

Electronic materials and components-Polymer types

Introduction

Polymer science is a broad field that includes many types of materials which incorporate long chain structures with many repeated units. One useful way of categorising polymers for the requirements of electronic assembly is by functional behaviour. In the strictest sense these categories are not fixed, or even particularly precise, and you should be aware that some materials can fit into more than one category:

Elastomers are flexible or 'rubbery' materials which can readily be deformed, and return rapidly to almost their original shape and size once released from stress, thus making them able to form reliable seals. Natural and synthetic rubbers are common examples of elastomers

Plastics are materials which can be shaped or moulded under appropriate conditions of temperature and pressure, and then hold their shape. In contrast to elastomers, plastics have a greater stiffness and lack reversible elasticity

Some plastics, such as nylon and cellulose acetate, can be formed into fibres. These have different mechanical characteristics and are often regarded as a separate class of polymer.

The stress-strain relationships for these groupings are substantially different, as may be seen in Figure 1.

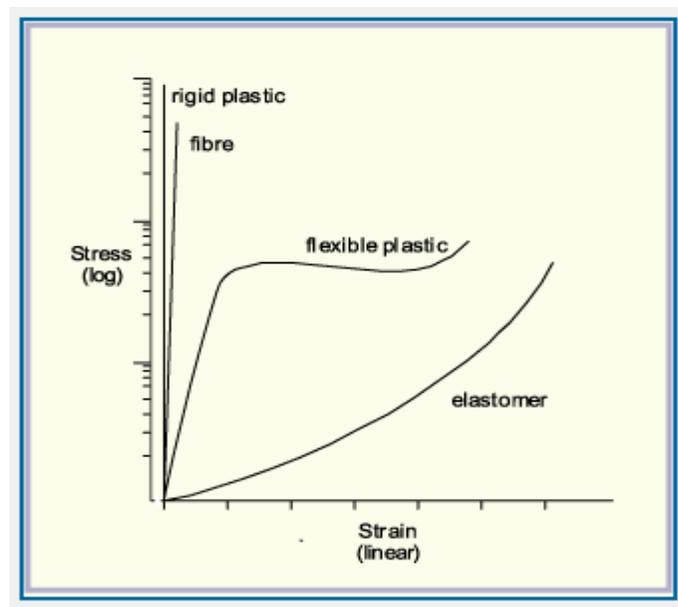


Figure 1: Stress-strain plots for typical polymeric materials

Adapted from: Odian 1970

A final functional category is that of adhesives, materials which will bond to a surface. These range in mechanical properties from rigid plastics to elastomers.

Table 1: Mechanical properties of typical polymeric materials

Property	Elastomers	Plastics	Fibres
Initial modulus of elasticity	0.1-1 MPa	10-100 MPa	1-10 GPa
Upper limit of extensibility (%)	100-1000	20-100	<10
Nature of stress deformation	Almost completely and instantaneously elastic	Partly reversible elasticity; little delayed elasticity; some permanent set	Some instantaneously reversible elasticity; some delayed elasticity; some permanent set
Effect of temperature upon mechanical properties	Elastic modulus increases with temperature (within a limited range)	Marked temperature dependency (over a wide range)	Little temperature dependency from -50°C to +150°C
Crystallisation tendency	Low (when unstressed)	Moderate to high	Very high
Molecular cohesion, cal/mol	1000-2000	2000-5000	5000-10,000
Representative polymers	Natural rubber Polybutadiene Polychloroprene Polyisobutylene Polysulphide	Amino resins Phenolics Polystyrene Poly(vinyl acetate) Poly(vinyl chloride)	Cellulose Polyamides Poly(ethylene terephthalate) Poly(vinylidene chloride) Silk

Elastomers

ASTM D-156611 defines an elastomer as a 'macromolecular material that returns rapidly to approximately the initial dimensions and shape after substantial deformation by a weak stress and release of the stress.' Such elongations typically exceed 100%.

The earliest-used elastomer was natural rubber, obtained from the sap of the rubber tree, which contains around 95% of a polymer whose repeating unit is isoprene. As polymer chemists evolved more and more polymers resembling natural rubber in properties, the term elastomer has grown to represent these materials, rubber being reserved for its original use.

Elastomers have three main functions in electronic assemblies:

to form an environmental seal

to provide mechanical strain relief

to give a means of conducting heat away from sources within the assembly.

Although used for many centuries in its raw form, a significant step forward was made when Charles Goodyear succeeded in 'vulcanising' natural rubber by heating it with sulphur to induce what is now understood to be cross-linking. The significance of the great performance improvement resulting from this treatment has led to the term 'vulcanisation' often being loosely used to describe the cross-linking of any elastomer.

Elastomers consist of long chain-like molecules, linked together to form a three dimensional network. Typically, an average of about 1 in 100 molecules are cross-linked: when this number rises to about 1 in 30, the material becomes more rigid and brittle. Most elastomers are thermoset materials, and cannot be remoulded, an exception being the class of materials known as 'thermoplastic elastomers'.

The most common elastomers used in electronics are silicones (Section 0), which are supplied either as thick pastes which can be dispensed, or as fully cured preforms. Silicones may be chosen because of their chemical inertness or, more commonly, because of their thermal performance. Silicone elastomers may also 'double' as adhesives.

Moulded cured elastomers can also be supplied with conductive filler materials, such as silver, copper, nickel and graphite. These gasket materials are intended to combine an environmental seal with shielding against electromagnetic interference (EMI).

Plastics

'Plastic' is a term which can cover a wide range of polymer materials, all of which can be moulded, for example to produce the body of a QFP component, the casing for a computer keyboard, the hand set of a mobile telephone or the encapsulant cover for a PLCC.

There are two main groups of plastic polymers, thermoplastics and thermosets:

Thermoplastics

Thermoplastics are supplied fully polymerised and remain permanently fusible, melting when exposed to sufficient heat, and potentially they can be recycled and reused.

Although some thermoplastics can have a crystalline microstructure, the essential feature of their structure is that there are relatively weak forces of attraction between the chains. These are overcome when an external force is applied (resulting in the plastic deforming) or when the material is heated, so that it becomes first soft and flexible and eventually a viscous melt. For each thermoplastic there is a specific temperature at which the material will start to distort, which is known as the 'heat distortion point'. However, when the material is allowed to cool it solidifies again. This cycle of softening by heat and solidifying by cooling can be repeated more or less indefinitely and is the basis of most processing methods for these materials.

Thermoplastics are usually supplied in the form of granular feedstock, which is heated, melted and moulded, and removed from the mould only when it has cooled below its 'heat distortion temperature'.

Examples of thermoplastics are polyethylene, poly(vinyl chloride), polystyrene, nylon, cellulose acetate, acetal, polycarbonate, poly(methyl methacrylate), and polypropylene.

Thermosets

A thermoset material is produced by a chemical reaction which has two stages. The first results in the formation of long chain-like molecules similar to those present in thermoplastics, but still capable of further reaction. This second stage of inter-linking the long molecules takes place at the point of use and often under the application of heat and pressure.

Since the cross-linking of the molecules is by strong chemical bonds, thermoset materials are characteristically quite rigid and their mechanical properties are not heat sensitive. Once cured, thermosets cannot again be softened by applying heat: if excess heat is applied to these materials they will char and degrade – as with eggs, once hard-boiled, they cannot be softened! Examples of thermosets are phenol formaldehyde, melamine formaldehyde, urea formaldehyde, epoxies, and some polyesters.

Thermoset raw materials are supplied in an uncured or partially cured state and fully cured during fabrication. The various stages of cure of a catalysed thermoset resin are known as 'A-stage' (uncured), 'B-stage' (partially cured), and 'C-stage'

(fully cured). Many moulding compounds and laminating fabrics can be processed whilst in the B-stage, and some must be kept refrigerated until ready to use.

Compared with thermoplastics, thermosets are much less soluble in organic solvents, and have harder surfaces. Inherently somewhat brittle, thermosets can be combined with reinforcements such as fibre-glass to form very strong composites.

Many thermoset mixes produce an 'exothermic' reaction, that is they give off heat during curing. The amount of heat generated will depend on the material and the amount of catalyst used. This effect needs to be taken into account when processing thermosets, particularly when producing large castings.

Adhesives

Adhesives can be classified by the method used for curing, and a number of different mechanisms have been developed to suit different applications:

Anaerobic adhesives are single-component materials which cure at room temperature when deprived of contact with oxygen. The curing component in the adhesive will not react with the adhesive as long as it is in contact with oxygen. The capillary action of this type of liquid adhesive carries it into even the smallest gaps to fill the joint.

In ultraviolet curing adhesives, the chemicals which would initiate curing are present, but are bound together and are inactive until exposed to UV light. The degree of cure depends on the UV intensity, and in some applications light may be physically blocked from reaching the polymer. In order to resolve this 'shadowing effect' problem, UV curing adhesives may have secondary curing activation systems, often using heat to ensure that the cure is complete.

Anionic reactive adhesives polymerise when in contact with slightly alkaline surfaces. In general, ambient humidity in the air and on the bonding surfaces is sufficient to initiate curing.

Activation adhesives are two part adhesives, where the solvent-based activator is applied to the surfaces to be bonded, often by spraying. Polymerisation begins as soon as the adhesive is applied to the activated surface.

Adhesive types

The lack of a detailed understanding of the adhesion process has not hindered progress in developing very strong adhesives for most materials. The only problem is that the wide range of chemical structures makes it impossible to produce an adhesive which is compatible with all polymers. It is always prudent to check

recommendations on suitable adhesives and surface preparation with the material manufacturers.

There are two main classes of adhesive for polymeric materials:

Solvent adhesives, which may be either a pure solvent which attacks the surfaces to be joined so that they fuse together, or a solvent containing some of the adherend material. This approach is used for polymers such as polystyrene and polymethyl methacrylate, the choice of solvent depending on practical issues such as the rate of evaporation

Organic adhesives based on rubbers or polymeric materials, which may be thermoplastic or thermosetting in nature.

The most versatile range of organic adhesives is that based on epoxy resins, and these are particularly widespread in electronics, although they are relatively expensive. The major advantages of epoxy adhesives are that:

No by-products are released on cure, so that only light contact pressure is necessary

They can be formulated to work well over a very wide temperature range

Epoxies have excellent resistance to moisture and chemicals

Shrinkage on cure is negligible, so that residual strains in the joint are small

Creep of the cured material is low

Epoxies can be cured at room or lower temperatures, although those cured at elevated temperatures are stronger.

There are however, the disadvantages that:

Care is needed when handling uncured epoxy resins

The shelf life of some formulations is limited

High temperature strength can only be achieved by sacrificing ductility.

Epoxy adhesives are sold either as two-part adhesives, where the epoxy resin is mixed with a catalyst just before use, or single-part materials, where the catalyst is incorporated during manufacture. Single-part adhesives are generally less reactive, needing to be heat-cured, and often require refrigerated storage to increase storage life.

Note that refrigerated materials generally need to be brought to room temperature before use, and it is unwise to try and accelerate this process. Remember to read the manufacturer's recommendations on storage life both before and after thawing!

Other adhesives you may encounter are:

Nitrile rubber adhesives: usually copolymers of butadiene and acrylonitrile, these are good adhesives in their own right, but also combine with phenolic resins to produce very good structural adhesives

Resorcinol adhesives are particularly good for bonding thermosetting plastics, but with a few exceptions (ABS, nylon, acrylic) are not suitable for thermoplastics

Cyanoacrylate adhesives can produce very strong bonds very quickly, even between dissimilar materials. The polymerisation reaction is triggered off by water or other weak base on the surfaces to be bonded. Cyanoacrylate adhesives are quite difficult to work with, having a low viscosity and exhibiting a slight ageing effect.

'Tailoring' polymers

The range of polymer materials available is enormous, as slight changes in the chemical make-up of the monomers or the conditions of polymerisation can result in dramatic changes in the material characteristics of the end of processed polymer.

Polyethylene is an example of a polymer which can be used in a wide variety of applications because it can be produced with different forms and structures. The first to be commercially exploited was called low density polyethylene (LDPE), which is characterised by a high degree of branching, which forces the molecules to be packed rather loosely. The resulting low density material is soft and pliable and has applications ranging from plastic bags and textiles to electrical insulation.

By contrast, high density (HDPE) or linear polyethylene demonstrates little or no branching, so that the molecules are tightly packed and the plastic can be used in applications where rigidity is important, such as plastic tubing and bottle caps. Other forms of this material include high and ultra-high molecular weight polyethylenes (HMW; UHMW), which are used in applications where extremely tough and resilient materials are needed.

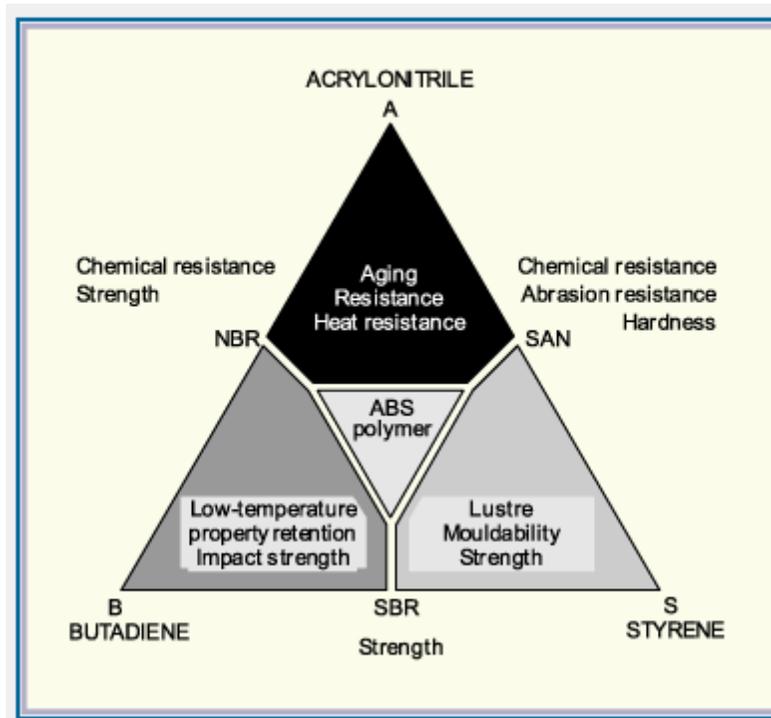
New materials can also be tailored by combining monomers with desirable properties. In some cases, these combinations are just physically mixed polymers, but more typically new 'co-polymers' are produced. Some types have a random structure of the constituent monomers, others may have a regular, repeating structure of the different materials:

A 'block' copolymer is made with blocks of monomers of the same type

A 'graft' copolymer has a main chain polymer built with one type of monomer, and branches made up of other monomers.

Nylon is an example of a common 'alternating copolymer' with two different monomers alternating along the chain. One useful material, which is in fact a 'terpolymer', is ABS. This is a combination of three monomers: acrylonitrile, butadiene and styrene, in varying proportions depending on the application (Figure 2). A rigid but tough material, it is used for water pipes, refrigerators and Lego bricks!

Figure 2: Some possibilities for variation in the composition of ABS copolymers



To obtain the desired properties, the chemist takes into account three key factors: the chemical composition of the building blocks; the possible shape of the polymer chains they can produce; and the alignment of these chains within the final product. A wide range of fillers and additives can then be used to modify the properties of the material. In fact, the plastics industry depends on additives to convert polymers into materials which have useful properties and improved ease of processing – one commentator even makes the point that 'polymer plus additive equals plastic'! Different combinations can produce synthetic products as unlike as nylon tights and vinyl flooring.

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