

POLYMERS

PROPERTIES AND BEHAVIOUR

A polymer is a large molecule containing hundreds or thousands of atoms formed by combining one, two or occasionally more kinds of small molecule (monomers) into chain or network structures. The *polymer materials* are a group of carbon-containing (organic) materials which have molecular structures of this sort. Polyethylene, polystyrene and the epoxy resins are well known examples. Macromolecules occur widely in living organisms: these *natural polymers* are frequently of very complex and specialised molecular structure. The polymers used in engineering are for the most part wholly synthetic and are of much simpler structure. The only natural polymers of major engineering importance are timber and natural rubber. Natural rubber, together with the synthetic rubbers, finds little application in civil engineering,

Molecular Structure

Linear Chain Polymers (Thermoplastics)

Polyethylene (PE) is an important hydrocarbon polymer which has a simple molecular structure. The molecular chain is built of carbon atoms each covalently bonded also to two hydrogen atoms, and, thus the PE polymer has the formula $-(CH_2)_n$ where n measures the chain length. In commercial PE materials n is generally in the range 1000 to 10 000, so that the linear chains have a length-to-thickness ratio similar to a piece of household string a few metres long.

Other important linear polymers with carbon chain molecular backbones are polypropylene (PP), polyvinyl chloride (PVC) and polytetrafluorethylene (PTFE). PP differs from PE in that one of the pair of hydrogen atoms attached to alternate carbon atoms along the chain is replaced by a methyl CH_3 group. PP is therefore also composed of only carbon and hydrogen and like PE is a hydrocarbon polymer.

In polyvinylchloride, chlorine atoms are attached to the main carbon chain, replacing one in four of the hydrogen atoms in the PE structure. In PTFE, all the hydrogen atoms are replaced by fluorine (F), giving a linear polymer. Other carbon chain linear polymers include polyacrylonitrile (PAN) (from which carbon fibre is made), polymethyl methacrylate (PMMA, the leading acrylic polymer) and polyvinyl acetate (PVAC).

Other important materials are based on linear chain polymers in which the chain backbone itself contains other atoms besides carbon (heterochain polymers). For example, the polyamides (or nylons) incorporate the amide link at intervals in the chain, and in polyesters, such as polyethylene terephthalate (PETP, used mostly as polyester fibre), the ester appears periodically along the chain.

Polymers which have simple and regular molecular structures, such as PE, PP, PTFE and PETP, can form crystallites in the solid state, within which the molecular chains are aligned regular manner. The efficient packing of the molecules increases the density and maximises the forces of attraction acting between adjacent chains. Nevertheless, the long molecular chains do not easily organise themselves into a crystalline lattice during

cooling from the melt, and the solid polymer materials invariably comprise mixtures of crystalline and amorphous regions.

The proportion of crystalline material is about 50 per cent in LDPE but may be as high as 90 per cent in HDPE. In solid polymers the crystalline regions are roughly spherical, and grow but from central nuclei during solidification from the melt. The spherulitic morphology and hence the physical properties of the solid are considerably influenced by the rate of cooling.

Several of these semi-crystalline polymers (notably PE, PP, the polyamides PA and the polyester PETP) have civil engineering uses as fibres. The polymers are drawn to high strains to form the fibres, producing a fibrillar rather than a spherulitic morphology, in which the molecular chains are oriented roughly parallel to the fibre axis. The primary chemical bonds of the chain lie along the fibre axis, which enhances the strength and modulus of the materials in this direction.

A number of linear chain thermoplastics however are completely amorphous (noncrystalline); examples are polystyrene (PS) and the acrylics such as PMMA. The failure of these polymers to form any crystalline regions may be attributed to the presence of bulky side groups along the chain. The solid polymer is composed of a myriad of randomly entangled polymer chains, which at normal temperatures (say 20 deg C) are locked together wherever the chains cross. The long chains are not cross-linked by chemical bonds but by physical intertwining. At these temperatures, the material is stiff (with an elastic modulus very similar to that of network thermosets) and generally brittle. As the temperature rises the thermal molecular motion gradually increases to allow chains to free themselves and move under an applied stress; thus the modulus falls and the tendency to creep increases.

It is possible to identify a characteristic temperature, *the glass transition temperature* T_g , at which large-scale molecular movement becomes possible and in the region of which the mechanical and other properties show major changes. The value of T_g for PMMA is about 105 deg C and for PS about 95 degC. As the temperature rises further beyond T_g the material becomes progressively more mobile, turning without obvious discontinuity into a viscous melt.

In the partially crystalline polymers the individual polymer chains pass from amorphous to crystalline regions and back again. The crystallites serve as cross-links in an amorphous matrix. Since the T_g of the amorphous material may be below or around the normal temperature of use, the crystalline regions stiffen the material, producing generally tough, leathery solids. The forces acting between the molecules within the crystallites themselves are not very strong and the melting temperatures are invariably rather low.

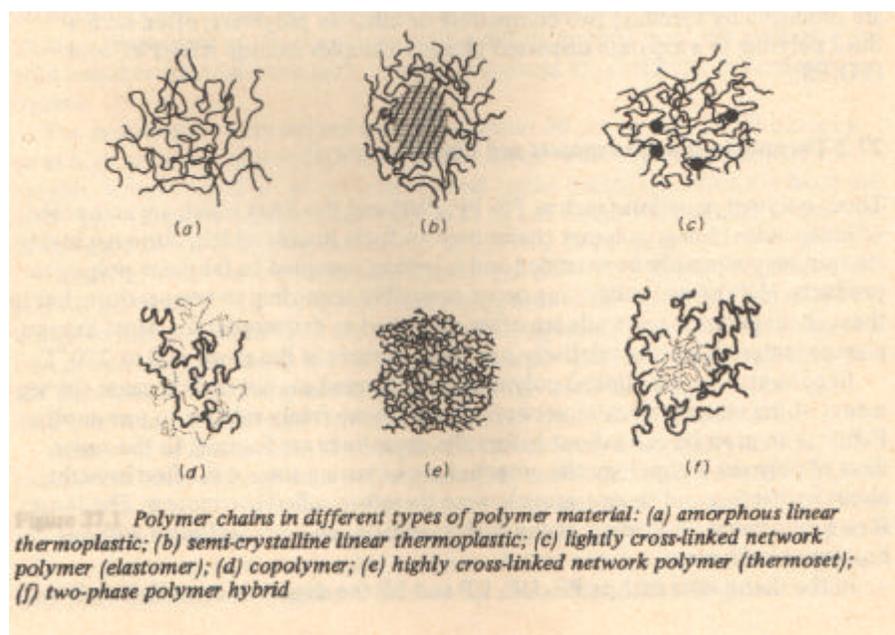
In summary, the linear chain thermoplastics fall into two main groups. First there are those like PE, PP, PA, PC and PETP which are crystalline and are used either above or not far below their glass transition temperatures. They are generally tough, versatile materials, and have important uses as pipe and conduit, film, and fibre. Second, there are those like PMMA and PS which are wholly amorphous and which are used below their glass transition temperature. They are generally stiff, transparent, and brittle.

Network Polymers (Thermosets)

Several major families of materials consist of polymer networks rather than essentially linear chains. Polymer networks may arise either by cross-linking preformed linear chains, in a two-step polymerisation; or directly in a single step to form a more or less randomly interconnected three-dimensional macromolecule of indefinite extent. Examples of the first type are the epoxies and unsaturated polyesters, extensively used with glass fibre-reinforcement, in which relatively short linear *prepolymer* chains are cross-linked at the curing stage. Polyethylene itself may be converted into a network polymer by chemical or radiation cross-linking.

The thermoset polymers have essentially random network structures and this rules out the possibility of regularly organised domains within the solid. Such materials are therefore inherently amorphous and share some of the characteristics of inorganic glasses which are similarly amorphous and macromolecular.

The extensive cross-linking of the thermosets result in their mechanical properties being much less sensitive to changes in temperature compared with thermoplastics or elastomers. They are generally stiff and strong but usually brittle and are widely used in fiber-reinforced composites, adhesives, and surface coatings.



Elastomers are also amorphous in the unstrained state, but in some elastomers sufficient alignment of the molecular chains may occur at high strain to permit some temporary strain-induced crystallisation. This has an effect on the stress-strain diagram, producing a marked increase in modulus at very high-strains.

Elastomers are network polymers based on linear chains above their glass transition temperatures. This implies that their cross-linking is not as strong as the thermosets and this accounts for their rubbery elasticity.

Mechanical Properties

The mechanical behaviour of polymers is directly related to the degree of orientation of the molecules and the amount of cross-linking by covalent bonds. The modulus of a polymer is the average of the stiffness of the bonds and can be estimated based on the volume fraction of the covalent bonding. Hence the expected modulus of various polymers can be computed (for temperatures less than the glass transition temperature) as shown on the following diagram.

