
POLYMERS

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From the chemical point of view, polymers comprise long molecules in which the same basic unit is repeated many times. Polyvinyl chloride, P.V.C., a typical polymer consists of vinyl chloride units linked together. Polymers occur widely in nature. In the inorganic world, rocks, clays and sands are all polymers based on units containing silicon and oxygen. In the organic realm, the structural materials of living organisms are polymers: cellulose in plants and proteins in animals. The products of metabolism of plants and animals may also be polymeric. One important example is natural rubber — a long chain of isoprene units. This substance occurs in certain trees, notably species of *Hevea* as a latex: a suspension of polymer particles in a watery serum.

Polymers have been produced synthetically during the past half-century with increasing frequency. Most of the familiar plastics are synthetic polymers. Many useful rubbers, for example Buna (butadiene), Buna S (butadiene and styrene), Perbunan (butadiene and acrylonitrile) and Neoprene (chloroprene), have been made from simple compounds, and recently rubber itself has been replicated. Synthetic fibres also are now household materials. The building units of the synthetic polymer industry, the simple molecules from which the more complex ones are built, derive from two principal sources: petroleum and coal tar.

In physical properties most polymers fall into one of the three classes — plastics, rubbers and fibres. Some polymeric materials can be stretched to many times their initial length, yet on releasing return to their original dimensions. These are called rubbers. Plastics cannot be reversibly deformed in this manner, and are often hard and glassy. Nylon and other high polymers are characterised by marked readiness to form fibres strong along their length but often weak laterally. Such man-made fibres can be spun woven or knitted into fabrics. The characteristic elastic properties of rubbers are associated with the fact that although their molecules are exceedingly long, the different parts of the molecular chains can undergo independent thermal vibrations. The result is that in the unstrained state the molecule has a random, kinked configuration. Application of stress, causes the kinked molecular chains to straighten out, thus permitting large-scale deformation. On releasing the stress, the molecules return to their irregular arrangement, and so a piece of rubber contracts to its original dimensions.

A possible transitory configuration of a rubber molecule (omitting side chains) may be illustrated by bending a wire at intervals representing the

distance between carbon atoms, at a valence angle of $109^{\circ}28'$ and in spatial direction determined by the throw of a die.

Because long rubber molecules entangle and only occasionally slip when the material is stretched, the elastic property of the individual molecules is conferred on the mass.

Rubbers

Two million tons of natural rubber come from the cultivated trees of Malaysia, Indonesia, Thailand and Ceylon. When the bark of the *Hevea Braziliensis* is cut, a milky white latex flows out slowly. Solid rubber is obtained from latex by adding methanoic and ethanoic acids, whereupon a spongy coagulum is formed which may either be dried in air (to give pale crêpe) or in smoke (to give smoked sheet).

Before they can be shaped to form useful articles, rubbers must be softened or "masticated" by kneading between rollers or rotors. This process produces reduction in the chain length of the rubber molecules. The shortened rubber molecules slide over one another more easily, and so the resilient material acquires plasticity. This is measured by the Mooney plastimeter and similar instruments.

When the softened rubber has been shaped it has to be vulcanised to regain its elasticity, increase its strength and reduce its sensitivity to changes of temperature. Vulcanisation is achieved by chemical cross-linking (i.e. bridging) of the individual polymer molecules to give a three-dimensional molecular network such that the giant molecule of vulcanised rubber in the classical sense may well be the whole of the piece. Vulcanisation can be accomplished by the use of many agents, notably sulphur, under the influence of heat and pressure. Accelerators and activators are chemicals used to reduce the time and temperature necessary to achieve the optimum elastic properties.

Fillers are incorporated in rubber to achieve special properties desired in the vulcanised product or to cheapen the mix. Carbon black increases tensile and tear strengths and enhances the abrasive resistance of rubbers so markedly that it confers improved wearing properties: features of great importance in tyres and similar applications. For increased heat resistance, asbestos is used as a filler. Cotton fibres are chosen as fillers for improved toughness, and mica powder for electrical applications.

The vulcanising ingredients, fillers and other additives are incorporated following mastication. The formulation of a rubber compound to meet specific requirements is of ten difficult, and calls for knowledge and experience.

Synthetic rubbers are materials exhibiting special properties long sought. Thus neoprene and butadiene-acrylonitrile rubbers display resistance to oils and solvents, whereas silicone rubbers show outstanding heat resistance.

Styrene-butadiene and butyl rubbers can replace natural rubber in many applications and are regarded as general purpose substituents of natural rubbers. These however process differently, butyl rubbers being unique in their low permeability to air.

Natural rubber and many of the synthetics may also be processed directly in the latex form to produce such familiar articles as latex foam cushioning, rubber gloves and balloons. Latices are also used in paper-making, textile treatments and in many other applications. This is a growing branch of industry with special appeal to the colloid chemist,

Efforts to make "artificial natural rubber" succeeded only as recently as 1955 when in Milan, Italy, Professor Guilio Natta managed to produce cis-Polyisoprene (Isoprene Rubber) by ionic polymerisation of isoprene.

Plastics

The molecules of plastic materials are of considerable size but are more rigid and less prone to the independent thermal vibrations which characterise the molecules of rubbery polymers. The hardness of these materials may be enhanced by crystallisation.

There are two main types of plastics: thermoplastics and thermosets. Thermoplastics, which include polythene, PVC, nylon, and polystyrene, can be reversibly softened by heating. The process of softening thermoplastics by heating them — and hardening them by cooling — can be repeated over and over again because the chains of molecules of thermoplastic materials remain unaltered after heating. Thermoplastics, therefore, are not used to make objects that must resist high temperatures.

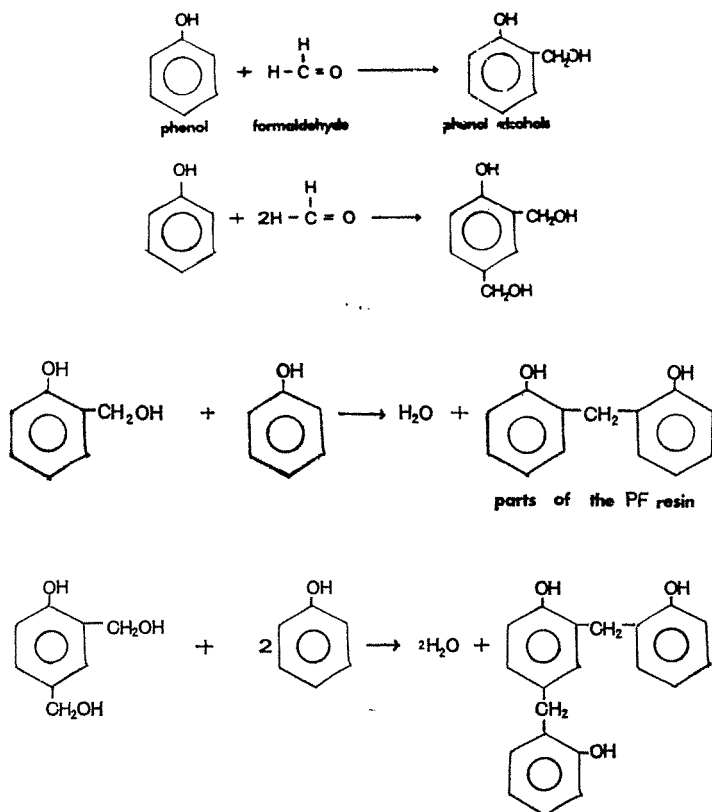
Thermosets, which include polyester resins (often reinforced with fibre-glass), phanolic, urea resins and melamine resins, are irreversibly hardened by heating. They can be softened and hardened only once when they are first heated. This is because their chains become permanently cross-linked in the process. Chemical cross-linking of the polymer molecules responsible for the permanent hardening of thermosetting material after heating is analogous to vulcanisation of rubber. Articles made from thermosetting materials therefore have good heat resistance.

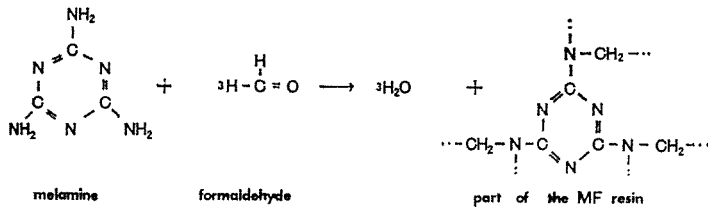
Plastics are being increasingly used in industry and in the home. They are often used as a substitute for traditional materials such as wood, iron, glass and ceramics. Frequently they cost less and perform better. Here is a list of some important properties found in all plastics:

Rot and corrosion resistance, Good electrical insulation, Good thermal insulation, Lightweight (especially the expanded or foam varieties), Flexibility or rigidity, Ease of colouring "right through", Strength, Ease of moulding, Low cost (and hence suitable for mass production).

Individual plastics, however can be made with very distinct properties.

Polythene is an electrical insulator both at high and low frequencies; but the housewife knows it as the versatile and welcome replacement for household porcelain, china, glass and vitreous enamelware. Plasticised polyvinyl chloride stands up extremely well to drastic weather and is popular in the form of thin sheeting and as cable sheathing. Polystyrene can be crystal-clear and sparkling in refrigerator liners in the kitchen, beakers in the bathroom and lampshades in the livingroom. When reinforced with fibre glass, polyester has amazing strength and is already replacing metal for many car components such as heater units, lorry cabs, sports car bodies and boat hulls. Phenolformaldehyde (PF resin) and melamine-formaldehyde (MF resin) mouldings and castings are widely used in electrical applications such as switches, plugs and sockets. Polystyrene, polymethyl methacrylate, nylon and an extensive range of other polymers are contributing to the high standard of living now considered a birthright.





The plastics industry is just over thirty years old and growing fast. Plastics are used everywhere — at home, in building construction, in transport and communication, on the beach, in sports arenas, schools and nurseries, on farms, in factories and in hospitals.

In the kitchen, washing-up bowls and opaque squeeze bottles are made of polythene, door handles of phenolic resin, transparent fruit squash bottles of PVC, unbreakable crockery of melamine resins, refrigerator liners of polystyrene and insulating ceiling tiles of expanded foamed polystyrene. In the PVC) and gliders (nylon or polystyrene) and gramophone records of PVC. beakers of polythene or polystyrene and lavatory seats of phenolic resin. In the living room carpets are frequently made from nylon or other synthetic polymeric textiles, washable wall coverings of PVC — coated paper, lampshades of polystyrene, upholstery of flexible PVC, curtain tracks (rigid PVC) and gliders (nylon or polystyrene) and gramophone records of PVC. In the wardrobe much plastic material is used in clothing. Fashionable wear and raincoats are made of flexible PVC and so are composition shoe soles; buttons are made of formaldehyde or polyester while nightwear and tights are made of brushed nylon.

Plastics are widely used for rainwater pipes and guttering (rigid PVC), water tanks (polythene), electric plugs and sockets (phenolic and urea resins), electric cable sheeting (flexible PVC) wall cladding and corrugated roofing (rigid PVC). Acrylic sheets and panes are used in canopy barrel roof vault and dome roof applications. Prefabricated house units and packaged house mouldings are being extensively used in building construction because they are light and need no painting. Houses, and recently a whole town named Plasticite in France, have been built almost entirely of plastics but restrictive building codes have been enacted partly due to opposition from traditionalists in the building trade unions and partly due to fire risks.

In transport, plastics are replacing metal for many car components such as heater units (polyester), washer bottles and fuel tanks (polythene), distributor caps (phenolic resins) and small gears (nylon). Larger components such as long cabs, sports car bodies and boat hulls are being manufactured in glass-reinforced polyester. In the transportation fields, shipping containers range from various bottles (or carboys) of 15 gallons capacity and drums of 55 gallons capacity which are made of polythene to flexible barges (or

dracmes) of 10,000 gallons capacity used for transporting oil, which are made of nylon and neoprene. The newly developed baggage expediter is moulded from glass-reinforced polyester resin and is designed to speed up the loading and unloading from jet airlines. Space travel and satellite communications would be impossible without many of the tiny components which can be made only with plastics. High temperature plastics are used in nose cones of missiles because during re-entry into the earth's atmosphere the nose cone of a rocket heats up to 16,000°C for about 20 seconds. It has been found that certain phenolics and phenyl silanes when reinforced with glass, asbestos or quartz fibres are ablative. Ablation in rocketry refers to the erosion of the hot outer side of the cone while enough of the inner part remains undamaged to provide necessary structural strength. As the temperature rises, some additional cross-linking of the polymer occurs. The outer layer is broken down by the heat and flakes off and the exposed fibres melt to form a highlyreflective surface which resists further erosion and reflects the heat away from the surface. The low conductivity of the resin protects the instruments inside the cone.

The eye-appeal and strength of plastics are put to advantage in air-beds (flexible PVC) so common in summer on the beach; squeaky toys and dolls (flexible PVC) in the nurseries; construction kits and models (polystyrene and polythene) as visual aids in schools; play-balls and handle grips (flexible PVC) and even artificial ski slopes (polythene).

Wherever you look you will find plastics helping to extend man's scope — and his life. The precooked packed foods, so popular in developed countries, include the instant breakfast polyester-film pouch which is kept in boiling water for ten minutes and scrambled eggs and precooked bacon are ready to serve. Flouroplastics are literally extending man's life as minute quantities of them are used in replacement of heart valves, joints and even arteries. The Starr-Edwards artificial heart valve is made of silicone rubber and a ring of PTFE (polytetrafluroethene), both chosen for their chemical inertness so that they they cause minimum tissue reaction. This heart valve is placed in position by sutures made of polyester fibre coated with PTFE. Plastics are very popular and versatile. PTFE is put to great industrial and domestic use. Because of its excellent non-stick properties it is used in thin coatings as a nonstick surface for cookware and is often used for lining food mixing equipment when sticky products such as chocolate, dough and coffee are being handled. As it has a very low coefficient of friction, it is used as greaseless bearing and for lining the skis of transport planes which have to land and take-off in icy conditions and for lining bearings operating under corrosive conditions or at elevated temperatures. It is used in electric insulators, wire covering, valve seats, seals and gaskets.

Fibres

Synthetic fibres made from various plastic polymers are used in products varying from heavy tow ropes to fine textiles. The basic requirements for fibres for textiles include a high tensile strength and a melting point (between 200°C and 300°C). This is high enough for garments to be ironed without damage but not so high that spinning the fibre in its molten condition (i.e. extruding it through very fine holes of a spinneret) becomes impossible. Synthetic fibres may be extruded from a solution of the polymer in a volatile solvent (excluding any solvent used in dry cleaning), e.g. cellulose acetate in acetone, and then evaporating the solvent. Some synthetic fibres are not attacked by moths, bacteria and fungi and have press-retaining properties superior to natural fibres. However they frequently have low softening temperatures which necessitate caution in ironing. They can also cause allergies. For high strength a primary requirement to any polymer is a minimum molecular length. In a fibre moreover powerful forces must exist between the chains to hold them together; hence the importance of molecular order and the close-packing of chains so that attractive forces (hydrogen bonds) are developed between adjacent components of the chains. These bonds link together chains in polymers containing hydroxyl groups (cellulose acetate), amino groups (polycaprolactam) and some other groups. In the polymerisation products of ethylenic and closely allied hydrocarbons (polythene, polypropene) interaction between chains is due to intermolecular dispersion forces of attraction which are weaker than hydrogen bonding. The cohesion of the chains must be amenable to temporary breakdown as the strength of a hydrogen bond and/or other secondary interchain connection is only one tenth that of the single covalent bond between carbon atoms. Otherwise the chains could not move in relationship to one another as they must during extrusion, when cohesion is lost on heating and re-established on cooling.

Monomers (Starting Molecules) of Nylon in commercial production:

Nylon —6	NH ₂ (CH ₂) ₅ COOH	
Nylon —6,6	NH ₂ (CH ₂) ₆ NH ₂	and COOH (CH ₂) ₄ COOH
Nylon —7	NH ₂ (CH ₂) ₆ COOH	
Nylon —6,10	NH ₂ (CH ₂) ₆ NH ₂	and COOH (CH ₂) ₈ COOH
Nylon —11	NH ₂ (CH ₂) ₁₀ COOH	
Nylon —12	NH ₂ (CH ₂) ₁₁ COOH	

The names in the first column are derived from the numbers of carbon atoms in the monomer molecules.

All polymers used for making fibres have a crystalline structure. In some cases, such as in polythene and Nylon — 6, 6, crystallinity develops only when the fibre is drawn. The specific properties of a fibre reflect the detailed structure of its chains, for example the melting points of Nylon — 6 and Nylon — 6, 6 are 215°C and 265°C respectively.

An important property of all crystalline polymers is their CRYSTALLINE MELTING POINT (T_m), which is the temperature at which crystalline structure or molecular order disappears and the substance becomes liquid. For a fibre T_m must be well above room temperature.

When polymers are heated they change physically at a temperature called T_g (glass transition temperature) before the crystalline structure melts. At T_g the thermal motion of the chain segments becomes sufficient to lend the chain a certain flexibility and the retarding effect of the interaction with adjacent segments of other chains is overcome. Below T_g , polymers are in the glass state, that is, they are hard, rigid and rather brittle (and are transparent if the polymer is amorphous but opaque if the polymer is crystalline).

For stretched rubber (crystalline polymer)

$$T_g = -80^\circ\text{C} \text{ and } T_m = 15^\circ\text{C}$$

There are various textile fibres with specific uses. Rayon yarns which may be viscose or cuprammonium are regenerated cellulose fibres in which 15% of the hydrogen atom in the — OH groups have been replaced in a cross-linking operation after the natural polymer has been dissolved and reprecipitated as very fine fibres. They may be monofilament (i.e. single filament extruded as a unit), multifilament (i.e. more than one filament extruded through small openings in a die and then twisted to form a single thread) or staple (i.e. cut into small pieces and then spun), with a high lustre or delustred by colourless pigments.

Textile rayon is used in a wide variety of fabrics, both alone and blended with other fibres, because rayon is readily dyed and is resistant to mildew and moths. High tenacity rayon is used as a cord to reinforce automobile, truck and aircraft tyres.

Nylon yarns have high tenacity, wet strength, extensibility and abrasion resistance. They are used in hosiery, parachutes, glider ropes, transmission and conveyor belting, cordage, fish lines, tyre cord and fabrics. Coarse monofilament nylon is used in toothbrushes, paintbrushes and in tennis rackets. Polyacrylonitrile is made into textile fibres which have moderate strength, low stretchability, low heat conductivity, and low softening point. They are used in light-weight, warm, wrinkleresistant and good-wearing fabrics.

Polyolefin fibres consist of polypropene (or polythene) extruded into fibres in the molten state followed by cooling in a water bath. They have

a limited use in dress fibres and are used in protective clothing and in carpets.

Natural and synthetic fibres (elastomers) are extruded into elastomeric fibres with polyurethane. Spandex elastic fibres consisting of 85% polyurethane, are superior to natural rubber in resistance to oxidation, chafing and dry-cleaning damage. They have excellent resistance to abrasion, ultra-violet light, weathering, chemicals and cosmetics and are used in foundation garments, swim-wear, surgical hose and other elastic products.

The development of optimum properties in any given application of polymers is often a matter of some nicety calling for technological skill and experience as an extensive knowledge of advanced chemistry, physics and engineering is required, coupled with a first-hand practical acquaintance with the raw materials.