Electronic materials and components - Polymer materials and properties

Introduction

A very wide range of polymer materials has been developed. This section briefly describes epoxies, the most versatile and pervasive of the thermosets, and some common thermoplastic and elastomeric materials.

Table 1 lists typical comparative mechanical properties for key polymers. It is important to realise that, within the range of grades that exist for a particular material, there can be significant differences in mechanical properties.

Table 1: Mechanical properties of typical polymeric materials

<table>
<thead>
<tr>
<th>Common name</th>
<th>Chemical name</th>
<th>Specific gravity</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
<th>Flexural modulus (GPa)</th>
<th>Max. operating temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABS (high impact)</td>
<td>acrylonitrile butadiene styrene</td>
<td>1.04</td>
<td>40</td>
<td>8</td>
<td>2.2</td>
<td>70</td>
</tr>
<tr>
<td>Acrylic</td>
<td>polymethyl methacrylate</td>
<td>1.18</td>
<td>70</td>
<td>2</td>
<td>2.9</td>
<td>55</td>
</tr>
<tr>
<td>Epoxies</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LDPE (low density) polyethylene</td>
<td>0.92</td>
<td>10</td>
<td>400</td>
<td>0.2</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>Polycarbonate</td>
<td></td>
<td>1.15</td>
<td>90</td>
<td>100</td>
<td>2.8</td>
<td>115</td>
</tr>
<tr>
<td>Polyester e.g. polyethylene terephthalate</td>
<td>1.6</td>
<td>50</td>
<td>2</td>
<td>9.0</td>
<td>130</td>
<td></td>
</tr>
<tr>
<td>PTFE polymer tetrafluoroethylene</td>
<td>2.1</td>
<td>25</td>
<td>200</td>
<td>0.5</td>
<td>180</td>
<td></td>
</tr>
<tr>
<td>PVC (flexible) poly(vinyl chloride)</td>
<td>1.3</td>
<td>15</td>
<td>300</td>
<td>0.007</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>PVC (rigid)</td>
<td></td>
<td>1.4</td>
<td>50</td>
<td>60</td>
<td>3.0</td>
<td>90</td>
</tr>
<tr>
<td>Silicones</td>
<td></td>
<td>1.4</td>
<td>5</td>
<td>450</td>
<td></td>
<td>240</td>
</tr>
</tbody>
</table>

Note that the figures given are approximate mid-points, and for any material there will be a wide range of properties, depending on the formulation and polymerisation/cure conditions.

Polymer materials

Epoxies
Epoxies first became commercially available in Germany in the 1930s, and by the 1950s began to be used as coatings and casting resins despite their high price. Today, PCBs using epoxy monopolise the marketplace, and epoxies are widely found in structural adhesives, structural composites and fibre-glass.

Epoxies may be cured at room temperature using amine catalysts, or cured at up to 180°C using amines or anhydrides to give superior thermal and physical properties. Most laminates are cured at around 150°C under pressure.

The most important epoxies are the epichlorohydrin-bisphenol-A types. Bisphenol-A is prepared by reacting phenol and acetone; epichlorohydrin is produced directly from the petroleum fraction propylene. In the presence of a catalyst, the two react to form a long chain molecule having carbon atoms and benzene rings interspersed along the backbone (Figure 1). In each molecular unit there are two pairs of carbon atoms, each pair of which shares an oxygen atom to form the epoxide group. It is this pair which opens in the presence of a curing agent to form the cross-linked, cured epoxy resin.

![Figure 1: The epoxide group in two different uncured epoxy resin structures](image)

Acrylics are transparent, light-stable resins that have been manufactured since the early 1930s. The clarity and weather-resistance of cast acrylic explains its major commercial application for glazing, and acrylic fibres are used both for fabric and fibre optic applications.

Poly(methyl methacrylate) (PMMA) is a linear carbon-chain compound with a relatively low softening point, which has a higher strength than most thermoplastics, although it is brittle. It has low moisture absorption and is resistant
to alkalis, dilute acids, detergents and greases, but will dissolve in alcohols, ketones and chlorinated solvents.

**Silicones**

Other polymers have a skeleton of carbon atoms: silicones are unique in that the skeleton is of silicon. Silicones range widely in molecular weight, and have a corresponding range of properties between light oils, greases and elastomers. Silicone resins cure to form solid but flexible materials which are impervious to moisture and have relatively high thermal conductivity.

Care has to be exercised in the selection and use of silicone elastomers:

Certain types produce acetic acid during cure, which can have an adverse effect on some types of metallisation

Silicone fluids (monomers and low molecular weight polymers) are very effective release agents (which can make bonding problematic) and inhibit solder wetting

Acrylics and urethanes will dewet on silicone surfaces, so that silicone elastomers cannot be used in assemblies intended for subsequent conformal coating.

**Additives**

All thermoplastic, thermoset, and elastomeric materials are generally compounded before processing, with a variety of additives to modify the optical, mechanical or surface properties of the plastic. These include vulcanising and curing agents, accelerators, pigments, catalysts, antioxidants, plasticizers, and tack enhancers.

Some additives modify the polymer properties by physical means (plasticizers, lubricants, impact modifiers, fillers or pigments); others act by chemical change (heat stabilisers, antioxidants, UV stabilisers and flame retardants). All must be carefully chosen to be compatible with the processing method and the intended application of the finished product.

Some additives are organic and inorganic ‘fillers’. These modify the mechanical properties of the structure, but are often primarily included to reduce cost. Adding filler to the resin is normally carried out at elevated temperatures, where surface tension and viscosity are both low. This encourages good wetting of the filler by the polymer, so that intimate contact between filler and polymer is maintained even when the material is deformed or exposed to water or other liquids or vapours.

In general, adding fine particles to polymers makes them more rigid, but also reduces their breaking strain and ‘toughness’, roughly in proportion to the volume of filler. Fibrous fillers behave differently: provided that the volume loading is sufficiently high, the length-diameter ratio sufficiently large, and the fibres
themselves strong, the tensile strength, stiffness and flexural strength are determined largely by the filler rather than the resin. The properties may be markedly ‘anisotropic’, that is, the properties are not the same in all three axes. For example, glass mat reinforcement gives properties which are uniform in only two dimensions, not three.

A good reinforcing additive:

is stiffer and stronger than the polymer matrix

has good particle size, shape, and surface character for effective mechanical coupling to the matrix

preserves the desirable qualities of the polymer matrix

achieves the design objectives at lowest net cost.

Glass fibre is by far the most widely used fibre reinforcement, the result of having desirable properties for reinforcement and a moderate price (about the same as common plastics). The glasses used are all based on silica, with smaller quantities of other inorganic oxides. Compositions are identified by code letters: the cheapest, and most commonly used, is ‘E-glass’; ‘S-glass’ has higher strength; ‘C-glass’ has improved resistance to attack by water and acids.

**Mechanical properties of polymers**

**Density**

Unreinforced plastics have densities in the range 830-2200kg/m3. This compares with values of 2700kg/m3 for aluminium and 8000kg/m3 for stainless steel. Expanded polystyrene foam (used as a packaging and insulating material) can have a density as low as 10kg/m3, although structural foams usually have a density of at least 500kg/m3. The major advantage this low density gives plastics is that their strength/stiffness to weight ratios compare favourably with apparently much stronger materials. For example, on a stiffness to cost ratio there is little to chose between aluminium alloy, alloy steel, polypropylene and PVC. The choice of material can then be based on ease of manufacture and factors such as chemical or corrosion resistance and weatherability.

**Strength and stiffness**
An important property of materials is their response to the application of a force, which can be classified into two main types of behaviour:

Elastic materials return to their original shape once the force is removed

Plastic materials will not regain their shape and instead flow, behaving like a highly viscous liquid.

Most materials demonstrate a combination of elastic and plastic behaviour, showing plastic behaviour after an ‘elastic limit’ has been exceeded. This behaviour is strongly dependent on temperature.

Plastics are generally stronger in compression than in other modes, and the values for tensile and flexural properties in Table 2 appear to restrict the use of unreinforced plastics in load bearing applications. However, their favourable strength to weight ratios and manufacturing benefits compared with metals make plastics preferable in many applications, giving the designer the challenge of compensating for low strength and stiffness by good engineering design. Usually this involves devising shapes which will give a sufficiently rigid construction, whilst using thin sections to facilitate easy moulding and fast production.

Table 2: Comparative mechanical properties of selected structural materials

<table>
<thead>
<tr>
<th></th>
<th>unreinforced plastics</th>
<th>aluminium</th>
<th>stainless steel</th>
<th>reinforced plastics</th>
</tr>
</thead>
<tbody>
<tr>
<td>tensile strength</td>
<td>10-100 MPa</td>
<td>170 MPa</td>
<td>740 MPa</td>
<td>100-1700 MPa</td>
</tr>
<tr>
<td>modulus</td>
<td>0.2-3.5 GPa</td>
<td>70 GPa</td>
<td>210 GPa</td>
<td>3-150 GPa</td>
</tr>
</tbody>
</table>

Of course the strength and stiffness of plastics can also be increased significantly by reinforcement (with glass or carbon fibres), and it is this approach which is adopted for the printed wiring board laminate.

Note that the yield strength of any plastic varies considerably with temperature: a strength range of greater than 2:1 over the temperature range -20°C to +70°C is typical. As the temperature is increased, the material becomes more flexible, and so for a given stress the material deforms more.

It should be kept in mind that short-term strength and stiffness values give a guide to the nature of the plastic, but should not be used in design calculations because plastics are sensitive to temperature and tend to creep and recover. As a general rule the long term strength of plastics decreases as the service temperature increases.
**Toughness**

Plastics exhibit a wide range of behaviour when subjected to impact forces. Whilst acrylic and polystyrene are brittle and fracture like glass, some plastics are very tough: polycarbonate is virtually unbreakable and is widely used in vandal-proof outdoor light fittings and safety helmets; nylon is used in industrial gears; ABS is used for crash padding in cars.

Unfortunately, comparing impact behaviour is difficult because different test methods use sample geometries with varying degrees of stress concentration. As the ranking of materials depends on the test method, designers have to be very careful when choosing a plastic on the basis of its tabulated impact strength, to ensure that the results quoted were obtained in a test which simulates closely the service conditions of the product.

In general, plastics will become brittle if they are subjected to sub-zero temperatures and/or contain severe stress concentrations, such as sharp corners and notches, and these conditions should be avoided whenever possible. Other factors known to lead to embrittlement include the use of excessively high melt pressures during injection moulding, which causes high residual stresses. Other areas of weakness in moulded plastics include weld lines and regions of highly oriented material, which will be strong in the orientation direction but relatively weak in the transverse direction. A common method of improving the impact strength of brittle plastics, such as polystyrene, is to add rubber fillers, but this is usually at the expense of strength and stiffness.

**Fatigue**

Two types of fatigue failure are observed:

‘Creep failure’ or ‘static fatigue’ which occurs when a thermoplastic is subjected to a constant load for a prolonged period. The higher the stress, the shorter will be the time to failure.

More conventional fatigue failure, when parts are subjected to the repeated action of a relatively low stress which would not cause failure in a single application. Studies have shown that fatigue cracks can be initiated and propagated in plastics, just as in metals, although cracks generally develop within the wall thickness of the moulding rather than start from the surface.

Depending on the application, failure may be the result of less than a complete fracture. For example, when stressed, transparent plastics develop crack-like features (‘crazes’) and other plastics may whiten, a change in appearance which may end their useful life.
**Operating temperature**

The glass transition temperature (Tg) is the temperature at which the links in the polymer start to weaken and become more flexible. At temperatures above Tg, sections of the polymer backbone are relatively free to move, whereas below Tg their motion becomes frozen, with only small scale molecular motion remaining. Over a temperature range of only 5–10°C, the material thus becomes more rubber-like rather than rigid (or ‘glass-like’). This phase transition is reversible and will leave no permanent effect on the polymer unless it is broken or allowed to distort whilst in the abnormal state.

A knowledge of Tg is essential in selecting polymers, which are compounded to produce the required Tg for the application. In general, elastomers have values of Tg well below room temperature, and structural polymers have values above room temperature. One example is of poly(vinyl chloride) (PVC), which is normally a brittle solid at room temperature, with a Tg of 83°C. It is therefore suitable for use for domestic cold water pipes, but not for hot water. However, by adding a small amount of plasticizer, the Tg can be lowered to −40°C, turning the PVC into a material which is soft and flexible at room temperature, and can be used for applications such as garden hoses. But even a plasticized PVC hose can become stiff and brittle in a severe winter, in the same way that natural rubber becomes brittle when cooled in liquid air, which is below its glass transition temperature of −70°C!

In general, the maximum continuous operating temperature is determined for thermoplastics by the heat distortion point, or for thermosets by the glass transition temperature (Tg), as above these temperatures the polymer is not sufficiently mechanically stable. The glass transition temperature is particularly significant in the case of:

Thermoset materials used to make printed wiring boards, where the mechanical strength is lower above Tg, which can lead to distortion and warping during unsupported reflow soldering

Encapsulation resins, where exceeding Tg can cause excessive stresses on embedded components. This is caused by differences in the rate of expansion, as resins above Tg typically show large increases in TCE.

**Elastomer properties**
Elastomers are affected by the environment more than other polymers. Thermal ageing usually increases cross-linking and the chain length of the elastomer, thus increasing stiffness and hardness and decreasing elongation. Radiation has a similar effect.

Elastomers are sensitive to oxidation and in particular to the effects of ozone. Ultraviolet radiation acts in a similar way to ionising radiation, so some elastomers do not weather well. Environmental effects are especially noted on highly stressed parts. Some elastomers are particularly affected by hydrolysis, and complete chemical reversion has been experienced, where the polymer depolymerises back to a liquid state.

Some changes occur also when elastomers are subjected to continued stress:

Creep refers to a change in strain when stress is held constant

Compression set is creep that occurs when the elastomer has been held in compression

Permanent set is deformation remaining after a stress is released.

The hardness of elastomers is a measure of their resistance to deformation measured by pressing an instrument into the elastomer surface. Special instruments have been developed, the most common being the Shore durometer. Figure 2 shows the hardness of elastomers and plastics. On the Shore A scale, 0 is soft and 100 is hard. On this scale, a rubber band is 27, and a car tyre is 70, with squeegees being rather harder still (typically in the range 70 to 95).
Flammability

Flammability has little direct impact on any electrical or mechanical parameters (although additives can cause slight modification to the resin properties), but is extremely important from the point of view of safety. Polymers are used in many electronic devices, from radios to aircraft and the materials used in making the electronic circuits within these devices must not cause or dramatically assist combustion.

The most usual flammability tests are those specified by the American Underwriters’ Laboratories (UL). For historical reasons, related to the use of PCBs in racked systems, these are carried out on test strips of standardised dimensions clamped vertically, with a defined flame applied for 30s and then removed. In 94V-0, the highest UL grade, the polymer has to self-extinguish within 10s, with no drips of flaming molten material. Materials with lower specifications (94V-1, 94V-2) are allowed longer to self-extinguish.

The rationale behind the choice of time-scales is that heating caused by fault over-current is the most common source of ignition, and fuse protection will operate within 30s. Although it is not realistic to expect freedom from burning while a source of ignition is present, the polymer should not remain alight afterwards. The
tests are applied both to materials such as base laminates and solder resists separately and to their combination in the completed PCB.

The UL tests are practical tests on real products, and have been criticised on the grounds that they are biased towards testing PCBs rather than other components, results may be affected by factors such as surface roughness and sample thickness, and the test method is difficult to standardise and operator-dependent to some extent, being based on simple equipment. For this reason UL tests may not reflect the inherent flammability of the resins themselves.

A supplementary method, preferred by bulk polymer suppliers, is the so-called Critical Oxygen Index (COI), also known as the Limiting Oxygen Index (LOI). This is the lowest percentage of oxygen in a nitrogen stream passing a specimen under test in which the specimen will remain burning under specified conditions. The technique requires extensive laboratory facilities, but is more reproducible than the UL test. However, the user will probably argue that the COI result requires interpretation, whereas UL test relate directly to the practical application.

For most applications, fire retardant additives are included in the resins used to make board laminates whence, for example, the name ‘Fire Retardant version 4’, or FR-4. Note that this term applies to the base material of which the PCB is made, and does not describe the additives.

However, such additives (most commonly brominated compounds) frequently greatly increase the harmful by-products of combustion. Since the Falklands War and Kings Cross fire, end-users have become aware of the dangers from such smoke and fumes. There is consequently a fine balance to maintain between meeting a tight flammability specification and avoiding excessive use of possibly harmful materials.

Author: Martin Tarr

Source: http://www.ami.ac.uk/courses/topics/0211_pmp/index.html