Exhibit 1012

FOURTH EDITION

MATERIALS FOR ENGINEERS AND TECHNICIANS

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FLS v. Metso

R. A. HIGGINS

Newnes

Materials for Engineers and Technicians

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To
the memory of my father

Victor Higgins
1882–1942
Watchmaker

As a small boy, standing by his workbench,
I learned how to harden steel and brass.

Exhibit 1012
FLS v. Metso

Materials for Engineers and Technicians

Fourth Edition

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19 Plastics materials and rubbers

19.1 Introduction

Nylon, one of the most important man-made fibres, was developed in the USA in the years just before the Second World War but made its glamorous debut to the public in the form of ladies' stockings in the spring of 1940. The production of polyethylene (polythene) started in England in 1941 and who today has not come across the 'polythene bag'. Both nylon and polythene are typical of the materials generally referred to as 'plastics', or more properly as 'plastics materials' – but *never* as plastic materials because of course many substances, including metals, undergo *plastic* deformation when the applied stress is great enough.

Though both polythene and nylon are relatively new materials, plastics and rubbers development began much earlier. The technology of rubber, for example, began in 1820 when a British inventor, Thomas Hancock, developed a method for shaping raw rubber; whilst some twenty years later, in the USA, Charles Goodyear established the 'vulcanisation' process by which raw rubber was made to 'set' and produce a tough, durable material, later to be so important in the growth of the motor-car industry.

Shortly afterwards, the plastics cellulose nitrate and celluloid were developed from ordinary cellulose fibre, and when, in the early years of the twentieth century, Dr. Lee Bakeland, a Belgian chemist, introduced the material which was ultimately named after him – 'bakelite' – the plastics industry could be said to have 'arrived'. It is interesting to note that since this book was first published, the *volume* of plastics materials produced annually has exceeded the volume of steel.

At present, the use of plastics continues to increase rapidly as new materials are developed. For example, modern cars include many items made from plastics and could we now exist without the plastic carrier bags and plastics bottles. Currently, polythene and PVC between them account for more than half of the plastics produced in the European Union. They are followed by polypropylene, polystyrene and polyethylene terephthalate and then the more expensive ABS, polyurethanes and nylons.

19.2 Types of plastics

Bakelite differs from either polythene or nylon in one important respect. Whereas the latter substance will soften repeatedly whenever they are heated to a high enough temperature, bakelite does not. Once moulded to shape, it remains hard and rigid and reheating has no effect – unless the temperature used is so high as to cause it to decompose and char.

Plastics materials can be classified into three groups (Figure 19.1):

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1 *Thermoplastic materials* – substances which loose their rigidity whenever they are heated, so that they can be moulded under pressure with the new shape being retained on cooling.
2 *Thermosetting materials* – substances which undergo a definite chemical change during the moulding process, causing them to become permanently rigid and incapable of being softened again. The process is not reversible. Materials used in conjunction with glass-fibre for the repair of the bodywork of decrepit motor cars fall into this class.
3 *Elastomers* – substances which are characterised by very high elasticity but a very *low modulus of elasticity*, i.e. great extensibility when stressed, and the capacity for very large rapidly recoverable deformation. Think of a rubber band.

The term *polymer* is used for the very large organic molecules which are involved in plastics.

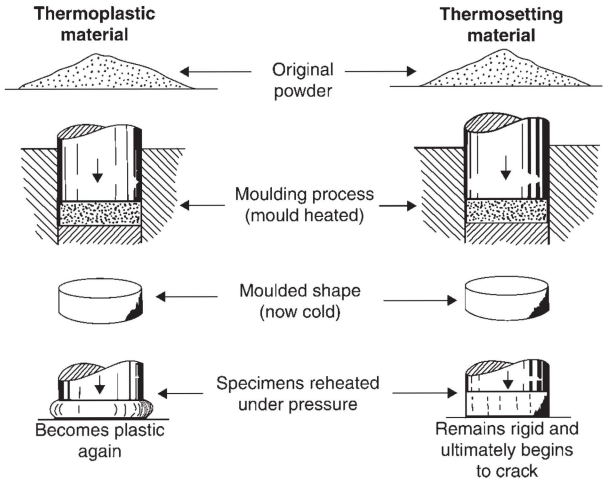


Figure 19.1 *The behaviour of thermoplastic and thermosetting materials when reheated under pressure.*

19.2.1 Raw materials

Raw materials used in the manufacture of plastics traditionally come from two main sources:

1 Animal and vegetable by-products such as casein (from cow's milk), cellulose (mainly from cotton fibres too short for spinning) and wood pulp, common products being cellulosics.
2 Petroleum by-products obtained during the refining and 'cracking' of crude oil, common products being polythene, PVC and polystyrene. This method is responsible for the bulk of plastics manufacture.

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Commercial plastics generally involve the addition to basic polymers of additives to modify properties, e.g. plasticisers to enhance flexibility (see later in this chapter) and antioxidants to inhibit degradation.

19.2.2 Composition of plastics

All plastics are polymers. Polymers are very large organic molecules, based on the element carbon, and made by the successive linking together of small molecules. The term 'organic' in chemical nomenclature has a similar connotation to its current use in farming practice in that it implies that only living materials and substances derived therefrom are involved. Organic chemical compounds are associated mainly with those derived from either living or once-living matter and can be regarded as the material which constitutes the skeletons of plants, from blades of grass to conifers some hundred metres tall, whilst petroleum, from the by-products of which most of our plastics are derived, was produced by the decay and fossilisation of vegetable matter, millions of years ago. In addition to the element carbon, most plastics contain hydrogen, whilst many contain oxygen. A smaller number contain other elements, the chief of which are nitrogen, chlorine and fluorine.

All organic substances exist in the form of molecules, within which individual atoms are bound together by very strong covalent bonds. The molecules in turn are attracted to each other by much weaker forces known as van der Waals forces. See Chapter 2 for a discussion of such bonds. Plastics materials consist of a mass of very large molecules, termed 'polymers', made by successive linking together of small molecules, called 'monomers'. Converting monomers into a polymer is termed 'polymerisation'. As a result each polymer molecule contains several thousands of atoms tightly bound one to the other by covalent bonds.

19.2.3 General properties of plastics materials

When visiting the wild and more remote parts of Europe's coastline one finds, cast up by the tide, along with the seaweed and driftwood, a motley collection of plastics bottles. Because of its low relative density and comparative indestructibility, this plastics junk will presumably congregate in increasing quantity, as yet another example of Man's careless pollution of his environment.

This fact illustrates some of the more important properties of plastics generally:

1 They are resistant both to atmospheric corrosion and to corrosion by many chemical reagents.
2 They have a fairly low relative density – a few will just float in water, but the majority are somewhat more dense.
3 Many are reasonably tough and strong, but the strength is less than that of metals. However, since the relative density of plastics is low, this means that many have an excellent strength-to-weight ratio – or *specific strength* as it is often termed.

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4 Most of the thermoplastic materials begin to soften at quite low temperatures, and few are useful for service at temperatures much above 100°C. Strength falls rapidly as the temperature rises.
5 Most plastics have a pleasing appearance, and can be coloured if necessary. Some are transparent and completely colourless.

19.3 Thermoplastics

In thermoplastics materials, the carbon atoms are attached to each other by covalent bonds in the form of a long chain – this in polythene is a chain of about 1200 carbon atoms in length. Strong binding forces operate between the molecules in the chains with just van der Waals forces between chains. These van der Waals forces will be stronger the closer the molecules are together. Furthermore, it is easy to imagine that a considerable amount of entanglement will exist among these long chain-like molecules (Figure 19.2). When such a solid is heated, vibration within the molecules becomes greater so that the distances between molecules becomes greater and so the forces of attraction between them will decrease (in a similar way, the force acting between two magnets becomes smaller the further they are moved apart). Then such a material will be weaker and less rigid, so that it can be moulded more easily – hence the term thermoplastic for such materials.

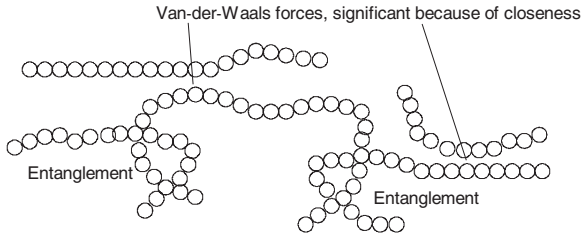


Figure 19.2 *Thermoplastics molecular chains.*

The household plastics material we call 'polythene' is more correctly known as 'polyethylene'. It is made from the gas 'ethylene', a by-product of the petroleum industry. In the ethylene molecule there is a weak double covalent bond (indicated in figures as = in Figure 19.3(i)) between two carbon atoms as a result of the sharing of four electrons between them. Such a double bond is not a sign of extra strength but of greater instability and suitable chemical treatment causes this bond to break. When this occurs simultaneously amongst many molecules of the gas, the resultant units (Figure 19.3(ii)) are able to link up, forming long chain molecules of polyethylene (Figure 19.3(iii)). This type of chemical process is known as *polymerisation*, and the product is called a *polymer*. The simple substance from which the polymer is derived is called a *monomer*, so in this case the gas ethylene is the monomer of poly-ethylene.

Sometimes the term *mer* is used in this context. A mer is a single unit which, though it may not exist by itself, occurs as the simplest repetitive unit in the chain molecule. Figure 19.4 thus shows the mer in polythene.

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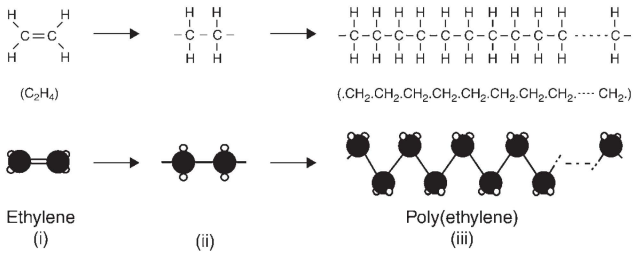


Figure 19.3 *The polymerisation of ethylene to polyethylene. The lower part of the illustration shows the arrangement of the carbon and hydrogen atoms.*

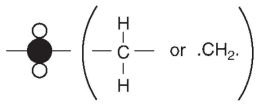


Figure 19.4 *The polythene mer.*

Frequently, a polymer molecule is built up from different monomers, arranged alternately in the chain. Such a substance is called a *copolymer*. In this way, molecules of vinyl chloride and vinyl acetate can be made to polymerise (Figure 19.5). The result is the plastics material polyvinyl chloride acetate, formerly used in the manufacture of LP gramophone records. It is in fact possible to use more than two monomers in making a copolymer. Thus acrylonitrile can be made to co-polymerise with butadiene and styrene to produce acrylonitrile-butadiene-styrene or 'ABS' as it is usually known industrially.

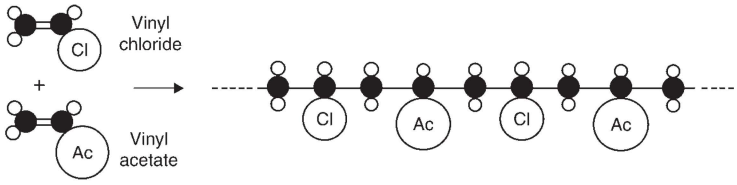


Figure 19.5 *The formation of a copolymer (polyvinyl chloride acetate).*

Some super-polymers consist of chain molecules built up from very complex monomers. This often leads to the operation of considerable forces of attraction between the resultant molecules at points where they lie alongside each other; consequently, such a material lacks plasticity, even when the temperature is increased. Cellulose is a natural polymer of this type.

19.3.1 Plasticisers

In 1846, Dr. Frederick Schönbein, of the University of Basle, produced cellulose nitrate by treating ordinary cellulose with nitric acid. When heated, it proved to be slightly more plastic than ordinary cellulose. This is because the 'nitrate' side branches (Figure 19.6(ii)), which became attached to the chain molecules as a result of the treatment with nitric acid, acted as 'spacers' which separated the chain molecules and so reducing the forces of attraction between them.

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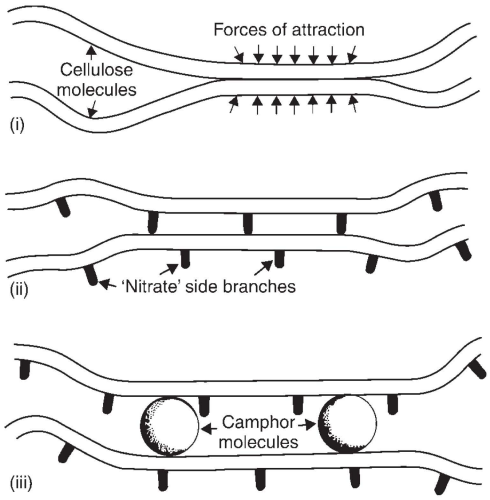


Figure 19.6 *The function of a plasticiser.*

In 1854, Alexander Parkes, the son of a Birmingham industrialist, began to experiment with cellulose nitrate, with the object of producing a mouldable plastic from it. He found that, by adding some camphor to cellulose nitrate, a mixture was produced which passed through a mouldable stage when hot. Not long afterwards, this substance was produced commercially under the name of 'celluloid'. The bulky camphor molecules separate the chain molecules of cellulose nitrate by even greater distances, so that the forces of attraction between them are reduced further. Thus the camphor is termed a *plasticiser* (Figure 19.4(iii)). Celluloid is a very inflammable material, and this fact has always restricted its use. Before other plastics materials were freely available, much celluloid was used in the manufacture of dolls and other children's toys, often with tragic results when these articles were brought too near a fire.

19.4 Thermoplastic materials

The following are commonly encountered thermoplastic materials.

19.4.1 Vinyl plastics

Presumably the term 'vinyl' is derived from 'vin' (as in 'vineyard') since the aromatic nature of some vinyl compounds is reminiscent of that of wine. Some of the vinyl compounds undergo polymerisation of their own accord, 'monomers' linking together spontaneously at ambient temperatures to form 'polymers'. Often they begin as 'watery' liquids, but, if allowed to stand for some time, become increasingly viscous as polymerisation proceeds, ultimately attaining a solid glass-like state (Figure 19.7). Of these plastics materials, polyethylene (PE), polyvinyl chloride (PVC), polypropylene (PP), polyethylene terephthalate (PET)

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and polystyrene (PS) in total account for over 80 per cent of the world's plastics market. In this section the structural formulae of the units derived from the monomers are given to show the relationship of these polymers to ethylene.

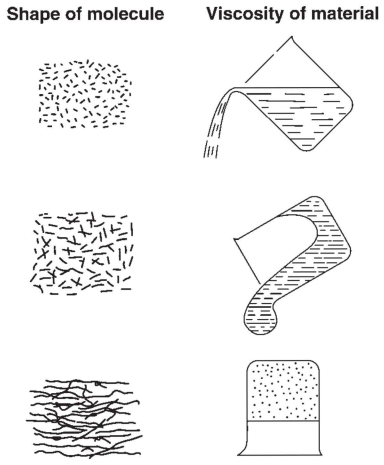


Figure 19.7 *Stages in the spontaneous polymerisation of some vinyl compounds.*

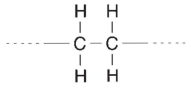


Figure 19.8 *Polyethylene.*

1 *Polyethylene (polythene) PE (Figure 19.8)*
This is probably the best known of the thermoplastics materials. It has an excellent resistance to corrosion by most common chemicals and is unaffected by foodstuffs. It is tough and flexible, has a high electrical resistivity, has a low density, and is easily moulded and machined. Since it is also comparatively cheap to produce, it is not surprising that polythene finds such a wide range of applications.

Polythene is available in several different modifications. Low-density polythene (LDPE) consists of molecules containing many side branches (Figure 19.9(i)) and is usually about 50 per cent crystalline (see Section 20.2), i.e. about half of it can be considered to be packed in an orderly manner in the solid – like atoms in a crystal. High-density polythene (HDPE) is approximately 90 per cent crystalline, because it consists principally of linear, unbranched molecules which can more easily be packed together to give the orderly arrangement necessary for a crystalline structure. Being harder, it is used principally for the manufacture of bottles and similar utensils by blow-moulding (see Section 20.5). Its particular feature is that it has a superior resistance to environmental stress cracking.

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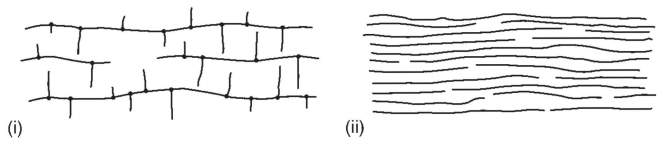


Figure 19.9 *Different molecular structures in polythene. (i) LDPE – here side-branching of the molecules increases the distance between adjacent chains. This reduces van der Waals forces so that LDPE is softer and weaker than HDPE (ii) where there is no side-branching. In (ii) the unbranched molecules lie closer together in a more orderly manner, so that crystallinity can be greater.*

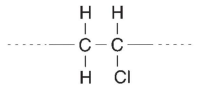


Figure 19.10 *Polyvinyl chloride.*

2 *Polyvinyl chloride (PVC) (Figure 19.10)*
The gas vinyl chloride was discovered more than a century ago. It was found that, on heating, it changed to a hard, white solid, later identified as polyvinyl chloride. Having rather a high softening temperature, PVC was difficult to mould, and it was not until the late 1920s that it was discovered that it could be plasticised. By adjusting the proportion of liquid plasticiser used, a thermoplastic material can be produced which varies in properties from a hard rigid substance to a soft rubbery one. Consequently, during the Second World War, and since then, PVC has been used in many instances to replace rubber. Protective gloves, raincoats and garden hose are examples of such use. PVC can be shaped by injection moulding, extrusion, and the normal thermoplastic processes. It can also be compression-moulded without a plasticiser, to give a tough, rigid material such as is necessary in miners' helmets. The effects on strength and ductility of PVC relative to the degree of plasticisation are indicated in Table 19.1.

Table 19.1 *Mechanical properties (average) of PVC related to the degree of plasticisation*

Degree of plasticisation	*Tensile strength MPa*	*Elongation %*
None	55	20
Low	35	200
High	17	400

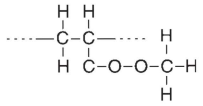


Figure 19.11 *Polyvinyl acetate.*

3 *Polyvinyl acetate (PVA) (Figure 19.11)*
This polymer softens at too low a temperature for it to be much use as a mouldable plastic, but it is useful as an adhesive, since it will stick effectively to almost any surface. It is supplied as an emulsion with water; when used in the manner of glue, the water dries off, leaving a strong adhesive polyvinyl acetate film for bonding the parts together. It is possibly best known as an emulsion with water, as the basis for 'vinyl emulsion paints'. The introduction of these was certainly a boon to those of us who, in our earlier days, battled with 'glue-size' based 'distemper' for our home decoration.

4 *Polyvinyl acetate/chloride copolymers*
These have already been mentioned (Section 19.3). In these, the very high softening temperature of PVC is reduced by combining it with

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vinyl acetate to form a copolymer of lower softening temperature. The LP gramophone records made from this have been superseded by polycarbonate compact discs.

5 *Polyethylene-vinyl acetate (EVA)*
This is a copolymer of ethylene and vinyl acetate in which the proportions of vinyl acetate are varied between 3 and 15 per cent to produce materials with different ranges of properties. The principal features of EVA are high flexibility, toughness, clarity and a high resistance to stress cracking, together with resistance to damage from ultraviolet radiation and ozone.

The rubbery nature and glossy finish of some forms of EVA make it useful for meat packaging and for cling-wrap purposes. Other forms are used for the moulding of automotive parts, ice-cube trays, road-marker cones, medical equipment, turntable mats and garden hose, whilst a harder cross-linked form is used for shoe soles. EVA is also the basis for a number of hot-melt adhesives.

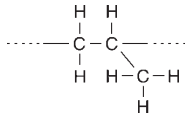


Figure 19.12 *Polypropylene.*

6 *Polypropylene (PP) (Figure 19.12)*
This is similar in structure and properties to polyethylene but it has a higher temperature tolerance. Whilst PE is produced from the gas ethylene, PP is polymerised from the gas propylene. PP is stronger than PE and is used for a wide variety of mouldings where greater strength and rigidity, than can be obtained with PE, are required. The higher melting point of PP as compared with HDPE make it more suitable for fibre manufacture, whilst large amounts are also produced as clear film for wrapping cigarettes and crisps.

7 *Polypropylene-ethylene copolymers*
A disadvantage of PP is that it becomes brittle at about 0°C as the amorphous regions of the polymer become glassy (see Section 20.2). To reduce this tendency PP is co-polymerised with PE. If 5–15 per cent PE is used, toughness is increased without loss of rigidity. Such copolymers are used for pipes and pipe fittings, cable insulation and ropes. But increasing the amount of PE to 60 per cent produces a rubbery copolymer, such elastomers being resistant to atmospheric attack.

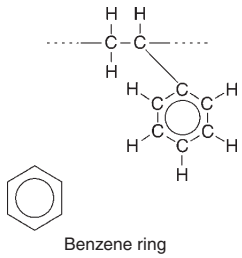


Figure 19.13 *Polystyrene: the 'ring' of carbon atoms is the nucleus of a benzene molecule and the significance of the circle in its centre is to indicate that all the valency electrons joining its six carbon atoms are shared equally by the six.*

8 *Polystyrene (PS) (Figure 19.13)*
PS was developed in Germany before the Second World War and is made by the polymerisation of styrene, a chemical substance known since 1830. PS has become one of the most important of modern thermoplastic materials. It is a glassy, transparent material similar in appearance to PMMA and has a high electrical resistivity. In the homo-polymeric state (just the single PS polymer) it is brittle and for this reason toughened versions of PS are used for most engineering and many other applications. *High-impact polystyrene* (HIPS) is produced by the addition of some polybutadiene – a rubber – which is present in the structure as tiny spheres. However, PS is probably best known in its 'expanded' or foamed form (see Section 20.4), such a material being widely used for packaging.

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PS hollow-ware is fairly easy to identify as such since it emits a resonant 'metallic' note when tapped smartly. PS can be cast, moulded, extruded and shaped easily by the ordinary methods of sawing, filing and drilling. Mouldings in HIPS have a lower tensile strength than those in ordinary PS but a much higher impact value, particularly at low temperatures, for which reason they are extremely useful as refrigerator parts.

9 *Acrylonitrile-butadiene-styrene (ABS)*

The 'rubber toughening' of styrene has been described above and the same principle is carried further in ABS plastics materials which are copolymers of acrylonitrile, butadiene and styrene (Figure 19.14). Some of the butadiene polymerises as globules in HIPS but the remainder co-polymerises with acrylonitrile and styrene to produce a material of outstanding resistance to fracture by impact, combined with a high tensile strength and abrasion resistance. So much so that luggage made from ABS resists all but the most serious attacks by airport baggage-handling systems! ABS is resistant to acids and alkalis as well as to some organic solvents and is available in the form of moulding powders for use in injection-moulding and extrusion; sheet is also available for vacuum-forming processes.

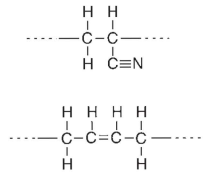


Figure 19.14 *ABS: the upper figure shows acrylonitrile and the lower figure butadiene. These are copolymerised to give ABS.*

Large amounts of ABS are used in the automobile industry where glass-fibre reinforced plastics are increasingly used for panel work. An added bonus for ABS and PP was that they could be chromium plated when used in radiator grilles and similar components. In recent years the fashion has turned away from 'chrome' in favour of more sombre hues so that now everything from car bumpers to hi-fi and TV cabinets and cameras are black. Of course, carbon black is much cheaper than increasingly expensive chromium. However, I suppose I must suppress this unwarranted cynicism!

Table 19.2 summarises the properties and uses of vinyls.

19.4.2 Fluorocarbons

The most important of these materials is *polytetrafluoroethylene* (PTFE). It can be regarded as polythene in which all of the hydrogen atoms have been replaced by atoms of the extremely reactive gas fluorine (Figure 19.15). Since fluorine is so chemically reactive, its compounds, once formed, are difficult to decompose. Thus PTFE will resist attack by all solvents and corrosive chemicals; for example, hot concentrated sulphuric acid does not affect it, whilst *aqua regia* (a mixture of concentrated nitric and hydrochloric acids which will dissolve gold and platinum) leaves PTFE unharmed. It will also withstand a wider range of temperatures than most plastics materials and can be used for continuous working between –260 and +250°C (+300°C for intermittent use). It is an excellent electrical insulator but above all it has the lowest coefficient of friction of any solid material, a feature which also makes it difficult to coat on to other surfaces.

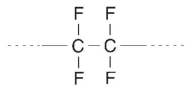


Figure 19.15 *PTFE.*

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Table 19.2 *Properties and uses of vinyl thermoplastics materials*

Compound		*Relative density*	*Tensile strength MPa*	*Chemical resistance*	*Safe working temp. °C*	*Relative cost*	*Typical uses*
Polythene PE	HD	0.95	30	Excellent	120	Low	Acid-resisting linings. Babies' baths, kitchen and other household ware. Piping, toys, fabric filaments.
	LD	0.92	13	Excellent	80	Low	Sheets, wrapping material, polythene bags, squeeze bottles, electrical insulation, bottle caps, tubing for ball-point pens, ink cartridges.
Polyvinyl chloride PVC	Un-plasticised	1.40	55	Good	70	Low	Domestic/industrial piping (rainwater, waste, etc.), light fittings, curtain rail (with metal insert), radio components, safety helmets, ducting, plating vats.
	Plasticised	1.30	35	Good	100	Low	Artificial leather cloth, gloves, belts, raincoats, curtains, packaging, cable covering, protective clothing.
Polyvinyl chloride/ acetate		1.3	25	Fairly good	70	Moderate	Gramophone records, screens, containers, chemical equipment, protective clothing.
Ethylene vinyl acetate EVA		0.94	25	Good	70	Moderate	Meat packaging, cling wraps, turntable mats, automobile parts, garden hose, car-door protectors, shoe-soles, road cones, surgical ware. Adhesives.
Poly-propylene PP		0.90	33	Excellent	100	Low	Packaging, pipes and fittings, cable insulation, battery boxes, refrigerator parts, sterilisable bottles and other uses where boiling water is involved, cabinets for TV and radio sets, fan blades, crates and containers, stackable chairs.
Poly-styrene PS	General purpose	1.05	45	Fairly good	80	Low	Moulded containers (food and cosmetic), boxes, toilet articles. *Foams*: ceiling tiles, heat insulation, packaging for fragile equipment.
	HIPS	1.02	20	Fairly good	80	Low	Radio and TV cabinets, vacuum cleaners, kitchen equipment, refrigerator parts, vending machine cups, cases for cheap cameras.
Acrylo-nitrile-butadiene-styrene ABS		1.01	35	Very good	80	Moderate	Pipes, radio cabinets, tool handles, protective helmets, textile bobbins, pumps, battery cases, luggage, typewriter and camera cases, telephone handsets, hairdriers, large amounts in automobile bodywork.

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Table 19.3 *Properties and uses of fluorocarbon thermoplastics*

Compound	*Relative density*	*Tensile strength MPa*	*Chemical resistance*	*Safe working temp. °C*	*Relative cost*	*Typical uses*
Polytetrafluoroethylene PTFE ('Teflon')	1.01	25	Excellent	250	Very high	Gaskets, valve packaging, inert laboratory equipment, chemical plant, piston rings, bearings, non-stick coatings (frying pans), filters, electrical insulation.

The high cost of fluorine – and hence of PTFE – at present restricts the use of this material except where its particular properties of low coefficient of friction (bearings and non-stick coatings for frying pans) and resistance to chemical attack (chemical plant) are utilised. Because of its very low coefficient of friction, bearing surfaces coated with PTFE can be used without lubrication at temperatures approaching 250°C. Similarly chemical plant carrying corrosive liquids can be used at that temperature.

Table 19.3 summarises the properties and uses of PTFE.

19.4.3 Cellulose-base plastics (cellulose esters)

Cellulose-base plastics are derived from natural cellulose, one of the world's most plentiful raw materials. It occurs in many forms of plant life but much of the raw cellulose used in the plastics industry is as cotton linters (cotton fibres too short for spinning to yarn). These 'cellulosics' were amongst the first thermoplastics materials to be developed. In the early days of the cinema, the film base was of cellulose nitrate. This was so inflammable that the unfortunate projectionist was often incarcerated, along with his film and a powerful carbon-arc 'lamp', in a fire-proof cabin in order to safeguard the audience.

This very dangerous 'nitrate' film has since been replaced by *cellulose acetate* (CA) for this, and other purposes, since CA is virtually non-flammable. Although only moderately strong and tough, CA is fairly cheap and is used for moulding a wide range of articles from pens and pencils to toys and toothbrush handles.

Cellulose acetate-butyrate (CAB) is tougher and more resistant to moisture than is ordinary CA and at the same time retains the other useful properties of CA. Because of its greater resistance to moisture, it is useful for the manufacture of handles for brushes and cutlery. Cellulose acetate-propionate (CAP) is slightly tougher and more ductile than the other cellulosics but is used for similar purposes. Table 19.4 summarises the properties and uses of cellulosics.

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Table 19.4 *Properties and uses of cellulosic thermoplastics*

Compound	*Relative density*	*Tensile strength MPa*	*Chemical resistance*	*Safe working temp. °C*	*Relative cost*	*Typical uses*
Cellulose acetate CA	1.3	35	Fair	70	Fairly high	Artificial leather, brush backs, combs, spectacle frames, photographic film base, mixing bowls, lamp-shades, toys, laminated luggage, knobs, wire- and cable-covering.
Cellulose acetate-butyrate CAB	1.18	35	Fair	70	Fairly high	Illuminated road signs, extruded pipe, containers.
Cellulose acetate-propionate CAP	1.21	55	Fair	70	Fairly high	Steering wheels, packaging, toothbrushes, door knobs.

19.4.4 Polyamides (PA)

Polyamides (PA) include a number of compounds better known by the collective name of *nylon*. The more common members of this series of polymers are designated nylon 6 (Figure 19.16), nylon 6.6, nylon 6.10, nylon 11 and nylon 12, of which the most popular forms are 6 and 6.6. In each case, the first digit indicates the number of carbon atoms in the repeating unit or mer in the polymer chain. Where there are two numbers, the full stops separating them are sometimes omitted. Where there are two numbers it means there are two different blocks which constitute the full repeating unit.

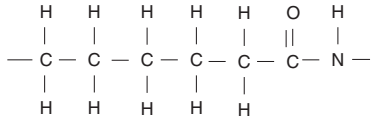


Figure 19.16 *The repeating unit for nylon 6.*

Although nylon 6.6 will always be associated with ladies' hosiery and underwear, it is in fact one of the most important engineering thermoplastics. It is a strong, tough, hard-wearing material with a low coefficient of friction. Its softening temperature is relatively high so that it can be safely heated in boiling water. However, nylons do absorb considerable amounts of moisture which reduces strength whilst increasing toughness. Nylons have very good resistance to most organic solvents, oils and fuels and are inert to inorganic reagents with the exception of mineral acids and chloride solutions containing Cl^- ions.

The high strength of nylon fibre claimed my personal interest and attention about half way through my rock-climbing career when nylon ropes were introduced. I soon realised that a nylon 'line' with an equivalent 'potential life-saving capacity' to that of the old hemp rope was but a fraction of the weight of the latter – a factor to be considered when a long trek in high mountain country was involved. The conservative 'hemp rope' school warned me that friction against rock

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could cause nylon to melt! However, it was never my intention to find myself dangling at the end of a long rope swinging pendulum-wise across a cliff face whilst wondering what the heck to do next. Hemp and manila ropes are still used on ships and in dockyards, but modern climbing ropes now are invariably synthetic fibres like nylon and polypropylene.

In addition to the use of nylon 6.6 in the fibre and textile field, nylons have many applications in engineering industries, particularly as wearing and moving parts where high impact strength is necessary. Small gears operating at low noise levels in music-reproduction equipment and electric clocks are examples. These polymers are injection moulded or extruded as rod, sheet or tube from which components can be machined. Some forms of nylon 6 are cast. The high-pressure lubricant molybdenum disulphide MoS_2 is sometimes added to nylon 6 destined for use as a bearing material. Table 19.5 summarises the properties and uses of polyamides.

Table 19.5 *Properties and uses of polyamide thermoplastics*

Compound	*Relative density*	*Tensile strength MPa*	*Chemical resistance*	*Safe working temp. °C*	*Relative cost*	*Typical uses*
Nylon 66 (PA66)	1.12	Moulded 60 Filaments 350	Good	140	High	Raincoats, yarn (clothing), containers, cable-covering, gears, bearings, cams, spectacle frames, combs, bristles for brushes, climbing ropes, fishing lines, shock absorbers.

19.4.5 Polyesters

These are sometimes of the 'setting' form (see Section 19.5) but one important member of the group is thermoplastic. This is polyethylene terephthalate (PET) – better known as 'Terylene'. Like nylon, this was originally produced as a 'man-made' fibre developed in Britain during the Second World War and adopted by the textile industry. Since then, uses of PET have developed further, first in the injection moulding of electrical components and then to the manufacture of bottles for a wide range of beers and soft drinks. When these drinks contain dissolved gases, such as CO_2 to give the 'fizz', under pressure, diffusion of the gas through the walls of the PET bottle can take place. Such diffusion is more rapid through an amorphous (glassy) structure than through a crystalline structure, hence the forming process is controlled to produce a highly crystalline structure. Thus the process of 'stretch blow moulding' was developed. In this process, extruded PET tube is heated and then simultaneously stretched and blown into the mould. The temperature and speed are controlled so that just below the glass transition temperature (see Section 20.2) very small crystals are formed from the amorphous structure. Because the crystals are very small, the bottle retains its transparent appearance and is also strong. The stretching of the PET in two directions during the blow moulding promotes the crystallisation process. Nevertheless, to make such bottles completely gas tight, they

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can be given an outer coating of polyvinylidene chloride (PVDC). This is important to prevent the ingress of oxygen which would spoil the contents of beer bottles.

Polycarbonates (PC) are structurally line-chain thermoplastic polyesters. They have excellent mechanical properties – particularly high strength and high impact toughness. Since they are also transparent, they are useful for the manufacture of vandal-proof light globes and for babies' feeding bottles. Their temperature tolerance is good so that they are used in high-temperature lenses, coffee pots and the like. A combination of suitable optical properties, along with mechanical toughness, a high heat-distortion temperature, ease of processing and good solvent resistance has led to the use of PC for the manufacture of CDs and similar data-storage products.

Table 19.6 summarises the properties and uses of thermoplastic polyesters.

Table 19.6 *Properties and uses of polyester thermoplastics*

Compound	*Relative density*	*Tensile strength MPa*	*Chemical resistance*	*Safe working temp. °C*	*Relative cost*	*Typical uses*
Polythene terephthalate ('Terylene', 'Dacron') PET	1.38	Moulded 60 Fibres 175	Moderate	85	Moderate	*Fibres*: a wide range of clothing. *Tape and film*: music and recording tapes, insulating tape, gaskets. *Moulded*: electrical plugs and sockets. *Blow moulding*: bottles for beer and soft drinks.
Polycarbonate PC	1.2	66	Good	140	High	Very tough – protective shields (police vehicles), hairdryer bodies, telephone parts, automobile tail light lenses, tool handles, machine housings, babies' bottles, vandal-proof street light covers, safety helmets, CDs (music and data storage).

19.4.6 Polyacetals

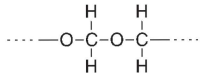


Figure 19.17 *Polyoxyymethylene.*

'Acetal resin' in its simplest form (homo-polymer) structure is a highly crystalline form of polymerised formaldehyde or polyoxymethylene POM (Figure 19.17). It has a high yield strength, both at ambient and at high temperatures, associated with a high modulus of elasticity. Resistance to creep is greater than with most other plastics. Impact toughness is high and is only slightly less at –40°C than at ambient temperatures but it is notch sensitive so that sharp corners in design are best avoided. It is a hard material with good dimensional stability whilst abrasion resistance is good and its coefficient of friction low. Moisture absorption is very low, chemical resistance high and electrical insulation properties good. Heat distortion temperature is very high – near its melting point. POM can be shaped by injection moulding or extrusion, though wrought forms cannot be shaped by heating and stretching. However, if necessary, it can

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be reground and used again. Its machining properties are excellent and are similar to those of alpha/beta brasses. But it is expensive.

Copolymer polyacetals contain extra CH_2 units in the polymer chain. They are generally less strong than the homo-polymer but tend to retain strength at elevated temperatures over longer periods. Polyacetals are particularly useful in applications requiring a high degree of dimensional accuracy, especially under conditions of varying humidity. Their combination of properties enables them to replace metals in many cases, e.g. die-casting.

Table 19.7 gives the properties and uses of the homo-polymer and the copolymer.

Table 19.7 *Properties and uses of polyacetal thermoplastics*

Compound	*Relative density*	*Tensile strength MPa*	*Chemical resistance*	*Safe working temp. °C*	*Typical uses*
Homo-polymer	1.4	70	Fairly good	95	Bearings, cams, gears, flexible shafts, office machinery, carburettor parts, pump impellers, car instrument panels, knobs, handles, water pumps, washing machine parts, seat-belt buckles.
Copolymer	1.4	60	Fairly good	95	

19.4.7 Acrylics

Acrylics are a group of vinyl plastics of which the most important is polymethyl methacrylate (PMMA). It is a clear, glass-like, plastics material better known as 'Perspex' in Britain or 'Plexiglass' in the USA and was developed during the Second World War for use in aircraft. Not only is it much tougher than glass, but it can easily be moulded. It is produced by the polymerisation of methyl methacrylate. Table 19.8 gives the properties and uses of PMMA.

Since it will transmit more than 90 per cent of daylight, and is much lighter and tougher than glass, it can be used in the form of corrugated sheets, interchangeable with those of galvanised iron, for use in industrial buildings. Lenses can be made from PMMA by moulding from powder. This is an inexpensive method of production as compared with the grinding and polishing of a glass blank. Unfortunately, PMMA lenses scratch very easily.

Table 19.8 *Properties and uses of acrylic thermoplastics*

Compound	*Relative density*	*Tensile strength MPa*	*Chemical resistance*	*Safe working temp. °C*	*Relative cost*	*Typical uses*
Polymethyl methacrylate PMMA ('Perspex', 'Plexiglass')	1.18	55	Fairly good	95	Moderate	Aircraft glazing, building panels, roof lighting, baths, sinks, protective shields, advertising displays, windows and windscreens, automobile tail lights, lenses, toilet articles, dentures, knobs, telephones, aquaria, double glazing, garden cloches, shower cabinets.

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19.4.8 High-temperature thermoplastics

The rapid development of plastics materials following the Second World War led to a demand for thermoplastics with higher temperature tolerance. Some of these materials are of complex structure and are produced by complicated processes; these matters will not be discussed here. One important point, however, which needs mention is that the linear chain molecules are built up from bulky ring-type units. Van der Waals forces, acting between these large units in adjacent chain molecules, are therefore relatively high and this results in a high softening temperature, high thermal stability and exceptional heat resistance. The following are three such plastics:

1 *Polyimides*
These are, structurally, similar to the polyamides (nylons) and were the first of the high-temperature thermoplastics of this group to be developed in the early 1960s. As described above, these have bulky, complex ring structure units along the polymer chain and these give rise to increased van der Waals forces between the long-chain molecules so that a higher temperature is necessary to cause their separation – greater heat input causes the molecules to vibrate more vigorously until they separate. Thus polyimides have a very high heat resistance and are useful for high-temperature service. Even after exposure for 1000 hours in air at 300°C, about 90 per cent of the original tensile strength is retained.

2 *Polysulphones*
These are, in some respects, similar in structure to the polycarbonates, and have linear molecular chains containing the bulky benzene ring structure (Figure 19.18). These large units contribute to increased van der Waals forces and so higher softening temperatures. The polysulphones are more expensive than polycarbonates and are therefore only used when the properties of the latter are inadequate. The creep resistance of polysulphones is excellent and superior to that of polycarbonates. They have good temperature resistance and rigidity, also transparency. They do not burn readily and then do not present a smoke hazard. As a result, they are widely used in aircraft for parts of passenger-service units, e.g. air ducts and vents, call buttons, lights, loudspeakers. Polysulphones can be injection moulded, extruded and thermoformed.

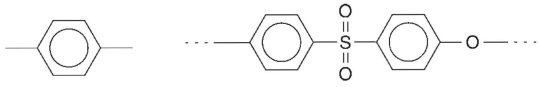


Figure 19.18 *The linear molecular chains contain the bulky unit shown on the left to give the polysulphone structure.*

3 *Polyether ether ketone (PEEK)*
These have outstanding heat-resistant properties as a consequence of the presence of the benzene ring as a unit in the linear polymer

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chains (Figure 19.19). In addition to its high softening temperature, it is resistant to oxidation and has low flammability. It is useful as a moulding material for aggressive environments. It has superior toughness and as a coating for wire it resists cuts and fracture caused by sharp corners. Fatigue resistance is very high.

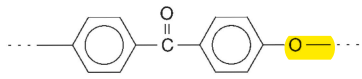


Figure 19.19 *PEEK.*

Table 19.9 gives the properties and uses of these high-temperature thermoplastics.

Table 19.9 *Properties and uses of high-temperature thermoplastics*

Compound	*Relative density*	*Tensile strength MPa*	*Chemical resistance*	*Safe working temp. °C*	*Relative cost*	*Typical uses*
Polyimides	1.42	90	Good	350	High	Seals, gaskets, piston rings, jet engine compressor seals, pressure discs, bearings, friction elements.
Polysulphones	1.24	70	Good	175	High	Hairdryers, oven, iron and fan heaters, microwave oven parts, pumps for chemical plant, transparent pipelines, hot-water dispenser cups for drinks machines, passenger-service unit parts in jet aircraft, integrated circuit boards.
Polyether ether ketone PEEK	1.28	92	Good	150	Very high	Aggressive environments (nuclear plant), oil and geothermal wells, high-pressure steam valves, aircraft and automobile engine parts, wire covering, filament for weaving high-temperature filtration cloth.

19.5 Thermosets

In thermosets, a chemical change is initiated during the moulding process, and 'cross-links', in the form of strong covalent bonds are formed between adjoining molecules. The powerful forces associated with these covalent bonds are greater than the van der Waals forces operating between the chain molecules in a thermoplastic substance. Consequently the molecules are unable to slide over each other and a strong rigid three-dimensional network is formed (Figure 19.20). Thus, *thermosetting* has taken place.

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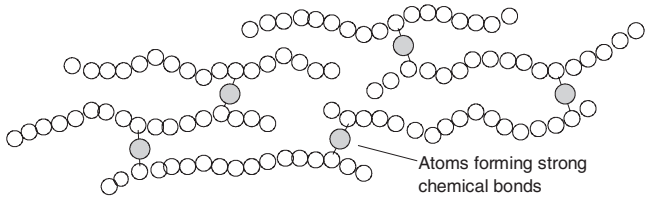


Figure 19.20 *Covalent bonds between neighbouring chains in a thermoset, resulting in a three-dimensional network.*

19.6 Thermoset materials

The following are examples of thermoset materials.

19.6.1 Phenolics

These are probably the best known of the thermosetting group of materials:

1 *Phenol formaldehyde (PF)*
The Crimean War (1853–56) is remembered chiefly for the military blunders which led to the decimation of the 'Gallant Six Hundred' in the Charge of the Light Brigade. Nevertheless, in contemplating this melancholy prospect – as Sir Winston Churchill might have described it – we should reflect on the heroic works of one, Florence Nightingale, whose efforts in the reorganisation and discipline of field hospitals reduced the death rate of wounded soldiers from 42 per cent to a little over 2 per cent. In those days, the badly wounded had little hope of survival as the inevitable *septicaemia* took control. The introduction of a new disinfectant known as 'carbolic acid' was, however, an important factor in this clinical revolution.

Carbolic acid – or phenol as we now know it – is a colourless, crystalline solid and a weak acid. It was used in 1907 by Dr. Leo Bakeland to develop the first synthetic plastics material 'bakelite'. This name became synonymous with plastics materials generally as the plethora of 'brown-bakelite-and-chrome' artefacts of the 1930s filled our homes, but we can't blame Dr. Bakeland for that!

The phenol molecule is based on that of benzene in that one hydrogen atom has been replaced by the –OH radical (Figure 19.21(i)). If phenol is mixed with a *limited* amount of formaldehyde (H.CHO) then the molecules of each react to form long-chain molecules (Figure 19.21(ii)). In this condition the material is brittle but thermoplastic, and can be ground to a powder suitable for moulding. This powder (or 'novolak') contains other materials, which on heating will release more formaldehyde, so that during the final moulding process, cross-links are formed between the chain molecules (Figure 19.21(iii)), (Figure 19.22). The resulting 'network' structure represented in Figure 19.21(iii) can only be shown two-dimensionally on flat paper, but it is in fact a three-dimensional cage-like network in which the units have 'set' *permanently*. Since a non-reversible chemical reaction has taken place, phenol formaldehyde cannot be softened again by heat.

Exhibit 1012
FLS v. Metso

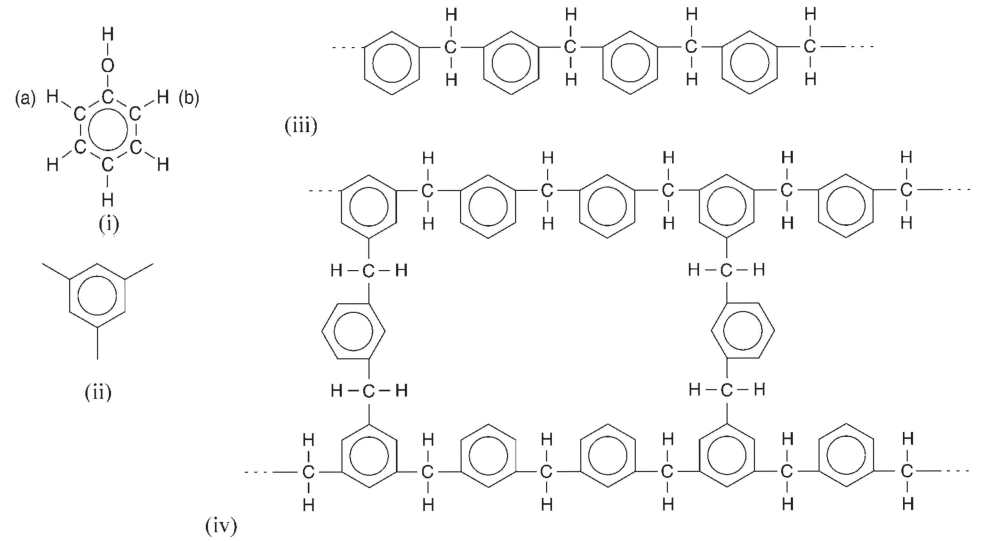


Figure 19.21 *(i) The phenol molecules and (ii) its representation in the following molecules, the –OH and H atoms which take no part in the reaction have, for clarity, been omitted. (iii) The long chain molecule when phenol reacts with formaldehyde, (iv) the network structure produced on heating with more formaldehyde during moulding.*

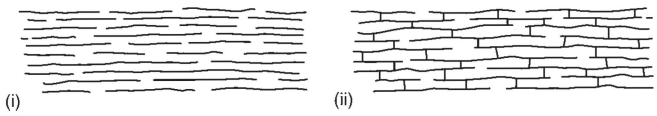


Figure 19.22 *Thermosetting in a polymer material: (i) illustrates the structure at the 'novolak' stage, here the material is still thermoplastic and the chain molecules are held together only by van der Waals forces, (ii) shows the effect of thermosetting, here the linear molecules are now held firmly together by powerful covalent bonds ('cross-links').*

This type of plastic is hard and rigid, but tends to be rather brittle in thin sections. However, it has a good electrical resistivity, so it is not surprising that the 'bakelite' industry grew in conjunction with the electrical industries from the late 1920s onwards. Various mouldings for wireless-cabinets, motor-car parts, bottle-tops, switchgear, electric plugs, door-knobs, and a host of other articles are commonly made from bakelite. In most of these articles, a wood-flour filler is used; but, if greater strength is required a fibrous filler (paper, rags, jute, or sisal) is employed.

2 *Urea formaldehyde (UF)*

These plastics are basically similar to the phenol-formaldehyde types since they depend upon the two-stage cross-linking reaction, but in this instance between molecules of urea and formaldehyde. The first stage of the reaction results in the formation of a syrupy material. This is mixed with the filler, to give a moist, crumbly mass. After

Exhibit 1012
FLS v. Metso

mixing with other reagents, this is allowed to dry out, producing the urea-formadehyde moulding powder.

The fact that urea-formaldehyde mixture passes through a syrupy stage makes it useful in other directions. For example, paper, cloth, or cardboard can be impregnated with it, and then moulded to the required shape before being set by the application of heat and pressure. Weather-resistant plywood can also be made using urea formaldehyde as the bonding material, whilst the syrup can also be used as a vehicle for colouring materials in the coating of metal furniture, motor cars, washing machines, and refrigerators with a layer of enamel.

3 *Melamine formaldehyde (MF)*
These plastics are of a similar type structurally to the two foregoing thermosets, but are much harder and more heat resistant. Moreover, they are most resistant to water and consequently find use in the household as cups and saucers, baths and sundry kitchen utensils, particularly where greater heat-resistance is necessary.

Table 19.10 gives the properties and uses of the above phenolic thermosets.

Table 19.10 *Properties and uses of phenolics thermosetting materials*

Compound	*Relative density*	*Tensile strength MPa*	*Chemical resistance*	*Safe working temp. °C*	*Relative cost*	*Uses*
Phenol formaldehyde ('bakelite, 'phenolic') PF	1.45	50	Very good	120	Low	Electrical equipment, radio-cabinets, vacuum-cleaners, ashtrays, buttons, cheap cameras, automobile ignition systems, ornaments, handles, instrument-panels, advertising displays, novelties and games, dies, gears, bearings (laminates), washing-machine agitators.
Urea formaldehyde ('urea') UF	1.48	45	Fair	80	Moderate	Adhesives, plugs and switches, buckles, buttons, bottle-tops, cups, saucers, plates, radio-cabinets, knobs, clock-cases, kitchen equipment, electric light-fittings, surface coatings, bond for foundry sand.
Melamine formaldehyde ('melamine') MF	1.49	50	Good	130	Moderate	Electrical equipment, handles, knobs, cups, saucers, plates, refrigerator coatings, trays, washing-machine agitators, radio-cabinets, light-fixtures, lamp-pedestals, switches, buttons, building-panels, automotive ignition-blocks, manufacture of laminates.

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FLS v. Metso

19.6.2 Polyester resins

Polyester resins of the thermoplastic type have already been mentioned in this chapter. These are of the 'straight-chain' molecule form, which are incapable of linking up with other adjacent chain molecules; they are therefore thermoplastic.

However, by using special monomers, polyesters can be produced with side-chains capable of forming cross-links between adjacent molecules and these therefore are 'setting plastics', of which some are of the cold-setting type. For example, if styrene is added to the liquid polyester, it provides the necessary cross-links, and the liquid gradually sets without the application of heat. Used with glass-fibre to provide reinforcement, these materials are useful in building up such structures as the hulls of small boats, wheelbarrows and car bodies. The glass fibre, impregnated with the liquid mixture, is built up a layer at a time on a suitable former. Pressure is not required, except to keep the material in position until it has set. These glass fibre/polyester resin composites are very strong and durable. See Table 19.11 for properties and uses.

Alkyd resins constitute a further group of polyesters. They are thermosetting materials originally introduced as constituents of paints, enamels, and lacquers. They have a high resistance to heat and a high electrical resistivity and are dissolved by neither acids nor many organic solvents. The resins are now available in powder form, which is generally compression-moulded. Liquid alkyds are used in enamels and lacquers for automobiles, stoves, refrigerators, and washing machines (Table 19.11).

19.6.3 Polyurethanes

Polyurethanes constitute a group of very adaptable plastics, comprising both thermoplastic and thermosetting materials. They are generally clear and colourless. One type is used in the manufacture of bristles, filaments and films.

Table 19.11 *Properties and uses of polyester (setting types) thermosetting materials*

Compound	*Relative density*	*Tensile strength MPa*	*Chemical resistance*	*Safe working temp. °C*	*Relative cost*	*Uses*
Polyester	1.3	40	Fairly good	95	Moderate	Adhesives, surface coatings, corrugated and flat translucent lighting-panels, lampshades, radio grilles, refrigerator parts; polyester laminates are used for hulls of boats, car bodies, wheelbarrows, helmets, swimming-pools, fishing-rods and archery-bows.
Alkyd resins	2.2	25	Fair	230	Moderate	Enamels and lacquers for cars, refrigerators and stoves, electrical equipment for cars, light-switches, electric-motor insulation, television-set parts.

Exhibit 1012
FLS v. Metso

In another group of polyurethanes, carbon dioxide is evolved during the chemical process necessary for establishing cross-links between the chain molecules. This carbon dioxide is trapped by the solidifying polymer, thus producing a foam. The mechanical properties of the foam can be varied by using different materials to constitute the polymer. Thus, some of the foams become hard and rigid, whilst others are soft and flexible. Rigid thermosetting polyurethane foams are used as heat-insulators, and for strengthening hollow structures, since they can be poured into a space where foaming and setting will subsequently occur. Aircraft wings can be strengthened in this manner. Flexible sponges, both for toilet purposes and for seat upholstery, are generally of polyurethane origin. See Table 19.12 for properties and uses.

Table 19.12 *Properties and uses of polyurethane thermosetting materials*

Compound	*Relative density*	*Tensile strength MPa*	*Chemical resistance*	*Safe working temp. °C*	*Relative cost*	*Uses*
Polyurethane PUR	1.2	Mainly foams	Good	120	High	Adhesives (glass to metal), paint base, wire-coating, gears, bearings, electronic equipment, handles, knobs. Foams are used for insulation, upholstery, sponges, etc. Rigid foams are used for reinforcement of some aircraft wings.

19.6.4 Epoxy resins

These are produced in a similar way to polyesters, i.e. by being mixed with a cross-linking agent which causes them to set as a rigid network of polymer molecules. They are used for manufacturing laminates, for casting, and for the 'potting' of electrical equipment. Excellent adhesives can be derived from the epoxy resins available as syrups, and they are particularly useful for metal gluing. The reader will no doubt be familiar with those two-component adhesives available at DIY stores – and be aware of how effective the cold-setting process really is if he gets the tube caps mixed! Table 19.13 gives the properties and uses of epoxy resin thermosets.

Solid epoxy resins are sometimes mixed with phenolic resins for moulding purposes.

19.6.5 Polyimides

These are high-temperature resistant polymers which can be either thermoplastic or thermosetting according to their formulation. They are available as film or as solid parts which retain mechanical properties at 300°C over long periods. Even at 500°C, properties are retained for a short time. Table 19.14 gives their properties and uses.

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Table 19.13 *Properties and uses of epoxy resin thermosetting materials*

Compound	*Relative density*	*Tensile strength MPa*	*Chemical resistance*	*Safe working temp. °C*	*Relative cost*	*Uses*
Heat-resistant type	1.15	70	Good	200	Fairly high	Adhesives (metal gluing), surface coatings, casting and 'potting' of specimens. Laminates are used for boat hulls (with fibreglass), table surfaces and laboratory furniture, drop-hammer dies. Epoxy putty is used in foundries to repair defective castings.
General purpose	1.15	63	Good	80	Fairly high	

Table 19.14 *Properties and uses of polyimide thermosetting materials*

Compound	*Relative density*	*Tensile strength MPa*	*Chemical resistance*	*Safe working temp. °C*	*Relative cost*	*Uses*
Polyimide	1.43	40	Good	300	Fairly high	Bearings, compressor valves, piston rings, diamond abrasive wheel binders.

19.6.6 Silicones

The polymers mentioned so far in this chapter are based on the element carbon, and are known as organic compounds. Unfortunately, they all soften, decompose, or burn at quite low temperatures. However, more than a century ago, it was realised that there was a great similarity in chemical properties between carbon and the element silicon. Since then, chemists have been trying to produce long-chain molecules based on silicon, instead of carbon, hoping that in this way materials would be discovered which lacked many of the shortcomings of carbon polymers. Common silicon materials include quartz, glass and sand – all substances which are relatively inert, and which remain unchanged after exposure to very high temperatures. Consequently, the more fanciful of our science-fiction writers have speculated on the possibility of a system of organic life, based on silicon instead of carbon, existing on the hot planets Venus and Mercury. Whilst their 'bug-eyed monsters' may remain a figment of the imagination, some progress has taken place here on Earth in producing polymers based on silicon, and called organo-silicon compounds, or 'silicones'.

Some of these compounds – of which sand is the basic raw material – have properties roughly midway between those of common silicon compounds, such as glass, and the orthodox organic plastics. Silicones are based on long-chain molecules in which carbon has been replaced by silicon and oxygen. They are available as viscous oils, greases, plastics and rubbers. All are virtually non-combustible, and their properties remain constant over a very wide temperature range. Thus, silicone lubricating oils retain their fluidity more or less unchanged at

Exhibit 1012
FLS v. Metso

temperatures low enough to make ordinary oils congeal. Similarly, silicone rubbers remain flexible from low sub-zero temperatures up to temperatures high enough to decompose ordinary rubbers. Silicones are water repellent, and are widely used for waterproofing clothes, shoes, and other articles, whilst silicone jelly is useful as a moisture-proof coating and sealing compound.

By forming still longer chain molecules, silicone plastics can be produced. These are very useful as an insulating varnish for electrical equipment designed to work at high temperatures. As moulding plastics, silicones are used in the manufacture of gaskets and seals for engineering purposes where high temperatures are involved, since they retain their plasticity and sealing efficiency under such conditions.

Silicone-resin paints provide durable finishes which clean easily, and which do not deteriorate appreciably. Such a finish applied to a motor car would normally outlast the car, and with a minimum of attention.

19.7 Elastomers

Christopher Columbus and his sailors may well have been the first Europeans to handle natural rubber since it was reported that some tribes of South American Indians played ball games well before the days of Pele. Natural rubber is in fact derived from the sap of the rubber tree *Hevea brasiliensis*. Following the work of Goodyear in vulcanising rubber, production grew rapidly in Brazil, the home of the rubber tree, and the city of Manaus, complete with an opera house and many other trappings of civilised living, mushroomed in the middle of the Amazon jungle as capital of a Rubber Empire. In 1876, however, some seeds of the rubber tree were smuggled out of Brazil by British botanists and planted in greenhouses in Kew Gardens. The young plants were sent to the Dutch East Indies (now Indonesia) and Malaya so that Britain was able to establish and control its own rubber industry. This naturally led to a severe contraction of the Brazilian rubber industry and a rather shabby Manaus is all that remains of its former glory.

19.7.1 Long chain molecules in rubber

In natural rubber, the long chain molecules are more complex in structure than in the simpler polymers such as polythene, and consist of chains of 44 000 or more carbon atoms in length. The monomer present in these rubber molecules is the carbon-hydrogen compound *isoprene*, so that natural rubber is really *polyisoprene*. When the isoprene mers are joined to form the large molecular chain (Figure 19.23), the side group makes the molecule rather 'lopsided' and this causes the molecule to bend into a folded or coiled form in order to accommodate these large side groups. Since these rubber molecules are folded and coiled, they possess elasticity in a similar manner to that of a coiled spring and immediately stress is applied there is an elastic response. Nevertheless, natural rubber stretches like dough when stressed, because the chain molecules slide past each other into new positions (Figure 19.24). This plastic flow takes place slowly because weak van der Waals forces acting between molecules are overcome progressively as entangled molecules become very slowly disentangled. For this reason, a piece of unvulcanised natural rubber is both *elastic and plastic* at the same time, and, once stretched, will not return to its original shape.

Exhibit 1012
FLS v. Metso

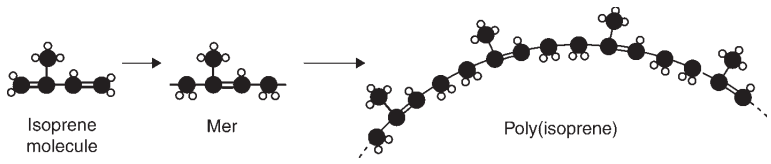


Figure 19.23 *The 'side groups', consisting of one carbon atom (the solid black circles) and three hydrogen atoms (the smaller open circles) cause the polyisoprene molecule to 'bend' into a coiled form.*

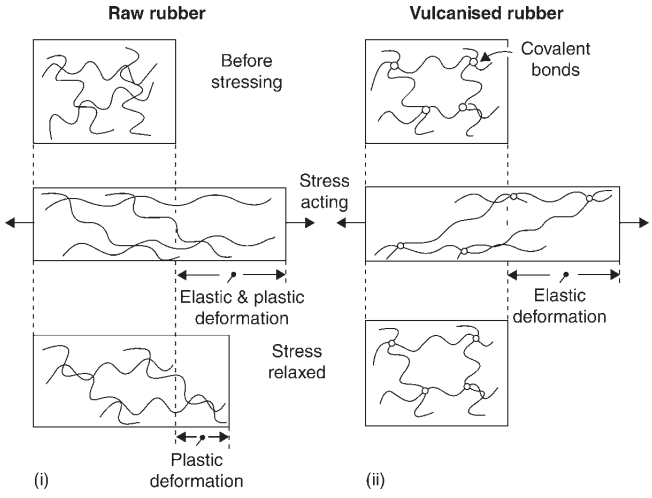


Figure 19.24 *Due to their folded or coiled form, rubber molecules become extended in tension but return to their original shapes when the stress is removed. In raw rubber (i) a steady tensile force will also cause separate molecules to slip slowly past each other into new positions because only weak van der Waals forces attract them to each other; so that when the force is relaxed some plastic deformation remains, though elastic deformation has disappeared. By vulcanising the raw rubber (ii) the chain molecules are covalently bonded at certain points so that no permanent plastic deformation can occur and only elastic deformation is possible. This disappears when stress is relaxed.*

19.7.2 Vulcanisation

When up to 3 per cent sulphur is added to rubber prior to moulding, 'vulcanisation' will occur if the moulding temperature is high enough. Atoms of sulphur form strong covalent bonds between the rubber molecules so that they are permanently anchored to each other. Thus, whilst the vulcanised rubber retains its elasticity due to the folded or coiled nature of its molecules, it retains its shape permanently because of the cross-linking. If the vulcanisation process is carried further – that is, if more sulphur is used – so many cross-links are produced between adjoining molecules that the whole mass becomes rigid and loses most of

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its elastomer properties. The product is a black plastics material known as 'ebonite' or 'vulcanite' and was used extensively some half century ago for the manufacture of such materials as fountain-pens, before other more suitable materials were developed.

The Japanese invasion of Britain's Far East rubber plantations in 1942 led to the development of synthetic rubber substitutes. In fact, synthetic polyisoprene was produced. Since those days, the properties of these synthetic rubbers have considerably improved and rubbers with new properties developed, so that the industrial output of synthetic rubbers now exceeds that of natural rubber. As with natural rubber, sulphur is used to provide the cross-linking atoms in the vulcanisation process for many of these synthetic rubbers, but in some cases oxygen cross-linking atoms are used, the oxygen atoms being provided by magnesium oxide or zinc oxide.

To be of value in engineering, a rubber must have a low 'hysteresis', that is, it must return within very close limits to its original shape following each successive deformation cycle of loading and unloading. It must also have a low heat build-up, i.e. heat generated as a result of friction (braking in a motor vehicle) or as a result of absorbing vibration energy, must be dissipated adequately.

19.7.3 Engineering elastomers

In addition to natural rubber, the more important elastomers in general use include:

1 *Natural rubber (NR) and polyisoprene (IR)*
The latter is manufactured from petrochemicals and has a molecular structure similar to that of natural rubber. Both are used for commercial vehicle tyres, anti-vibration and anti-shock mountings and dock fenders. They have good mechanical properties in respect of strength, high elasticity and low hysteresis in the important working range. Creep properties are also good. Unfortunately, the resistance to attack by oxygen and ozone is poor, though this can be overcome by the use of additives for most applications.

2 *Styrene-butadiene rubber (SBR)*
This is possibly the best known and most widely used of elastomers and was originally a replacement for natural rubber following the Japanese occupation of Malaya during the Second World War. It is a copolymer of styrene and butadiene with physical properties slightly inferior to those of natural rubber. Although ageing properties and abrasion resistance of SBR are slightly superior to those of natural rubber, it suffers greater from heat build-up. Nevertheless, it is widely used for car tyres where adhesion and wear resistance are of paramount importance. Heat build-up is not a great problem here since the modern car tyres are heavily reinforced and consequently have thin walls which lose heat more quickly.

3 *Butadiene rubber (BR)*
Butadiene rubber – monomer butadiene – is noted for its high resilience but poor tensile strength and poor tear resistance, for

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which reasons it is seldom used on its own but generally blended with other elastomers. Since it has a low heat build-up it is generally used for vehicle tyres – blended with natural rubber for truck tyres and with SBR for motor car tyres. BR imparts good tread wear to tyres and also has good low-temperature properties. It is also used as a sealant compound in caulking.

4 *Polychloroprene rubber (CR)*
Polychloroprene rubber – the monomer of which is chloroprene – is also known as *neoprene*. It has the good physical properties of natural rubber coupled with a much better resistance to oxygen, ozone and some oil products. CR retains its properties well up to 90°C but tends to become hard and stiff below –10°C. It finds use in a variety of products, such as diver's wet suits, anti-vibration mountings, conveyor belts, tank linings, hoses and cable sheathing.

5 *Acrylonitrile-butadiene rubbers (NBR)*
These are copolymers of acrylonitrile and butadiene and are usually called *nitrile rubbers*. The normal grades have quite good physical properties though slightly inferior to those of natural rubber and SBR. Nitrile rubber is relatively expensive and is used principally for sealing applications (gaskets) where its excellent resistance to oil products and its good temperature resistance (95°C) are essential. It is also used for hoses, conveyor belts and cable sheathing where similar conditions prevail.

6 *Butyl rubber (IIR)*
This is a copolymer of isobutane and small amounts of isoprene. It is cheaper than natural rubber to which its physical properties are, however, inferior. Since it has a very low permeability to air and other gases, it is used mainly for tyre inner tubes and also for the liners of tubeless tyres. It has excellent resistance to ozone and to ageing generally so that it is less apt to perish. 'Butyl' – as it is generally called – is also used for air-bags and supporting equipment, as well as for more general purposes such as hoses and tank linings since it is impervious to many chemicals.

7 *Ethylene-propylene rubber (EPM)*
This is a copolymer of the gases ethylene and propylene in which a quantity of either monomer can vary up to 65 per cent. During polymerisation, any weak double-bonds are 'used up' and the resulting rubber is therefore chemically inert so that, like polythene, it has good resistance to ageing, weathering and ozone attack. Its service-temperature range of –50 to +125°C is also good but it has poor resistance to some solvents and a rather high creep rate. Since EPM has good electrical insulation properties, it is often used for cable covering. A further *-diene* material is often added to provide extra cross-linking sites (thus toughening the polymer and increasing its heat tolerance). It is then designated EPDM and has a number of uses in the automobile industry.

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8 *Silicone rubbers (SI)*
In these materials, silicon and oxygen replace carbon in the polymer chains. They are expensive but their high temperature tolerance (200°C) makes them very useful for many purposes. Their resistance to low temperatures too is good but resistance to some oils and other organic liquids is only moderate. This can be improved by replacing some of the hydrogen atoms by fluorine, but at a great increase in cost.

Few of other synthetic rubbers are of such engineering significance. *Polysulphide rubber* has a good resistance to oils and solvents and is used as an internal coating for oil and paint piping. *Styrene-butadiene-styrene rubber* (SBS) is thermoplastic at temperatures above that of glass transition (see Chapter 20) so that it can be moulded by conventional methods. For this reason, it is used as a carpet-backing material and in some adhesives.

Table 19.15 summarises some of the properties of elastomers. The term resilience is used for the capacity of a material to absorb energy in the elastic range – a high resilience rubber ball will bounce to a much higher height than a low resilience one.

Table 19.15 *Properties of elastomers*

Elastomer	*Tensile strength MPa*	*Elong. %*	*Service temperatures °C*	*Resistance to oil and greases*	*Resilience*	*Uses*
Natural rubber	28	700	–50 to +100	Poor	Good	Tyres, engine mountings, flexible hoses, foamed padding, balloons, rubber bands.
Styrene-butadiene	25	600	–60 to +100	Poor	Good	Tyres, transmission belts.
Polychloro-prene	25	1000	–50 to +100	Good	Good	Car radiator hoses, gaskets and seals, conveyor belts.
Butyl	20	900	–50 to +100	Poor	Fair	Inner tubes, steam hoses and diaphragms.
Ethylene-propylene	20	300	–50 to +100	Poor	Good	Resistance to hot water and superheated steam, steam hoses, conveyor belts.

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20 Properties of plastics

20.1 Introduction

In the previous chapter we considered a polymer material as consisting of an intertwined mass of giant molecules each containing thousands of atoms. In thermoplastics materials, these molecules are attracted to each other by relatively weak van der Waals forces, whilst in thermosetting plastics they are joined to each other by strong, permanent covalent bonds. This means that whilst thermosetting materials are sometimes stronger than thermoplastics, they are inevitably more rigid and much more brittle. This chapter is about the properties of plastics, their testing, and the methods used to shape them.

20.2 Crystal and glass states

Most solid substances – metals, solids and minerals – exist in a purely crystalline form, i.e. the atoms or ions of which they are composed are arranged in some regular geometric pattern. This is generally possible because the atoms (or ions) are small and very easily manoeuvrable. With polymers, however, we are dealing with very large molecules which entangle with each other and are consequently much less manoeuvrable. As a result, only a limited degree of crystalline arrangement is possible with most polymers as they cool, and only restricted regions occur in which linear molecule chains can arrange themselves in an ordered pattern (Figure 20.1). These ordered regions are called *crystallites*.

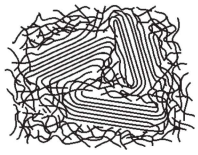


Figure 20.1 *'Crystallites' in a solid plastics material.*

Thus in a solid state, polymers can consist of both crystalline and amorphous regions. Highly crystalline polymers contain up to 90 per cent crystalline regions, whilst others are almost completely amorphous.

20.2.1 Melting points of polymers

A pure, completely crystalline, solid such as a metal or inorganic salt, melts at a single definite temperature called the melting point; this is because *single* atoms (or ions) are easily mobile and can change from the orderly crystalline state to the amorphous state of being a liquid. Amorphous and partly crystalline materials, however, start off with some degree of being amorphous and so they merely become progressively less rigid when heated and show no clear transition from solid to liquid, both being amorphous in this case. This is what we would expect since liquids become less viscous as the temperature rises – viscous liquids like treacle and tar flow more readily when they are heated. With highly crystalline polymers on the other hand, a sudden change in structure at a particular temperature, is shown by a change such as the rate of expansion. This is the point at which all crystalline regions have become amorphous – as happens of course when all crystalline metals melt to form amorphous liquids. For such polymer materials, this temperature is designated the melting point T_m (Table 20.1). As will be noted in Table 20.1, the

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greater the degree of crystallinity of polythene, the higher its melting point. Presumably this is because van der Waals forces are much greater in the crystalline regions since the molecules are closer together there.

Table 20.1 *Melting points of some crystalline polymers*

Polymer	*Melting point °C*
Polythene (PE) 50% crystalline	120
Polythene (PE) 80% crystalline	135
Polypropylene (PP)	170
Polyvinyl chloride (PVC)	212
Polyethylene terephthalate (PET)	255
Polyamide (Nylon 6.6)	265
Polytetrafluoroethylene (PTFE)	327
Polyether ether ketone (PEEK)	334

20.2.2 Glass transition temperature

At ambient temperatures, polymers may be either soft and flexible or hard, brittle, and glassy. When a soft, flexible polymer is cooled to a sufficiently low temperature, it becomes hard and glassy. For example, a soft rubber ball when cooled in liquid air shatters to fragments if any attempt is made to bounce it whilst it is still at that very low temperature. The temperature at which this soft-to-glassy change occurs is known as the *glass transition temperature* T_g (Table 20.2). For some plastics, T_g is above ambient temperature so that they only become soft and flexible when heated past T_g. Polystyrene is a polymer of this type. The polystyrene kitchen hollow-ware is hard and rigid at ambient temperatures and gives a characteristic 'ring' when lightly struck, but on heating above its glass transition temperature of 100°C it loses that rigidity. Below the glass transition temperature amorphous polymers have molecular chains which are unable to move when the material is heated and so it is stiff and rather brittle. When heated to above T_g, there is sufficient thermal energy for some motion of segments of the polymer chains to occur and so impart flexibility to the polymer.

Table 20.2 *Glass transition temperatures of some polymers*

Polymer	*Glass transition temp. °C*
Polythene (PE)	–120
Natural rubber (NR)	–73
Polypropylene (PP)	–27
Polymethyl methacrylate (PMMA)	0
Polyamide (Nylon 6.6)	60
Polyethylene terephthalate (PET)	70
Polyvinyl chloride (PVC)	87
Polystyrene (PS)	100
Cellulose acetate (CA)	120
Polytetrafluoroethylene (PTFE)	126
Polyether ether ketone (PEEK)	143
Polycarbonate (PC)	147

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20.2.3 Vicat softening temperature

This is a value which can be determined more precisely in numerical terms than either T_m or T_g, so that it offers a useful means of comparison between plastics materials as far as their response to temperature change is concerned (Table 20.3). It measures the temperature at which a standard indentor penetrates a specific distance into the surface of the plastics material using a standard force. During the test, the temperature is raised at a specified uniform rate and the penetration is recorded by a dial gauge micrometer. The *vicat temperature* is the temperature when the specified penetration (usually 1 mm) has been attained.

Table 20.3 *Vicat temperatures for some polymers*

Polymer	*Vicat softening temp. °C*
Ethylene vinyl acetate (EVA)	51
Cellulose acetate (CA)	72
Polyvinyl chloride (PVC)	83
Low-density polythene (LDPE)	85
Polymethyl methacrylate (PMMA)	90
Polystyrene (HIPS)	94
Polystyrene (PS)	99
Acrylonitrile-butadiene-styrene (ABS)	104
High density polythene (HDPE)	125
Polypropylene (PP)	150
Polycarbonate (PC)	165
Polyacetal	185
Polyamide (Nylon 6.6)	185

20.3 Mechanical properties

The strength of plastics materials is generally much lower than that of most other constructional materials. Nevertheless, plastics are light materials with a relative density between 0.9 and 2.0 so that when considered in terms of strength/weight ratio they compare favourably with some metals and alloys. Figure 20.2 indicates the types of stress/strain relationship obtained for different groups of polymers.

The mechanical properties of most engineering materials and alloys vary very little within the range of ambient temperatures encountered in service. This is to be expected since no structural changes occur (other than thermal expansion) until the recystallisation temperature (see Section 6.3.2) is reached and this is usually well above 100°C. However, with many polymer materials – particularly thermoplastic – mechanical properties vary considerably with temperature in the ambient region. The gradual reduction in van der Waals forces with rise in temperature will affect mechanical properties; at both T_g and T_m mechanical properties change. Thus, a thermoplastic polymer may have a tensile strength of, say, 70 MPa at 0°C, falling to 40 MPa at 25°C and to no more than 10 MPa at 80°C. As tensile strength falls with rise in temperature, there is a corresponding increase in percentage elongation (Figure 20.3).

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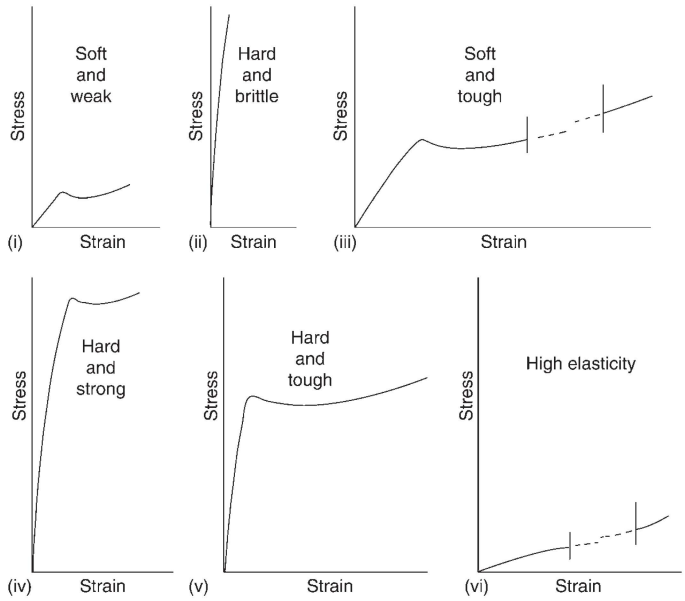


Figure 20.2 *Types of stress-strain diagram for different polymer materials (after Carswell and Nason). (i) Low elastic modulus, low yield stress, e.g. PVA and PTFE. (ii) High elastic modulus, low elongation, e.g. PF, PMMA and PS. (iii) Low elastic modulus, low yield stress but high elongation and high stress at break, e.g. PE and plasticised PVC. (iv) High elastic modulus, high yield stress, high tensile strength and low elongation, e.g. rigid PVC and modified PS. (v) High elastic modulus, high yield stress, high tensile strength and high elongation, e.g. nylons and polycarbonates. (vi) Very low elastic modulus, low yield stress and low tensile strength but very high elastic elongation, e.g. natural rubber and other elastomers.*

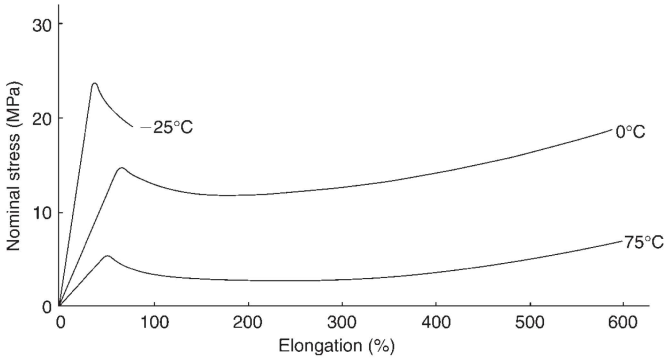


Figure 20.3 *Tensile stress-strain curves for low-density polythene at –25°C, 0°C and 75°C.*

20.3.1 Tensile testing

Clearly if mechanical tests on plastics are to have any meaning, then a *fixed testing temperature* must be specified. Thus BS 2782 (Part 3) requires a testing temperature maintained at 23 ± 2°C with an

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atmospheric humidity of 50 ± 5 per cent for many thermoplastics materials; moreover, the test-pieces must be maintained under these conditions for 88 hours prior to the test. In some cases, for example thermosetting plastics, this conditioning is unnecessary since the permanent covalent bonds between the polymer chains render these materials much less temperature sensitive.

Plastics materials are also very time-sensitive as far as mechanical testing is concerned. This is because the total deformation depends upon:

1 Bond bending of the carbon-carbon covalent bonds in the polymer chain – this is manifested as the ordinary elasticity and is an *instantaneous* deformation.
2 Uncoiling of the polymer chains – this gives rise to high elasticity and is *very time dependent*.
3 Slipping of polymer chains past each other – this produces *irreversible* plastic flow and is also *very time dependent*.

The sum total of deformation arising from (1), (2) and (3) is generally termed *viscoelastic*, and the rate of strain has a considerable effect on the recorded mechanical properties. Generally, as the strain rate increases so does the recorded yield stress and again BS 2782 (Part 3) lays down different conditions for different plastics as far as tensile testing is concerned. The speed of separation of the test-piece grips varies between 1 and 500 mm/min for different materials and forms of material.

The geometry of test-pieces also differs from that used in metals testing. Abrupt changes in shape cause stress concentrations which are likely to precipitate failure so tensile test-pieces are generally of the form shown in Figure 20.4

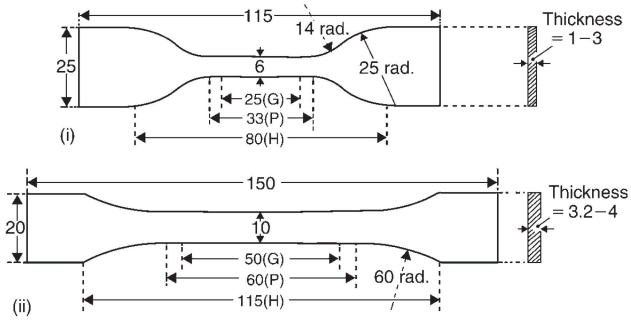


Figure 20.4 *Two forms of tensile test-piece for plastics. Gauge length G, parallel section P, distance between grips H (measurements are in mm).*

Many plastics do not obey Hooke's law, i.e. elastic strain produced is not proportional to the stress applied, so that it becomes impossible to derive the tensile modulus of elasticity (Young's modulus) since this value applies only to materials with Hookean characteristics. As an alternative, it is usual to derive the *secant modulus* of the material. This is defined as the ratio of stress (nominal) to corresponding strain at some specific point on the stress/strain curve. In Figure 20.5, the secant

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modulus associated with a strain of 0.2 per cent is shown and is, in fact, the slope of the line OS.

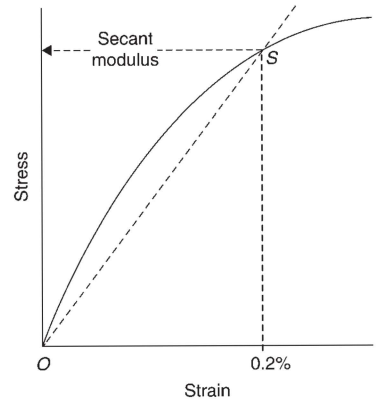


Figure 20.5 *The secant modulus for non-Hookean polymer materials.*

At the commencement of the tensile test, an initial force of w (usually about 10 per cent of the expected force necessary to produce 0.002 strain) is applied to 'take up slack' and straighten the test-piece. With this force applied the extensometer is set to zero. The force is then gradually increased (in accordance with the specified straining rate) until the necessary force W is reached to produce 0.2 per cent strain in the gauge length. The stress is then $(W - w)/A$, where A is the initial cross-sectional area of the test-piece at the gauge length used. Thus:

$$\text{secant modulus} = \frac{\text{stress}}{\text{strain}} = \frac{(W-w)/A}{0.002}$$

Other values of strain between 0.1 per cent and 2.0 per cent may be used, depending upon the type of material. The strain value must, therefore, be stated when quoting the secant modulus.

20.3.2 Hardness tests

Ball-indentation tests similar to those used for metals are applied to some of the harder plastics, e.g. ebonite and hard rubbers, and the hardness index is derived from the same principle, i.e.

$$\text{hardness} = \frac{\text{applied force}}{\text{surface area of impression}}$$

When using the Rockwell test (see Section 3.3.3) for these hard plastics materials, scales M, L or R are appropriate and the hardness index is prefixed with the letter denoting the test, i.e. M, L or R.

For other plastics, a form of indentation hardness test is used in which the depth of penetration is measured under the action of a standard force. In the *durometer* (which measures Shore hardness) two different

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indentors are available. Type A (Figure 20.6) is used for soft plastics materials and type D for hard plastics.

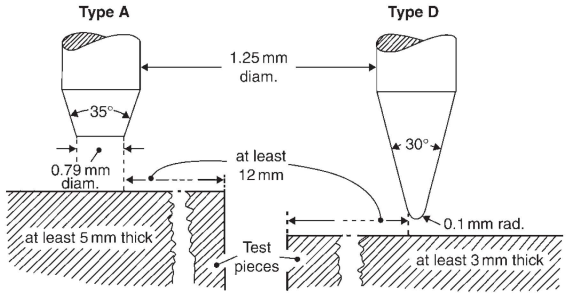


Figure 20.6 *Indentors used in the durometer (Shore hardness).*

As is the case when hardness testing metals, the thickness and width of test-pieces must be adequate, as indicated in Figure 20.6. The load is applied for 15 s whilst the conditions of temperature and humidity (23°C and 50 per cent humidity) specified in the case of the tensile test for plastics also apply here. In the Shore hardness test, the hardness index is related inversely to the depth of penetration. It was suggested earlier in this book (see Section 3.3) that values described as 'hardness indices' are in fact generally measurements of the resistance of a material to penetration rather than the resistance of its surface to abrasion. This is particularly true of plastics. Thus high-density polystyrene will resist penetration in tests of this type better than will polythene, yet the surface of polystyrene can be *scratched* much more easily.

20.3.3 Impact tests

Both Izod and Charpy tests are used to assess the toughness of plastics materials. Plastics fall into three groups as far as toughness is concerned (Table 20.4). In this table, those materials described as 'brittle' will break even when unnotched, whilst those described as 'notch-brittle' will not break unnotched but will break when sharp-notched. The 'tough' materials will not break completely even when sharp-notched. For this reason a variety of notches are used in impact testing of plastics (Figure 20.7), in order to suit the material under test and to make possible the production of comparable test results.

Table 20.4 *Relative impact brittleness of some common plastics*

Brittle	*Notch-brittle*	*Tough*
Acrylics	Polyvinyl chloride (PVC)	Low-density polythene (LDPE)
Polystyrene (PS)	Polypropylene (PP)	Some Acrylonitrile-butadiene-styrene (ABS)
Phenolics	High-density polythene (HDPE); some Acrylonitrile-butadiene-styrene (ABS)	Polyethylene-propylene co-polymers

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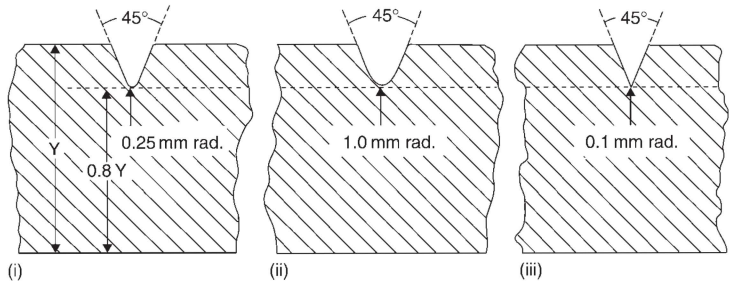


Figure 20.7 *Test-piece notches for impact tests on plastics materials. (i) and (ii) are used in the Izod test whilst all three are available for the Charpy test.*

20.3.4 Creep

Creep, the gradual extension under a constant force, must be considered seriously for metals if they are to work at high temperatures (see Section 3.5). Plastics materials, however, are much more prone to this type of deformation since they undergo the viscoelastic type mentioned earlier (Section 20.3.1). Creep rates, like other mechanical properties for polymers, are very temperature dependent. Even for a plastics raincoat, creep must be considered since it must be capable of supporting its own weight so that it can hang in a wardrobe possibly for long periods without slowly flowing towards the floor during a period of warm weather.

The creep curves shown in Figure 20.8 are typical of those for most thermoplastics materials. These show that the initial rate of creep is rapid but then the rate decreases to a lower constant rate, which for small stresses might mean no further change in creep. Naturally the greater the applied force the greater the creep rate and elongation and quite small rises of temperature will produce much greater rates of creep.

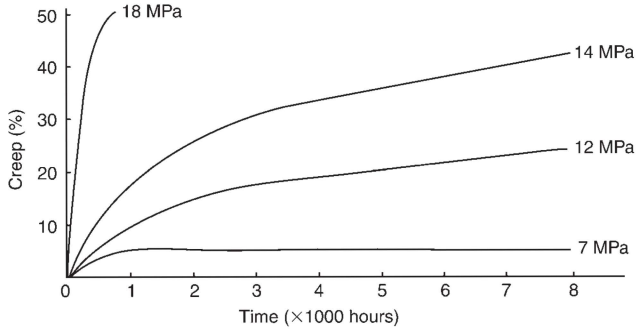


Figure 20.8 *Creep curves for cellulose acetate at 25°C. At a stress of 18 MPa, rapid creep soon leads to catastrophic failure, whilst at a stress of 7 MPa a small initial amount of creep ceases after about 1000 hours and no further measurable creep occurs.*

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20.3.5 Other mechanical tests

Other mechanical tests are used to measure compressive properties, tear strength, shear strength and deflection in bend under an applied load. All of these tests, together with those described briefly here, are dealt with in BS 2782: Part 3.

20.4 Additives

Various materials can be introduced into a polymer at the moulding stage by mixing the additive thoroughly with the moulding powder.

20.4.1 Fillers

Fillers are used principally in the interests of economy when up to 80 per cent of the moulding powder might be filler. Generally fillers are finely powdered, naturally occurring, non-polymeric substances which are readily available at low cost. Phenolic (bakelite)-type resins are nearly always compounded or filled with substances such as sawdust, wood flour, short cellulose fibres from wood pulp, or cotton flock; fillers like paper, rag and cotton fibres will increase the strength of bakelite. Some soft thermoplastics materials are blended with up to 80 per cent mineral solids such as crushed quartz or limestone. Here the plastics materials operate in much the same way as does cement with the aggregate in concrete. Thus some fillers serve to increase the strength and hardness and to reduce creep and thermal expansion.

20.4.2 Anti-static agents

The act of walking across a polypropylene fibre carpet can easily produce a considerable charge of static electricity, whilst most readers will be aware that the simple act of removing a synthetic-fibre garment, particularly in a dry atmosphere, will generate 'static' – a charge more than sufficient to create a spark capable of igniting a petrol-air mixture. One wonders how many unexplained fires are started in this way.

Since the valence electrons, i.e. the outer shell electrons, are held captive within the covalent bonds throughout a plastics materials, such a material is a non-conductor of electricity. In fact, most polymers are excellent insulators. It follows therefore that a plastics material can become highly charged with 'static' electricity because this static is unable to be conducted away. This may be undesirable or indeed hazardous and in such cases an anti-static substance is added to the mix. Additives to achieve this result are substances which will lower the electrical resistivity of the surface of the polymer, generally by attracting moisture to its surface since moisture is sufficiently conductive to provide a path by which the 'static' charge can 'leak' away.

Many such additions are 'waxes' in which the molecules are strong dipoles (see Section 1.4.8), i.e. they have a negatively charged end and a positively charged end. They therefore attract water molecules which also are dipoles, so that the two are held together by van der Waals forces. Such a strategy is of course not effective in very dry atmospheres (below 15 per cent humidity). Such 'waxes' can be added to PE and PS since their moulding temperatures are low enough to avoid decomposition of such additives. Other organic compounds (amines and

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amides), also phosphoric acid derivatives and sulphonic acids, are sometimes used for this purpose.

20.4.3 Flame retardants

Many plastics materials constitute a fire risk as witnessed by a number of home disasters in past years. Plastics foam fillings of cushions can be a fire hazard. To reduce such fire risks, flame retardants are used with the object of interfering with those chemical reactions underlying combustion. One such substance is hexabromocyclodecane (HBCD) which is incorporated in materials like polypropylene. If combustion of the plastics material begins, hydrogen bromide is released from HBCD as a vapour which immediately combines with those portions of the plastics molecule, generally –OH groups, which would otherwise burn and lead to a rapidly spreading conflagration. Thus combustion is stifled.

Some organic chlorides have a similar action in releasing hydrogen chloride which similarly neutralises the –OH groups. Their effectiveness can often be improved by the addition of antimony oxide. This reacts with the organic chloride in the flame producing antimony trichloride which increases flame retardation.

20.4.4 Friction modifiers

For two apparently flat surfaces in contact, whether metals or plastics, there will only be contact at a few high spots between them. At such points there is 'intimate' atomic contacts. Thus, friction between two plastics surfaces occurs because of the van der Waals forces at such contact points acting between molecules of two adjacent surfaces. In order to move one surface over another, such adhesion bonds have to be broken. Coefficients of friction for different plastics materials vary widely since the different groupings of atoms at molecule surfaces affect the magnitude of these van der Waals forces, such coefficients being as low as 0.04 for polytetrafluoroethylene (PTFE) and as high as 3.0 for natural rubber. Consequently, PTFE is widely used as a bearing material, as is nylon with a coefficient of 0.15 and ultra-high molecular weight polythene with coefficient varying from 0.08 to 0.2.

The addition of graphite to a plastics material will reduce the coefficient, as will particles of added PTFR and the high-pressure lubricant molybdenum disulphide. Such materials will reduce wear in bearings and bushings.

20.4.5 Other additives

Other additives include *colourants* which are either insoluble, finely divided pigments or soluble dyes, usually chosen for colour stability, inertness and non-toxicity. In some instances, pigments may act as a filler or serve some other purpose such as that of a stabiliser.

The addition of *asbestos* to a plastics material will increase its heat tolerance, whilst *mica* improves its electrical resistance.

20.4.6 Foamed or 'expanded' plastics materials

Foamed rubber was developed many years ago; now a number of polymers are available as 'foams'. 'Expanded' polystyrene is probably

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the best known of these. It is used as a very lightweight packing material for fragile equipment. Without one wonders how many of the cameras, computers and TV sets from the Far East would reach us intact. Up to 97 per cent of its volume consists of air bubbles so that it is useful as a thermal insulator and for the manufacture of DIY ceiling tiles, as well as being an excellent flotation material which, unlike cork, does not become waterlogged.

Polyurethane foams are available in two different forms, either as flexible foams for the production of sponges and upholstery, or as rigid foams used for the internal reinforcement of some aircraft wings. Both thermoplastic and thermosetting polymers (including some elastomers) can be foamed and four basic methods are available for introducing the gas packets into the polymer:

1 By mechanically mixing air with the polymer whilst the latter is still molten.
2 By dissolving a gas such as carbon dioxide into the mix under pressure. As hardening proceeds, the pressure is reduced so that the gas is released from solution, rather like the bubbles of carbon dioxide which are released from mineral water, or of course champagne, when the stopper is removed. The bubbles in this case are trapped in the hardening polymer.
3 A volatile component may be added to the hot mix. This vaporises during hardening, forming bubbles.
4 In some processes, a gas is evolved during the actual polymerisation process. This can be utilised to cause foaming. Alternatively, a 'blowing agent' may be added which will release gas when the mix is heated for the moulding process. This is useful for thermoplastics materials. A simple reagent of this type is sodium bicarbonate which releases carbon dioxide when heated. It behaves in much the same way when used as 'baking powder' with bubbles of carbon dioxide released during baking making a cake 'rise'.

20.5 Shaping plastics

Most of the larger plastics manufacturers supply raw materials in the form of powders, granules, pellets and syrups. These are purchased by the fabricators for the production of finished articles. As with metals, plastics can be purchased in the form of extrusions and sheet on which further work can be carried out.

The principal methods of fabrications are calendering, extrusion, moulding, blow moulding and vacuum forming, but raw materials available in liquid form may be cast.

20.5.1 Calendering

This is used to manufacture thermoplastics sheet, mainly PE and PVC. The calendering unit consists of a series of heated rolls into which the raw material is fed as heated 'dough' (Figure 20.9). The formed sheet is cooled by a chill roller. Fabric, paper and foil are coated with a film of plastics material using a similar process.

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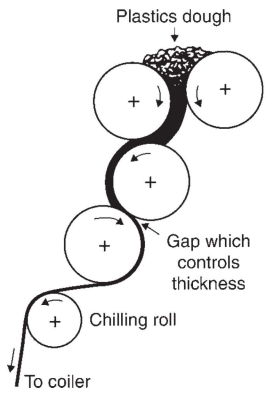


Figure 20.9 *The principles of calendaring.*

20.5.2 Extrusion

The principle of extrusion is shown in Figure 20.10. Here the plastic material is carried forward by the screw mechanism, and, as it enters the heated zone, it becomes soft enough to be forced through the die. The die aperture is shaped according to the cross-section required in the product.

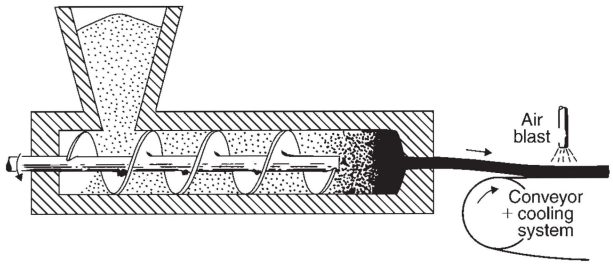


Figure 20.10 *The extrusion of plastics. Often known as 'screw-pump' extrusion.*

Man-made fibres are extruded using a multi-hole die, or 'spinneret'. Wire can be coated with plastics by extrusion, assuming that the machine is adapted so that the wire can pass through the die in the manner of a mandrel.

20.5.3 Moulding

Several important hot-moulding processes are commonly used:

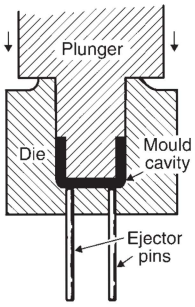


Figure 20.11 *One system of compression-moulding.*

1 *Compression-moulding* (Figure 20.11)
This is probably the most important, and is used for both thermoplastic and thermosetting materials, though it is particularly suitable for the latter. In either case, the mould must be heated, but for thermoplastic substances it has to be cooled before the work-piece can be ejected. A careful measured amount of powder is used and provisions are made to force out the slight excess necessary to ensure filling of the mould cavity. Machine and tooling costs are low compared to most other permanent mould casting processes.

2 *Injection-moulding* (Figure 20.12)
This is a very rapid response process and is widely used for moulding such materials as polythene and polystyrene. The material is softened by heating it in the injection nozzle. The mould itself is cold, so that the plastic soon hardens and can be ejected. The work-piece generally consists of a 'spray' of components, connected by 'runners' which are subsequently broken off. The operating cost is high due to the cost of machines and moulds.

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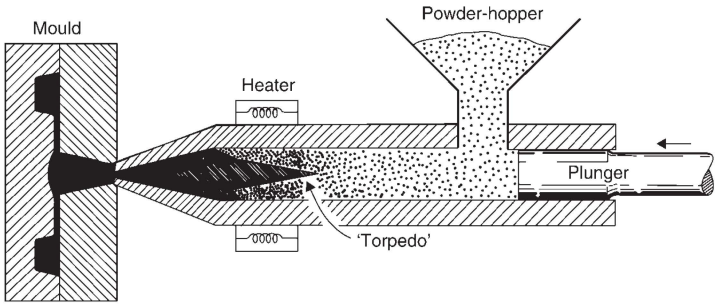


Figure 20.12 *The principle of injection-moulding.*

3 *Transfer-moulding* (Figure 20.13)
This is used for thermosetting plastics. The material is heated to soften it, after which it is forced into the heated mould, where it remains until set. Rather more intricate shapes can be produced by this process than by compression-moulding.

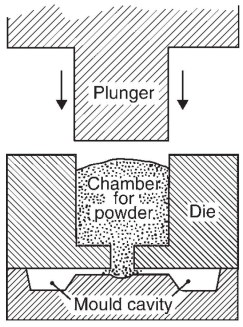


Figure 20.13 *Transfer-moulding.*

4 *Blow moulding* (Figure 20.14)
This is used to produce hollow articles. The plastic is first softened by heating and is then blown by air pressure against the walls of the mould. In the figure, extruded tube (parison) is being used. A variety of containers, e.g. bottles and coffee jars are produced in this way. It is mainly used with the thermoplastics of PET and polyalkenes.

A similar process, known as *stretch-blow moulding*, is used in the manufacture of PET drinks bottles. Here a preform is stretched and blown within the mould so that crystallisation of the PET occurs within the amorphous structure. This process provides increased yield strength and stability in bottles which can be filled with liquids at around 90°C.

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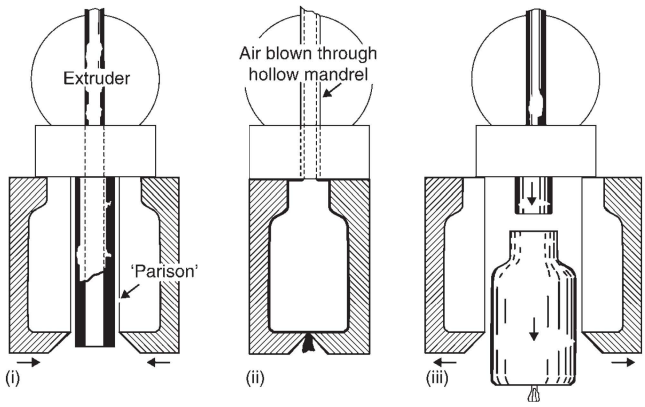


Figure 20.14 *Blow-moulding by interrupted extrusion.*

5 *Film-blowing* (Figure 20.15)
Film can be blown continuously from heated thermoplastics delivered straight from the extruder. This material has a nominal thickness of not more than 0.25 mm. The process is used for the manufacture of PE film and 'tube' for parting off as bags or other forms of packaging.

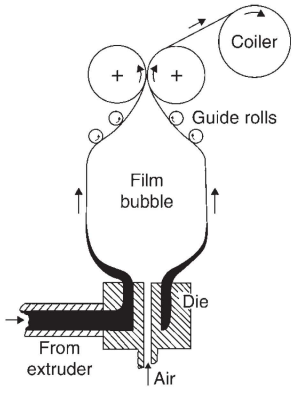


Figure 20.15 *Film-blowing of plastics bags.*

6 *Vacuum-forming* (Figure 20.16)
This is used in producing simple shapes from thermoplastics materials in sheet form. The heated sheet is clamped at the edges and is then stretched by the mould as it advances into position. The ultimate shape is produced by applying a vacuum, so that the work-piece is forced into shape by the external atmospheric pressure. It is used for shapes with essentially constant section thickness.

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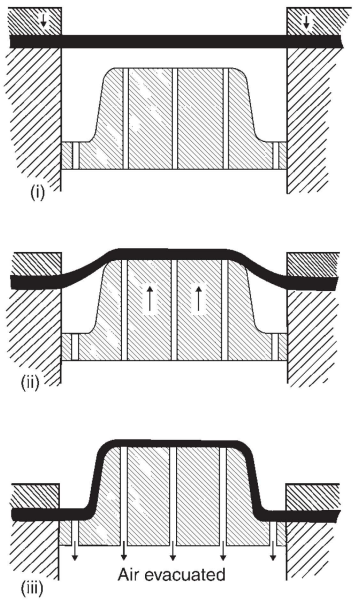


Figure 20.16 *Stages in a vacuum-assisted forming process.*

20.5.4 Casting

This is limited to those plastics materials whose ingredients are in liquid form, i.e. as monomers which polymerise in the mould. The mixed liquids are poured into the open mould and are allowed to remain at atmospheric pressure until setting has taken place. It is mainly used for simple shapes; operating costs can be very low.

Slush-moulding is essentially a casting process rather than the moulding process its name implies. It is used mainly for PVC, the mix being prepared as a thin paste which is injected into the mould. The mould is then rotated and heated until the paste forms a solid 'gel' on the inner surface of the mould. The excess fluid is then poured out and the *hollow* formed article removed from the mould. The process is used for the manufacture of dolls' heads and other semi-soft toys. The 'slush casting' of aluminium teapot spouts and of lead soldiers in former days, followed a similar method.

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