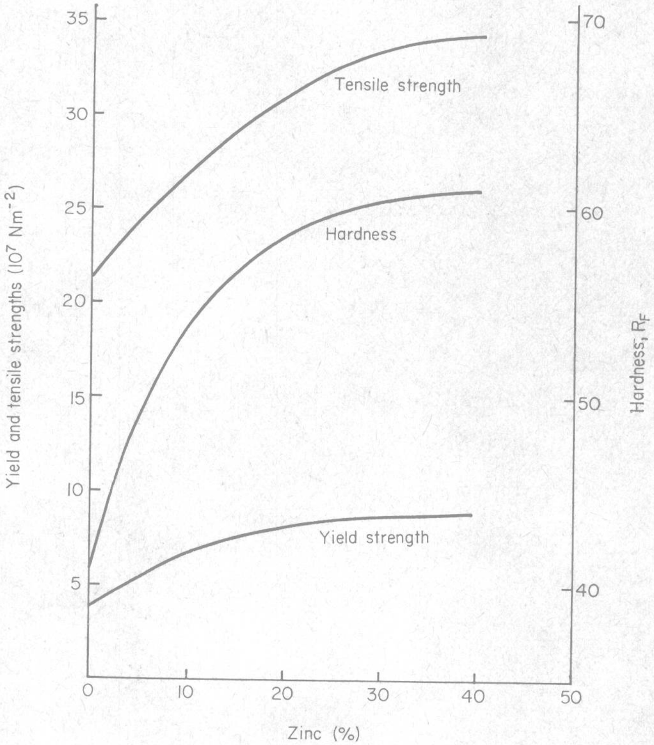

FIG. 1.2. Mechanical properties of annealed brasses.

1.3.2 The effect of grain structure

A more massive re-arrangement of the crystal structure of single phase metals can produce a structure consisting of a variety of crystals of different orientations. The adjacent crystals have dissimilar orientations so that a grain boundary is present (Fig. 1.3). The microstructures of single phase metals can be varied by changes in size, shape and orientation of the grains, and the grain structure will influence the mechanical properties of the metal. For example, the changes in ductility and tensile strength in an annealed 70/30 brass (Fig. 1.4) are a direct reflection of the grain boundary area within the brass and the effect that the boundary has on slip.

1.3.3 The introduction of a second phase

This can often have a strengthening effect by inhibiting the movement of dislocations. To illustrate this it is useful to consider the Fe–C phase

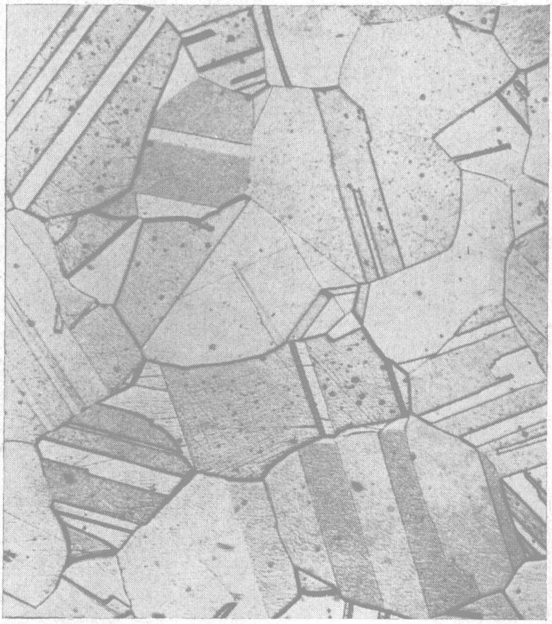

FIG. 1.3. Illustration of grain structure in a recrystallised 70/30 brass (× 100).

relationships since steel offers examples of the majority of reactions and microstructures available for adjusting material properties. We are also able to bring in another parameter—temperature—which, as we shall see later, has a profound effect on all materials.

TABLE 1.2

Effect on steel properties of varying the character of the disperse phase

Composite system			*Disperse phase variables changing:*		
Phase			*Shape*	*Size*	*Concentration*
Continuous	*Disperse*	*Property*	*Plate to round to fibre*	*Increasing*	*Increasing*
Iron	Carbides	Toughness	Increase	Decrease	Increase
		Hardness	Decrease	Decrease	Increase

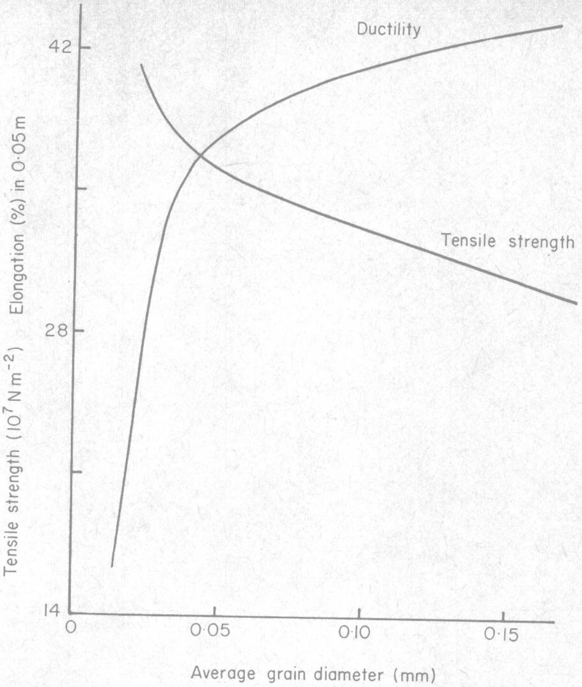

FIG. 1.4. The dependence on grain size of the mechanical properties of an annealed 70/30 brass.

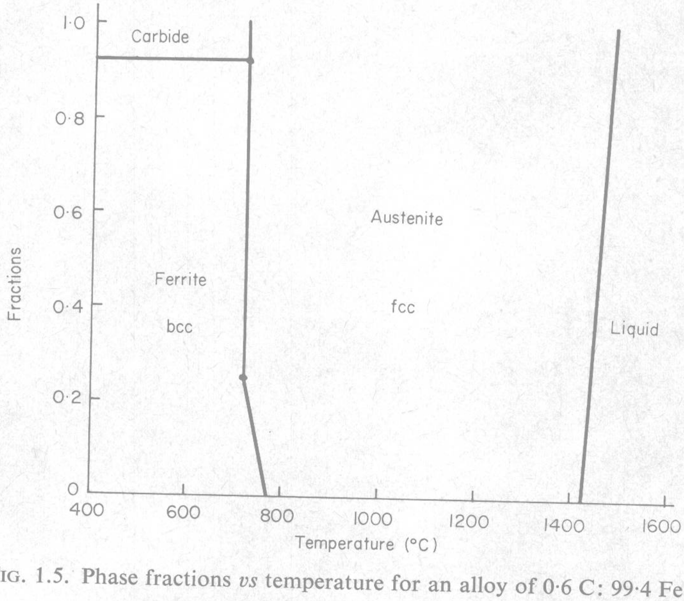

FIG. 1.5. Phase fractions *vs* temperature for an alloy of 0·6 C: 99·4 Fe.

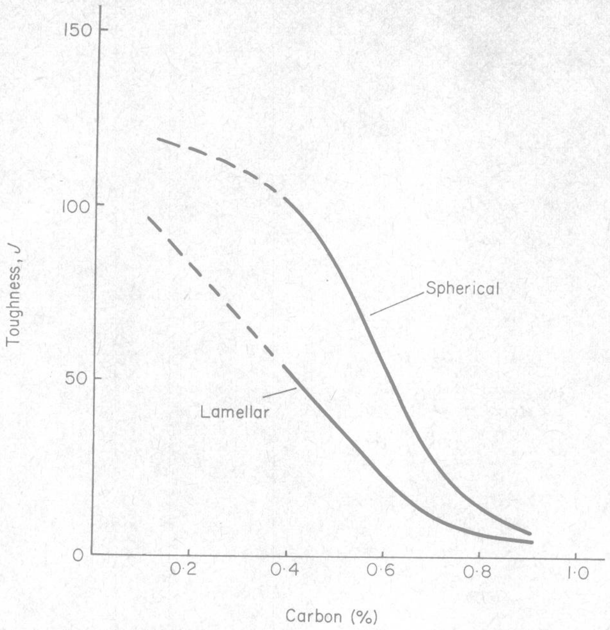

FIG. 1.6. Effect of carbon concentration and particle shape on the toughness of steel.

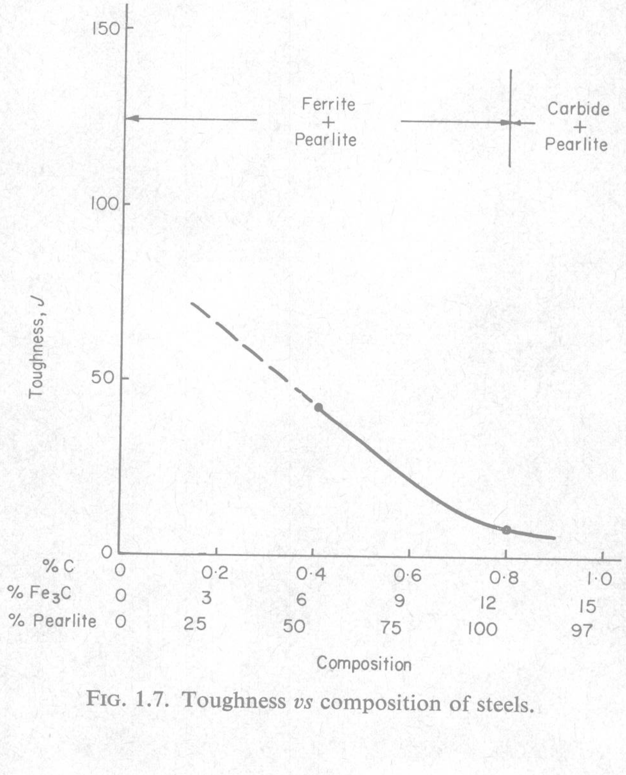

FIG. 1.7. Toughness *vs* composition of steels.

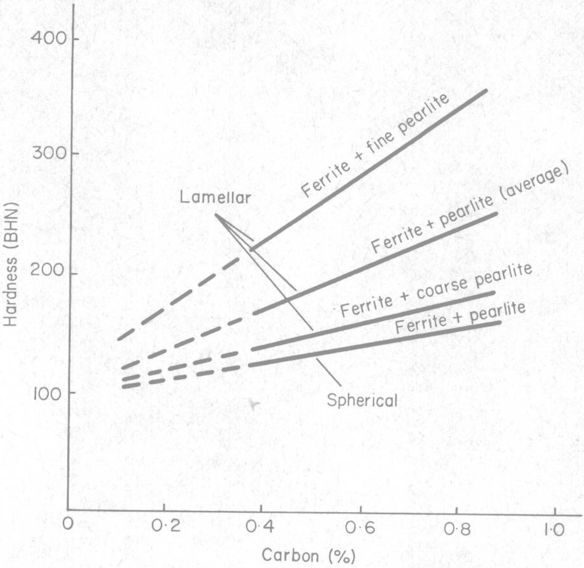

FIG. 1.8. Effect of particle size and shape and percentage carbon on hardness of steel.

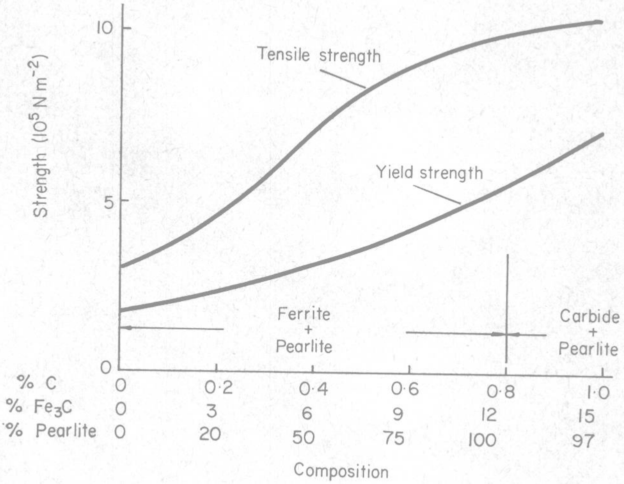

FIG. 1.9. Strength *vs* composition of steels.

Pure iron changes its crystal structure from body-centred to face-centred cubic as it is heated above 910°C and a subsequent phase change occurs at 1400°C. These changes and their effects on the solubility of carbon in iron are shown in Fig. 1.5.

In iron–carbide alloys, carbon in excess of the solubility limit must form a second phase, and this second phase has the chemical composition Fe_3C. The most familiar of the resulting structures is known as Pearlite; the mixture is lamellar and composed of alternate layers of ferrite and carbide. Pearlite is a specific mixture of two phases formed by transforming austenite of eutectoid composition to ferrite and carbide. However, it is possible to form mixtures by other reactions, although these microstructures will not be lamellar and consequently their properties will be different. Two other parameters will also affect the properties of these composite materials; these are the volume fraction and the size of the dispersed phase. A brief survey of the effects of these parameters is shown in Table 1.2 and Figs. 1.6, 1.7, 1.8 and 1.9.

Having considered metals and their properties in some detail we can now appreciate the wide variety of ways in which it is possible not only to select appropriate atoms but also to control their arrangements in space in order to create a whole range of physical properties.

1.4 CERAMICS

Ceramic materials contain phases which are compounds of metallic and non-metallic elements. There are many ceramic phases because:

(a) there are many possible combinations of metallic and non-metallic atoms;
(b) there may be several structural arrangements of each combination.

Most ceramic materials, like metals, have crystal structures. The electrons, however, are either shared covalently with adjacent atoms, or are transferred to produce ionic bonds. For this reason ceramic materials are in general highly stable. As a class they have higher melting temperatures than do metals or polymeric materials and they are also harder and more resistant to chemical attack. In some of the simpler crystals such as MgO, plastic slip, similar to metallic slip, can occur. Crystal outlines can form during growth as exemplified by the cubic outline of common salt.

In asbestos the crystals have a marked tendency towards linearity; in micas and clays the crystals form two-dimensional sheet structures and the stronger, more stable ceramic materials commonly possess three-dimensional framework structures with equally strong bonding in all three directions.

1.5 POLYMERS

We have seen that, in the case of metals and ceramics, the atom, the ion, and the unit cell are the important features of structure in determining properties. In the case of polymers, however, the polymer chain is the important feature, and it is the nature of the chain links (their size and shape), together with the ways in which the links are arranged to form the chain, the length of the chains, and the disposition of the chains in space, that determine the nature of the material. The simplest type of polymer—which we may describe as a one-dimensional macromolecule—consists of a single chain of backbone atoms and the most familiar member of this class is polyethylene, which is composed of ethylene molecules.

We can gain an idea of the size of the polyethylene chain if we appreciate that the length of the ethylene molecule is about 2×10^{-10} m long and that a typical polyethylene chain of some 50 000 links would be about 2×10^{-5} m long (in the region of a fiftieth of a millimetre).

The polyethylene chains are normally tangled and coiled in random directions like the filaments in a bundle of wire wool. By looking at Fig. 1.10(a) we see that the material is flexible because rotation can easily occur at each of the bonds, hence the molecule is readily deformed. It is tough because this movement will absorb sudden stresses. It is light because there is a large space/chain ratio (this is often increased by considerable branching of the main chain structure) and it has a low softening point because the chains can easily disentangle and slide past one another when thermal energy is supplied to the material. This latter characteristic, as we shall see later, is common to all thermoplastic materials which, providing excessive heat is not used, can be reprocessed.

1.5.1 Methods of creating specific properties

The flexibility of the polymer molecule, and hence the material, can be controlled by a variety of methods. It can be increased by the addition of plasticisers. Plasticisers, in simple terms, are liquids which fill up some of the spaces between the chains and so make it easier for them to move about relative to one another. This technique is most frequently used in PVC technology. Flexibility can also be increased by the technique of copolymerisation, whereby some of the polymer links in the chain are replaced by ones which can more easily be deformed.

(*a*) *Substitution in the chain*

Flexibility can be decreased by introducing a series of knobs or lumps into the chains thus restricting their movement by making it difficult for the links to rotate. The substitution of the bulky chlorine atoms and the even