

Polymers

Introduction to Plastics

Plastics are polymeric materials, a material built up from long repeating chains of molecules. Polymers such as rubber occur naturally, but it wasn't until the development of synthetic polymers around 1910 that the polymers tailored to the needs of the engineer first started to appear. One of the first commercial plastics developed was Bakelite and was used for the casing of early radios. During the Second World War, plastics such as nylon and polyethylene were used as a replacement material for other materials in short supply. Because the early plastics were not completely chemically stable, they gained a reputation for being cheap and unreliable. However, advances in plastic technology since then, mean that plastics are a very important and reliable class of materials for product design.

The mechanical properties of plastics tend to be inferior to most metals. Because of this, careful consideration must be given to using plastics for structural applications. Fibre reinforced plastics are extensively used where the mechanical properties of the base plastic material are not sufficient. However because of their relatively low weight, the ability to colour the plastics when manufacturing, and the ability to mould complex shapes relatively easily, plastics are extensively used for product casings and other applications where mechanical strength is not at a premium.

Plastics are not cheap materials. The cost of raw plastic materials is typically higher than steel but less than aluminium. However, because processing costs over large production runs are lower, the use of plastics can result in significantly cheaper products.

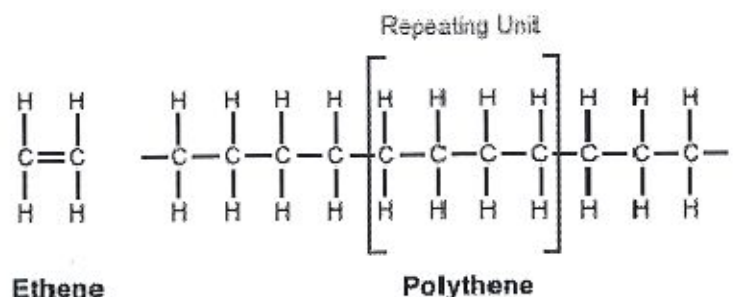
For applications requiring strength, the plastics can be reinforced by fibres, usually glass, which give the material added strength.

Polymers

In metals molecules arrange themselves into crystalline lattices. Polymers have molecules arranged into long strings of molecules.

Carbon is contained in all organic materials and can be easily linked to other materials such as hydrogen and oxygen because of its need to find four electrons. Carbon is the main ingredient in the long chained polymer molecules and forms covalent bonds with other materials. This carbon chain is known as the polymer backbone.

A simple chain of carbon and hydrogen gives butane (C^4H_{10}). These molecules are called monomers. Carbon though can form double or even triple bonds. By splitting the double bonds it is possible to link it to other molecules. By splitting the double bond of ethene (C_2H_4) and joining it to another ethene molecule the polymer poly(ethene), or polythene as it is commonly known is formed

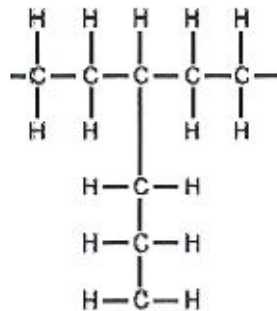


Other polymers can be easily produced such as polyphenylethene (polystyrene can be produced from phenylethene (styrene). These can be formed from 1000 to 50000 linked monomers).

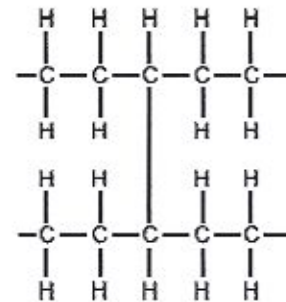
Polymers

To give strength, the chains can be altered. If a hydrogen atom is removed and replaced by a carbon atom then the chain can branch out. This will form another chain similar to the main chain. This creates a softer plastic with a lower melting point.

A cross linked polymer can be formed by removing two hydrogen atoms from the branch and growing a chain adjacent to the original molecule. Cross linking gives us plastics such as polyester, rubber and thermosetting resins.



Branched Chain Polymer



Cross linked polymer

Unbranched chains can form crystalline regions called spherulites. These regions are closely packed. Polythene is about 60% crystallising, solid fillers such as silica and alumina can be added to add stiffness to rubbers and other elastomers which do not crystallise. These fillers attach to the polymer chains creating a similar effect to crystallisation.

Copolymerisation is a process of combining two or more monomers forming a polymer. In this reaction there are no by products, when combined the monomers are mixed randomly making an irregular structure. Copolymerisation is useful allowing the original properties to be altered. For example PVC when pure is brittle. Copolymerisation with vinyl acetate create a flexible copolymer

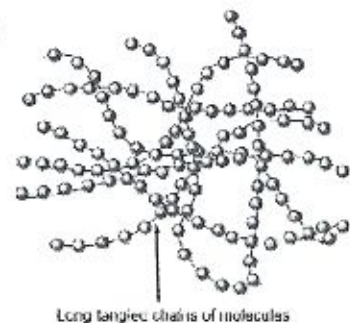
There are two main families of plastics, **thermosetting and thermoplastics**

Thermoplastics

Thermoplastics become soft when heated. They can be easily moulded and remoulded without significant degrading. Thermoplastics consist of long molecular chains with no regular structure (or very little regular structure).

There are many thermoplastics available:

- Polyethylene
- Polystyrene
- Polycarbonate
- Nylon
- Acrylic
- Acetal



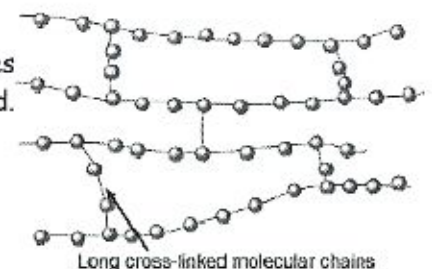
Long tangled chains of molecules

Thermosetting Plastics

Thermoset plastics are rigid plastics, resistant to higher temperatures than thermoplastics. Once set, a thermoset plastic cannot be remoulded.

There are several common thermoset plastics:

- Epoxies
- Polyester



Long cross-linked molecular chains

Polymers

Polymers

Polymer materials include plastics and rubbers whose atoms are arranged in long molecular chains known as polymers. The use of natural rubber, obtained from the rubber tree, began in the nineteenth century. Unfortunately natural rubber degrades or 'perishes' over a relatively short period of time and is readily attacked by solvents. It is not used much in engineering today except when mixed with synthetic rubbers. Developments over the last hundred years have seen the introduction of many new synthetic rubbers and plastics with many different properties. The raw materials that are used to make them come from oil distillation, coal, and some are from animal and vegetable substances.

The name 'plastic' is a little misleading. Plasticine, chewing gum and linseed oil putty are examples of materials which are truly plastic. They are easily deformed by tensile, compressive and shearing forces and retain whatever shape they are moulded into. Polymer materials are in fact quite elastic at normal temperatures and the name 'plastics' refers to their condition when they are being formed into shape. At this stage the raw material is often a resin which can be poured or injected into a mould. Alternatively the raw material may be a powder or granules which are heated into a liquid prior to moulding.

Polymers are made up mainly of carbon and hydrogen atoms but may also have oxygen, chlorine, and fluorine atoms attached to them depending on the type of plastic. Each polymer can contain several thousand atoms. If fully extended, they can be anything up to a millimetre long and possibly more. The polymers are intertwined and held together by covalent bonds. The strength of the bonds affects the properties of plastic materials and rubbers. Some are very flexible and easy to stretch whilst others are hard and brittle. Some will melt and burn at relatively low temperatures whilst others are heat resistant. The polymers of two common plastics, polyethylene (polythene) and polyvinyl chloride (PVC) are shown in diagram 1 (a) & (b).

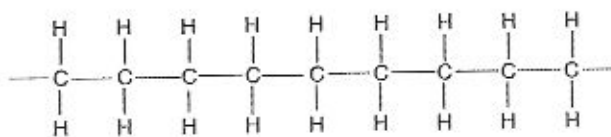


Diagram 1(a) the polythene polymer

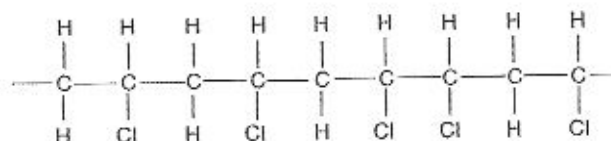


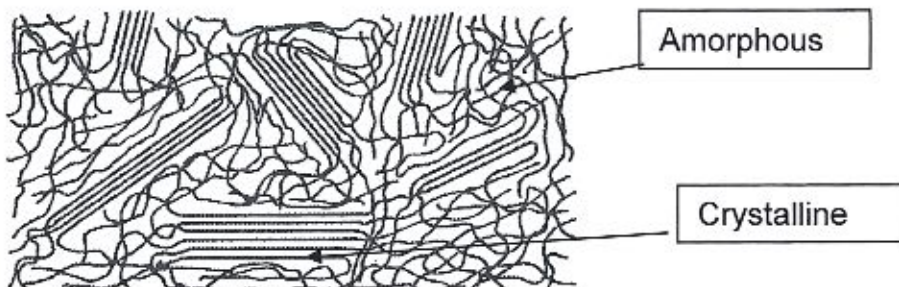
Diagram 1(b) the PVC polymer

Plastics can be part amorphous, where the polymers are randomly entangled, and part crystalline where the polymers become arranged in a geometric pattern.

These regions are called crystallites (diagram 2). The relative proportion of amorphous regions and crystallites varies with different plastics and the way in which they have been processed.

Polymers

Forces of attraction are set up between the polymers as they form. They are known Van der Waal forces and it is these that hold plastics such as polythene and PVC together.



Plastics can be subdivided into thermoplastics, thermosetting plastics and rubbers.

Diagram 2 Crystalline and amorphous regions

Thermoplastics can be softened and remoulded by heating whereas thermosetting plastics cannot. Rubbers are polymer materials known as elastomers which have the property of being able to return to their original shape after large amounts of deformation.

Thermoplastics

Some thermoplastic materials are soft and flexible at normal temperatures whilst others are hard and brittle. When heated the hard thermoplastics will eventually soften and become flexible. The temperature at which this occurs is known as the glass transition temperature denoted by the symbol T_g . Further heating eventually causes the material to reach its melting temperature which has the symbol T_m . Diagram 3 shows how the properties of a thermoplastic change with temperature.

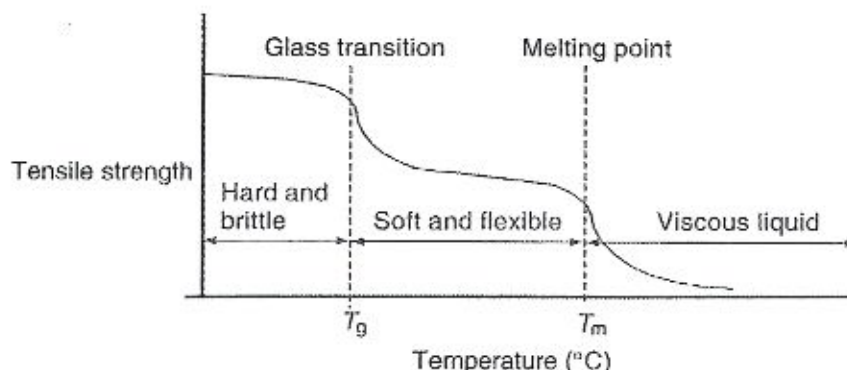


Diagram 3 Change of thermoplastic properties with temperature

Polymers

Some common thermoplastic materials and their uses are listed in Table 1.

Polymer	Common name	Properties	Applications and uses
Polyethene	Low-density polythene	Tough, flexible, solvent resistant, degrades if exposed to light or ultra-violet radiation	Squeeze containers, packaging, piping, cable and wire insulation
Polyethene	High-density polythene	Harder and stiffer than low-density polythene with higher tensile strength	Food containers, pipes, mouldings, tubs, crates, kitchen utensils, medical equipment
Polypropene	Polypropene	High strength, hard, high melting point, can be produced as a fibre	Tubes, pipes, fibres, ropes, electronic components, kitchen utensils, medical equipment
Polychloroethene	Polyvinyl chloride or PVC	Can be made tough and hard or soft and flexible, solvent resistant, soft form tends to harden with time	When hard, window frames, piping and gutters. When soft, cable and wire insulation, upholstery
Polyphenylethene	Polystyrene	Tough, hard, rigid but somewhat brittle, can be made into a light cellular foam, liable to be attacked by petrol based solvents	Foam mouldings used for packaging and disposable drinks cups Solid mouldings used for refrigerators and other appliances
Methyl-2-methylpropenoate	Perspex	Strong, rigid, transparent but easily scratched, easily softened and moulded, can be attacked by petrol based solvents	Lenses, corrugated sheets for roof lights, protective shields, aircraft windows, light fittings
Polytetrafluoroethylene	PTFE	Tough, flexible, heat-resistant, highly solvent resistant, has a waxy low-friction surface	Bearings, seals, gaskets, non-stick coatings, tape
Polyamide	Nylon	Tough, flexible and very strong, good solvent resistance but does absorb water and deteriorates with outdoor exposure	Bearings, gears, cams, bristles for brushes, textiles
Thermoplastic polyester	Terylene	Strong, flexible and solvent resistant, can be made as a fibre, tape or sheet	Textile fibres, recording tape, electrical insulation tape

Table 1 Common thermoplastics and uses

Thermosetting plastics

Thermosetting plastics, which are also called thermosets, undergo a chemical change during the moulding process. Strong covalent bonds are formed between the polymers that are known as cross links. The cross-links may consist of a single atom or a small chain of atoms that form in the mould during what is known as the curing process. As a result, the bonding forces are much stronger than the Van der Waal forces and once formed the cross-links cannot be broken. Thermosetting plastics are generally harder and more rigid than thermoplastics and cannot be softened or melted by heating.

Filler materials are very often mixed in with the raw materials for thermosetting plastics prior to moulding. These improve the mechanical properties and include wood flour, shredded textiles, paper and various other fibres and powdered materials. Some common thermosetting plastics and their uses are listed in Table 2.

Polymers

Table 4.10 Common thermosetting plastics

Polymer	Common name	Properties	Applications and uses
Phenolic resins	Bakelite	Hard, resistant to heat and solvents, good electrical insulator and machinable, colours limited to brown and black	Electrical components, vehicle distributor caps, saucepan handles, glues, laminates
Urea-methanal resins	Formica	As above, but naturally transparent and can be produced in a variety of colours	Electrical fittings, toilet seats, kitchen ware, trays, laminates
Methanal-melamine resins	Melamine	As above, but harder and with better resistance to heat. Very smooth surface finish	Electrical equipment, table ware, control knobs, handles, laminates
Epoxy resins	Epoxy resins	Strong, tough, good chemical and thermal stability, good electrical insulator, good adhesive	Container linings, panels, flooring material, laminates, adhesives
Polyester resins	Polyester resins	Strong, tough, good wear resistance, and resistance to heat and water	Boat hulls, motor panels, aircraft parts, fishing rods, skis, laminates

Table 2 Common thermosets and uses

Rubbers

The polymers in rubbers are known as elastomers. They are longer and tend to be more complex than other polymers (Table 3). Elastomers can be made up of more than 40000 atoms and when the material is unloaded; they are intertwined and folded over each other in a random fashion.

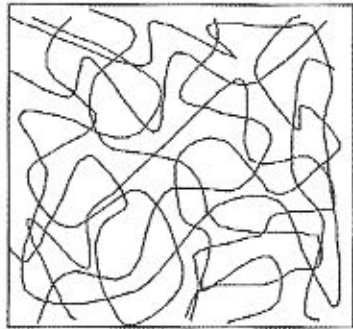
Table 4.11 Common types of rubber

Type of rubber	Properties/origins	Applications and uses
Natural rubber	Obtained as latex from the rubber tree. Perishes with time and is readily attacked by solvents	Not used for engineering purposes except when mixed with synthetic rubbers
Styrene rubber	Synthetic rubber developed in USA during Second World War as a substitute for natural rubber. Also known as GR-S rubber. Resistant to oils and petrol	Blended with natural rubber and used for vehicle tyres and footwear
Nitrile	Synthetic rubber with close resemblance to natural rubber. Resistant to mineral and vegetable oils and can withstand moderately high temperatures	Used in engineering for oil seals, gaskets and hoses
Butyl rubber	Synthetic rubber with good resistance to heat and temperature. Impermeable to gases	Used in engineering for tank linings, moulded diaphragms, inner tubes and air bags
Silicone rubber	Synthetic rubber with good solvent resistance and which retains its properties over a wider temperature range than other types. Remains flexible from -80°C to 300°C	Widely used in chemical and process plant for seals and gaskets where a wide variation in temperature is likely. Also in aircraft where low temperatures are experienced at high altitude

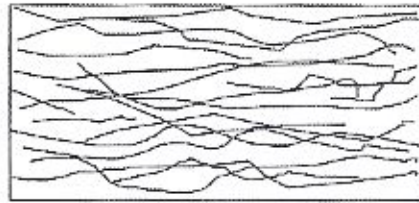
Table 3 Common types of rubber

Polymers

When loads are applied to rubber, the elastomers behave rather like coiled springs which become aligned as the material is stretched. This gives the material its elastic properties. If the loading is excessive, the forces between the polymers may be insufficient to prevent them from sliding over each other. This will ultimately lead to failure, or produce permanent deformation. In this condition the rubber is said to be both elastomeric and thermoplastic (diagram 4).



Unloaded elastomers



← Load →
Elastomers aligned under load

Diagram 4 Elastomer behaviour

When sulphur or certain metal oxides are added to the rubber during manufacture, cross-links are formed between the polymers. These are similar to those formed in thermosetting plastics and the process is known as vulcanising. The cross-links enable the rubber to retain its elasticity and return to its original shape when loaded almost to the point of failure. The addition of larger quantities of sulphur causes the rubber to lose some of its elasticity. If sufficient is added, it becomes hard and brittle and its properties are then very similar to the hard thermosetting plastics.

Worksheet

1	What are the main constituent elements of polymers?
2	What are Van der Waals forces?

Polymers

3	What change takes place in thermoplastic materials at the glass transition temperature?
4	Which thermoplastic material is widely used in moulded and granular form in packaging?
5	What is the common name for polychloroethane
6	What is the main behavioural difference between thermoplastics and thermosets?
7	What happens during the curing process in thermosetting plastic materials?
8	Which kind of rubber retains its flexibility over a temperature range of between -80°C and 300°C ?
9	What is vulcanising and what effect does it have on the properties of rubber?