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# Practical Guide to High Performance Engineering Plastics



David J. Kemmish



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# Preface

High-performance engineering plastics are used in a vast range of applications and environments. They are becoming increasingly important because of the trend towards more reliable and higher-performance machines and devices.

Typically there are multiple suppliers for each material and hundreds of individual product grades. Materials are usually selected on the basis of combinations of properties rather than a single key parameter. The result can be a bewildering array of possibilities.

This book aims at the development of a working knowledge and understanding of high-performance engineering plastics. It starts with a simple, practical overview of key properties and principles. In each of the subsequent chapters there are sections on production chemistry, product forms, properties, processing and applications. There is a strong bias towards materials and concepts which are used in practice.

The materials covered include examples of high-performance polyethersulfones, polyetherimides, polyphthalamides, polyphenylenesulfides, polyaryletherketones, polyamideimides, polyimides, polybenzimidazole, liquid crystalline polyesters and perfluoropolymers.

The reader will develop the ability to understand why materials are chosen for certain applications, why those materials have particular properties, and how those properties can be modified. This will facilitate conversations with materials suppliers and end-users. It will help to identify the best and most cost-effective solutions.



# 1 Overview of Key Properties and Underlying Principles

## 1.1 Introduction

High-performance engineering plastics are used in a vast range of applications and environments. The hierarchy of performance (and often cost) is commonly represented by simple diagrams. Many suppliers publish 'performance pyramids'. The highest cost (and by implication the highest performing) products are shown at the top. Sometimes the diagram is refined to show whether the polymer is amorphous or crystalline.

However, it is entirely possible for a material to have excellent performance in one area and poor performance in another. Different diagrams emphasise different properties. The most expensive material may not be the best-performing solution. Even if we consider individual performance parameters, for example, resistance to radiation or chemicals, the actual performance will be dependent upon which chemical or which type of radiation we are referring to. Accordingly, these simplistic representations are of very limited use.

It is the purpose of this book to review the main classes of commercial high-performance plastics in sufficient depth to allow the reader to make meaningful comparisons between materials. The emphasis will be on understanding the materials as well as presenting their key properties. The reader will develop the ability to have in-depth discussions with material suppliers.

This chapter looks at many of the properties which are critical to performance. It also considers the relationships between the structure and properties of polymers and how the latter can be improved by the use of fillers and reinforcements.

Chemistry and structure will determine the fundamental performance of a particular class of materials. However, the specific properties of the thousands of individual grades should always be checked with the suppliers.

## **1.2 Key Properties**

In this section we will consider key properties under the headings:

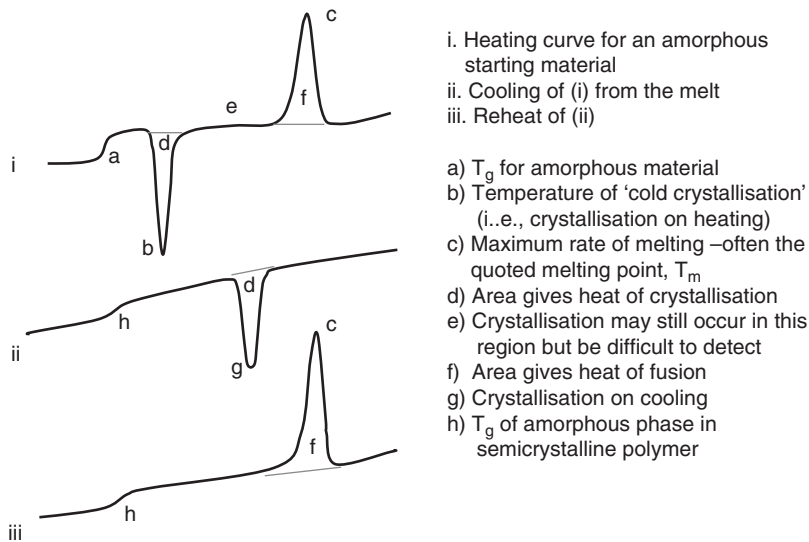
- Short-term temperature performance
- Long-term temperature performance
- Chemical resistance
- Radiation resistance
- Fire, smoke and toxicity
- Mechanical performance
- Electrical properties
- Colour and colour measurement

### **1.2.1 Short-term Temperature Performance**

The three parameters most commonly used to define short-term temperature performance are the glass transition temperature ( $T_g$ ), melting point ( $T_m$ ) and heat distortion temperature (HDT). In addition, the coefficient of thermal expansion (CTE) describes how the dimensions of the material respond to temperature changes.

The  $T_g$  is the temperature of onset of segmental mobility in the polymer chains. In fully amorphous thermoplastics, this is generally the temperature at which useful properties are lost because the chains can now flow past one another – the material has become a viscous liquid. The  $T_g$  is highest for materials with a rigid chemical backbone because these require the most thermal energy for the onset of segmental mobility. This is favoured by ring structures (e.g., phenylene, imide) by the presence of polar groups which are involved in electrostatic interactions, by hydrogen bonding, and by bulky groups that restrict bond rotation.

Differential scanning calorimetry (DSC) (Figure 1.1) is probably the commonest method used to measure the  $T_g$ . It detects the increase in heat capacity associated with the extra modes of molecular movement. The transition occurs over a range of temperatures. It is worth knowing if the number quoted reflects the onset or the midpoint of the process; different suppliers may have different protocols. The  $T_g$  increases with increasing molecular weight, and is also affected by rates of cooling and heating. Crystallising an amorphous polymer (in systems in which this is possible) will increase and broaden the temperature of the transition because the crystals constrain

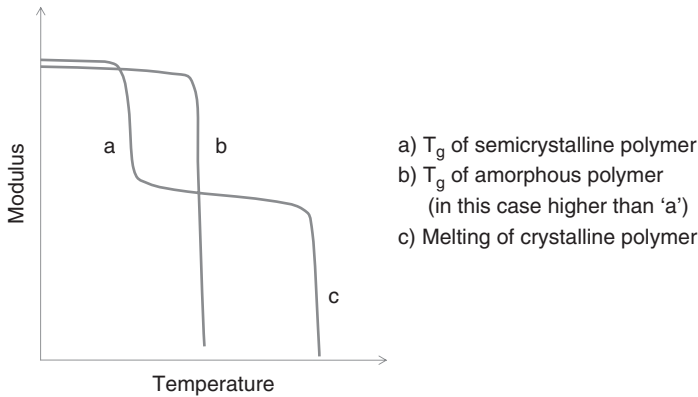


**Figure 1.1** Generic DSC Curves for a Crystallisable Polymer

**Basic Explanation:** DSC measures the rate of heat flow into a sample as the sample is heated through a temperature profile. The curves are plots of heat flow rate versus temperature. In this case endothermic heat flow is plotted in the positive direction. DSC detects changes in heat capacity (for example a step in the heat flow rate at  $T_g$ ), crystallisation processes (exothermic), melting processes (endothermic) and also exo or endothermic degradation. The heat, cool reheat series of experiments is useful because the second reheat is independent of the initial thermal history of the sample.

the mobility of the amorphous phase. It may also make the  $T_g$  more difficult to detect because the change in heat capacity will be smaller due to the reduction of the amount of amorphous material and its constraint by crystals. The  $T_g$  can also be detected by measuring the CTE as a function of temperature – it is higher above the  $T_g$ . Dynamic mechanical thermal analysis (DMTA) (**Figure 1.2**) is a sensitive method to detect this type of transition. DMTA can also be used to detect other onsets of mobility in the polymeric chains, and these may also be associated with step changes in properties.

$T_m$  is the temperature at which the crystalline structure of a ‘crystalline’ polymer becomes thermally unstable, resulting in a phase transition from solid to liquid. The resulting endotherm is readily detected using DSC (**Figure 1.1**). For a polymer to crystallise it must have a regular structure that can fit into the ordered three-dimensional array of a crystal. (In the amorphous phase, the polymer chains are arranged rather like a random pile of spaghetti, whereas in the crystalline phase they have an ordered three-dimensional structure. Liquid crystalline structures are described in **Chapter 9**).



**Figure 1.2** DMTA Modulus Curves for Amorphous and Semicrystalline Polymers

Basic Explanation: DMTA applies a cyclic load to a sample (typically at around 1 Hertz) and measures the resultant force and amplitude at the other end/side of the sample. This allows calculation of modulus and also the phase difference ( $\delta$ ) between the applied and resultant signals. This phase difference is greatest when the applied frequency resonates with a molecular motion, for example close to  $T_g$ . Hence DMTA  $\tan \delta$  peaks are a very sensitive mechanical manifestation of this type of transition and are observed close to the sharp drop in modulus. DMTA curves can often indicate the composition of polymer blends and whether the phases are miscible, in which case there is a single  $T_g$ .

Many polymers cannot crystallise and do not have a melting point. Some may thermally decompose before they melt. Even ‘crystalline’ polymers are invariably only semicrystalline with a mix of crystalline and amorphous phases. This is because the amorphous chains are too entangled and constrained by the growing crystals to be able to rearrange into crystalline structures with 100% efficiency. Crystallinity is important for the development of chemical resistance, retention of mechanical properties above the  $T_g$  and fatigue performance. It usually renders the material opaque (although this is dependent upon the size and orientation of the crystallites). For many polymers, there is a relationship between the  $T_g$  and  $T_m$  such that:

$$T_g \text{ (Kelvin)} / T_m \text{ (Kelvin)} \sim 2/3 \tag{1.1}$$

A high  $T_g$  is associated with a high  $T_m$ . However,  $T_m$  can be reduced by limiting the size of the crystals by the incorporation of non-crystallisable units in the polymer backbone. The high surface-to-volume ratio of smaller crystals increases the entropy of mixing on melting and reduces  $T_m$ . This effect can be used if a high  $T_g$  is required but the resulting  $T_m$  would be too high for melt processing – perhaps because the melt would be thermally unstable. Polymers usually exhibit a range of melting points

reflecting the range of crystal perfections and crystal sizes. This range is readily observed by DSC. Most commercial literature will quote the temperature of the maximum endothermic heat flow as measured by DSC but academic articles may use the temperature at which the last trace of crystallinity disappears extrapolated to a zero heating rate. Occasionally we might see references to a higher ‘thermodynamic’  $T_m$ . This is calculated to be the melting point of an infinitely large, perfect crystal. In detailed comparisons of the  $T_g$  and  $T_m$  for different polymers, it is important to know exactly what was measured and how it was done.

Idealised DSC and DMTA traces with basic explanations are shown in **Figures 1.1** and **1.2**, respectively.

HDT, also known as deflection temperature under load (DTUL), measures the temperature at which a material distorts by a certain amount under a particular stress. The typical stress used is 1.82 MPa, but values are also commonly quoted for 0.45 MPa and 8 MPa. It is a quick and convenient method for comparing the performance of different materials. However it provides much less information than plots of flexural modulus *versus* temperature, and such plots should be requested from suppliers as part of the material selection and design process. HDT can be predicted to some extent from the  $T_g$  and  $T_m$ . In amorphous materials, there is a dramatic drop in strength at the  $T_g$ ; HDT is close to the  $T_g$  and reinforcement increases HDT by only 10–15 °C. In semicrystalline materials, the crystals effectively act as reversible ‘crosslinks’ in the amorphous phase, and the drop in properties at the  $T_g$  is much less pronounced. HDT is close to the  $T_g$  for unreinforced semicrystalline materials but reinforcement can raise HDT to close to the  $T_m$ .

The CTE describes the way in which dimensions change as temperature increases. It changes with temperature, crystallinity and orientation. It is higher above the  $T_g$ . The single numbers commonly shown in data tables are only a guide, and more detailed numbers should be requested from the suppliers. The CTE is important in terms of achieving dimensional tolerances but also because variations and mismatches in CTE can give rise to warpage as temperature changes. Fillers reduce the CTE but oriented fillers with aspect ratios can make the CTE more anisotropic. (In materials such as liquid crystalline polymers, anisotropy can be decreased by the addition of glass fibres.) The CTE increases above the  $T_g$ , and so a high  $T_g$  offers a relatively low, stable CTE over a wide range of temperatures.

### **1.2.2 Long-term Temperature Performance**

Changes in performance over the longer term can result from purely physical changes (e.g., creep) or chemical changes (often due to oxidation). The former is usually characterised by a creep modulus and the latter by a continuous-use temperature (CUT) or relative thermal index (RTI).

*Creep modulus* is used to characterise the way in which deflection under load increases as a function of time, temperature and load. This phenomenon is known as ‘creep’ and arises from the viscoelastic nature of polymers: over sufficiently long timescales the molecules can undergo viscous flow as well as undergoing a recoverable elastic response. The apparent creep modulus is calculated from the strain under a particular load, and is a function of time and temperature.

*CUT (or the more strictly defined RTI)* (Underwriters Laboratories (UL) 746B) is essentially the temperature at which 50% of properties are retained after 100,000 hours of ageing. However, CUT is sometimes quoted for much shorter time periods. These may be as low as 3000 hours or 6000 hours where this represents the required product lifetime (e.g., in automotive applications). The relationship between half-life and temperature typically follows the Arrhenius relationship, which is familiar to all chemists and which is described in the UL standards. This means that performance lifetime decreases exponentially with increasing temperature. Half-life may improve dramatically as temperature is reduced. To illustrate this point, lifetime might improve by a factor of two for a temperature decrease of only 10 °C. This is because the rate of oxidation is reduced by a factor of two. Conversely a claim to ‘double lifetime’ may be offset by only a small increase in service temperature. Material suppliers will have data for specific resins. Knowing which property was measured – typically this might be dielectric strength, tensile strength or tensile impact strength – is important. The CUT is useful for comparisons between materials, but their actual maximum acceptable service temperature will be dependent upon which properties are important for a specific application as well as the required product lifetime. The CUT characterises thermal ageing but, as we describe later, there are other types of environmental ageing (e.g., due to ultraviolet (UV) light or attack by chemicals).

In general, the ‘chemical rules’ that govern the oxidative stability of polymers are:

- a) Aromatic groups are more stable than methylene groups
- b) High bond strength is desirable (C-F is preferable to C-H or C-C)
- c) The oxidation resistance of C=O is better than that of methylene
- d) Aromatic C-H is better than aliphatic C-H
- e) There should be no easy chemical pathway for decomposition (e.g. ‘unzipping reactions’)

It is possible for materials to have a high HDT but a low CUT. For example, some polyamides (nylons) may have a high  $T_m$  due to hydrogen bonding but poor oxidative stability due to the presence of aliphatic C-H. The CUT can sometimes be improved by the incorporation of oxidative stabilisers.



### **1.2.3 Chemical Resistance**

Failure in chemical environments may occur through actual reactive chemical attack (e.g., hydrolysis) but also through environmental stress cracking, swelling and dissolving. Material suppliers usually supply extensive lists of chemical resistance data. However, these may not offer a mechanistic explanation for the effects, and they may sometimes lack data under stress or at elevated temperatures.

Usually the supplier will be able to give, at the very least, some degree of confidence about the performance of a material in a particular environment. If definitive information is not available then application specific testing may be necessary. This is very often the case in environments in which the material is also under fatigue loading. It is very important to know whether the material is crystallisable and, if so, what level of crystallinity has been developed. Crystals resist the ingress of solvent, and dissolution of crystals is energetically unfavourable. As a result, crystallinity can profoundly affect chemical resistance. A 'semicrystalline' material with less than a typical level of crystallinity (perhaps as a result of degradation or an incorrect thermal history) can have severely compromised chemical resistance. Residual stress in a moulding will usually reduce chemical resistance and facilitate environmental stress cracking. Annealing procedures can be used to increase crystallinity and reduce residual stress (although the precise conditions will be dependent upon the objective). Fillers and fibres may also act as a weak point in terms of their own chemical resistance and by allowing wicking effects along the filler/fibre to polymer interface. It may be important to consider the environmental resistance of any surface treatments or sizing agents used on the fibre.

Actual chemical attack is often easy to predict from standard reaction chemistry. For example, polyesters, polyamides and polyimides are likely to undergo hydrolysis or be attacked by acids and alkalis; aromatic rings will be subject to attack by electrophiles and halogens.

Environmental stress cracking (ESC) is harder to predict. It can give rise to surface crazing, microcracks or even sudden failure. It occurs because environmental resistance is less when a material is under stress. Accordingly it can be important to test materials in environments under stressed conditions. Material suppliers will typically have this capability and will make it available for sufficiently large applications. In more extreme situations the material will swell or dissolve even in the absence of stress.

To some extent these effects, from ESC to solubilisation, can be predicted using solubility parameters. A solubility parameter is a measure of the cohesive energy between molecules. Materials with similar solubility parameters are predicted to be highly compatible and even to form mutual solutions. Simplistically, this translates to 'like dissolves like'. Very simple single-parameter approaches have severe limitations. However, knowing the Hansen solubility parameters for a particular polymer and comparing these with the environment in

question can be worthwhile. The Hansen approach considers three separate components of the solubility parameter: dispersion forces, polar forces, and hydrogen bonding. The parameters for polymers and small molecules can be readily calculated using standard tables and a group contribution approach [1]. The polymer can be positioned on a three-dimensional graph showing the three parameters. Chemicals which fall close to this position are predicted to be of particular concern with regard to ESC, swelling and even dissolving. The predictions can provide very valuable insights, and help to select materials for testing. However, they should not be relied upon. Factors such as the level of crystallinity, crosslinking, stress, and actual chemical attack can be critical. Actual test results are always required.

Solvent absorption can often be described using Fickian or modified Fickian diffusion kinetics. However, in practice, a polymer undergoing very substantial solvent absorption is unlikely to be selected.

#### **1.2.4 Radiation Resistance**

Radiation resistance can be predicted from chemical structure. It is important to distinguish between high-energy radiation (X-rays; gamma rays; fluxes of particles such as helium nuclei and electrons) and low-energy radiation (e.g., UV light, visible light). For example, polytetrafluoroethylene (PTFE) has excellent UV resistance and poor resistance to high energy radiation whereas polyaryletherketone (PAEK) exhibit the opposite effect.

For high-energy radiation it is important to avoid low-strength chemical bonds. Aromatic rings and double-conjugated bonds generally improve resistance to high-energy radiation in comparison with saturated bonds or C-F bonds. This is because the wide range of energy levels associated with resonance structures can dissipate the energy over a range of bonds in the structure. Loss of an electron due to ionisation in one area is compensated by electron redistribution without the breaking of chemical bonds. However, defects in the polymer structure can be points of weakness. Most material suppliers will have data showing properties as a function of radiation exposure. Other environmental factors may increase the rate of degradation. Temperature, pressure and oxidising environments tend to reduce radiation resistance. The effect is expected to be greater in the amorphous phase and particularly above the  $T_g$ .

UV radiation can cause degradation by initiating the formation of free radicals. In the presence of air these can form hydroperoxides, which decompose to produce more reactive radicals in an auto-accelerating process. This is sometimes referred to as 'photo-oxidation'. Fluoropolymers can have excellent UV resistance because of the strength of the C-F bond. Predicting the performance of polymers in the presence of UV light can be complicated because small amounts of impurities (e.g., catalyst residues or UV-absorbing chromophores) can facilitate the initiation of

photo-oxidation. Additives are used to improve UV stability (although many are too volatile or thermally unstable to be used in high-temperature polymers). It is wise to enquire if stabilising additives are present because these may also affect other properties. Accelerated ageing under UV light is a common test, and there are several standards to reflect the different types of illumination, temperature, humidity and environment.

### **1.2.5 Fire, Smoke and Toxicity**

Organic materials will burn under oxidative conditions with sufficient applied heat flux. However, resistance to combustion and the toxicity of the resultant smoke varies widely. Simple laboratory scale tests can be used to compare the flammability of materials. The limiting oxygen index (LOI) is essentially the oxygen concentration required to support flaming combustion, and is temperature-dependent.

In the UL94 test, a controlled energy source is applied to a test specimen for a specified period of time. The rating is dependent upon the time for which the material burns, and how it burns after removal of the heat source. The three vertical ratings (V-0, V-1, V-2) indicate that the material was tested in the vertical position and self-extinguished after a specified period of time. V-0 is the best rating and it is typically given down to a critical sample thickness. It is easier for thinner samples to support combustion, so lower numbers for critical thickness indicate better properties. V-2 indicates that the sample dripped flaming particles.

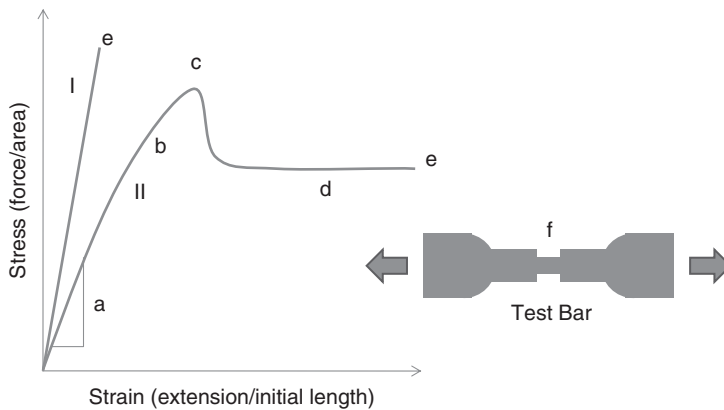
Basic tests such the LOI and UL94 are useful but do not reflect real fire situations. In recent years, cone calorimetry has become a key laboratory-scale test. Samples are typically exposed to radiant heat fluxes of  $\leq 100 \text{ kW/m}^2$ . Rates of heat release can be measured throughout the experiment using oxygen depletion calorimetry (which calculates the heat released from the quantity of oxygen used in the combustion process). The test can provide information on mass loss, heat release as a function of time, time to ignite, peak heat release rate, time to peak heat release, total heat release, and level of smoke. It is also possible to analyse the combustion gases and to assess smoke toxicity. Typically, measurements will be made at a range of heat fluxes (e.g., 25, 50, 75 and  $100 \text{ kW/m}^2$ ). At lower fluxes, the samples may not combust and so produce remarkably good smoke results and toxicity results! Another form of heat-release calorimeter was developed by Ohio State University (OSU; Columbus, OH, USA). The OSU test measures the temperature (and hence enthalpy) increase of the gas stream leaving the device. It has been recognised by the USA Federal Aviation Administration (FAA) as a test for the assessment of aircraft interiors. For example, a material may have a maximum peak heat release rate of  $65 \text{ kW/m}^2$  and a maximum 2-minute total heat release of  $65 \text{ kWminutes/m}^2$ . Hence, a material may be said to pass OSU '65/65' or '50/50'. Various studies have compared cone calorimetry and OSU testing; there are several FAA publications available through the US National Technical Information Service.

Aromatic polymers (i.e., those containing benzene rings) are energetically stable and tend to produce char in fire situations. The char reduces heat transfer and obstructs the transport of degradation products to the surface, where they contribute to the combustion cycle and heat-production cycle. The benefits of char can be enhanced by fillers (especially those which act as a barrier to mass transfer of degradation products and also reinforce the char layer). Many high-performance polymers have excellent fire resistance without the use of additives (which can sometimes produce toxic and corrosive gases). Fluoropolymers exhibit very low flammability but produce toxic and corrosive products in fire situations.

### 1.2.6 Mechanical Performance

#### 1.2.6.1 Strength, Modulus and Stiffness

The strength of a plastic material is characterised in terms of the stress at which it yields and/or ruptures. Typically, it is measured on a dumb-bell-shaped specimen which is 'pulled' on a machine that measures stress *versus* the applied strain. Typical stress–strain curves are shown in **Figure 1.3**. The initial part of the curve is elastic, and stress is proportional to strain. At higher stresses, there is evidence of viscous rather than elastic behaviour and, at the yield point, the material undergoes macroscopic



- I. A brittle material with elastic response up to fracture
- II. A lower modulus ductile material which yields and then cold draws
- a) Elastic region, modulus (stress/strain) given by the gradient
- b) Onset of curvature indicates inelastic behaviour, deformation may not be recoverable
- c) Yield point and formation of a 'neck'
- d) Cold Drawing
- e) Fracture
- f) Neck formed on yielding

**Figure 1.3** Typical generic stress–strain curves.

localised flow. A ‘neck’ is initiated at the point of yielding, and the load drops because of the decrease in the cross-sectional area of the sample. Yielding continues until strain hardening (orientation) increases the stiffness in that locality, and then the adjacent un-necked regions yield. In this way, the neck moves along the test piece in a process known as ‘cold drawing’. Relatively brittle materials break before the yield point. Fibre-reinforced resins typically show a higher modulus and strength but break before yielding. Although it is common to quote yield stresses for unfilled material, in practice a material that has reached its yield stress has probably undergone considerable irrecoverable deformation. Energy is force multiplied by distance, so the energy absorbed is proportional to the area under the stress–strain curve.

The modulus is the ratio of stress to strain. It is measured in the initial elastic part of the curve where stress is proportional to strain. For a given geometry, it is a measure of the stiffness. However, stiffness (i.e., resistance to bending) is very much a function of geometry, and is greatly enhanced by increased thickness. Hence, plastic components can have stiffness comparable with metal by judicious use of ribs or other design features which increase the effective thickness.

The modulus is often described as a ‘true’ material property. However, care should be taken to characterise the material being measured. For example, injection moulding may produce components in which fibres are aligned along the surface of mouldings. This will create a component with a flexural modulus higher than predicted from the measured tensile modulus.

### *1.2.6.2 Time-dependent Properties: Fatigue and Creep*

Creep arises due to the viscous flow of plastic materials under load. Hence, the apparent (‘creep’) modulus decreases with time as deflection increases. Designers must use the creep modulus appropriate to the time, temperature, and load seen in a given application. There may also be creep rupture data because prolonged loading times can give rise to rupture at lower loads than are measured in short-term tests.

Plastics are also subject to failure due to cyclic (fatigue) loading. This is typically characterised in terms of cycles to failure for a given loading pattern, frequency, temperature and environment. It can be a very important limitation. For example, in some plastics the fatigue strength after  $10^7$  cycles may be as little as 20% of the ultimate tensile strength measured in a short-term tensile test. Unfortunately, fatigue testing is time-consuming and relatively expensive. Fast, accelerated cycling rates can result in temperature increases and misleading results. Stress concentrators (e.g., sharp corners; surface scratches; abrupt changes in geometry) reduce fatigue performance. Impurity particles (e.g., specks of metal or degraded polymer) can also act as stress concentrators. Most manufacturers provide high-temperature fatigue data, but environmental fatigue data can be hard to come by. Many environmental fatigue tests are

undertaken in actual end-use simulations (e.g., in the bench testing of compressors). Subtle variations in polymer structure may give rise to changes in fatigue performance, and this creates a barrier to changing materials in existing applications.

### **1.2.6.3 Impact Performance**

Impact assesses the performance of materials at high strain rates. Some materials are ductile at low strain rates but brittle at high rates of strain. A ductile failure involves gross plastic deformation and high energy absorption. A brittle failure will involve only (or very largely) elastic deformation and relatively low energy absorption. This occurs when the rate of strain energy release that results from crack growth exceeds the energy required to create new crack surfaces. Once this critical strain energy release rate is exceeded, the crack will propagate without any further external energy input. If the material is ductile, then yielding and gross deformation of the material will absorb the released energy and, in the absence of further external energy input, crack propagation will slow and eventually stop. Many materials will undergo a transition from ductile to brittle behaviour under appropriate conditions. Conditions which often tend to favour brittle failure include: low temperature, high strain rate, thicker specimens, sharper notches, bigger and/or sharper defects (cracks, impurities), reinforcement, fillers and crystallinity.

The Charpy and Izod tests use notches of known radius to produce a well characterised flaw from which the crack can propagate. As well as measuring the total energy absorbed, it is possible to use instrumented tests in which the energy absorbed can be followed throughout the failure process. For example, it can be important to know the energy at which crack propagation commences or at which irreversible damage occurs. It can also be useful to inspect the fracture surfaces using optical microscopy or scanning electron microscopy. Very often it is possible to see a distinctive craze site at the point of initial crack propagation as well as evidence of any changes in crack velocity or ductile yielding. The brittle failure may also be seen to have started from a defect or foreign body which acted as a stress concentrator.

### **1.2.6.4 Wear**

Resistance to fatigue, environmental chemicals and high temperatures combined with hardness tend to produce good performance in wear situations. The temperatures and forces at the surface can be further reduced by additives such as: PTFE; fluorocarbon and silicone oils; graphite; molybdenum disulfide; and boron nitride. All of these agents reduce the coefficient of friction at the interface.

Wear test data are very much dependent upon test conditions. For example, wear face temperature is dependent upon the geometry of the specimen and the test rig. Wear rate data are often quoted at particular values of the product of applied pressure (P)

and velocity (V). PV is sometimes said to be a measure of the energy input to the system. However, this tells us little about the temperatures reached, and wear mechanisms can change according to whether a given PV is produced using high P and low V or low V and high P. For example, in some polymers, low pressure and high velocity results in lower wear because the mechanism is predominantly interfacial rather than cohesive. It is commonplace to run tests with at least two regimens; high pressure and low velocity (as might be found in thrust washers), and low pressure and high velocity (as might be found in dynamic seals). PV may be increased stepwise to determine the limiting PV for the material. In practice, PV values are only a guide, and application-specific data are usually required.

### **1.2.6.5 Gear Design**

In comparison with metals, plastic gears can offer lower cost, lower weight, less noise, better corrosion resistance, lower inertia, self-lubrication, and greater design flexibility. Unfortunately, design data are often in short supply and require a highly empirical approach. However, many manufacturers have sufficient data to allow gears to be designed for a testing phase under realistic conditions. Such testing is usually essential.

Gears can fail by several mechanisms. Tooth breakage can occur due to overloading or fatigue or even as a result of tooth wear. Plastic flow can be beneficial at low levels – it allows gears to ‘bed in’ and reduces the need for high tolerances. However, excessive plastic flow leads to rapid failure. It is often the result of frictional heating, and this can be reduced by the incorporation of lubricating additives. Rapid cyclic fatigue stresses may also increase tooth temperature and lead to tooth deformation. In some cases, teeth may even fold over on themselves. Surface stresses can cause adhesive wear, but there can also be abrasive wear (due to wear debris or environmental particles) or fatigue-related pitting.

Many suppliers now publish gear design guides. A gear tooth is basically a cantilever beam fixed at one end. Manufacturers can often provide data on allowable bending stresses as a function of the number of contact cycles, lubrication type, pitch line velocity, temperature, and surface of the opposing gear. Unfortunately, it is not just a matter of bending stresses; contact between the teeth also results in compressive, tensile and frictional forces. It is possible to calculate the surface stresses using contact mechanics and compare these with published limits for the materials if the data are available. Ultimately there is no substitute for prototype testing using a real moulded gear.

### **1.2.7 Purity and Outgassing**

Polymers can introduce a wide variety of impurities into the environment. The level of impurities may not be inherent to the material but be dependent upon the nature of the manufacturing process (especially the efficiency of any extraction steps).

Wear particles produced by abrasion are critical in everything from the manufacture of silicon wafers to medical implants and satellites. Other impurities can be separated into those which can be extracted and those which are locked in the polymer matrix. In the latter case it might be possible to ignore them if sufficient evidence is available. Polymers can often contain metal particles from process equipment, and may also be contaminated with various metallic ions. Volatile compounds (e.g., oligomers, polymerisation solvents) can volatilise ('outgas') and this can be a serious problem for many applications. For information on analytical methods, see **Section 1.3**.

### **1.2.8 Electrical Properties**

Dielectric strength, arc resistance and the comparative tracking index: These are different measures of the strength of a material as an insulator. Dielectric strength is the voltage gradient at which breakdown occurs. Arc resistance is the ability to resist a high voltage arc without forming a conductive track. The comparative tracking index measures electrical breakdown on a surface by formation of a carbonised track in the presence of an electrolyte. Carbonisation tends to be easier in polymers which contain aromatic groups because they are already that much closer to the structure of carbon.

Surface and volume resistivity are important to define the performance of conductive compounds. Definitions vary but, in general, a surface resistivity of  $10^9$ – $10^{11}$  ohm/sq is said to be 'antistatic',  $10^7$ – $10^9$  is 'dissipative' and  $<10^6$  ohm/sq is 'conductive'. All the polymers in this book are insulators. However, antistatic, dissipative and conductive properties can be obtained by the use of controlled amounts of conducting fillers. These include milled carbon fibres, carbon powder and carbon nanotubes. Highly conducting electromagnetic shielding grades may contain stainless-steel fibres, nickel-coated carbon fibres or simply rely on metallisation of the final component. Controlling the resistivity can be difficult because it drops rapidly as the filler content approaches the 'percolation threshold' (the point at which each fibre touches at least one other fibre to form a continuous conducting network). Various strategies have been developed to reduce this effect. However, it is often found that the precise resistivity is dependent upon the moulding conditions and the level, dispersion, and distribution of the filler at the point in the moulding actually being measured. Carbon nanotubes are typically used at low loadings to produce a material with uniform conductivity at very small scales, excellent surface finish, good flow properties and low particulate generation.

The dielectric constant is the ratio of the capacity of a condenser to the capacity of the same condenser with air as the dielectric. Hence, if we want to produce a small-size condenser, then a high dielectric constant is required. However, if we want to insulate the components of an electrical network, then a low dielectric constant is best. Polymers containing polar groups with significant dipoles tend to have high dielectric constants.



### **1.2.9 Colour and Colour Measurement**

Pigments can be used to produce a reasonable range of colours even in high-temperature polymers. This can be important in certain applications (e.g., to mark different types of components). However, most engineering applications are not sensitive to the actual colour of the component. Small variations in colour (even if they do not affect properties) can cause concern to end-users. They are particularly obvious if different batches are combined (e.g., in welded products or in the weaving of fibres).

Colour measurement can be undertaken with standard colorimeters and should be done on materials moulded under real conditions. Colours can be modified. In some cases this may be quite crude (e.g., the use of titanium dioxide may lighten a dark polymer but could also affect its mechanical properties). However, in other cases, the use of subtle toners and optical brighteners can control colour and even make amorphous materials appear surprisingly bright and clear.

Visual colour assessment is notoriously difficult and depends very much on the observer (who may have some degree of colour blindness) and the lighting conditions. Quality-control tests are often undertaken using colorimeters. These use various types of standard lighting and attempt to simulate the sensitivity of the human eye to the three primary colours. The result is usually expressed in terms of three parameters chosen from one of several 'colour spaces'. For example, in the popular  $L^*a^*b^*$  colour space,  $L^*$  indicates lightness,  $b^*$  covers the range yellow-to-blue and  $a^*$  green-to-red. The limitations of the human eye mean that these three colour space parameters appear to cover the range of perceptions available to the human visual system. Differences between samples can be reduced to a single parameter for quality-control purposes. For example, the square root of the sum of the squares of the differences in each parameter is known as  $\Delta E$ . However, the colorimeter method has limitations. In contrast to colorimeters, spectrophotometers measure the intensity of reflected light at all wavelengths. The results can be used to calculate  $L^*a^*b^*$  values but are more accurate and contain more information. By combining the spectral power distribution of the illumination with the spectral reflectance of the sample, it is possible to predict  $L^*a^*b^*$  under a range of possible illuminations. Samples showing 'metameric' behaviour will look the same under one light source but different under another. The spectral reflectance curves will be different, but a colorimeter using a single light source may report that the colours are identical or give a misleading assessment of colour variation in different lighting conditions. In situations where colour matching is critical or complex, it is often important to use spectrophotometer data to gain the fullest and most accurate information.

## **1.3 Structural Characterisation**

The published structures of polymers are, in reality, simplifications showing the principal repeat units. Whereas small molecules follow the law of constant composition, the same cannot be always said for different grades and sources of polymers. For

example, different samples may have different molecular weight and molecular-weight distributions. The breadth of the molecular-weight distribution is important. Low-molecular-weight material will tend to degrade mechanical properties and thermal properties, whereas high-molecular-weight material will increase melt viscosity and make processing more difficult. There may be different end groups that can affect a wide range of properties (e.g., thermal stability, crystallisation rate). Polymers may have the same overall composition but varying distributions of different monomers along the polymer backbone, which can affect many properties (e.g.,  $T_m$ ). The chains may also contain defects due to side reactions and various distributions of branch points, which can affect thermal stability and processing characteristics. There may be impurities (e.g., residual monomer; metal ions; catalyst residues; polymerisation solvent or oligomers; other low-molecular-weight material). There may also be more macroscopic impurities (e.g., high-molecular-weight or crosslinked gel particles; specks of degraded polymer or monomer; particles of metal from processing equipment). Voids can profoundly affect the properties of mouldings.

Sometimes subtle variations in structure will have been introduced deliberately but in other cases they are just consequences of complex polymerisation chemistry or monomer impurity. In this section, we will consider some of the techniques that can be used to characterise these effects. There are independent laboratories which undertake this type of analysis, some of which have considerable expertise in characterising certain classes of materials. In some cases, this is because they were once the analytical departments of major chemical companies involved in the original research, development and manufacturing operations. Many universities can also provide access to these capabilities.

Molecular weight is often assessed by making simple measurements of polymer melt viscosity. It is important to know the shear rate used because viscosity will, in general, decrease with increasing shear rate as a result of shear thinning. (Shear thinning occurs because the molecular coils distort in the direction of flow as a result of the applied stress.) Perhaps the simplest viscosity test is the melt flow index (MFI). This measures the mass of melt extruded through a die under a given weight in a given period of time at a given melt temperature. Effectively it measures shear rate under a given load, so this is a variable shear rate, fixed shear stress test. In practice, the shear rates are always low because the operator needs to collect a manageable amount of sample. Melt viscosity is dependent upon molecular weight raised to the power 3–4, so it is very sensitive to changes in molecular weight (see Section 1.4.3). However, this technique gives us limited information about the actual molecular weight or molecular-weight distribution. The latter is usually measured by gel permeation chromatography (GPC), also known as size exclusion chromatography (SEC). This involves passing a solution of polymer through a column which separates molecules according to their size. In triple-detector GPC, an array of three detectors (light scattering, viscometry, concentration) then gather information which allows the direct determination of absolute

molecular weight, molecular-weight distribution, molecular size, conformation and branching. Triple-detector GPC has largely superseded earlier GPC techniques which gave molecular-weight distribution relative to a standard (usually polystyrene). The results of the older technique are not comparable (the weights are in ‘polystyrene equivalents’) unless corrected.

Fourier transform infrared spectroscopy (FTIR) can be used to detect individual types of chemical group based on their infrared (IR) absorption characteristics. It can also be used to ‘fingerprint’ materials. Its use may be dependent upon whether the group under investigation occurs at a part of the IR spectrum that is free from other interferences. The technique can also be combined with microscopy to look at very small areas of materials. This can be especially useful for identifying small defects (e.g., foreign particles). FTIR is also used to characterise end groups. FTIR fingerprints can be used to certify the identity of a material (although it can be difficult to assess the significance of any small variations observed).

Mass spectrometry (MS) sometimes combined with separation techniques such as gas chromatography (GC-MS) or liquid chromatography (LC-MS) is useful for looking at relatively small molecules. It can be sensitive down to extremely low concentrations. These molecules may show-up in the vapour headspace when the sample is heated or be found in extracts produced by heating or refluxing the polymer in solvents. This technique can detect the residues of monomer and polymerisation solvents, which give insights into the production processes. Sometimes samples can be thermally degraded and the volatile fragments analysed by MS techniques. The range of degradation products gives an insight into degradation processes and also the underlying polymer structure. For larger molecules, oligomers and sometimes actual molecular-weight distributions, mass analysis laser desorption ionisation-time-of-flight (MALDI-TOF-MS) allows mass spectrometry of some very-high-molecular-weight species.

Nuclear magnetic resonance (NMR) tends to be less sensitive to small differences in structures but can be useful to detect end groups when they are distinct from the rest of the structure. End groups such as fluorine, chlorine or methoxy (in an otherwise aromatic polymer) would be readily detected. NMR can also be used to determine the principal species in the main backbone, and often gives information on the sequence distribution of these species along the polymer backbone.

Metal ions and other elemental impurities can be detected by techniques such as inductively coupled plasma atomic emission spectroscopy (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS) and X-ray fluorescence (XRF). These have largely superseded atomic absorption (AA) methods, and allow simultaneous detection of many elements. Macroscopic pieces of metal can be detected by conventional X-ray imaging and computed tomography (CT) techniques.

Finally, we should not forget the value of indirect techniques such as DSC. DSC is fast, simple and inexpensive. It does not give direct structural information but can be very sensitive in picking-up changes (e.g., differences in crystallisation rates). These differences can then be investigated by more direct methods.

## **1.4 Processing Considerations**

The materials in this book range from those which are readily extruded and injection-moulded to those which require processing techniques derived from powder metallurgy. Each chapter will review processes for the polymer being described. Here we will make some general comments about the economics and basic principles (e.g., development of crystallinity and residual stress).

### **1.4.1 Economics**

The economics of using a particular polymer should be seen in terms of the cost of the final product and, often, its ultimate disposal: the total system cost. This may be as much to do with the processing route as the raw material cost.

Machining products from plastic stock shapes can be the most economic option for small production runs. Indeed, for small runs, machining may be the process of choice, even with readily processed thermoplastics. However, for larger production runs, where the cost of making a mould is spread over many parts, injection moulding is usually preferable to machining. This means that materials which can be injection-moulded offer considerable cost advantages for high-volume applications. As we shall see, not all high-performance plastics can be injection-moulded.

Product densities can vary widely, and the cost per cubic centimetre is usually more important than the cost per kilogramme. There are an increasing number of examples where an expensive polymer is used at the critical point in a component but is combined, often via overmoulding, with less expensive materials.

High-performance plastics are often used to replace metal. Metals have much higher specific gravity than plastics, so material costs should be compared in terms of volume and not mass. Metal processes typically involve machining, die casting, or press forming. Machining metals gives excellent dimensional control but is very time-consuming. Die casting often requires secondary machining operations although sometimes metals (e.g., aluminium) can be cast to a final net shape. Die cast moulds tend to have shorter lives than plastic injection moulds. As part complexity and part numbers increase, it is very likely that plastic will become more cost-effective than metals. Relative to machining and die casting, press-formed metal parts can be inexpensive to produce. However, it is often the case that a single plastic component can replace several metal

components that have to be assembled into a final part. Where plastics do need to be assembled there can be many options, including snap-fits and latches as well as adhesives, thermal welding, and screws. Metal inserts can also be included in the moulding process or added afterwards using press-fit, ultrasonic or thermal methods. Assembly cost savings can be very significant. In addition, plastics offer many other advantages over metals, which are discussed in the next section.

### **1.4.2 Metals versus Plastics**

Many industries have a long history of using metal, and fail to consider alternative designs in plastic. Metals generally retain properties to higher temperatures; have a much higher modulus; lower CTE; and higher thermal and electrical conductivity. They perform relatively well when thin walls are required (e.g., in panels for automobiles). However, plastics offer many advantages over metals, including: reduced weight; greater design freedom; resistance to denting and corrosion; sound-absorption properties; electrical-insulation properties; and reduced need for painting. In addition, plastic compounds can offer: controlled electrical and thermal conductivity; magnetic properties; increased specific gravity; and enhanced modulus and strength. The economics of metal and plastic processing are considered in **Section 1.4.1**, but plastic can often be the less expensive option (especially for complex geometries and large production runs).

Optimised plastic parts will be different to metal parts. Typical design features for injection-moulded products include those listed below:

- Ribs, V-shaped sections and even curved or domed surfaces compensate very effectively for the lower modulus of plastics. By using these different designs, plastic components can often have equal rigidity to their metal counterparts
- Corners will be radiused to reduce stress concentrations
- Wall thicknesses will tend to be uniform to reduce differential cooling and hence internal stresses and warpage. Bosses will be designed so as to avoid variations in wall thickness
- Thick sections may be cored to reduce residual stress and sink marks, and to use less material
- Mould flow paths will be from thick-to-thin sections to prevent freezing of the upstream material and hence poor packing, residual stress and sink marks in thicker sections
- Walls will be angled to allow easy ejection from the moulds

- Gates will be positioned to take into account residual stress and the formation of weld lines when flow fronts meet

Material suppliers offer design guidelines for their materials, and may also offer design services which include finite element and mould-flow analyses. It is wise to get the material supplier to comment on any proposed design.

### **1.4.3 Melt Flow**

Melt flow characteristics will determine the ease of processing and the range of available processing options. This can have a critical influence on the cost of using a particular material. Simplistically, we might categorise materials as ‘easy to injection mould’, ‘hard to injection mould’, or ‘not injection-mouldable’.

High-performance polymers must have rigid chain structures to develop high temperature properties. These chain structures can produce viscous melts which are hard to process. To some extent this is offset by the use of high melt temperatures but ultimately materials decompose before they form a reasonable viscosity melt. Accordingly, materials described as just ‘injection mouldable’ might be hard to process.

Melt viscosity is the ratio of stress to the rate of strain and has the units of  $\text{Ns/m}^2$ . For most polymer processes, we refer to shear rate, shear strain, and shear viscosity. However, elongational viscosity can also be important for flow processes involving stretching. Branching can create polymers with similar shear characteristics but dramatically different stretching flows. The viscosity of polymers decreases with increasing shear rate because the coils of polymer chains start to deform to comply with the direction of flow. This process is known as ‘shear thinning’. It is important to measure viscosity at a shear rate that is relevant to the process being used. The characteristics of shear thinning are also dependent upon factors such as molecular-weight distribution. Two grades of a nominally identical type of polymer may behave differently at different shear rates: one may have a higher viscosity at one shear rate and a lower viscosity at another.

MFI (International Organization for Standardization (ISO) 1133) is a very simple measure of melt flow characteristics. It is the number of grammes of material extruded from a die in a particular time under a particular applied stress. Effectively it is a fixed stress, variable shear rate test. However, the shear rates used must be fairly low to manually capture the extrudate. Typically, they are in the range expected for extrusion processes but much lower than those found in injection moulding. A higher melt flow index number indicates a lower viscosity. When comparing materials, it is important to know the weight used to drive the MFI grader piston (i.e., the stress applied), the temperature and the die diameter. Not all MFI numbers are directly comparable. MFI tells us nothing about the shear rate dependence of viscosity (although

some insight can be gained by taking the ratio of MFI values at two different applied stresses). Melt elasticity may be assessed by measuring the swelling ratio after the die. Although MFI is a very basic test, it allows the operator to directly experience the flow characteristics of the material.

Capillary flow rheometry measures the stress required to force the melt through a capillary at a variety of shear rates. It is a simple way to characterise shear thinning, and typically results in a plot of viscosity *versus* shear rate. In the author's opinion, this is the minimum information needed to assess the flow of a material. Rotational methods (e.g., cone and plate rheometers) provide more information but they may be limited to lower shear rates.

It is always possible that the material will thermally degrade during the test, and it is wise to check the melt stability of all high performance materials. Instability can often be detected by visual observation of the extrudate. The effect can also be measured in terms of the change in viscosity as a function of time in the rheometer. For example, the material can be left at the melt temperature in the barrel of a capillary rheometer and measurements taken at various time intervals. Thermally unstable materials are sometimes better characterised by measurement of solution viscosity or by GPC techniques because the result will not be affected by degradation during the time spent at melt temperatures.

Fillers will usually increase viscosity. It is important to consider the size and length of fillers and reinforcement relative to any dies used. In some cases, filler can be broken up during the measurement process.

#### **1.4.4 Crystallisation and Crystallinity**

In semicrystalline polymers, the development of crystallinity is essential to achieve optimum mechanical properties, fatigue resistance, and chemical resistance. Polymers will crystallise if they can fit into a thermodynamically favourable three-dimensional regular array; if they have sufficient chain flexibility to rearrange into such a structure on the available timescale; and if the process can be started at a point of nucleation. Crystallisation does not occur below the  $T_g$  because the chains cannot rearrange into crystals without a high degree of segmental mobility.

The process starts with the formation of a nucleus of critical size. This may occur on the surface of some impurity or arise as a result of random fluctuation in the melt. At low temperatures it is relatively easy to form a nucleus of critical (i.e., stable) size because there is relatively little thermal energy to break it apart, so the nucleation density is relatively high. However, the polymer chains lack thermal energy and so 'reel' into the crystalline surface relatively slowly. At high temperatures the opposite effect occurs; high energy means that nuclei tend to be unstable but the rate of chain

movement is high. Accordingly, there is a maximum rate of crystallisation between the  $T_g$  and  $T_m$ . This is often characterised in terms of the temperature at which the rate reaches a maximum and the half-life at that temperature. However, for fast-crystallising polymers, the crystallisation process on cooling is often complete by the time the temperature of the maximum achievable rate of crystallisation is reached. This means that the peak of the DSC exotherm on cooling will be at a higher temperature than is observed on heating because both processes will be complete before the maximum possible rate is reached. However, if cooling is sufficiently fast, it is possible to quench crystalline materials to the amorphous state. The required cooling rate can be very high, and sometimes a thin sample of melt (e.g., in a DSC pan or compression-moulded between aluminium foil) has to be quenched by immersion in iced water to produce an amorphous material.

In general, crystalline lamellae will grow outwards from the point of nucleation to produce spherical structures known as 'spherulites'. These eventually impinge on each other and the rate of crystallisation decreases. The overall crystallinity is the product of the volume fraction of space filled by spherulites and the proportion of crystallinity within the spherulite. For useful properties, the volume fraction of space filled by spherulites should be 100%, otherwise fully amorphous regions will remain and act as points of weakness. For a given polymer, the crystallinity within the spherulite will be dependent upon its thermal history. Higher temperatures provide more energy for the rearrangement of chain entanglements and so will produce higher levels of crystallinity. However, we may have to wait longer for the process to occur, and clearly the rate of formation of crystals is reduced as we approach the  $T_m$ .

In practice, mould temperatures have to be set above the  $T_g$  to produce mouldings with crystalline surfaces. The optimum temperature will be dependent upon the rate of crystallisation of the polymer and the influence of higher mould temperatures on cycle time. Higher temperatures will reduce the cooling rate but increase the injection moulding cycle time and so adversely affect process economics.

Crystallinity can be checked by measurement, but moulders often rely on control of thermal history to ensure adequate crystallisation. In extreme cases, too low a mould temperature will result in a visibly amorphous, translucent skin on the moulding. This can be removed by annealing above the  $T_g$ , but it is better to use a correct mould temperature. Crystallinity can be increased by annealing (especially at high temperatures).

Crystallinity can be measured by several techniques, as shown below:

- X-ray diffraction: Crystallinity is determined from the ratio of the areas of the crystalline and amorphous peaks. Sharper peaks suggest higher crystal perfection. It is also possible to determine crystalline orientation by looking at the variations in intensity observed in the rings seen in two-dimensional diffraction patterns



- Density changes: Crystallisation increases density and so a two-phase model of crystalline and amorphous phases can be used to calculate crystallinity from the densities of amorphous and 100% crystalline material. The latter can be calculated from the unit-cell dimensions of the crystal as determined by X ray crystallography. In practice, density measurement is often simple and highly accurate but can be difficult to interpret if the sample contains voids or fillers
- DSC: This looks at the area of the melting peak after subtraction of any crystallisation process that occurred during the DSC heating scan. This technique can require very careful interpretation. It is not always possible to detect all the crystallisation occurring during heating; peak integration limits can be difficult to determine and enthalpies measured at different temperatures should be corrected using heat capacity data. This technique works best for samples in which crystallisation does not occur during heating. Such samples might have been slowly cooled or annealed at high temperatures. In this case, the melting peak has clear limits and the heat of fusion is proportional to the degree of crystallinity
- FTIR: In some cases, crystalline conformations give rise to specific IR absorptions. These can then be used to assess the degree of crystallinity

#### **1.4.5 Dimensional Tolerances and Stability**

Dimensional tolerances and dimensional stability can be critical for engineering plastic applications. Liquid crystalline polymers have a morphology that is particularly suited to high-precision moulding; this is discussed in **Chapter 9**.

For a given polymer, shrinkage will be dependent upon temperature drop, cooling rate, forming pressures and orientational anisotropy. Dimensional changes after moulding may result from processes such as: stress relaxation; post-crystallisation; moisture absorption; or thermal expansion and contraction.

CTE is greater above the  $T_g$ . Accordingly, high- $T_g$  materials offer a low, stable CTE over a wide range of temperatures. As explained above, the highest values of  $T_g$  tend to be found in amorphous polymers.

Shrinkage is much greater for crystalline materials because of the density changes associated with crystallisation. It is reduced by the use of fillers, but fillers with significant aspect ratios can become oriented and increase anisotropy. Accordingly, crystalline materials present much greater challenges when high dimensional tolerance and dimensional stability is required. In practice, shrinkage numbers provided by suppliers can only be approximate: the actual value will depend on the precise moulding conditions. As a result, mould cavities are normally made slightly too small and adjusted accordingly.

Differential shrinkage causes problems by giving rise to part warpage. Differential shrinkage can result from: variation in mould temperature; differential cooling; orientation; variation in melt pressures. For example, if surface layers cool faster than the interior, then the result will be internal stresses and/or voids and sink marks. Molecular orientation will tend to relax after moulding, giving rise to further internal stresses and potential warpage effects. Often these effects become pronounced if the part temperature increases because relaxation gives rise to an increase in configurational entropy.

Components can be annealed just above their use temperature to reduce residual stresses. In some cases, parts are machined to near final shape, annealed to release any tendency to warp, and then machined again to the final shape. Most manufacturers will provide annealing guidelines for their materials.

### **1.4.6 Recycling**

High-performance engineering plastics are expensive. There is often scope for in-process and end-of-life recycling. This is particularly true of the thermally stable thermoplastics. Recycling may increase fibre breakage, colour and levels of degraded specks, but it is often possible to use a reasonable level of recycled product. Recycled materials tend to be available from secondary processors, partly because the original manufacturers would need to compare the price of feedstock for recycling with their internal cost to manufacture 'virgin' product.

## **1.5 Property Improvement**

### **1.5.1 Reinforcements, Fillers and Additives**

Fibre reinforcement is the most effective way of enhancing the strength and modulus. Glass fibres and carbon fibres are commonly used. Aramid fibres are used in some applications. In an appropriately formulated compound, the strength and modulus are derived from the fibres. The role of the matrix is to transmit stress to the fibres, to hold the fibres in position, and to protect the fibres from abrasion and chemical attack. Hence, many of the key environmental properties can be predicted from the strengths and weaknesses of the matrix.

To utilise fibre properties it is essential to transmit stresses to the fibre. At the end of each fibre there is an ineffective length which is under a lower stress than the rest of the fibre because of the limitations of the matrix to fibre stress transfer processes. This length is shorter if there is a better fibre-matrix interface. If stress transfer to the fibre is poor or the fibre is too short, then the fibre will debond from the matrix rather than ultimately breaking under applied stress. This leads to failure at a low strength.

Accordingly, the key parameters for a fibre-reinforced matrix are the:

- Nature of the matrix
- Properties of the fibre
- Quality of the fibre-matrix interface
- Orientation of the fibres
- Volume fraction of the fibres
- Distribution of fibre lengths

The orientation and distribution of fibres can be assessed by observation of polished surfaces. Fibre-length distribution is typically measured by image analyses of fibres suspended in a solution of polymer after dissolution of the matrix or by isolation of glass fibres by pyrolysis.

Achieving a good interface requires a compatible surface chemistry and a method to bring fibres into close contact with the polymer. Many processes can damage the fibres, and fibres can also be extremely difficult to handle. Nearly all fibres are protected by a sizing agent which holds fibre bundles together and prevents fibre damage. Various sizing agents have been developed which are compatible with high-temperature polymers. Carbon fibres are typically surface-oxidised before sizing; silanes are used to treat glass to improve compatibility.

The most common process used to make fibre-reinforced compounds is twin-screw extrusion. This technology can be bought 'off the shelf'. It often dramatically reduces fibre length from several millimetres to hundreds of microns. Special feeders have been developed to add fibres to twin-screw extruders, and damage and breakage of fibres is often reduced by adding fibres downstream of the initial melting process.

Processes have been developed to produce polymer pellets with continuous fibres oriented along their full length. These are based on chopping fibre tows or rovings which have been pultruded with molten polymer through a special die. Fibres types include glass, carbon, aramid and stainless steel. Fibre lengths can be >1 cm and very-high-fibre contents can be obtained. The long fibres form a remarkable reinforcing network. In glass-fibre products, the matrix can be removed by pyrolysis to leave the original shape of moulded articles retained in the structure of the reinforcing fibres. Conventional twin-screw-produced products would be reduced to a small heap of very short fibres. These long fibre-reinforced products offer several advantages, including improved impact resistance, rigidity, creep resistance and dimensional stability. They

are injection-mouldable. They are particularly suitable for metal replacement, where they offer weight reduction, corrosion resistance and lower manufacturing costs (e.g., in automobiles). They can also show high conductivity and excellent electromagnetic shielding properties.

Most glass fibre that is used is general-purpose E glass. However, there are also more chemically resistant glasses (ECR glass), higher-strength glasses (S glass), low dielectric glasses (D glass) and high-purity silica fibres. Carbon fibres are available in a range of combinations of strength and modulus. However, the compatibility of the size, the surface chemistry, and the degree of fibre breakage on processing are as important as the properties of the fibre itself. Fibres are typically available as tows, rovings, chopped strands, milled fibres, and in various weaves.

Talc and mica can be used to reduce the CTE, shrinkage and warpage. As platey fillers they also offer some reinforcing effect. Graphite powder, irradiated PTFE powders, boron nitride and molybdenum disulfide are used in tribological grades to reduce coefficients of friction. Whisker reinforcements (e.g., potassium titanate) are occasionally used.

A wide range of materials are available at the nano scale, and many interesting effects have been reported. The two most important classes of nanofiller in engineering plastics are nanoclays and carbon nanofibres.

Nanoclays rely on exfoliation of clay platelets via an intercalating agent which conventionally lacks stability in the presence of high-temperature polymers. There are various ways to address this problem, but in practice the use of nanoclays in high-performance polymers is severely limited. If it were possible then we might expect improved barrier properties, stiffness, HDT, and fire resistance.

In contrast, multi-walled nanotubes are finding a significant number of applications following their availability at competitive prices. Producing nanotube compounds remains challenging, and most products contain more than the theoretically required amounts of tubes. In general, mechanical reinforcement with nanotubes is often disappointing, especially given their exceptional mechanical properties. However, they are being used to produce materials with controlled resistivity and hence controlled electrostatic dissipation. They are typically used at low loadings to produce a material with uniform conductivity at very small scales, excellent surface finish, good flow properties, and low particulate generation. The products compare favourably with those based on more macroscopic reinforcements (e.g., milled carbon fibres which suffer from less uniform conductivity and higher wear particle generation). Recently, another form of carbon has become available, exfoliated graphene nanoplatelets, that may offer several advantages. Boron nitride is available as fibres and as nanotubes.

### **1.5.2 Continuous-fibre Thermoplastic Composites**

Most engineering plastic fibre reinforcements take the form of discontinuous carbon or glass. However, there are also product forms which utilise high loadings of continuous fibres with controlled orientations. These continuous-fibre products are referred to as 'composites' (although the term is also sometimes used for discontinuous reinforcements). High levels of continuous reinforcement with controlled orientation produce exceptional strength and stiffness together with very low CTE. Properties per unit weight are comparable with those of metals. Thermoplastic composites offer several advantages over conventional thermosetting composites in which low-molecular-weight materials are crosslinked around a high loading of carbon fibres. These advantages include:

- Potential for high-volume, low-cost manufacturing
- Ease of recycling
- High thermoplastic toughness and damage tolerance
- No shelf-life issues. No chemistry occurring during part fabrication
- Potential for welding, fusion, bonding and repair

Given these properties, it is surprising that greater use is not made of such materials. However, relative to injection-moulding compounds, thermoplastic composites are expensive and difficult to process. The need to wet a large area of fibre means that the polymer must have good flow properties. Examples include: polyphenylenesulfide (PPS), PAEK, polysulfones, polyetherimide (PEI) and polyamides. The production of such materials often involves proprietary processes. Some processes merely bring the polymer into contact with the fibre, leaving the final forming process to individually wet the fibres with the polymer melt. This allows for a low-cost precursor but often limits the quality of the parts that can be produced. More advanced impregnation processes produce low-void products (such as uni-directional pre-impregnated tape), in which there is a strong interface between the polymer and the fibre, and a high degree of wetting and distribution of fibres. It is possible to assess the quality of a product by polishing and looking for voids but also by simply snapping a piece of tape and looking for evidence of loose fibres and fibre pull-out. Properties in the fibre direction will be dominated by the fibre and tell us little about the composite. Transverse properties such as transverse tensile and flexural strength provide more information about the quality of impregnation. Other key tests include damage-tolerance measurements (e.g., damage area, compression after impact).

Fibre-impregnation techniques include:

- Direct melt impregnation: this can be difficult with high-viscosity polymers
- Melt processes assisted with volatile plasticisers: one way to reduce the melt viscosity
- Powder impregnation: electrostatic or aqueous dispersion followed by melt pultrusion through a die
- Fibre co-mingling: to produce a drapeable product that is relatively easily wetted and uniformly impregnated on melt forming

Having produced a precursor material (well-wetted or not), it is necessary to form the product into a shape. In principle, high-volume manufacturing should be a key advantage for thermoplastic composites over thermosets. Press lamination, thermoforming and pultrusion are relatively simple. However, autoclave lamination requires expensive bagging materials, lengthy heating and cooling, and the use of autoclaves. Thermoplastic materials also lack the tack and drape properties of thermosetting tapes, so can be harder to use in automated tape-laying processes. Various automated techniques have been developed. In fibre placement with *in-situ* consolidation, a robot lays down tape onto a tool as it is heated with hot gas, lasers or IR and is consolidated *in situ*. This requires void-free, smooth, pre-impregnated tapes because the forces involved will not promote significant fibre wetting. Other processes use automated layup followed by press consolidation. A continuous compression moulding process has been developed to produce rails, beams and profiles. 'Composite flow moulding technology' allows pultruded rods to be converted into articles (e.g., screws, fasteners, bone plates) while maintaining the length and orientation of fibres.

### **1.5.3 Blends**

There have been many attempts to blend high-performance polymers with the objective of reducing cost and/or enhancing aspects of performance. Researchers are often seeking synergistic effects as well as mere combinations of properties. In general, blends can be classified as 'miscible' or 'immiscible'. Truly miscible blends have a single  $T_g$  and only one phase. Miscible blends are quite rare. Immiscible blends show varying degrees of phase compatibility and multiple values of  $T_g$ . Often these can be detected easily by techniques such as DMTA. DSC is less sensitive but can also be useful. Compatible phases can manifest very fine phase structures because favourable interactions between the polymers mean that high surface-to-volume ratios (i.e., large phase interface areas) are not energetically unfavourable. Such blends are often easy to manufacture using twin-screw extrusion. In these situations, it is critical to know which phase is continuous because this phase will dominate the properties

(e.g., environmental resistance). In general, the lower-viscosity phase will tend to encapsulate the higher-viscosity phase, and very approximately the composition of the phase inversion point is related to the ratio of the two resin viscosities. It can also be possible to produce interpenetrating networks. Scanning electron microscopy is useful to determine phase structures if the components can be differentiated (e.g., by selective extraction or elemental analyses). Compatibility can be enhanced by adding materials which are compatible with both phases. Sometimes this can take the form of block copolymers with the compatibility of each block matched to each material, but it can also be achieved by encouraging chemical reactions between the polymers.

## 1.6 Food Contact and Medical Devices

### 1.6.1 Food Contact

Materials used for food contact will have been subject to a special approvals process. This is done in the USA by the Food and Drug Administration (FDA) and in Europe by the Scientific Committee on Food (SCF). This process ensures that materials in contact with food do not transfer their constituents to the food in such a way as to endanger human health or affect food quality. A key element of the tests is to characterise the migration of impurities into food simulants. Very often specific methods have to be developed. The migration may be subject to specific limits for particular monomers or additives, or an overall limit for all migrating substances. It is critical to know if you are using a food-contact grade and if the component manufacturer is required to undertake specific migration testing on the final article. Approval may be conditional on final-article testing and it is important that these requirements are met by the manufacturer of that article.

### 1.6.2 Medical Devices

In recent years, there has been an increasing trend towards the use of high-performance plastics in medical applications. For example, Solvay have introduced an entire family of implantable polymers under the trade name 'Solviva Biomaterials'. This includes materials based on polyetheretherketone, self-reinforced polyphenylene, polyphenyl-sulfone and polysulfone.

ISO 10993 defines three classes of medical-grade plastic. The most demanding class (often referred to as 'implant' or 'permanent' grade) is used in implantable applications with a duration of >30 days. There are also <30-day 'prolonged' implantable applications and short-term 'limited-use' applications. The recommended tests depend on the type of body contact and the duration of that contact. Material suppliers will usually file *in-vitro* and *in-vivo* data together with manufacturing information with regulatory bodies (e.g., FDA). This facilitates the approval of devices. Typical tests

for an implantable grade include genotoxicity, haemolysis, cytotoxicity, biostability, sensitisation, pyrogenicity, and chemical analysis. Materials are often manufactured to Good Manufacturing Practice (GMP) standards (e.g., as defined in ISO 13485). Ultimately, it is the device and not the material that is approved because the suitability of the material will depend on the nature of the device. However, a record of successful and perhaps similar device applications will greatly facilitate future approval of a given material.

The specific advantages of implantable grade plastics vary with the material, and can include:

- Imaging properties that, unlike metals, do not produce artefacts in X-ray, CT and magnetic resonance imaging (MRI). These properties can also be tailored using additives such as barium sulfate or tantalum wire to mark the position of key components
- Tailoring modulus to be closer to bone than can be achieved with metals. This reduces the demineralisation of bone structure due to stress shielding
- Sterilisability with steam, gamma radiation, or ethylene oxide
- Lower density, lower thermal conductivity, and more colourable than metals. This leads to lighter, less noticeable implants
- Ease of forming into complex shapes. Sometimes these can be specific to the patient and crafted during or shortly before surgery
- No release of metal ions. Some metals have been implicated in allergic reactions and other undesirable effects
- Lower visibility through the skin compared with metals such as titanium

## **1.7 Notes and Caveats on Reading the Materials Chapters**

The remainder of this book introduces the main classes of high-performance engineering plastics. Each chapter contains sections on production chemistry, product forms, properties, processing and applications with a bias towards those features that are used in practice.

A literature search for each class of material typically reveals thousands of academic articles, producer publications, press releases and patents. It is not possible to give a definitive list of references for each chapter. However, certain key articles and patents are identified (especially for the process chemistry). Patents are required to disclose sufficient information to be enabling and will contain a summary of the background



to the invention. A recent patent can therefore provide a route to older patents and publications covering the entire history of a product. Many of the patents cited here will provide the starting point for such an exploration. Once the names of the key inventors and/or the manufacturers (past and present) are identified, together with a few keywords, it can be possible to find detailed descriptions of the underlying technology. This applies to production routes and applications. Patents are freely available from searchable Internet databases provided by the United States Patent and Trademark Office (USPTO) and The European Patent Office (Esp@cenet Portal). The USPTO allows Boolean searches of its entire database, and worldwide searches are possible on the Esp@cenet portal. Full-text patents can also be downloaded.

Manufacturers often do not reveal chemical structures and product formulations in their standard literature. In the following chapters, a particular effort is made to discuss the structures of the materials and to give references to helpful patents. Sometimes the structures are obvious but on other occasions an opinion has been formed from the academic and published literature. This may not always be accurate; in particular there will, no doubt, be minor changes to copolymer compositions. In addition, successful trademarks are often used for an increasing number of somewhat different chemistries which serve a particular range of customer needs.

The best sources for properties data will invariably be the manufacturers' websites and technical service departments. A single polymer type can easily have dozens of grades, and some grades will have been developed in an attempt to address the weaknesses of the material.

The data tables presented here are for the purposes of illustration only and cannot give a complete picture of material performance. They have been compiled from various sources, and not all the test methods will yield strictly comparable results. Data and product comparisons should always be checked with the manufacturers. However, coupled with the structure–property principles explained throughout the book, they will help to provide a framework against which to navigate the hundreds of manufacturer's datasheets.

In reviewing data tables and product comparisons, it is wise to remember that not all the sources from which data are gathered are 100% reliable. Some properties such as chemical resistance depend on several factors (e.g., moulding conditions, stress, temperature, concentration). Accordingly, it is always essential to talk to the suppliers and check data carefully for accuracy and relevance to the application conditions before committing to expenditure, selecting, or deselecting a material.

In such discussions it is worth distinguishing between numbers in datasheets and the numbers in actual specifications. Datasheets may be based on 'typical' (often average) values whereas specifications will be based on minimum values that all batches of

the product should meet. It is common for specification numbers to be lower than datasheet numbers. This may reflect variations due to testing, but there can also be batch-to-batch variations in the product itself.

Manufacturers' websites and the trade literature provide numerous examples of applications. Often manufacturers can describe success in closely related applications which will provide the necessary confidence for the specific testing of applications.

## **Reference**

1. D Van Krevelin in *Properties of Polymers*, Elsevier, Amsterdam, The Netherlands, 1990.

# 2 Polyarylethersulfones and Polyaryletherimides

## 2.1 Introduction

Commercial polyarylethersulfones (PAES) and polyaryletherimides are generally amorphous, melt-processable thermoplastics with, in many cases, fairly comparable values of the glass transition temperature ( $T_g$ ). Simplistically, the ether group imparts chain flexibility, leading to melt processability and toughness, whereas the sulfone and imide groups impart rigidity and polarity to the chain, producing a high  $T_g$ . The  $T_g$  is typically in the range 220–265 °C, but can be up to 311 °C in the case of certain polyetherimides. The useful properties of amorphous materials are lost above the  $T_g$  and chemical resistance and fatigue performance can be limited. Hence, various attempts have been made to improve these properties by creating melt-processable, crystalline polyetherimides such as ‘Aurum’, which is discussed in this chapter.

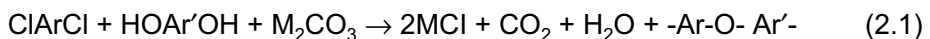
Polyethersulfones and polyetherimides often compete for similar applications, and end-users may have to choose between them. Typical applications utilise properties such as temperature performance, and perhaps low flammability and clarity, but these can be limited by certain aspects of environmental resistance and fatigue performance. Examples include: connectors and sockets; pump components; sight glasses; steam-sterilisable medical devices; cookware; coffee pots; projector lamp grills; lamps holders; lamp reflectors; aircraft interiors; and engine sensors.

## 2.2 Chemistry and Manufacturing

### 2.2.1 Polyethersulfones

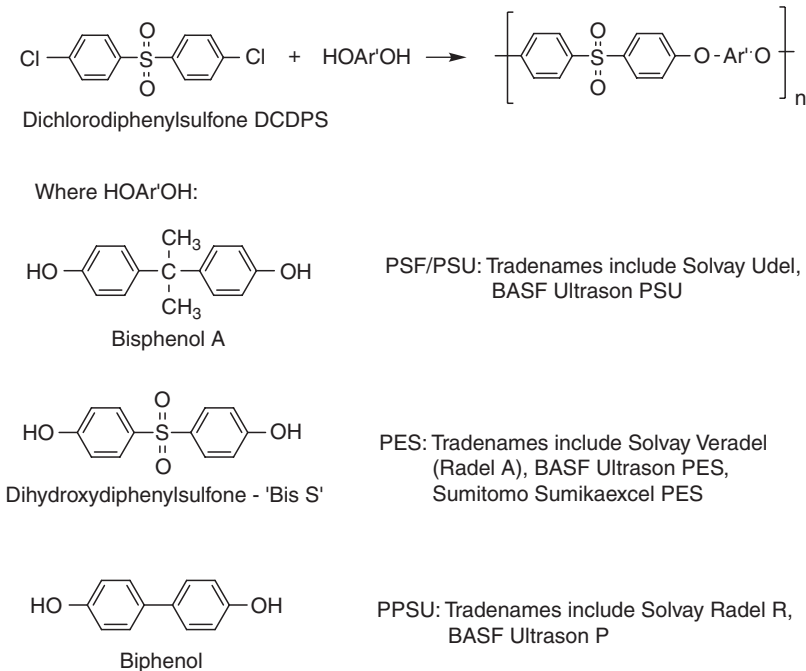
Polyethersulfones are produced by several companies such as BASF, Solvay and Sumitomo.

The standard nucleophilic polyetherisation route involves displacement of a sulfone-activated chloride by phenoxide anions. The general reaction is shown below where Ar is a sulfone-activated aromatic and M is usually sodium or potassium:



The most common chloromonomer is dichlorodiphenylsulfone (DCDPS). The most common bisphenols in order of increasing resultant  $T_g$  are: bisphenol A, 4,4'-dihydroxydiphenylsulfone and biphenol [1–3]. The basic reaction and resulting structures are shown in **Figure 2.1**. Manufacturers do not always publish the structures of commercial grades. **Figure 2.1** links tradenames to structures but there may be variations (especially if minor comonomers are taken into account). **Table 2.1** lists short- and long-term thermal properties. It can be seen that the  $T_g$  increases as the rigidity and polarity of the chain increases. Materials based on bisphenol A have a lower continuous-use temperature (CUT) because of the presence of aliphatic C-H groups. Accordingly, the properties section of this chapter will tend to emphasise higher-CUT materials. It is also possible to obtain an even higher  $T_g$ , for example, by introducing bis (benzene sulfonyl) diphenyl groups (**Figure 2.2**) which could be achieved using the dichloro or dihydroxy monomer.

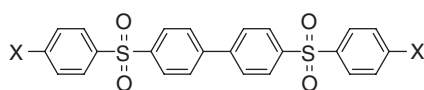
Molecular weight can be controlled using reaction stoichiometry, and various end-capping agents can be used. End groups may affect properties, and it can be useful to know which end groups are present and how well end-group distributions are controlled. Possible end groups include hydroxy, chlorine, phenate salts (potassium, sodium) and various monofunctional monomers.



Note that commercial grade structures may vary and may contain comonomers.

**Figure 2.1** Synthesis and structures of polyethersulfones

Table 2.1 Properties of polyethersulfones						
Material	Polysulfone (PSU)	PSU	Polyethersulfone (PES)	PES	Polyphenylsulfone (PPSU)	PPSU
	Unfilled	30% Glass	Unfilled	30% Glass	Unfilled	30% Glass
T <sub>g</sub> /°C	185	185	220	220	220	220
Melting point (T <sub>m</sub> )/°C	None	None	None	None	None	None
Heat distortion temperature (HDT)/°C	174	181	204	214	207	210
CUT/°C	160	160	180	-	160	-
Tensile strength, MPa	70	107	83	130	70	120
Tensile elongation, %	75	2	50	2	90	2
Flexural modulus, GPa	2.7	7.6	2.9	8.2	2.4	8.1
Unnotched Izod, J/m	NB	-	NB	540	NB	640
Notched Izod, J/m	69	69	76–120	60–90	694	75
Coefficient of thermal expansion (CTE)/10 <sup>-6</sup> m/m/°C	57	-	49	-	56	-
Limiting oxygen index, %	26	32	39	41	38	-
Density, g/cm <sup>3</sup>	1.24	1.49	1.37	1.59	1.29	1.53



where X = OH or Cl

Figure 2.2 Monomer unit used to increase T<sub>g</sub>

Manufacturers vary in terms of preferred polymerisation and extraction processes. In the case of bisphenol A, the disodium salt is made before the reaction with DCDPS. However, with other monomers, the phenate is generally produced *in situ* by the reaction with potassium carbonate in the presence of the dichloromonomer. The solvent is a dipolar aprotic solvent and can be diphenylsulfone, *N*-methyl pyrrolidone, sulfolane and dimethylacetamide. Water is evolved during the reaction. The polymer-extraction process is dependent upon the solvent and the technical preferences of the manufacturer. At the end of the reaction, metal chlorides can be removed by filtration and/or extraction with water from the solidified or the molten reaction mixture. The polymer may be recovered from solution by coagulation with a non-solvent followed by filtration; solvent evaporation; or by extraction of solvent from a solidified reaction mixture using solvents such as acetone. It can be worth enquiring which solvent and extraction method was used to better understand residual impurities and outgassing performance. The final stages may include melt filtration, devolatilisation, and extrusion into pellets. A wide range of compounds is manufactured.

Although the basic manufacturing technology is quite old, there are many recent patents covering improvements and blends. These include materials with greatly reduced colour, improved transparency and brightness [4], fire-retardant grades [5], and fire-resistant fluorinated sulfones [6]. PAES are blended with polyaryletherketones (PAEK) to improve chemical resistance, and ketone-containing copolymers have been developed [7] to provide better integration of the properties of both classes of material. Blends with polyetherimide can have improved resistance to ultraviolet (UV) light [8].

### **2.2.2 Polyetherimides**

Polyetherimides are produced by Sabic (formerly GE Plastics). A crystalline polyetherimide ('Aurum') is available from Mitsui and DuPont.

The structures of various polyetherimide monomers are shown in **Figure 2.3**. Bisphenol A is a relatively inexpensive starting material used in other Sabic products such as polycarbonate. Its dianhydride derivative (bisphenol A dianhydride (BPADA)) can be used to make a range of polymers based on different diamines.

The most well-known polyetherimide is probably Ultem 1000, which is manufactured by Sabic. It is made from BPADA and metaphenylene diamine (MPD) (see **Figure 2.4**). The flexibility of the ether and isopropyl groups produces a melt-processable imide-containing structure. However, these flexible groups also reduce the thermal performance *versus* pure imides because increasing chain flexibility reduces the  $T_g$ . In addition, the methyl groups reduce oxidative thermal stability but, because these contain primary hydrogens and are pendant to the main chain, the effect is not as marked as it might be. The relatively high ratio of carbon-to-hydrogen reduces the flammability of the polymer. Unfortunately, Ultem 1000 lacks the symmetry to crystallise.

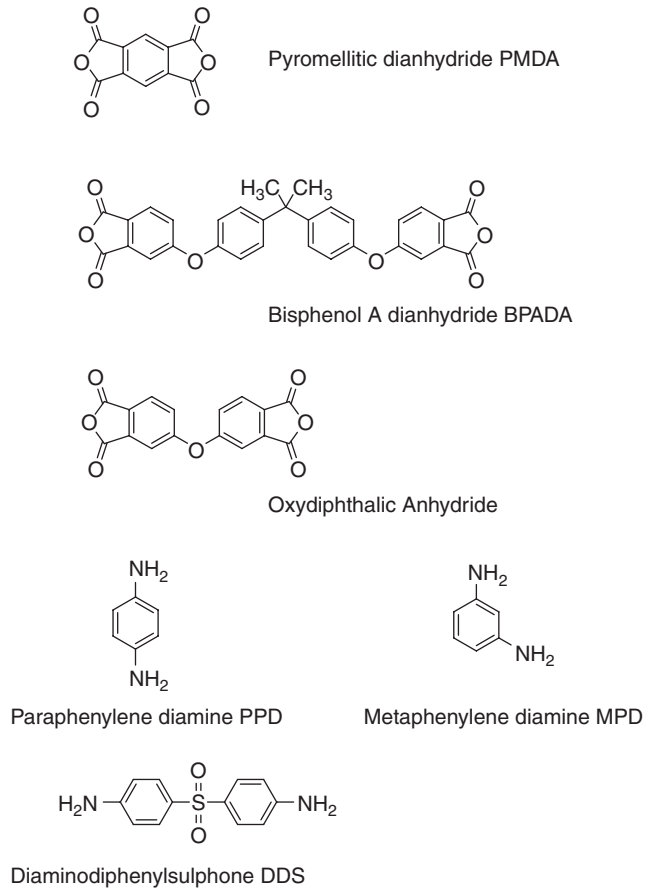


Figure 2.3 Structures of dianhydrides and diamines

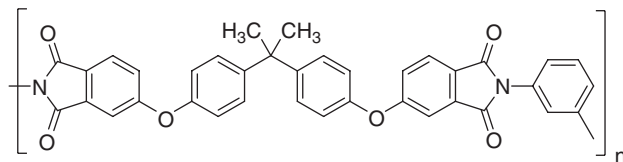


Figure 2.4 Structure of Ultem 1000

The structures of other Ultem grades are not commonly published but can be found in the literature [9]. Using paraphenylenediamine (PPD) produces an amorphous polymer with better solvent resistance and a somewhat higher  $T_g$  (Ultem 5000). Ultem 6000 is based on MPD reacted with a mixture of BPADA and pyromellitic dianhydride (PMDA). The less flexible PMDA further increases the  $T_g$ .

The use of diamino diphenylsulfone (DDS) in reaction with BPADA produces high- $T_g$  ethersulfoneimide polymers (Ultem XH (e.g., XH6050)). An even higher  $T_g$  can be achieved by replacing some or all of the BPADA with 4,4'-oxydiphthalic anhydride. The author believes that this may be the basis of the Sabic Xtem series of polymers [10, 11] which can have a  $T_g$  as high as 311°C. Table 2.2 lists the  $T_g$  of the Ultem and Extem series of polymers.

Sabic have also developed a flexible copolymer consisting of BPADA, MPD and polydimethylsiloxane known as Siltem [12, 13].

It is also possible to produce polyetherimides which crystallise (often relatively slowly). For example, Mitsui Chemicals developed Aurum (Figure 2.5) which is now sold by Dupont. These materials can have a high  $T_g$ . Various attempts have been made to improve the level and rate of crystallisation, for example, by blending with lower- $T_g$ , faster-crystallising polyetherimides [14]. In the early 2000s, Mitsui Chemicals introduced 'Super Aurum'. This material can have a lower  $T_g$  (190 °C) than Aurum but crystallises in the mould. Aurum-type materials are the basis of some of the thermoplastic resins sold by DuPont under the tradename Vespel.

## 2.3 Properties and Processing

Table 2.1 lists the properties of common polyethersulfones. However, Solvay have recently introduced a product with a  $T_g$  of 265 °C. The sulfone group is fully oxidised and so is relatively stable to thermal oxidative attack. It is highly polar, which increases the  $T_g$  but water absorption also increases as the proportion of sulfone increases. Hence, polyethersulfone (PES) has the highest water absorption. However, actual hydrolytic stability is very good, which leads to resistance to extreme aqueous environments such as boiling water, steam, or strong acids and alkalis. This can contrast with many polymers which contain hydrolysable groups such as esters, amides, imides or carbonates.

Polysulfone (PSU) typically has the lowest cost and best colour and clarity, but also has a relatively low CUT,  $T_g$  and limiting oxygen index (LOI). This can be explained by the presence of the aliphatic, bulky, flexible isopropyl group. PES offers higher thermal performance than PSU and chemical resistance which is intermediate to PSU and polyphenylsulfone (PPSU). PES is soluble in a limited number of organic solvents, including methylene chloride, dimethylacetamide and dimethylformamide. Ketones and aromatic hydrocarbons can lead to stress cracking. The incorporation of a biphenyl unit in PPSU increases impact strength, reduces notch sensitivity, imparts very good steam sterilisability, and improves resistance to environmental stress cracking in organic solvents. However, it can still be attacked by ketones, methylene chloride, and aromatic hydrocarbons.



**Table 2.2 Properties of polyetherimides**

Material	Ultem 1000	Ultem 2300	Ultem CRS5001	Ultem CRS5311	Ultem XH6050	Extrem XH1005	Extrem XH2315	Extrem UH1006	Siltem*	Aurum	Aurum
	Unfilled	30% Glass	Unfilled	30% Glass	Unfilled	Unfilled	30% Glass	Unfilled	Unfilled	Unfilled	30% Glass
T <sub>g</sub> /°C	217	217	225	225	247	267	267	250/305	198	250	250
T <sub>m</sub> /°C	None	None	None	None	None	None	None	None	None	388	388
HDT/°C	190	210	207	215	217	235	254	242	-	238	245
CUT/°C	170	180	-	-	-	-	-	-	-	-	-
Tensile strength, MPa	110	168	100	160	98	103	156	120	60	92	165
Tensile elongation, %	60	3	50	3	25	15	3	20	-	90	3
Flexural modulus GPa	3.5	8.9	3.1	8.9	3.2	3.1	8.9	3.5	1.7	2.9	9.5
Unnotched Izod	1335	430	2082	-	NB	1850	1387	1950	NB	-	-
Notched Izod (both in J/m)	32	85	64	-	69	44	86	75	406	90	120

**Table 2.2 Continued**

Material	Ultem 1000	Ultem 2300	Ultem CRS5001	Ultem CRS5311	Ultem XH6050	Extem XH1005	Extem XH2315	Extem UH1006	Siltem*	Aurum	Aurum
CTE/ $10^{-6}$ m/m/ $^{\circ}$ C	56	-	-	-	50	50	-	46	-	55	-
Limiting oxygen index %	47	50	-	-	45	43	-	47	48 (estimated)	47	-
Density, g/cm <sup>3</sup>	1.27	1.51	1.28	1.51	1.31	1.31	1.52	1.37	-	1.33	1.56

\*Properties will depend on siloxane content.  
Adapted from G. Haralur, G. Kailasam and K. Sheth, inventors; GE, assignee; US 02304060 A1, 2009 [19]

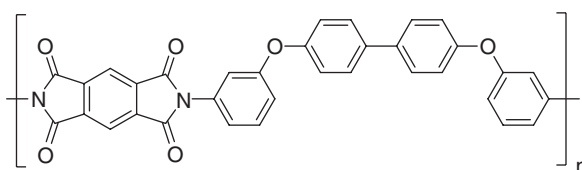


Figure 2.5 Structure of Aurum

There are several sulfone blends, some of which are commercially available. Acudel (Solvay) is described in the patent literature as an immiscible blend of PPSU and PSU. It is aimed at the cost-performance gap between PPSU and PSU, and has better toughness and chemical resistance than PSU. Blends with PAEK are not miscible but are fairly compatible. It is possible to form a fine dispersion of PAES in PAEK, retaining at least some of the superior chemical resistance of the crystalline PAEK. PAES can impart lower cost, lower mould shrinkage and lower warpage [15–17]. Such blends may be the basis of some of the Avaspire-modified polyetheretherketone (PEEK) grades sold by Solvay.

Table 2.2 lists the properties of some polyetherimide-based materials. The range of Ultem resins offers  $T_g$  in the range 217 °C to 247 °C and a CUT of 170–180 °C. As amorphous, high- $T_g$  materials they offer high dimensional stability and tight tolerances over a wide temperature range due to low and consistent shrinkage and low coefficient of thermal expansion (CTE). They have high modulus and strength combined with low flammability and smoke emission as well as good hydrolytic stability. The LOI is 47%, higher than that for many other high-performance engineering plastics. Some grades of Ultem (e.g., Ultem 1000 series) have been around for many years, and there are a wide range of qualifications and approvals (including for food contact, water contact, and medical devices). As amorphous materials, the chemical resistance can be limited. The CRS 5000 series of resins have enhanced resistance to strong acids, bases, aromatics and ketones.

Siltem grades can offer low flammability and flexibility combined with lower toxicity than fluoropolymers in fire situations.

Extrem XH and UH resins extend the performance of Ultem to even higher temperatures, with  $T_g$  values of 250 °C and 311 °C, respectively. In addition, they can show unusually good chemical resistance for amorphous resins. For example, they can be resistant to aliphatic alcohols, hydrocarbons, automotive and aircraft fluids and fully halogenated hydrocarbons. Resistance to phenols is poor, and performance in ketones can be marginal. The imide link means that resistance to strong alkalis remains limited. Very rigid backbone structures make materials progressively more difficult to process. This can be addressed to some extent by blending with other

resins. This can include other polyimides to produce intermediate  $T_g$  values [17], or crystalline resins such as PAEK [10].

Polyetherimides are often blended with other resins. Blends with polycarbonate combine the heat-, chemical- and scratch-resistance of Ultem with the impact strength, flow and economy of polycarbonate. Blends with PPS possess the infrared (IR)-soldering capability, excellent flow, and chemical resistance of PPS with low flash and improved mould cycle times. This allows PPS to compete with higher-cost liquid crystalline polymers which claim zero flash as a significant competitive advantage.

Blends with PAEK are of particular interest because they combine the chemical resistance and processability of PAEK with the high-temperature properties of polyetherimides. Ultem 1000 is miscible with many PAEK (e.g., polyetheretherketone (PEEK), PEK) in all proportions [14]. The result is an increase in the  $T_g$ , reduced crystallisation rate, very little change in melting point ( $T_m$ ) and reduced overall crystallinity. The blends can offer an increased  $T_g$  combined with good chemical resistance at lower polyetherimide (PEI) levels. Addition of PEI to PAEK reduces the overall cost. Such blends find uses where PAEK-like performance is required in combination with increased heat distortion temperature (HDT). There are also applications in which the PEI component of the blend is used above its  $T_g$  as a melt adhesive [18]. Blends of PEEK and Extem offer many PEEK-like properties such as chemical resistance, hydrolytic stability, processability and wear resistance. Extem enhances performance between the  $T_g$  of PEEK (143 °C) and the  $T_g$  of Extem, and improves dimensional stability [10]. Blends of PEEK with Siltem produce materials with improved ductility that may be suitable for applications such as the insulation of wire and cable [19].

Comparisons are often made with polyethersulfone resins. It was previously possible to compare Ultem 1000 with grades of PES in a relatively simple manner. However there is now a wide range of base resins and associated blends and compounds. Simple comparisons between Ultem and PES or PPSU are less straightforward than they used to be. Indeed, Sabic give presentations in which they present at around 17 different grades to compete with specific aspects of PSU, PES and PPSU. Simplistically, however, polyetherimides might offer lower density and higher strength, stiffness, LOI and UV resistance. Extem-type polyetherimides can offer higher values of  $T_g$  ( $\leq 311$  °C), although Solvay now offer a transparent polysulfone with a  $T_g$  of 265 °C. Some polyethersulfones might offer better resistance to strong alkalis and to hydrolysis, as well as better colour, toughness, CUT and melt flow. However, such comparisons are not always clear-cut. For example, some grades of Ultem are toughened by blending with polycarbonate and some grades of sulfones contain UV stabilisers. Accordingly the end-user should contact suppliers of both classes of resins and compare the best on offer from each while paying particular attention to the properties mentioned above.

There can also be important differences in chemical resistance to materials such as brake fluid, petrol, aromatic hydrocarbons, alcohols, acetates, ketones, trichloroethylene and motor oil.

Aurum is unusual in its ability to crystallise. It has a high  $T_g$  (250 °C) in relation to its  $T_m$  (388 °C). This suggests small imperfect crystals and annealing after moulding is required to develop crystallinity. It is reported to have good chemical resistance to oils, petroleum fuels and methylethylketone but it remains susceptible to strong alkalis. It is resistant to hard radiation.

Ethersulfones and etherimides are processable on conventional thermoplastic processing equipment. In general, they can be injection-moulded, extruded, blow-moulded, compression-moulded and thermoformed. Typical melt temperatures and mould temperatures are high to assist mould filling and reduce moulded-in stress. In general, higher- $T_g$  materials will be expected to have higher melt viscosities, and processing windows will become progressively smaller. Under these conditions, blends with other polymers (e.g., PAEK) may help processability as well as adding interesting performance characteristics. Materials that do not crystallise exhibit low mould shrinkage, and this is an advantage for applications requiring close dimensional tolerances.

## **2.4 Applications**

Product forms include: injection mouldings; extruded profiles; extruded stock shapes; as well as fibre film, foam, honeycomb and continuous-fibre composites. A wide range of compounds is available.

Aerospace applications are driven by light weight; fire smoke and toxicity performance (including low heat release on burning), processibility; and, for interiors, aesthetic considerations. Applications include personal service units, window surrounds, handles, seat components, ventilation grills, oxygen-mask containers, fasteners, and lighting units. Sabic have launched a new long carbon fibre-filled grade of Ultem which is lighter and stronger than the die-cast aluminium it replaces. It is used for interior components such as tray arms and meets Ohio State University (OSU) heat-release requirements. Low flammability Ultem honeycomb cores for composites can be rapidly thermoformed into a wide variety of complex shapes for ducting, luggage compartments, and galleys.

Food-contact applications require food-contact approval together with some combination of durability, impact performance, and cleanability, high-temperature dimensional stability, hot and superheated water resistance, resistance to food and

cleaning agents and, sometimes, transparency and ease of colouring. Examples include chopsticks, pumps in coffee makers, tea-maker components, food-processing equipment, sterilisable baby nursing bottles, microwave dishes, non-stick coatings (in combination with polytetrafluoroethylene (PTFE)) and transparent lids for deep-fat fryers and electric frying pans.

Automotive applications include high-temperature metallised lighting components such as foglamp and headlamp reflectors. Engine components such as sensor housings, connectors, fuse holders, oil-control pistons, throttle bodies, ignition components, thermostat housings and gearshift forks can reduce weight while combining tight tolerance with temperature and oil resistance.

In healthcare, USP class VI- and ISO 10993-compliant grades are available. Components can be durable, transparent and repeatedly sterilised. Examples include: healthcare sterilisation and transport containers, animal cages, sterilisation trays, surgical tools (e.g., skin staplers), secretion bottles, examination lamp housings, membranes, filters, dental equipment and laboratory equipment such as pipettes and petri dishes.

In telecommunications and electrical equipment miniaturisation, tight tolerance and environmental resilience are often critical. Applications include high-temperature edge and round multipin connectors, coil bobbins, terminal blocks, fibreoptic connectors, dip switches, liquid crystal display (LCD) projector internals, light-emitting diode (LED) reflectors and radomes. Materials can be injection-moulded and then plated to produce complex antenna systems. In electronic manufacturing, conductive chip carriers and trays can be moulded to high tolerances. Circuit-breaker pawls offer high dimensional stability, low creep, and low flammability and stiffness at high temperature. Consumer applications include hairdryers and hot combs. Siltem is targeted at flexible wire insulations where it can offer low flammability and low emission of toxic gases.

Industrial applications include sight glasses, pump components, hot-water pump impellers, gas flues, heat exchangers, filter bowls, bearing cages, expansion valves and fuel-cell components (e.g., methanol tanks). Sulfones find application in casings for alkaline batteries.

The crystallinity of Aurum combined with its high  $T_g$  means that some of its applications are closer to what would be expected of crystalline materials such as PAEK. This might include thrust washers and seal rings, jet-engine components, gears, valve seats, stripper fingers for high-speed copiers and bearing cages.

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# 3 Semi-Aromatic Polyamides (Polyphthalamides)

## 3.1 Introduction

Semi-aromatic polyamides (also known as polyphthalamides (PPA)) are combinations of aromatic and aliphatic functionalities. PPA are generally aimed at the performance gap between aliphatic nylons such as PA6,6 and PA6, and higher price polymers such polyaryletherketone (PAEK). They are crystalline and offer high strength and stiffness at elevated temperatures. However, the aliphatic functionality limits the continuous-use temperature (CUT). There is a range of product forms: glass-filled, impact-modified, mineral-filled, high-flow, flame-retardant, high-reflectivity and electrical grades. They find uses in a wide range of applications, including under-bonnet automotive components, electronic devices and domestic appliances.

## 3.2 Chemistry and Manufacturing Processes

Semi-aromatic polyamides are generally combinations of aromatic and aliphatic functionalities. They invariably contain 1,4 and sometimes 1,3 phthalic acid, so they are also known as PPA. Fully aliphatic polyamides offer limited thermal performance. Polymers made from aromatic diacids and aromatic diamines (commonly known as 'aramids') have superb properties, and are the basis of high-performance fibre products such as Kevlar. However, they lack melt processability. This is improved by the use of aliphatic monomers and aromatic monomers. As we shall see, quite complex combinations of monomers are used to achieve the required performance combinations. There are several suppliers of PPA including Arkema, DuPont, EMS Grivory, Evonik, Mitsui, and Solvay (formerly Amoco).

Figure 3.1 shows the generic polymerisation reaction together with the structures of the most commonly used diacids (terephthalic acid (T), isophthalic acid (I), adipic acid) together with various diamines. In the standard nomenclature, 'T' and 'I' are combined with a number indicating the length of the aliphatic monomers. Therefore, nylon 6T might be assumed to be made from hexamethylene diamine and terephthalic acid. Based on structure–property considerations, 6T looks like an interesting high-temperature material. However, the melting point ( $T_m$ ) is too high for melt processing without significant thermal degradation. Accordingly, comonomers are used to reduce the melting point.

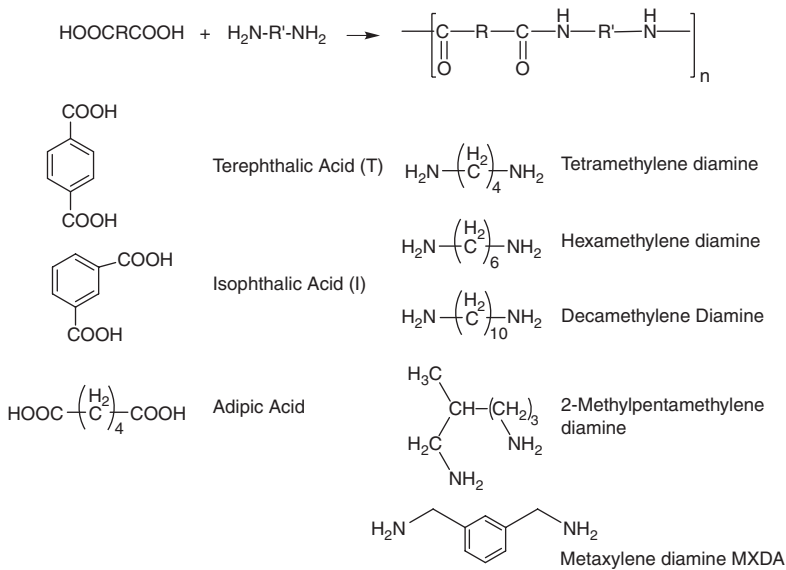


Figure 3.1 Synthesis of polyamides

The combination of aromatic diacids is sometimes represented in the product name. For example, PA 6T is produced from hexamethylene diamines and terephthalic acid, whereas PA 6T/6I would be a copolymer of hexamethylene diamines with both acids. Units designated '6.6' can be produced by the reaction of adipic acid and hexamethylenediamine. However, many copolymers are simply referred to as 6.T or 6.T/X, and this tells us little about the exact nature of the '6' unit or the presence of other monomers. There is a wide range of possible copolymer compositions, and these are used to 'tune' the exact thermal characteristics of particular products. Copolymers are often necessary to reduce the  $T_m$  to acceptable levels. For example, mixtures of terephthalic acid and isophthalic acid can be copolymerised with hexamethylene diamine and 2-methylpentamethylenediamine to produce polymers with values of  $T_m$  in the range 280–330 °C [1]. DSM have found that combinations of 4T and 6T produce polymers with  $T_m$  which are very high but well below the thermal decomposition temperature [2]. A very recent DSM patent illustrates ongoing research into ever more complex copolymer compositions, in this case involving mixtures of short- and long-chain diamines [3].

Manufacturers do not routinely disclose comonomer compositions. However, the structures of common commercial grades can be found in the patent literature, often linked to actual product trade names. Information can also be available on the proportions of acid and amine end groups, the nature of endcapping, as well as molecular weight and mechanical properties as a function of composition [4–12]. Table 3.1 shows how  $T_m$  and the glass transition temperature ( $T_g$ ) can be affected

**Table 3.1 Thermal properties as a function of molar composition of high-performance polyamides**

Terephthalic acid mol %	Isophthalic acid mol %	Adipic acid mol%	Hexamethylene Diamine mol%	2-Methylpenta-methylene diamine	Glass transition temperature ( $T_g$ )/°C	$T_m$ /°C	Trade name reported to be related to this type of structure
65	25	10	100	0	126	311	Amodel 1000
65	0	35	100	0	100	325	Amodel 4000
55	5	40	100	0	94	303	-
50	5	45	100	0	88	296	
60	0	40	100	0	95	317	
50	0	50	100	0	84	305	
55	0	45	100	0	88	312	Amodel 6000
100	0	0	50	50	125	305	Zyrel HTN 501

by composition, and relates these to the compositions of Amodel 1000, 4000 and 6000 and Zytel HTN. Other commercial products with structures disclosed in the literature include Mitsui Arlene CH230 (6.6/6.T), EMS-Grivory HT1 (6.T/6.I) and EMS-Grivory HT2 (6.6/6.T).

Polymers can also be produced using longer-chain diamines such as 10T/X made by Evonik or the similar HT3 (10.T/6.T) made by EMS-Grivory. The decamethylenediamine used in these products can be derived from castor oil, and the product is marketed for its performance and environmental credentials. The use of 6T units to control the  $T_m$  in 10T polymers is described in detail in a patent by EMS-Grivory [12]. A 65:35 10T:6T composition has a  $T_m$  and  $T_g$  of  $\sim 280$  °C and 121 °C, respectively.

Polyamide polymerisation can be achieved by gradually removing water from an aqueous mixture of the monomers. The process takes place under pressure at high temperatures [8]. Solid-phase post condensation can be used to increase molecular weight [7]. The chemistry lends itself to continuous processing [13, 14]. A two-stage process might involve the formation of a low-viscosity, low-molecular-weight pre-polymer which is subsequently post-polymerised in the solid phase or in the melt (e.g., via melt extrusion). There are also three-stage processes involving precondensation, solid-phase polymerisation, and polymerisation in the melt [15].

Polyamides can be compounded with a wide range of reinforcing fibres and other fillers. The presence of aliphatic groups means that thermal stabilisers and anti-oxidants are used [6]. Other important additives include fire-retardants [16] and toughening agents [17].

A slightly different class of semi-aromatic polyamide is made by condensing adipic acid and *m*-xylylenediamine (MXDA). This type of product is known as PMXD6, and is sold by Solvay under the trade name 'Ixef' [18].

### **3.3 Properties and Processing**

Section 3.2 illustrates the exceptionally versatile chemistry of semi-aromatic polyamides. However, certain structure–property principles limit the performance of polyamides, notably effects involving oxidative stability and moisture absorption.

The combination of crystallisable structures and hydrogen bonding between the amide groups mean that  $T_m$  are typically close to or  $>300$  °C. Many grades are glass fibre-reinforced and the heat distortion temperature (HDT) routinely approaches the  $T_m$ . However, the presence of aliphatic C-H groups is a major weakness, and the relative thermal index (RTI) is commonly  $\sim 115$ – $140$  °C. This is not a problem for all applications. The RTI is based on a 100,000-hour half-life and many

applications (e.g., automotive-engine components) require much shorter lifetimes. Care should be taken when comparing loosely defined CUT values: some will be quoted for as little as 500 hours! Much effort has been put into improvement of the CUT. Recently, DuPont introduced 'Shield Technology', which combines a special set of stabilising additives with a new polymer backbone and polymer modifications. The resulting products have more than twice the lifetime and are targeted at conventional polyphenylenesulfide (PPS) applications in which they can also offer higher levels of toughness.

Moisture absorption is a problem for many polyamides. It causes dimensional instability and reduces the  $T_g$  and mechanical properties. Data tables often list properties as a function of humidity (e.g., dry 'as moulded' and at a standard relative humidity). In the case of semi-aromatic polyamides, the rate of moisture absorption may be very slow, and they may not have reached equilibrium at the time of testing (or an accelerated equilibration regimen may have been used). Knowing the conditions under which measurements were made and the sensitivity of key properties to moisture is important. In extreme cases, the  $T_g$  may drop below the service temperature, or components may seize or warp due to dimensional changes. However, the effect of moisture is less than that seen in aliphatic polyamides. The effect on mechanical properties at room temperature can be relatively small. This can be an advantage for PPA *versus* aliphatic polyamides.

Moisture absorption is an inevitable consequence of hydrogen bonding between water and amide groups. It is reversible and so can be less of a problem at service temperatures  $>100\text{ }^\circ\text{C}$  where the environment effectively dries the polymer. The effect is reduced with fewer amide groups and more hydrophobic chains. Semi-aromatic nylons have lower moisture absorption than aliphatic ones. Similarly, 10T would be expected to have lower moisture absorption than 6T. The higher-temperature aliphatic nylons (e.g., PA4.6) tend to have large proportions of hydrogen-bonding groups and can absorb relatively large amounts of water.

Flammability properties are inherently limited by aliphatic content. Many materials are rated 'horizontal burn' (HB) in UL94. However, grades containing flame-retardants (many of which are non-halogen-based) are available, and V-0 ratings can be achieved.

Aromatic content generally improves chemical resistance compared with aliphatic polyamides. However, the amide group is susceptible to hydrolysis and can be attacked by sufficiently strong acids and alkalis. Glycols and alcohols as well as water attack these materials aggressively only at high temperatures. Product literature from Amodel states that it has excellent resistance to hydrocarbons, greases, oils, chlorofluorocarbons, chlorinated hydrocarbons, ketones, esters, higher alcohols, alkalis, and gamma radiation but performs less well in methanol, strong acids and

methylene chloride. As always, a lot depends on stress, concentration, time, and temperature. Performance in phenol is described as ‘unacceptable’. Manufacturers will have specific performance data.

PMXD6 has relatively low thermal properties ( $T_g = 85\text{ }^\circ\text{C}$  and limited long-term thermal oxidative stability) but some of its other properties are exceptional. It typically contains  $\leq 60\%$  glass reinforcement (tensile strength, 280 MPa; flexural modulus, 24 GPa) and yet it has excellent flow properties. It can be used to produce very high strength, very high stiffness thin-wall components with excellent scratch-resistant surface finishes.

Table 3.2 shows the properties of some semi-aromatic polyamides and also the aliphatic polyamide nylon 6,6. For comparison, PA 4,6 would have a  $T_m$  of  $295\text{ }^\circ\text{C}$ , a  $T_g$  of  $75\text{ }^\circ\text{C}$ . The data are taken from Evonik datasheets, which allow comparison of 6T/X and 10T/X in unfilled and glass-reinforced forms. These numbers can be used as a baseline for comparisons with other materials such as DSM 4T materials, 6T products from Solvay, DuPont and EMS Grivory. The 6T material chosen has a  $T_m$  and  $T_g$  similar to those of Amodel 1000. The lower- $T_g$  resins (e.g., Amodel 4000 and Amodel 6000) can have a HDT comparable with that of Amodel 1000 when reinforced because of their high  $T_m$ . Up to 60% (or even 66%) glass-filled grades

Table 3.2 Properties of semi-aromatic polyamides					
Material	Vestamid M1000 ‘6T/X’	Vestamid M1000 ‘6T/X’	Vestamid M3000 ‘10T/X’	Vestamid M3000 ‘10T/X’	PA 6,6*
	Unfilled	50% Glass	Unfilled	50% Glass	Unfilled
$T_g/^\circ\text{C}$	125	125	125	125	60
$T_m/^\circ\text{C}$	315	315	285	285	260
HDT/ $^\circ\text{C}$	126	293	128	276	80
Tensile strength at break/MPa	90	230	73	215	73
Tensile elongation at break/%	3	1.6	5	2.2	40
Tensile modulus GPa	3.6	17	2.7	15.5	2.4
Flammability UL94 3.2 mm**	HB	HB	HB	HB	HB
Moisture absorption % (23 $^\circ\text{C}$ , 50% humidity)	0.3	0.2	0.15	0.08	
Density, g/cm <sup>3</sup>	1.2	1.64	1.1	1.58	1.12
* For comparison, PA 4,6 would have a melting point of $295\text{ }^\circ\text{C}$ at a $T_g$ of $75\text{ }^\circ\text{C}$					
** Halogen-free, flame-retardant grades can have V-0 ratings					

are available for some polymers. Moduli of ~23 GPa are achievable. However very highly filled systems may have limited flow and be suitable only for thicker parts.

In comparison with PA66, 6T is said to offer better: heat resistance; dimensional stability; resistance to chemicals and hydrolysis; stiffness; and tensile strength; it also offers lower absorption of humidity. Impact strength and processability are slightly lower. In comparison with 6T, 10T is said to offer better: resistance against hydrolysis; moisture uptake; chemical resistance; processability; impact strength; and elongation at break. The HDT, tensile strength and stiffness are lower. Such comparisons are dependent upon the precise composition of the polymer and compound.

The advantages of PPA compared with other polymers have been described, as listed below:

- *Versus* liquid crystalline polyesters (LCP), PPA can offer better weld line strength and dynamic stress performance
- *Versus* polyethersulfone (PES)/polyphenylsulfone (PPSU), PPA can offer better resistance to chemicals and environmental stress cracking (PES/PPSU are amorphous)
- *Versus* PPS, PPA can offer better toughness and elongation up to break, and can be better for dynamic stress
- *Versus* PA46, PPA can offer lower water absorption, better dimensional stability and mechanical properties that are less susceptible to moisture

Semi-aromatic nylons can be processed using standard thermoplastic techniques. However, they must be dried according to manufacturer recommendations. Failure to do so can result in poor part appearance, drooling at machine nozzles, and brittleness due to reduction in molecular weight. The drying temperature and drying time need to be limited to avoid resin discolouration; desiccant dryers are recommended. High mould temperatures are required to develop full crystallinity. For Amodel, mould temperatures >135 °C are required to produce parts with the best chemical resistance, dimensional stability and HDT. Excessive melt temperatures and residence times can give rise to degradation.

### **3.4 Applications**

PPA are generally aimed at the performance gap between aliphatic nylons such as PA6,6 or PA6 and high-price polymers such as PAEK. There is a wide range of

product forms, including glass-filled, impact-modified, mineral-filled, high-flow, flame-retardant, high-reflectivity and electrical grades.

PPA are found in a wide range of under-bonnet automotive applications. Benefits include adequate heat aging resistance for automotive lifetimes, easy processing with good surface appearance, high stiffness and strengths at elevated temperatures, hydrolysis resistance, dimensional stability, surface appearance, paint adhesion and weldability. Examples include tank flaps, electrical water pump and thermostat housings, engine mount orifice bodies, digital water valves, capless fuel filler systems, fuel filter housings, exhaust-gas recirculation components, air-intake manifolds, oil coolers, heater core end caps, snap-fit electrical terminals, moulded-in-place gaskets, control system enclosures, noise encapsulation devices, and engine covers.

Complex electronic components can be produced from high flow grades. Benefits can include resistance to hot and humid environments and compatibility with lead-free soldering technologies. Applications include light-emitting diode (LED), surface mount technology components, connectors, motor parts, and controller housings. PPA are used in connectors and sockets for serial advanced technology attachment connectors, notebook memory backplanes and memory cards. Flow is inferior to LCP but toughness and weld-line strength are better. Halogen-free flame-retardant grades reduce the relative advantages offered by inherently fire-retardant LCP. Laptop base frames can be made from flame retardant grades. LED require durable, highly reflective sockets. PPA can offer a light natural colour and high-reflectivity whites combined with good ultraviolet and dimensional stability as well as excellent adhesion to metal and silicone. This allows the creation of longer-lasting, more robust and more efficient LED. Thermally conductive grades can improve heat management.

Many small domestic appliances such as power tools and gardening equipment contain PPA components. The conventional connectors currently used in many domestic appliances (e.g., washing machines, clothes dryers) are being converted to surface mount technology, thereby creating further opportunities for PPA.

Conventional rubber components are fastened and fixed using composite structures that contain a metal component. PPA can remain stable at vulcanisation temperatures to provide a lightweight, corrosion-resistant alternative. Complex parts can be manufactured inexpensively by injection moulding. The composite components are used in a wide variety of applications, including shock-absorbing bearings and buffers or reinforced seals.

PMXD6 resins offer very high strength and stiffness in thin-wall components with an excellent, scratch-resistant surface finish. They can look and feel like metal, and are used in aesthetic components such as mobile-phone housings, shaver heads, electric iron parts, sewing-machine components, automotive door handles, mirror housing and headlamp surrounds.



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# 4 Polyphenylene Sulfide

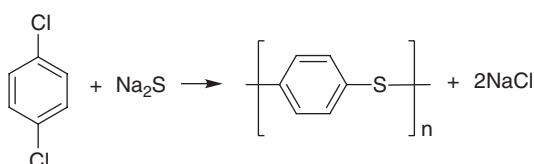
## 4.1 Introduction

Polyphenylenesulfide (PPS), (also known as polyarylene sulfide (PAS)), has a glass transition temperature ( $T_g$ ) of 90 °C , a melting point ( $T_m$ ) of 280 °C , a glass-reinforced heat distortion temperature (HDT) of >250 °C and a continuous-use temperature (CUT) of ~220 °C. It is strong, rigid, highly crystalline, has excellent flow properties, absorbs little moisture, is relatively inert to many chemicals and to hydrolysis, and is inherently fire-retardant (limiting oxygen index (LOI) ~50%). It has a wide range of industrial, electronic, automotive, aerospace and domestic-appliance applications. It is relatively inexpensive but compared with, for example, polyaryletherketone (PAEK), it has lower temperature performance and toughness and a greater tendency than liquid crystalline polyesters (LCP) to flash on moulding.

## 4.2 Chemistry and Manufacturing Processes

PPS is typically manufactured by the reaction of sodium sulfide and 4,4' dichlorobenzene in *N*-methylpyrrolidone (NMP). The simple reaction scheme shown in **Figure 4.1** hides a remarkable degree of mechanistic complexity. A wide range of modifications and/or post-treatments are used to produce commercial products. Many of these are described in patents from companies such as DaiNippon Ink, Idemitsu, Kureha, Philips, Toray and Ticona. This section describes some of the key developments.

The earliest commercial route [1] was developed by Phillips Petroleum. It utilised the production of reactive sodium sulfide by dehydration of aqueous sodium



**Figure 4.1** Synthesis of PPS

sulfide in the presence of NMP. This was then polymerised with dichlorobenzene. The PPS precipitated on cooling and was washed to remove NMP and sodium chloride. The polymerisation has several unusual features reflecting the complexity of the underlying mechanism. For example, NMP is not merely a solvent but also transforms the sodium sulfide into a soluble nucleophile, and the production of high-molecular-weight material at even low conversions results from differences in particular  $S_NAr$  ionic reaction rates [2]. PPS made by this early route is typically oxidatively heat-treated in a process known as ‘curing’ (3,4). This can be carried out in the solid state at temperatures below the  $T_m$ . The PPS remains thermoplastic, and the curing process should not be confused with the crosslinking, curing processes used in thermosets. ‘Cured’ PPS shows increased melt viscosity and toughness but a reduced rate and level of crystallisation. ‘Curing’ darkens the polymer.

Higher molecular weight, ‘linear’ PPS can be made by adding alkali metal carboxylates to the sodium hydroxide, hydrogen sulfide and sodium hydrogen sulfide used in the production of the sodium sulfide [5]. The material can have higher elongation and impact strength than cured PPS and can produce better fibre properties. Kureha have developed processes to produce high-molecular-weight, linear PPS without using polymerisation aids such as the salts of organic acids [6, 7]. Branch points can also be deliberately introduced (e.g., by using trichloro monomers) and this can further improve certain properties.

In addition to curing, there are several other post-treatment processes. Crystallisation temperatures can be increased by treatment with aqueous non-oxidising strong acids or the salts of such acids with weak bases. This is said to be due to the neutralisation or acidification of basic end groups such as  $SNa$  [8]. Various precipitation-based fractionation techniques have been developed to separate high-molecular-weight material from oligomers [9]. This improves mechanical properties and outgassing characteristics.

The complexity of the polymerisation reaction and the range of possible post-treatments create opportunities for patenting 40 years after the original process was developed. Most manufacturers continue to file patents on improvements in the process and products. Some of these products are radical step changes (e.g., cyclic PPS is a fairly recent development) [10, 11]. Other examples include the further development of branched products, high purity grades, copolymers, improved extraction methods, and the use of lithium salts instead of sodium sulfide (because lithium chloride is soluble in NMP).

An end-user considering using a new grade of PPS may find it interesting to search for patents using the name of the manufacturer and the polymer type; in the patent literature this is often termed ‘polyarylene sulfide’. It may be possible to identify the technology used to produce the new grade.

### 4.3 Product Forms, Properties and Processing

PPS is highly crystalline, has high melt flow, and is supplied with  $\leq 70\%$  filler, thereby improving strength and reducing warpage and cost. In addition to the basic resin types (cured, high-molecular-weight linear, branched), PPS can also be modified by the use of fibre reinforcements, fillers and blends with other polymers. Grades are available for medical, pharmaceutical and repeat-use food-contact applications. The unfilled resin is fairly brittle, and PPS is usually employed with  $\sim 40\%$  glass-fibre reinforcement. There are also reduced chlorine grades and toughened grades. Recently, Toray introduced a microcell-expanded PPS foam sheet. **Table 4.1** lists the properties of some types of PPS. The CUT is typically in the range 200–240 °C. The LOI, at  $\sim 50\%$ , is high, but degradation products can include sulfur dioxide, carbonyl sulfide and mercaptans. Resistance to gamma radiation and neutron radiation are good, but PPS has limited resistance to degradation by ultraviolet radiation. Moisture absorption (and the associated swelling and dimensional change) is very low. Chemical resistance is generally very good. PPS is resistant to many non-oxidising organic solvents, but amines, aromatic compounds and halogenated compounds may have some effect at elevated temperatures. It can be resistant to liquid gases and fuels, methanol, ethanol, hot engine oil, greases, antifreeze, dilute acids and alkalis, and is not subject to hydrolysis. Special grades have been developed to resist attack of hot water on the resin–fibre interface in glass-fibre reinforced grades. However, it is chemically decomposed by oxidising acids such as nitric acid; it will dissolve in aromatic hydrocarbons and chlorinated aromatic hydrocarbons  $>200$  °C; and can be attacked by carbon tetrachloride, nitrobenzene

**Table 4.1 Properties of PPS**

Material	Linear	Linear	Linear
	Unfilled	40% Glass/mineral	60% Glass/mineral
$T_g/^\circ\text{C}$	90	90	90
$T_m/^\circ\text{C}$	280	280	280
HDT/ $^\circ\text{C}$	110	260	270
Tensile strength, MPa	90	195	145
Tensile elongation at break, %	3	1.9	1.2
Flexural modulus, GPa	3.8	14	16.7
Notched Izod, $\text{kJ/m}^2$ (J/m)	3	10	6
Unnotched Izod $\text{kJ/m}^2$ (J/m)	50	34	-
LOI, %	-	47	53
Coefficient of thermal expansion (CTE), $10^{-6}$ m/m/ $^\circ\text{C}$	52	-	-
Density, $\text{g/cm}^3$	1.35	1.66	1.95



and concentrated hydrochloric acid. Chemical resistance is reduced above the  $T_g$ . Permeability is generally low. In comparison with polyethersulfone (PES), PPS is opaque, has lower toughness and greater flashing, but better chemical resistance and a higher CUT. The tensile and flexural strengths of glass-filled PES are higher than for glass-filled PPS between the  $T_g$  of PPS (90 °C) and the  $T_g$  of PES.

Linear PPS is said to have better strength, toughness, purity, weld-line strength and colourability than cured PPS. Cured PPS is said to show better elevated temperature creep resistance and dimensional stability. Cured PPS has already been thermo-oxidatively treated, so it may show less marked changes during thermal ageing. Simple comparisons of short-term and/or room-temperature properties are not sufficient to assess the relative merits of different PPS types. It is always worth asking for data at the proposed operating conditions. For example, differences in the tensile or flexural strength of glass-reinforced linear or cured PPS become much smaller at high temperatures.

Lack of toughness and a tendency to flash in injection moulding are amongst the commonly quoted limitations of PPS. There are various reduced flash grades, including blends with polyetherimide and polyphenylene oxide. Blends of PPS and polyetherimide can possess the infrared soldering capability, excellent flow and chemical resistance of PPS while showing low flash and improved moulding cycle times. This allows PPS to compete with higher-cost liquid crystalline polymers, which usually claim zero flash as a significant competitive advantage. PPS can be blended with LCP to reduce cost, improve the LCP weld-line strength or to further improve the flow of PPS. Various toughened PPS grades have been developed. Work to address this weakness continues decades after PPS was first introduced [12].

PPS can be processed using normal thermoplastic processing techniques. Depending on the grade, it can be injection-moulded, extruded, blow-moulded, powder-coated and even converted to multilayer or biaxially oriented films. Extrusion can be used to produce rods, slabs, pipes, films, sheets and coated wires. Very complex blow mouldings can be produced using special blow-moulding grades, and this has opened up important new applications. The high flow of PPS makes it ideally suited to the production of thermoplastic continuous-fibre composites and long fibre-reinforced compounds. PPS can be converted into mono- and multifilament fibres and non-woven fabrics. Finishing processes include welding, machining, laser marking, adhesive bonding, painting, printing and metalising.

Although PPS is very hydrolytically stable and moisture absorption is low, it should be dried before processing to prevent splay marks and other cosmetic defects. Crystallinity is important to develop elevated temperature properties because the  $T_g$  is relatively low. A minimum mould temperature of 140 °C is recommended to produce fully crystalline mouldings. Crystallinity can be further developed by annealing for

1 or 2 hours between 200 °C and 230 °C. Most PPS is used for its combination of mechanical endurance, chemical resistance, and dimensional stability at high temperatures. Therefore most processors will be concerned to develop adequate crystallinity. In most cases, adequate control of thermal history is assumed to result in a reproducible level of crystallinity. Annealing can reduce tensile strength, elongation and impact strength, but increases the modulus and chemical resistance. The measurement and development of crystallinity in PPS is the subject of a report available from the US Department of Energy (DOE) [13].

PPS shows excellent flow and can fill very-thin-walled parts. Unfortunately, it is easily prone to flash, and costs can be increased by secondary flash-removal operations. Flash can be reduced by using moulds built to high tolerances, but this can become a problem as the mould starts to wear. Unfortunately, many highly filled grades are highly abrasive.

#### **4.4 Applications**

PPS finds uses in various under-the-bonnet applications which take advantage of its environmental resistance and CUT of 200 °C. This includes intake manifolds, components for exhaust gas systems and turbochargers, water-pump impellers, thermostat housings, engine mounts, seal housing, gasket carriers, fuel-pump impellers, servo pistons, transmission sensors, fuel-pump housings mounted within fuel tanks, and vacuum-pump components.

In recent years, blow moulding has become an important processing technology. Automotive applications include air ducts for turbocharged diesel engines, intake manifolds, cooling systems, water tanks, and heat shielding piping. Gas heating systems use PPS flue pipes.

Industrial applications include fibres for filter bags, braided sleeves, flue gas filters, protective clothing and dryer belts; pump housings and impellers, valve components, chemical-tank linings, dishwasher spray arms, pipe linings, composite and long-fibre outer reinforcements for pipes, and oil field equipment.

Domestic appliance uses include components for irons, kettles, coffee machines, hairdryers and microwave ovens. These may be circuit-breakers, relay housings, bob-bins, connectors, impellers, frying-pan handles, hairdryer grills, steam-iron valves, toaster switches, hot-water valves, light-reflector housings, and ink-jet cartridges.

Electronic applications include surface mount connectors, chip carriers, telephone jacks, integrated circuit card connectors, high-density complex interconnects, head-lamp reflectors, alignment critical devices for splicing optical cables, sockets, relays, switches, circuit-breakers, semiconductor polishing rings and electronic device

packages. Complex components can be produced via techniques such as laser direct structuring. Special grades of PPS can be used for transistor encapsulation where high flow, low ionic content, low coefficient of thermal expansion (CTE) and high resistance to moisture transmission are key properties. PPS is chosen because of its high dimensional stability (including during soldering processes), good heat and chemical resistance, inherent flame retardancy, and ease of moulding into thin sections. PPS competes with LCP in many applications in the electrical/electronic market. Parts made from both materials can be attached to circuit boards by surface mount technology using convection, infrared reflow or vapour-phase soldering. PPS and LCP are commonly supplied with 30–50% glass-fibre reinforcement and have a HDT of >260 °C and 300 °C, respectively, and a CUT of 200–240 °C. LCP allows longer flow lengths, thinner sections, shorter cycle times and lower levels of flash. PPS offers better weld-line strength. Blends of PPS and LCP can reduce the cost of LCP.

PPS is a popular matrix resin in continuous-fibre composites with glass, carbon and aramid fibres. Its composites are used in the leading edge of wings and in several ribs, panels and beams on the Airbus A340 and A380. Compared with PAEK composites, PPS materials lack temperature performance and toughness, but are less expensive and can be processed at lower temperatures. Possible applications include fasteners, floor beams, door and fuel tank access panels, thermal and fire barriers, and stiffeners.

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# 5 Polyaryetherketones

## 5.1 Introduction

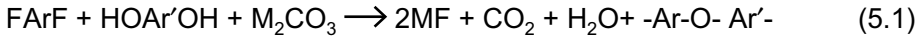
Polyaryetherketones (PAEK) are high-temperature, crystalline, true thermoplastics. The glass transition temperature ( $T_g$ ) is typically 140–180 °C, although higher values are possible by copolymerisation with rigid units (e.g., sulfone, biphenyl). Melting point ( $T_m$ ) values are typically 330–390 °C. At processing temperatures, viscosity is similar to many other thermoplastics, and typical thermoplastic processing techniques can be used. The materials can be 30–40% crystalline, which results in good resistance to chemicals and fatigue. PAEK offer a combination of properties that goes far beyond temperature resistance. They include resistance to wear, chemical environments, hydrolysis, sterilisation and fire together with biocompatibility, purity, low smoke and toxic-gas generation and electrical performance. They are produced by a range of companies, including Arkema, Evonik, Gharda, Jilin Super Engineering Plastics, Polymics, Solvay and Victrex. The latter is the leading supplier with the longest product history. PAEK are found in almost all industry sectors, and are available as pure resins, compounds, blends, composites, films, coatings and medical grades.

PAEK are commonly described in terms of an ‘E’ (ether group) and a ‘K’ (ketone group). For all *para* structures, temperature performance increases as the ratio of relatively polar and inflexible K units increases. The most common PAEK are polyetheretherketone (PEEK), polyetherketone (PEK), polyetherketoneetherketoneketone (PEKEKK) and Polyetherketoneketone (PEKK). Their structures are described in the next section. PAEK are the subject of a recent technology update published by iSmithers Rapra [1].

## 5.2 Chemistry and Manufacturing

The standard nucleophilic polyetherisation route involves the displacement of a carbonyl activated fluoride by phenoxide anions. Diphenylsulphone is used as a high-temperature solvent (typically at ~320 °C) and the phenate is produced *in situ* by the reaction of the bisphenol with alkali metal carbonates. The general

reaction is shown below, where Ar is a ketone-activated aromatic and M is usually sodium or potassium:



The routes to PEEK, PEK, polyetheretherketoneketone and PEKEKK are shown in Figure 5.1 and are widely described in the literature [2–5]. At the end of the polymerisation, the solidified polymerisation mixture contains polymer, diphenylsulphone, and alkali metal fluorides. The diphenylsulphone is removed with acetone and the

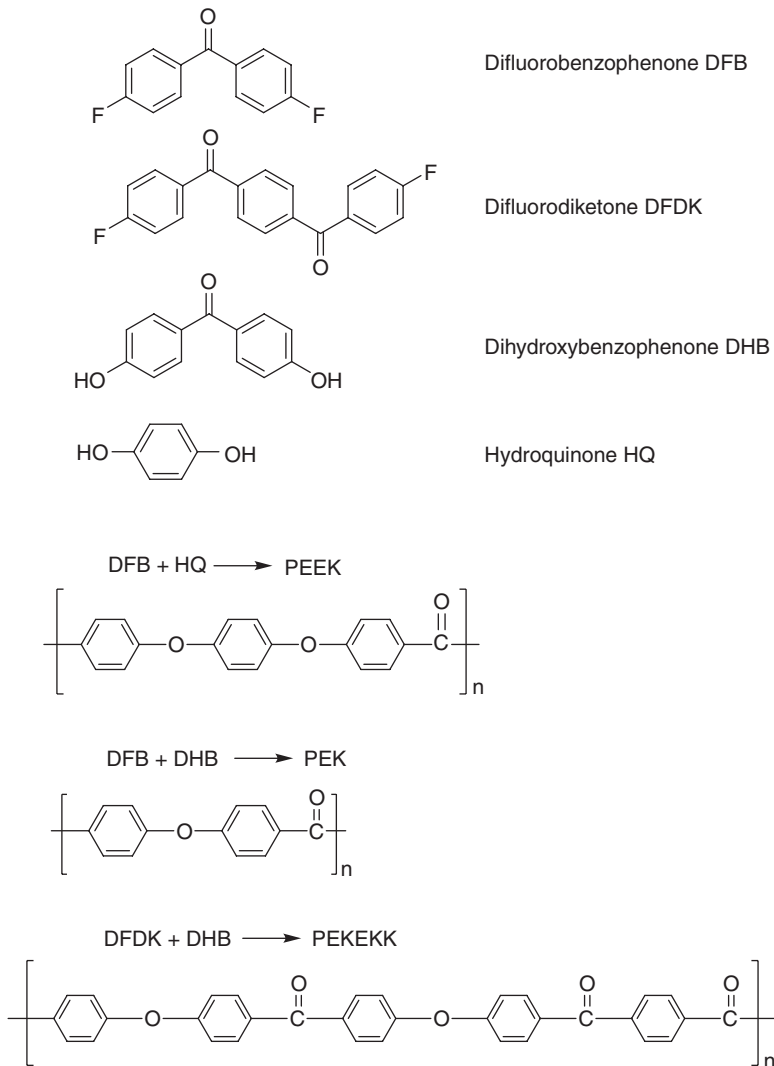


Figure 5.1 Monomers and routes to PAEK

metal fluorides by extraction with water. Various attempts have been made to use cheaper chloromonomers. For example, a recent patent describes the production of PEK from the alkali metal salt of 4,4' hydroxychlorobenzophenone [6, 7].

PEKK is produced by an electrophilic process from diphenyl ether and phthaloyl chlorides [8]. It is one of the few PAEK that would be difficult to make by nucleophilic routes because of the complexity of the monomer required. The high  $T_m$  of linear, 100% *para* PEKK means that it is made from terephthaloyl (T) chloride and isophthaloyl chloride (I). Crystalline PEKK is typically 80:20 T/I, whereas the amorphous grades used for thermoforming are 60:40 T/I. The isophthaloyl groups limit the size of crystals and hence reduce their  $T_m$ , together with crystallisation rate and overall crystallinity. There is also an electrophilic route to PEEK from phenoxyphenoxybenzoic acid [9] and PEKEKK has previously been made using electrophilic processes.

Product forms include powders and granules, fine powders, compounds with a wide range of fillers and reinforcements, continuous-fibre composites, films, fibres, coating dispersions, stock shapes and foams. There are a wide range of speciality products, including wear, electrostatic-dissipative, high-purity, coloured, radio-opaque, antimicrobial, laser-markable, and authentication grades. Some of these are produced by resin manufacturers, but others are available from specialty compounders (e.g., RTP, Sabic LNP).

PAEK can be blended with a range of other polymers (although the blend components must have sufficient thermal stability). Most blends are immiscible, but many PAEK are miscible with polyetherimide (PEI) (Ultem) in all proportions [10]. The addition of PEI increases the  $T_g$  and can be used to build the heat distortion temperature (HDT) while retaining crystalline chemical resistance properties. PEI can also be blended with PAEK to obtain melt adhesive effects [11]. Blends with Extem are used to enhance thermal performance [12] and polyimidesiloxane copolymers can be blended with PEEK to improve flexibility [13]. Polyphenylene sulfide (PPS) is crystalline, and blends will retain a good degree of chemical resistance [14–16]. Blends with polybenzimidazole (PBI) can show exceptional wear performance [17–21]. Liquid crystalline polyester (LCP) blends have improved flow properties. Blends with polysulfones and PPS are immiscible. PES is amorphous and can reduce mould shrinkage and warpage [22, 23]. Fluoropolymers are commonly added to wear-resistant compounds.

### 5.3 Properties and Processing

The short-term thermal performance of commercial PAEK is summarised in **Table 5.1**. Longer-term, continuous-use temperature (CUT) are typically 180–260 °C depending on the property measured. PAEK will degrade at elevated temperatures, especially in the presence of air and transition metal catalysts such as copper. Degradation can often be detected by changes in crystallisation rate or colour and can result in the formation of gels and carbonised black specks during melt processing.

**Table 5.1 Properties of PAEK**

Material	PEEK	PEEK	PEEK	PEEK	PEEK	PEEK	PEEK	PEEK	PEEK	PEEK**
	Unfilled	30% glass fibre	40% carbon fibre*	Unfilled	30% carbon Fibre	Unfilled	30% glass fibre	Unfilled	30% glass fibre	Unfilled (crystalline)
T <sub>g</sub> /°C	143	143	143	157	157	162	162	162	162	163
T <sub>m</sub> /°C	343	343	343	374	374	387	387	387	387	360
HDT/°C	152	328	345	165	368	172	172	172	380	175
Tensile strength, MPa	100	180	250	110	250	115	200	115	200	110
Tensile elongation at break, %	45	2.7	1.6	20	2.2	20	2.5	20	2.5	12
Flexural modulus GPa	4.1	11.3	28	4.1	22	4.1	11	4.1	11	4.5
Notched Izod, kJ/m <sup>2</sup> (J/m)	7.5 (83)	10 (115)	8.5	6.9	8.0	6.0	11	6.0	11	-
Unnotched Izod, kJ/m <sup>2</sup> (J/m)	NB	60 (725)	40	-	45	NB	70	NB	70	-
Coefficient of thermal expansion, 10 <sup>-6</sup> m/m/°C	47	-	-	-	-	45	-	45	-	-
Limiting oxygen index (LOI), %	35	-	-	-	-	-	-	-	-	40
Density, g/cm <sup>3</sup>	1.32	1.51	1.44	1.32	1.41	1.30	1.53	1.30	1.53	1.31

\*Higher values can be obtained with specialist carbon fibre grades  
 \*\*PEKK chemistry is quite versatile, grades with a T<sub>g</sub> of 172 °C are available

The mechanical properties of typical unfilled and reinforced grades of PAEK are shown in **Table 5.1**. In interpreting manufacturer's literature it can sometimes appear that lower molecular-weight-grades have higher short-term properties (e.g., modulus). This may be due to slightly higher degrees of crystallinity in the faster-crystallising lower-molecular-weight resins or perhaps better wetting and less breakage of fillers and fibres in some production processes. However, higher-molecular-weight material may indeed show better long-term properties (e.g., fatigue resistance). Continuous carbon fibre-reinforced PAEK (which may contain  $\leq 68\%$  carbon fibre) has exceptional strength and stiffness properties. The wear resistance of tribological grades is excellent.

Chemical resistance is generally very good and hydrolysis resistance is excellent. The semi-crystalline structure of PAEK resists swelling and ingress of chemical environments, and the dissolution of crystals is energetically unfavourable. Material suppliers produce extensive chemical-resistance tables. These include automotive fluids, jet fuel, hydraulic fluids, refrigerants, and oilfield semiconductor manufacturing chemicals. However, performance can be limited in certain environments (e.g., halogens, very strong acids, strongly oxidative environments, high-temperature aromatics and amines). Resistance to ultraviolet radiation is limited, but resistance to hard radiation (gamma rays, and so on) can be very good.

PAEK do not support combustion in air, produce little smoke, and burn in excess oxygen to produce carbon dioxide and water. However, the limiting oxygen index (LOI) is not especially high (e.g., 35% in PEEK). Fire performance can be enhanced by the addition of fillers.

The extraction processes used in PAEK production can result in very pure polymers in terms of metal ions and volatile organic compounds (outgassing).

PAEK are good electrical insulators in a wide range of environments and temperatures. However, the comparative tracking index can be relatively low, reflecting the ease of degradation to conducting char. The polar carbonyl groups mean that dielectric constants and dissipation factors are inferior to those of fluoropolymers.

PAEK can usually be processed using virtually all the standard technologies. They can be injection- and compression-moulded, extruded into film, sheet and fibre, oriented, powder- and dispersion-coated, blow-moulded, laser-sintered, converted into thermoplastic composites, welded, metallised, adhesively bonded and machined. Although moisture does not result in chemical degradation, it can produce moulding defects, and PAEK need to be dried before processing. Melt temperatures are typically 30–60 °C above the  $T_m$ . A suitable cooling regimen is required to produce crystalline components. This will involve an injection mould temperature in excess of the  $T_g$ . Amorphous material may appear as a brown skin on the surface. This should not

be confused with thermal degradation. If necessary, it can be removed by annealing, but it is better to use correct mould temperatures. Annealing is sometimes used to increase crystallinity and/or to remove residual stress.

## **5.4 Applications**

Transport (aerospace and automotive) applications are driven by factors such as the ease of fabrication, weight, mechanical properties, wear resistance, chemical resistance (e.g., to jet fuels, hydraulic fluids, brake fluid), rain-erosion resistance, and fire, smoke and toxicity performance.

Aircraft applications include: radomes, pylon fairings, fuel-tank manhole covers, hub caps, thermoformed cabin interior panels (often PEKK laminated with polyvinylidene fluoride), window surrounds, passenger service units and lamp housings, hinge-bracket assemblies, seat lumbar support adjusters, headrests and seatbelt guides, wiring blocks, cable ties, braided tubes, conduit interconnection systems, fuel-tank vents, oil cooling system impellers, air-conditioning fans, and cover films for thermal acoustic and burn-through insulation. PAEK thermoplastic composites are used less than their PPS counterparts because of cost and higher processing temperatures, but offer higher toughness and temperature performance. Potential applications include fuselage panels, fasteners, floor beams, spars, ribs, thermals and fire barriers and stiffeners. A range of composite fasteners, bolts, nuts, inserts and brackets is made using composite flow moulding technology.

In automotive applications, high-volume injection-moulded components offer greater design flexibility and are often less expensive than their metal counterparts. Transmission components include seal rings, self-lubricating (usually containing PTFE) thrust washers, bearing retainers and cages, bearings, bushings, vacuum pump vanes and vane tips, oxygen sensors, steering column sleeves, lamp sockets, fuel management components, antilock brake system tappets and plungers, and fork pads. PAEK gear applications include worm gears for steering adjustment and gears for air conditioning, seat adjustment and electronic power steering systems. Compared with metal gears, PAEK offer design flexibility, reduced weight, corrosion resistance, reduced fabrication cost, lower noise, and the ability to run without lubrication.

Extraction of oil and gas offer many opportunities for PAEK. Oil and gas extraction can involve temperature and pressures of 200 °C and 140 MPa, respectively, combined with hydrogen sulfide, methane, brine, carbon dioxide and crude oil. The cost of equipment failure means that the industry uses the more expensive PEK, PEKEKK as well as PEEK. Typical applications include data-logging tools, sensor housings, data and power cables, electrical connectors, bearings, bushings, seals, backup rings, compressor components, radio frequency identification tags, cable ties and energy-absorbing



springs for sealing systems. Recently, there has been a lot of interest in PAEK pipes that offer low permeability, low sensitivity to rapid gas decompression, erosion and wear resistance, and high strength, fatigue and creep performance. PAEK are used as liners in a range of umbilicals and, in the future, may be used as deep-ocean risers with superior buoyancy to their steel counterparts.

Electronic-device applications include high-performance connectors and wiring systems. PEEK is used in wiring for nuclear power stations because of its resistance to radiation, temperature and chemicals. Lead-free solders require high process temperatures. LCP offer the necessary temperature performance but may lack mechanical performance and weld-line strength. PPS offers high flow and dimensional stability, but can be limited by its temperature performance. Mobile-phone applications include battery gaskets, hinges and the use of film in speakers and microphones. Office machine applications include gears, split fingers and bushings for copiers and printers, as well as lamp holders for digital projectors. PAEK film is also finding uses in flexible printed circuit boards.

PAEK have important applications in the production of semiconductors and displays. This includes robotic wafer handling wands as well as wafer transport and storage devices. PEEK/PBI blends are used in robotic wands for extreme environments. Benefits include low particle generation due to wear, electrostatic discharge performance, high purity and low outgassing in vacuum, ability to handle hot wafers, no additives, and the production of complex geometries by injection moulding. The high level of purity and low wear particle generation increase device yield. PAEK are also used in chemical mechanical polishing rings because of wear life and in the plasma etch environment. PAEK test and burn in sockets survive the test environment with only very small changes in dimensions.

Industrial and chemical process applications include static compressor components together with moving components which require excellent fatigue life. Examples include valve plates, bearings, piston rings, labyrinth seals, scroll compressor tip seals, star gears and rotors. The slight plastic flow compared with metal allows components to 'bed' into their environment, and thereby respond to a degree of damage and wear. PAEK can reduce noise and vibration and increase efficiency. There are many applications in textile and weaving equipment, including lubricant-free wear plates, chain belt parts, as well as yarn and thread guides with over-moulded ceramic inserts. Analytical equipment makes extensive use of the environmental resistance of PAEK. PAEK films and membranes are used in heat exchangers and separation processes.

Food-contact applications are mostly found in food processing factories (although PAEK are used in steam contact components in espresso machines). Factory applications include conveyor-belt chains, scraper blades, pump impellers, and spray cleaning heads.

Consumer applications include strings for tennis racquets and violins, together with vacuum-cleaner components and portable camping stoves.

Short- and long-term implantable medical devices are made from PAEK, which can offer all of the benefits described in **Section 1.6.2**. Short-term applications include: tubing and catheters (e.g., for stent delivery in minimally invasive surgery), heat-shrinkable tubing for wiring protection, sterilisable diagnostic devices, drug-delivery and blood-management devices (e.g., dialysis equipment), laparoscopes, surgical instruments, surgical head restraints, endoscopes, endoscopy camera housings, dental tools, electrosurgical devices, analytical equipment, chromatography, and bio-hazard handling. Long-term applications include many spinal devices, bone pins, screws and plates, joint replacements (including wear-resistant surfaces), hip prostheses, dental implants, finger implant stems, cardiac pumps and pacemakers.

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# 6 Polyamideimides

## 6.1 Introduction

The imide group appears in a very diverse range of polymers. These can be amorphous or crystalline true thermoplastics or they can be non-melt-processable. They can even contain thermosetting functionality. The polyimide group is usually formed by the reaction of a dianhydride with a diamine. Here we look at polyimides containing amide functionality that can be injection-moulded and then thermally cured to increase imidisation and molecular weight. In this way, many of the advantages of injection moulding can be obtained while accessing the properties of high-performance imides. Excellent strength and stiffness are retained to high temperatures and combined with dimensional stability, wear performance and environmental resistance.

## 6.2 Chemistry and Manufacturing [1–3]

There are many possible varieties of polyamideimide (PAI) but probably the best known is Torlon PAI manufactured by Solvay (formerly Amoco). PAI can also be obtained from Toray. Torlon-type PAI can be made by two routes. Trimellitic anhydride acid (TMA) is the key raw material.

The most well-known route involves condensation of trimellitic anhydride chloride with various diamines in dipolar aprotic solvents such as *N*-methylpyrrolidone or dimethylacetamide. Depending on subsequent thermal and other treatments, the reaction can produce polymers with varying degrees of polyamic acid along the backbone (**Figure 6.1**). The products can vary in terms of the diamines used, the molecular weight, and the degree of imidisation. Some of these materials can be melt-processed by extrusion and injection moulding. However, they then require a further thermal curing process which needs to be carefully controlled and can take ~18 days to complete. This is essential to increase imidisation and molecular weight. It also leads to substantial crosslinking. Having originally benefited from thermoplastic processing, the product ceases to be thermoplastic.

The second route involves the reaction of TMA with diisocyanates such as 4,4'-diisocyanatediphenyl methane. This route is said to give rise to more complex structures and lower melt stability but can be used to produce material for wire enamel and coating applications.

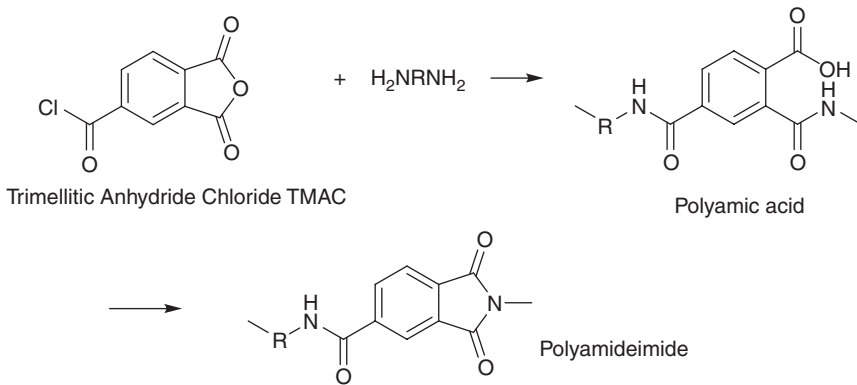


Figure 6.1 Synthesis of PAI

Determining the monomers used in commercial grades is made more difficult by the lack of solubility of the fully cured resins. However, it can be done using nuclear magnetic resonance (NMR) [1]. For example, Amoco's Torlon 4000T (the base resin used in injection-moulding grades of Torlon) has been shown to be based on trimellitic anhydride chloride with a 70:30 mixture of 4,4'-oxydianiline and *m*-phenylenediamine (Figure 6.2). It is also possible to use NMR to determine the distribution of amide-amide, amide-imide and imide-imide groups along the polymer backbone. Monomers commonly referred to in the literature include 4,4'-oxydianiline, *m*-phenylenediamine, 4,4'-diaminodiphenylmethane and 4,4'-diisocyanatediphenyl methane. However, the presence of aliphatic groups might be expected to lower thermal stability. They were not found in Torlon 4000T.

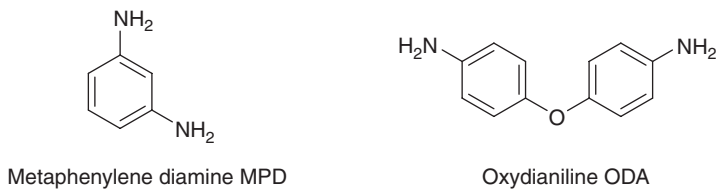


Figure 6.2 Diamines

### 6.3 Properties and Processing

Table 6.1 summarises the typical properties of PAI. Various compounds are available, including 30% glass fibre, 30% carbon fibre and various combinations of graphite and polytetrafluoroethylene. Torlon PAI has exceptional strength and stiffness for an injection-mouldable material, and these are retained to high temperature. Specific strength is comparable to that of some metals. The glass transition temperature is 275 °C and

Table 6.1 Properties of polyamideimides

Material	Torlon	Torlon	Torlon
Composition	-	30% Glass fibre	30% Carbon fibre
HDT, °C	278	282	282
Tensile strength, MPa	192	205	203
Tensile elongation at break, %	15	7	6
Flexural modulus, GPa	5.0	11.7	19.9
Notched Izod, J/m	142	79	47
Unnotched Izod, J/m	1062	504	340
CTE, 10 <sup>-6</sup> m/m/°C	31	16	9
LOI, %	45	51	52
Density, g/cm <sup>3</sup>	1.42	1.61	1.48

heat distortion temperature (HDT) can range from 278 °C (unfilled) to 284 °C depending on the grade. Compressive strength, toughness and wear resistance are very good. The continuous-use temperature of unfilled and 30% glass-filled material ranges from 200 °C to 220 °C. The limiting oxygen index (LOI) is high (45%). The coefficient of thermal expansion (CTE) of filled PAI can nearly match that of many metals. Thermal conductivity is low.

PAI can resist attack by most common hydrocarbons, chlorinated solvents and many acids at moderate temperatures. However, it can be attacked by strong bases, steam, some amines and some high-temperature acids. Water absorption limits the maximum acceptable rate of heating. Above this rate blistering and distortion can occur unless the absorbed water has time to diffuse out of the part.

All high-performance engineering plastics need correct processing to develop optimum properties. PAI seeks to gain the advantages of a polyimide while remaining injection mouldable. Special moulding and post-cure conditions are required and correct processing techniques are critical. PAI can be injection-moulded, extruded and compression-moulded. Injection moulding can require heavy-duty, high-rate machines, hydraulic accumulators and special screw designs. PAI has a high melt viscosity and is reactive in the melt state. Accordingly it is not possible to simply reduce melt viscosity by increasing melt temperature. Residence time needs to be carefully controlled and hot runners are not recommended. Mould shrinkage is low. The resin will closely match mould surfaces and will not accept undercuts unless moveable mould features are used. Jetting can be an issue resulting in internal voids. Recommended mould temperatures are typically 160–220 °C. The appearance of injection-moulded parts may be good, but molecular weight is relatively low and ‘curing’ is essential to develop strength, toughness, wear properties, chemical resistance and temperature performance.

The curing process involves a series of temperature steps up to ~260 °C. Depending on geometry and thickness, it may take  $\geq 18$  days to complete. Water is lost during curing but many resultant parts are near net shape. Some machining may be required to achieve tolerances or to add in certain features. Moulded or extruded parts can be machined like soft steel or acrylic resins. Wear surfaces may need to be re-cured after machining. Joining is possible via a range of mechanical techniques or with a range of adhesives. PAI can be insert-moulded with polyphthalamides; the amide chemistries allow the formation of a strong bond without the use of adhesives.

## 6.4 Applications

PAI is used in industrial, aerospace, chemical processing, semiconductor manufacturing, teletronics and laboratory equipment applications. Key benefits include high strength and rigidity, dimensional stability, environmental resistance, conformability, dimensional stability, wear performance, creep resistance, low CTE, impact resistance, lightweight *versus* metals and self lubrication (in some grades).

PAI has replaced aluminium in labyrinth seals in centrifugal compressors, offering greater reliability, increased efficiency and run times. Tighter clearances reduce leakage and increase compressor efficiency. Excellent wear properties and conformability are said to increase the lifetime by a factor of 2–3 over aluminium. Labyrinth seals can be very large (1.5 m across and 8 cm thick). At the other end of the size scale, and in spite of processing challenges, PAI has been precision micro-injection-moulded to produce tiny components for cardiovascular repair devices. The parts are much less expensive than machined metal components, and operate under load at high temperature and several thousand revolutions per minute.

Industrial applications include pump housings, compressor valve plates and motor end caps. Wear grades are used for various lubricated and non-lubricated bushings and bearings, thrust washers, wear pads, piston rings, slides, bearing sleeves, clutch rollers, and seals. Extruded thin-wall bearings can compete with bronze alternatives. High-speed sewing-machine bobbins operate at high temperatures without lubrication. Because of their lack of rigidity they have greater compliance, thus they are more forgiving than their stainless-steel counterparts. PAI have also been used to produce gears. Check balls provide excellent sealing surfaces without damaging metal components, and are used in automotive transmissions where they withstand high temperatures and pressures and hot transmission oil.

PAI aircraft clip nuts can be used to secure interior trim, flooring and fairings. They survive high torques and yet have sufficient elongation to clip easily into place. They are lighter than metal nuts and do not damage protective coatings on the metal structures. PAI has been used to replace titanium jet engine air return grills. Electronic applications include chip nests and sockets and electrical connectors.



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# 7 Polyimides

## 7.1 Introduction

The imide group appears in a very diverse range of polymers. These can be true thermoplastics, not melt-processable or even contain thermosetting functionality. Here we look at the ‘non-melting’ polyimides, which are typically formed by sintering processes. This can increase part cost. However, non-melting polyimides outperform thermoplastic materials in some types of applications. They offer excellent high-temperature and wear performance combined with radiation resistance and low outgassing.

## 7.2 Chemistry and Manufacturing

The generic reaction most often used to produce polyimides is shown in **Figure 7.1**. **Figure 7.2** shows various commonly used dianhydrides and diamines. In the first stage, a polyamic acid is produced by reaction in a polar solvent such as *N*-methylpyrrolidone. This is followed by a dehydration reaction which may be driven by a combination of heat, azeotropic agents (e.g., toluene) or chemical dehydrating agents (e.g., acetic anhydride combined with pyridine). The chemistry is extremely versatile,

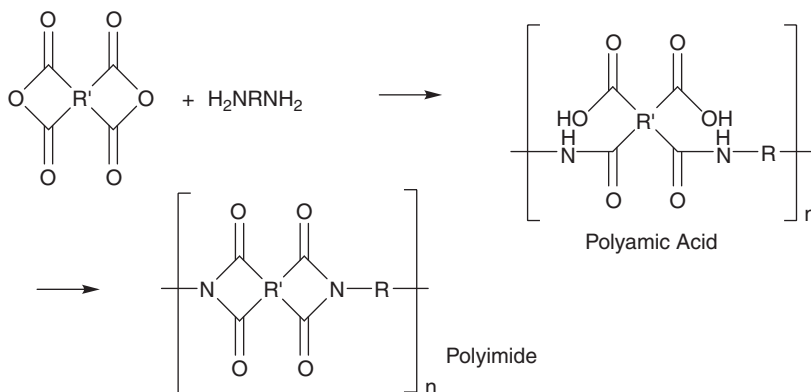


Figure 7.1 Generic synthesis of polyimides

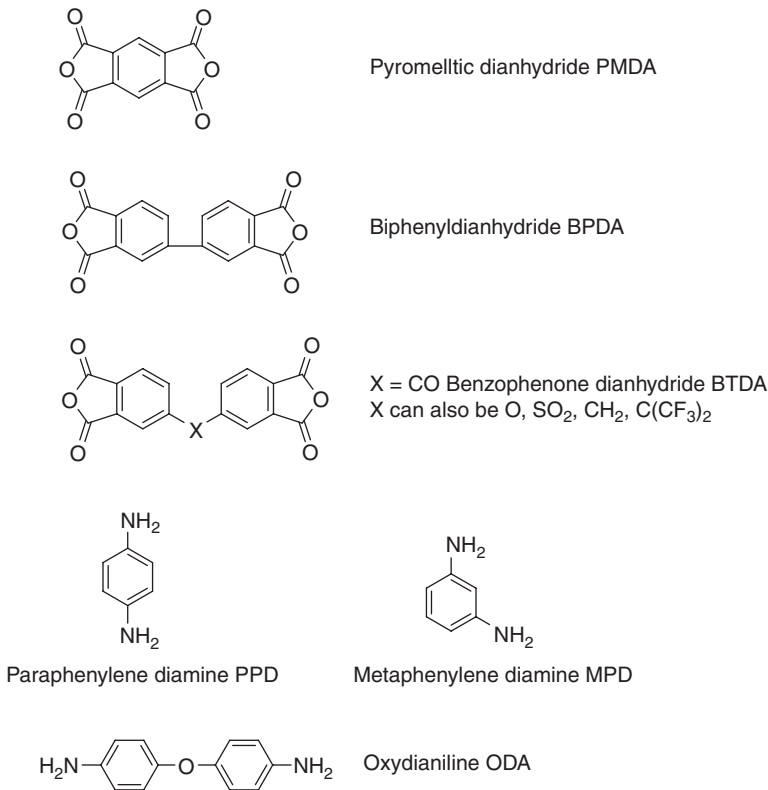


Figure 7.2 Dianhydrides and diamines

and a wide range of products can be made. Possibly the best known polyimide is Vespel, manufactured by DuPont, but other manufacturers include Evonik, Ensinger (Tecasint), Daelim (Plavis), Ube (Upimol) and Saint Gobain (Meldin).

The traditional grades of DuPont Vespel SP (and Kapton film) are made by the reaction of pyromellitic dianhydride (PMDA) with di(4-aminophenyl) ether (oxydianiline (ODA)). The reaction chemistry is described in the early patents [1–3] and is the basis of Vespel S.

Ube Industries produce two polyimides based on biphenyltetracarboxylic dianhydride (BPDA) with ODA to produce Upimol R or paraphenylenediamine (PPD) to produce Upimol S. The structures of these materials are shown in Figure 7.3. The PPD-based polymer lacks any flexibilising ether functionality and offers an especially high heat distortion temperature (HDT). It is easy to envisage that a range of properties could be obtained by using combinations of *p*- and *m*-phenylene diamines. Research continues into improved polyimides. For example, DuPont have filed patents on blends of polyimides derived from PMDA/ODA and BTDA/(PPD/

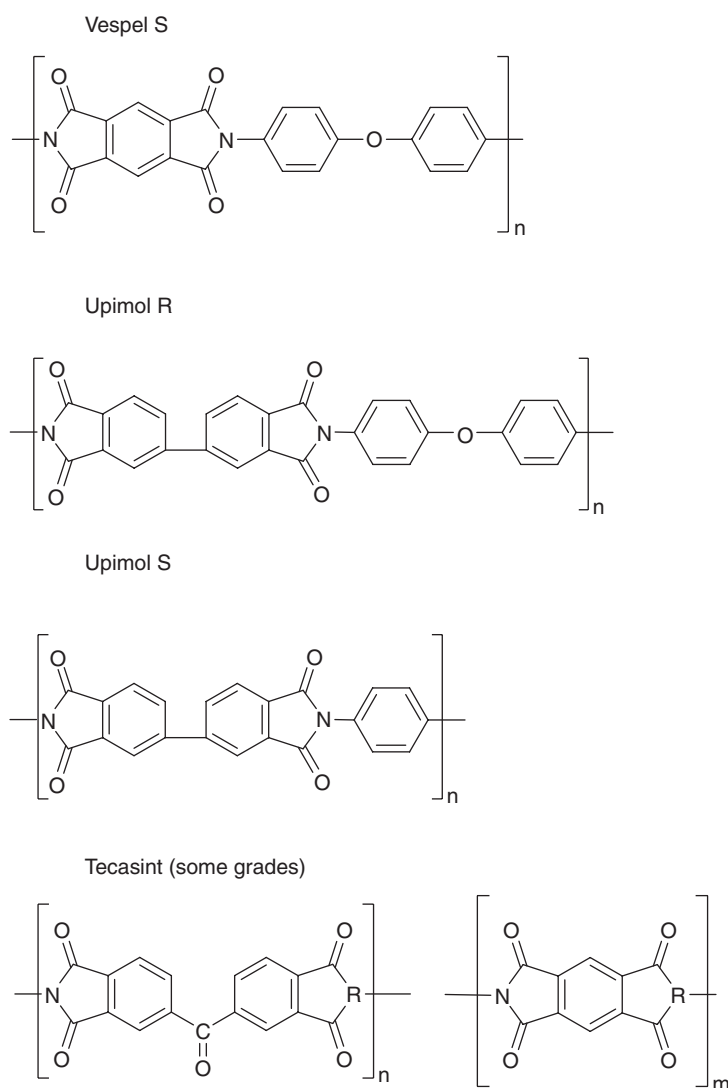


Figure 7.3 Structures of Vespel S, Upimol R, Upimol S and Tecasint (some grades)

MPD) which offer improved properties such as reduced moisture absorption [4]. Recently, DuPont introduced a higher-temperature Vespel polyimide, Vespel (SCP), which also has improved chemical and wear resistance and dimensional stability.

Ensinger produce a range of polyimide shapes, including copolymers with the general structure shown in Figure 7.3. Similar types of structures are described in the patent literature, which also shows how materials can be prepared from the reaction of diisocyanates and dianhydrides [5].

Polyimide chemistry is very versatile. As well as moulding compounds, they are also used in coatings, adhesives and as composite matrices. Examples include thermo-setting polyaminobismaleimides (e.g., Kinel) produced by the reaction of aromatic amines with maleic anhydride. These are crosslinked in the mould and can be compression-moulded, transfer-moulded or even injection-moulded with thermoset injection-moulding machines. The glass transition temperature ( $T_g$ ) may be  $\sim 300$  °C. Fluorinated polyimides (e.g., Avimid K, Avimid N) are used as matrices for continuous fibre-reinforced composites.

### 7.3 Properties and Processing

Table 7.1 shows the properties of some representative polyimides. Vespel SP is possibly the best known of this class of material, and it is a useful baseline for comparison with other polyimides. Vespel SP has no  $T_g$  or melting point ( $T_m$ ) below the decomposition temperature. It displays an almost linear decay of properties with temperature, and very low high temperature creep. The HDT is  $\sim 360$  °C. Vespel SP is 25–50% crystalline, whereas amorphous ST grades have higher toughness and little or no crystallinity. ST grades have about double the elongation of SP materials. Some Vespel parts can function continuously at 300 °C (340 °C in an inert atmosphere) with excursions up to 500 °C or at cryogenic temperatures. Filler systems include graphite and polytetrafluoroethylene (PTFE) or molybdenum sulfide. Wear performance can be excellent up to very high pressures and velocities. Outgassing is low (once water has been removed) and resistance to radiation is high, with little or no property changes observed up to 1000 MRad. Compliance can be higher than for a thermosetting material, which

Material	Vespel SP	Upimol R	Upimol S
Composition	PMDA/ODA	BPDA/ODA	BPDA/PPD
HDT, °C	360	Up to 360	Up to 500
Tensile strength, MPa	86	118	84
Tensile elongation at break, %	7	5	2
Flexural modulus, GPa	3.1	4.2	8.1
Notched Izod, J/m	80	75	20
Unnotched Izod, J/m	747	930	110
Coefficient of thermal expansion (CTE), $10^{-6}$ m/m/°C	54	57	47
LOI, %	53	-	-
Density, g/cm <sup>3</sup>	1.43	1.39	1.47

helps with sealing applications. Dimensional stability is limited by changes due to moisture absorption. Vespel SP is subject to hydrolysis, and cracking may occur in water or steam >100 °C. It is susceptible to attack by alkalis, strong acids and oxidising agents. It has good resistance to most many organic solvents, although some swelling and property reduction may be observed at elevated temperatures. The limiting oxygen index (LOI) is high (53%). Properties can be reduced after prolonged exposure to sunlight and weathering conditions.

Some polyimides can offer even higher heat resistance. DuPont recently introduced Vespel SCP. Upimol S (made by Ube) offers a HDT up to a remarkable 500 °C. Other polyimides have defined  $T_g$  (e.g., the  $T_g$  of Ensinger's Tecasint materials is 260–400 °C). The HDT gives only a 'snapshot' of high-temperature mechanical properties, and may not be quoted for very high temperature-performance materials. Plots of the modulus versus temperature can be particularly useful for comparing different polyimides, and are available from most suppliers on request.

This class of polyimides cannot be extruded or injection-moulded. Stock shapes can be made by isostatic (ISO) sintering, and direct formed (DF) parts are made to final near net shape and then sintered. In significant quantities, direct formed parts are significantly less expensive than machined parts. Direct forming and machining can be combined to produce high tolerance and complex components. Direct formed parts are produced with unidirectional pressure. This causes the tensile strength and elongation to be higher and thermal expansion lower in the plane perpendicular to the force than in the direction parallel with the force. Machined parts can offer better properties than those which have been direct formed. It is important to know which method was used to generate data and whether the same method will be used to make the proposed components.

## **7.4 Applications**

Polyimides are extensively used in high-temperature wear applications. Examples include thrust washers, sleeve bearings in transmissions, dry running piston rings, unlubricated vanes in vacuum pumps, bushings, wear pads in jet engines, exhaust gas systems, bushings, copier bearings, wire guides, and rollers. Low creep properties mean that they are also used in high-temperature valve seats and, if there are leakage problems, with metal seals at high temperature and pressure.

In aerospace applications, polyimides offer many metal-like characteristics but with lower weight, better friction, vibration damping and stealth characteristics than metals. Cast metal parts can often be converted to polyimide parts reinforced with various fillers and fibres. For example, engine tube clamps (which attach hydraulic, hot gas and electrical lines) survive extremes of temperature, saltwater and de-icing fluids. Aircraft wear applications include bushings, seals and shrouds.

Polyimides are used in the handling of hot glass. Parts benefit from low wear, low thermal conductivity, good impact performance, extreme temperature resistance and low oil absorption compared with carbon graphite alternatives. Enhanced product durability reduces downtime and overall manufacturing costs. Other high-temperature components include seals, bushings, bearings and insulators for a wide range of equipment from injection-moulding machines to welding torches.

In semiconductor processing, polyimides can offer high purity, low outgassing, low wear, high tolerances, temperature performance, as well as resistance to etching conditions, process gases and solvents. They are used in planarization retaining rings, vacuum pads, wafer clamping rings, bearings, insulators, wafer handling end effectors, wear strips, wafer guides, test holders and etch chamber components.

The low coefficient of thermal expansion (CTE) improves leak control in seal rings and reduces the chance of seizure of bearings. Hardness at high temperature, combined with a degree of compliance, allows polyimides to be used as covers for embossing rolls.

Polyimides can show low outgassing which is improved after gamma irradiation. They are used in vacuum applications with high levels of radiation as well as in satellites, radiation-resistant pipe seals and other components. Vespel literature has described the 'ideal' application as 'a sliding electromechanical component of an assembly which is exposed to radiation in a vacuum at a continuous working temperature of 315 °C'.

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# 8 Polybenzimidazole

## 8.1 Introduction

Polybenzimidazoles (PBI) offer exceptionally high thermal performance, stability, strength and fire resistance. In the most commonly produced version, the glass transition temperature ( $T_g$ ) is 427 °C, the limiting oxygen index (LOI) is 58%, and compressive strength ~400 MPa. PBI finds a wide variety of application in extreme environments. Unfortunately, pure PBI is not thermoplastic and has to be processed using techniques more familiar in powder metallurgy. However, melt-processable blends have been developed, and these can benefit from some of the exceptional properties of PBI.

## 8.2 Chemistry and Manufacturing

A wide variety of PBI-type materials can be made from the condensation of a tetrafunctional amine and an aromatic dicarboxyl compound (Figure 8.1). The reaction of most practical significance (Figure 8.2) takes place between tetraaminobiphenyl and diphenylisophthahlate. It produces the product commonly known as Celazole PBI from PBI Performance Products which was originally developed by Celanese and later by Hoechst Celanese. However, other PBI products are available. For example, a PBI-based polymer has been introduced by HOS-Technik in Austria and Gharda Chemicals produce two PBI materials shown in Figure 8.3 using a single monomer route from 3,4 diaminobenzoic acid or 3,4 diamino-4'- carboxydiphenyloxide (Figure 8.4).

For the purposes of this chapter, the PBI referred to is the product shown in Figure 8.2. It can be produced using a two-stage process [1]. The first stage, melt polymerisation,

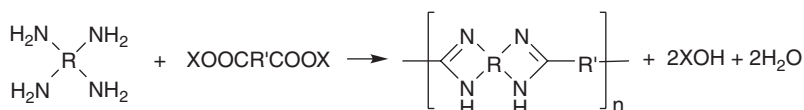


Figure 8.1 Two monomer route to polybenzimidazoles

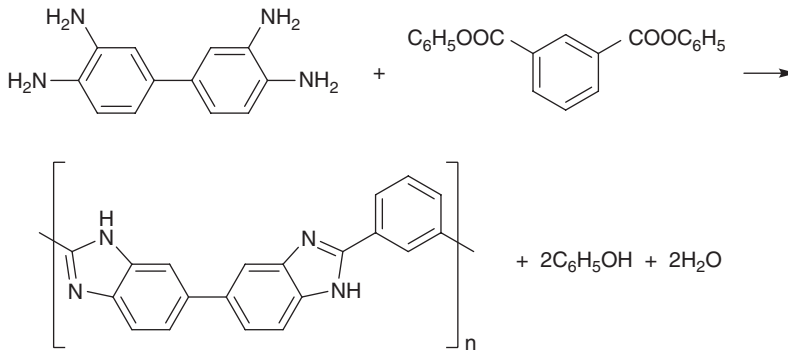


Figure 8.2 Route to celazole PBI

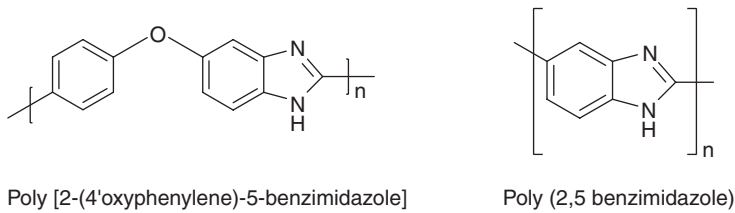


Figure 8.3 Polybenzimidazoles available from Gharda Chemicals

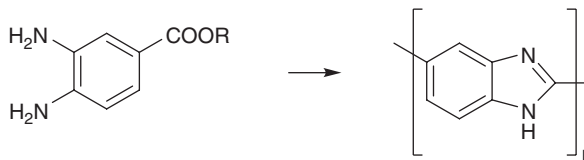


Figure 8.4 Single monomer route

takes place at 170 °C and yields a foamed prepolymer. This is cooled, pulverised and subjected to further polymerisation at higher temperatures. Several specific conditions are required to develop high molecular weight, which can be assessed by measuring solution viscosity in concentrated sulfuric acid.

The resulting polymer is extremely difficult to process; when it was first discovered, it was described as an 'intractable brick dust'. However, PBI is now available in stock shapes, fibres and injection-mouldable blends.

Compression moulding has been described in various patents. It can involve long cycle times as well as temperatures and pressures approaching 500 °C and 10,000 psi, respectively. [2]. However, it was subsequently discovered that water-plasticised

porous PBI powder can be compacted at room temperature before sintering using powder-assisted hot isostatic pressing. The porous powders are made by spraying PBI solutions into a 'mist' of non-solvent. They can be cold-compacted and then sintered in a graphite powder bed at 1–3 kpsi and 425–500 °C. The process is described in a series of patents [3–6].

PBI can be dissolved in dipolar aprotic solvents such as dimethylacetamide (DMAC), dimethylsulfoxide and *N*-methylpyrrolidone. Films, membranes, fibres and coatings can be produced from solutions containing ~26% PBI in DMAC. Lithium chloride is added to prevent gelation and can be subsequently washed out with water. In fibre production, DMAC is evaporated after the spinneret, and fibre properties further developed by hot drawing. Shrinkage in fire-resistant fabrics can be prevented by dipping the hot-drawn fibres in sulfuric acid to form an imidazolium salt.

A wide variety of PBI blends have been investigated. Blend constituents include polyetherimides, polysulphones and aramids. Sometimes these are made by solution blending before the formation of fibres or films. Blends with polyaryletherketone are important because they allow the creation of injection-mouldable PBI products. The blending methods range from simple twin-screw extrusion to the use of solvents and coupling agents [7–12]. Recently, this has been extended to include blends of polyetheretherketone (PEEK), PBI and polyetherimide (PEI) in which the  $T_g$  of the PEEK phase is increased by the presence of PEI [13].

### 8.3 Properties and Processing

The properties of PBI and various blends with PEEK are summarised in **Table 8.1**. Moulded PBI has a  $T_g$  of 427 °C and a heat distortion temperature (HDT) of 435 °C combined with exceptional compressive strength (400 MPa). Its outstanding chemical and thermal stability is derived from its aromatic 'stepladder' backbone. It can withstand temperatures of >700 °C for several minutes. It is extremely hard. PBI is said to retain useful strength to higher temperatures than polyimide or polyamideimide. The LOI is 58%. PBI is an ablative material leaving a mass of char after pyrolysis. The density of the base resin makes it a candidate for high-strength, low-weight applications. The coefficient of thermal expansion (CTE) is very similar to that of aluminium. According to specifications published on PBI stock shapes by Quadrant, grades of PBI can be resistant to alcohols, hydrocarbons, ethers, ketones and chlorinated solvents. However, resistance to acids and alkalis is limited. Presumably, hot aqueous acids attack PBI through reaction with the basic imidazole group to form the PBI-acid salt. PBI is available in high-purity and electrostatic-dissipative grades. Pure PBI components are made by the machining of shapes formed by the processes described in the previous section.

Material	PBI	PBI/PEEK	PBI/PEEK
	Unfilled	Unfilled	Carbon fibre
T <sub>g</sub> /°C	427	-	-
Melting point/°C	-	-	-
HDT/°C	435	-	-
Tensile strength, MPa	160	100	240
Tensile elongation at break, %	3	2.2	1.5
Flexural modulus, GPa	6.5	4.8	24
Notched Izod, kJ/m <sup>2</sup> (J/m)	(30)	25	25
Unnotched Izod, kJ/m <sup>2</sup> (J/m)	(590)	4	5
CTE, 10 <sup>-6</sup> m/m/°C	13–18	34	-
LOI, %	58%	-	-
Density g/cm <sup>3</sup>	1.3	1.3	1.4

Blends of PBI and PEEK combine the exceptional mechanical and thermal properties of PBI with the processability of PEEK. They provide high tensile strength and modulus as well as low creep even at temperatures up to 300 °C. These materials can be extruded or injection-moulded, although very high melt temperatures (450 °C) and mould temperatures (210 °C) may be required. Data available from PBI Performance Products compares the wear behaviour of lubricated PBI/PEEK blends with specific grades of PEEK, Torlon polyamideimide and Vespel polyimide (PI). PBI/PEEK and PI produced the best results. PEEK/PBI showed superior performance with consistently low wear factors, low coefficient of friction, and cool counter surface temperatures. Above certain speeds it was the only material to survive loads >2500 psi (although the grade of Vespel PI exhibited the highest absolute value of limiting pressure X velocity). Readers with extreme wear applications should contact suppliers for the most relevant data on their recommended grades. Nevertheless, the wear performance of PEEK/PBI is clearly exceptional.

## 8.4 Applications

PBI is an excellent material for thermal protective and sealing applications. It is used in the chemical process and oil industries where thermal stability and chemical resistance are key factors. Sealing applications include ball valve seats, hydraulic seals and backup rings. It is also used in thermal and electrical insulators, high-temperature electrical connectors, and in high-performance bearings and bushings. Rollers and pedestals for handling hot glass are made from PBI. It is used in insulating hot runner bushings for plastic-injection moulds; many molten plastics are said not to stick

to PBI. Excellent ultrasonic transparency means that PBI finds use in the probe tip lenses of ultrasonic scanning equipment.

Aerospace applications include missile nose cones, leading edge components and motor nozzles. PBI can also be used as a matrix for advanced composites which are prepared by impregnation with solutions of dimethylacetamide. The PBI matrix can be used as a precursor to carbon-carbon composites

PEEK/PBI is used to make compression vanes in high-rotation pneumatic tools. The vanes have exceptional wear resistance and modulus at high temperatures together with excellent resistance to oils and grease. The vanes were previously made from a phenolic thermoset which was more expensive and time-consuming to process and which required lubrication inside the compression chamber.

PBI components for gas plasma etching equipment are said to last longer than PI parts because of reduced rates of erosion. Purity and outgassing performance can be excellent. Applications for PEEK/PBI blends in the semiconductor industry include soldering tools, wafer transportation pods and chamber parts in spin-coating and etching processes. PEEK/PBI has been used to make end effectors ('hands') for robotic arms because of its high temperature resistance and strength together with low sloughing, high abrasion resistance and smooth surface finish.

PBI fibre does not burn in air, does not melt or drip and retains some flexibility and integrity even when charred. It is used in protective apparel for fire fighters and military personnel, aluminised crash rescue gear, aircraft fire blocking layers and wall fabrics, suits for racing car drivers, brake pads, rocket motor insulation and, if appropriate, as a substitute for asbestos fibre.

PBI-based membrane electrode assemblies are used in elevated-temperature polymer electrolyte membrane fuel cells.

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# 9 Thermotropic Liquid Crystalline Polyesters

## 9.1 Introduction

Thermotropic liquid crystalline polyesters (TLCP) can offer superb flow into thin sections coupled with zero flash, low coefficient of thermal expansion (CTE), low moisture absorption, high dimensional stability, high strength and stiffness, compatibility with lead-free soldering and low mould cycle times. Their properties are, however, anisotropic and they can suffer from limited weld line strength. They find applications in a wide range of fine, high-precision moulded devices.

## 9.2 Chemistry and Manufacturing

TLCP have unique properties because the molecules in the melt form ordered domains called micelles in which the chains are aligned in the same direction. This results from the rigidity of the molecules, which can be visualised by analogy as groups of tree logs floating down a river. The liquid crystalline state is intermediate between that of an isotropic liquid and a three-dimensional crystal. It is described as a 'mesophase' or 'mesomorphic structure' (from the Greek meaning 'intermediate form'). If the mesophase can be formed in solution the liquid crystal is said to be 'lyotropic', if it is formed by the action of temperature in the melt it is said to be 'thermotropic'. In the 'nematic' state the molecules are aligned parallel to one another along a common axis and exhibit one-dimensional order. In the 'smectic' state they also exist in layers and so have two-dimensional order. There are many types of liquid crystals but the ones of most importance in engineering plastics are main chain thermotropic polyesters which can be processed using conventional melt-processing techniques. (Some fibres such as Kevlar are solution-spun from lyotropic materials, but here we are less concerned with polymers used in high-performance fibres.) A given polymer can exhibit more than one type of mesophase depending on conditions such as temperature.

To form a liquid crystalline phase, a polymer must have a sufficient aspect ratio and a minimum rigidity. There are many varieties but they are sometimes classified into three basic types:

- I. Rigid, aromatic and linear
- II. Completely aromatic, rigid but containing crankshaft motions, side groups and/or kinks
- III. Semi-rigid containing flexible aliphatic spacers

Temperature performance and processing temperatures generally decrease in the order I>II>III. While it is useful, this is only a general classification, for example, some type-III TLCP can have improved heat resistance.

Manufacturers include Solvay (Xydar), Sumitomo (Sumikaexcel LCP), Ticona (Vectra and Zenite) and Toray (Siveras). The DuPont Zenite business was recently transferred to Ticona.

Some grades of Xydar are examples of type-I materials [1]. They can be produced from the polymerisation of biphenol, hydroxybenzoic acid (HBA) and terephthalic acid. Hydroxybenzoic acid alone cannot be used because the resulting polymer has a very high melting point ( $T_m$ ). Even with these comonomers the resulting all-*para* structure requires relatively high processing temperatures. **Figure 9.1** compares this type-I structure with the type-II materials that can be produced by the introduction of 2,6 naphthalene units based, for example, on hydroxynaphthoic acid (HNA), dihydroxynaphthalene or naphthadioc acid [2–4]. Vectra A is an example of a type-II material. HNA acts to disrupt the structure of the *para* oxybenzoyl units. This technique results in a lower heat distortion temperature (HDT), lower processing temperatures, and better flow properties. In a further variation, aminophenol can be added to produce polyesteramides. Type-III materials can contain aliphatic polyester units, giving improved flow but a lower HDT. For example, Unitika developed materials based on copolymers of polyethylene terephthalate and HBA [5–7].

As well as the classic structures presented here, the versatility of polyester chemistry allows the production of a wide range of structures. For example, more recent patents describe TLCP with repeat units derived from hydroquinone, terephthalic acid, isophthalic acid, 2,6 naphthalene dicarboxylic acid and HBA [8, 9]. Often these compositions are aimed at the use of lower-cost monomers as well as properties such as HDT and processing temperature. Some of the more recent patents provide summaries of the background with references to key historical patents [10].

The polymerisation reactions can be conducted using fairly typical polyester polycondensation chemistry. The reactants are usually acetyl derivatives of the hydroxyl compounds and dicarboxylic acids. These may be produced *in situ* by reaction with acetic anhydride. The reaction involves a progressive rise in temperature and reduction in pressure during which acetic acid is driven off the polymerisation mixture. If necessary, molecular weight can be further increased by solid-state polymerisation.



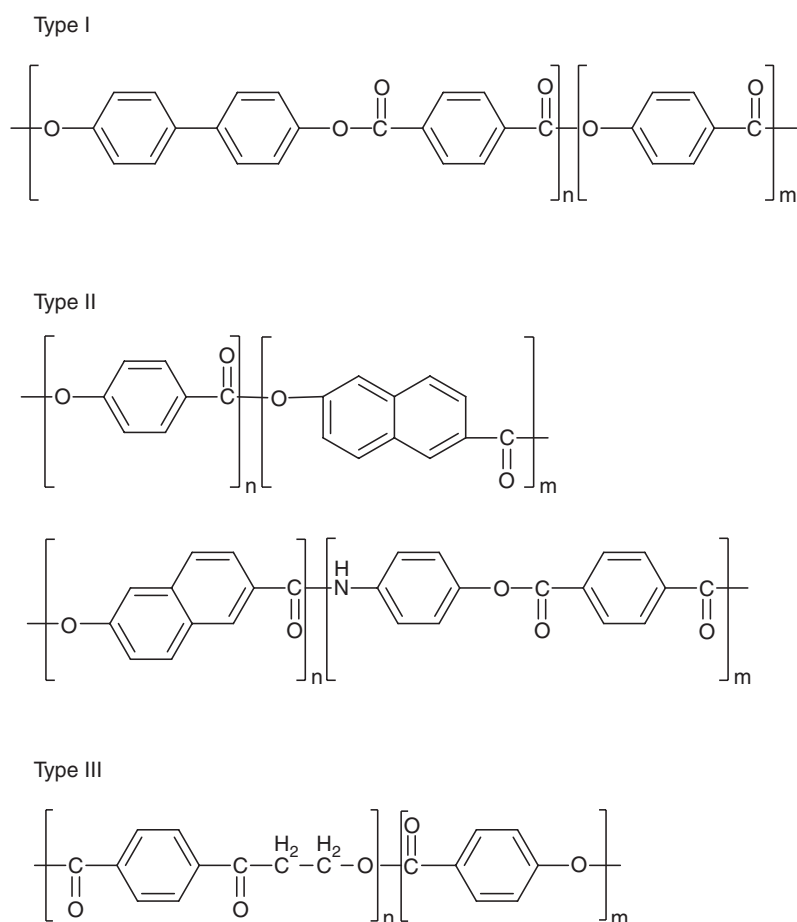


Figure 9.1 Examples of structures of TLCP

### 9.3 Properties and Processing

The mesomorphic structure has a profound effect on material properties. Under the action of shear and particularly tensile stresses, a very high degree of orientation can develop. TLCP mouldings have a much greater degree of orientation than conventional polymers. The melts are not particularly elastic, show extremely low die swell, and have low mould shrinkage.

This is in contrast to conventional polymers which are reluctant to orientate and will revert to the preferred random coil configuration once the orienting stress is removed. The reversion to random coils makes it difficult to obtain highly oriented components. Frozen in orientation results in frozen-in stress which can effect environmental resistance and cause lack of dimensional stability (especially at high temperatures).

Table 9.1 Properties of TLCP				
Material	Xydar	Vectra A	Vectra E	Vectra S
	30% Glass filled	30% Glass fibre	30% Glass fibre	35% Glass fibre
T <sub>m</sub> /°C	320	280	335	350
HDT/°C	271	235	276	340
Tensile strength, MPa	135	190	150	140
Tensile elongation at break, %	1.6	2.1	1.6	1.3
Flexural modulus, GPa	13.4	14.5	13.5	14.5
Notched Izod, kJ/m <sup>2</sup> (J/m)	(96)	24	20	14
Unnotched Izod, kJ/m <sup>2</sup> (J/m)	(430)	29	31	14
CTE/ 10 <sup>-6</sup> m/m/°C (flow/transverse)	3 to 7/40 to 80	6/23	7/20	1/23
Density g/cm <sup>3</sup>	1.60	1.62	1.61	1.67

Table 9.1 summarises the properties of some grades of TLCP. In general, TLCP offer many advantages, as shown below:

- Very high flow into thin sections (e.g., 0.15-mm walls in connectors)
- Very high modulus and tensile strength in the flow direction
- Short mould cooling times with no flashing
- Low moisture absorption and CTE (can be comparable with steel and ceramics), high dimensional stability
- High HDT (typically up to 340 °C, but some grades (e.g., type-III) are much lower)
- High continuous-use temperature (CUT) typically up to 260 °C, V-0 flammability, limiting oxygen index (LOI) typically up to ~50%, low smoke and toxic-gas generation
- High radiation resistance
- Low permeability
- Good chemical resistance (especially to organic solvents; polyesters are hydrolysed by acids and alkalis at elevated temperatures)

- Extremely low permeability to gases and water vapour
- High damping characteristics
- Low outgassing

Unfortunately this unique morphology also produces some important limitations. Mouldings tend to be highly anisotropic, have low weld-line strength, and fracture behaviour that resembles that of wood. This means that TLCP are ruled out in many applications, and tend to be used if their exceptional properties confer major advantages. In unfilled materials, rigidity in the transverse direction may be 30% of that in the flow direction. Properties can depend on wall thickness because thin walls cause a higher degree of orientation. In contrast to conventional polymers, anisotropy can be decreased by the addition of glass fibres. Injection-moulding grades are usually filled to reduce anisotropy, and the tendency of the oriented surface to fibrillate (i.e., fibrous surface layers start to peel off). Much effort has gone into developing grades with improved weld-line strength, and some limitations can be minimised by careful design of parts. Ultraviolet resistance is also limited.

TLCP can be processed using conventional methods such as injection moulding and extrusion. As with all polyesters, good drying is essential. Melt viscosities typically decrease continuously with increasing shear rate as a result of the nematic liquid crystalline structure of the melt. Very thin wall thicknesses can be achieved without flashing. In addition, low filling pressures allow the use of fine cores without positional distortion. When liquid crystalline polyesters (LCP) melt the melt maintains the high orientation of the solid phase. This relatively small change in the degree of order is associated with small energy flows which allow for faster cycle times. Process temperatures depend on grade but Vectra would typically be moulded using a melt temperature of 270–310 °C (higher for E and S series) and a mould temperature of 80–120 °C. Xydar might require a melt temperature of 320–360 °C and a mould temperature of 65–95 °C. High gloss finishes can be obtained. Surface finish tends to improve with higher mould temperatures. Grades are available for thermoforming, pipe and tube extrusion, coating of fiberoptic cables, and biaxial orientation. TLCP can be welded, adhesively bonded and metallised. In common with other materials, conductive paths can be directly deposited using techniques such as laser direct structuring. Low levels of TLCP can be used to reduce the viscosity of many other thermoplastics.

## **9.4 Applications**

TLCP components typically benefit from excellent flow into thin sections coupled with zero flash, low CTE, low moisture absorption, high dimensional stability, high strength and stiffness, and low mould cycle times.

TLCP components are compatible with a wide range of soldering technologies. However, the degree of resistance depends on the  $T_m$ , the HDT, and the loads on the component. Hence, grades of Vectra A resist soldering temperatures up to  $\sim 240$  °C, whereas the higher melting, higher HDT grades can operate at even higher temperatures. Lead-free solders can have temperature peaks  $\sim 270$  °C and here higher-temperature TLCP are often recommended. Correctly moulded TLCP components of the correct grade maintain their dimensional accuracy even after the soldering process.

Perhaps the best known applications of TLCP are various forms of fine, high-precision and dimensionally stable connectors. Ever-increasing degrees of miniaturisation create an increasing need for such products. These include mobile-phone connectors with 0.15 mm-thick walls, circuit board connectors, edge card connectors, central processing unit (CPU) socket connectors, secondary in line memory module card connectors, high-density interconnects, test socket connectors, heater plug connectors, miniature multimedia card readers, smart card readers, fiberoptic connectors and metallised interconnects. In mobile phones, TLCP find uses in SIM card connectors, input/output connectors, micro SD card connectors, flexible printed circuit board connectors, and also in housings for camera modules.

Applications also include base plates and lens holders in CD players, injection-moulded metallised mobile phone aerials, precision micro-moulded disc-drive components, electrostatic dissipative film guides, mobile phone frames, virtual-reality headsets, lead-free solderable relays, precision pushbutton casings, micro switches, components for night-vision scopes, miniature power convertor housings, tape drive chassis, surface mount relays, portable projector components, watch base plates, lamp sockets, microwave oven door panels, fuel cell components, sterilisable instrument trays, surgical staplers, skin stretchers, and precision needle-free syringes.

Mineral-filled TLCP are being increasingly used in thermoformed cookware such as muffin trays, oven plates and baking trays. Multilayer films can use the superb barrier characteristics of LCP in food- and non-food packaging applications. Various techniques, for example, involving rotating dies, have been developed to produce biaxially oriented film and tubing. Applications of tubes include endoscopic, laparoscopic and urological instruments which benefit from improved stiffness, compressive strength and crush resistance. There is increasing interest in the use of TLCP to produce flexible circuits.

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# 10 Polyphenylenes

## 10.1 Introduction

The polyphenylenes described in this chapter are marketed by Solvay under the trade name Primospire. They were originally developed by Maxdem in California, USA, and marketed as Parmax SRP. The technology was acquired by Mississippi Polymer Technologies in 2000 and then bought by Solvay. As of November 2010, Solvay suspended production of these very interesting materials but continue to research improved methods for their manufacture.

## 10.2 Chemistry and Manufacturing

The original key patent [1] describes a polyphenylene backbone substituted with organic groups. These groups enhance solubility and make it possible to reach high molecular weights. This gives rise to the type of polyphenylene structure often found in product literature (Figure 10.1). However, later patents [2, 3] describe more processable polymers that contain kinked and flexible segments. Phenylketone is a popular solubilising side group, 1,3 phenylene is a popular kinked unit and 1,4 (phenoxybenzoylphenylene) has been described as a main-chain flexible unit.

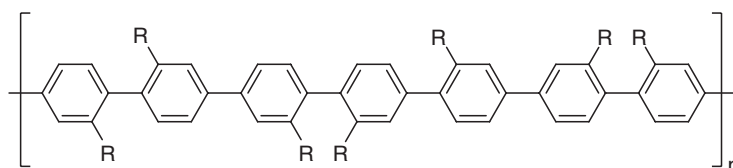


Figure 10.1 Generic polyphenylene structure

The patent literature discloses that the commercial material Primospire 250 is a copolymer of paraphenylene substituted with a phenylketone group together with an unsubstituted *m*-phenylene [4]. More rigid, less processable grades would probably have lower *m*-phenylene content. US 5976437 [3] describes how such a polymer might be made. The monomers are 1,3 dichlorobenzene and 2,5 dichlorobenzophenone,

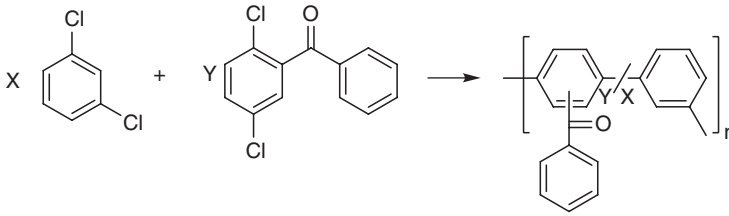


Figure 10.2 Synthetic route from US 5976437 [3]

both of which are relatively inexpensive (Figure 10.2). However, the coupling reaction takes place in *N*-methylpyrrolidone (NMP) in the presence of nickel chloride, sodium iodide, triphenylphosphine and zinc.

Blends can be used to improve the modulus of other polymers. Blends with Radel R [5] can be miscible, and partial miscibility is reported with polyaryletherketone [4]. Polyphenylene-reactive monomers have also been developed and incorporated into a range of different polymer types [6, 7]. This can potentially provide a generic method for improving a wide range of materials.

### 10.3 Product Forms, Properties and Processing

Typical properties are summarised in Table 10.1. The advantages of polyphenylenes are listed below:

- Very high strength and stiffness without reinforcement; they are often referred to as self-reinforcing polymers
- High compressive strength
- Outstanding mechanical performance in cryogenic conditions
- Inherent flame resistance (limiting oxygen index (LOI) ~50%), very low smoke emission and ablative performance
- Chemical resistance which is exceptional for an amorphous material, outperforming some crystalline materials in acids
- Isotropic performance and dimensional stability further enhanced by low moisture absorption, mould shrinkage and coefficient of thermal expansion (CTE)
- Transparent grades with exceptional surface gloss/mirror finish and aesthetics
- Do not have liquid-crystalline character and so do not show poor weld-line strength, transverse properties, compressive strength or a fibrillated structure



Table 10.1 Properties of polyphenylenes		
Material	PR120	PR250
	Compression and extrusion grade	Injection moulding and extrusion grade
Glass transition temperature ( $T_g$ )/°C	158	168
Melting point/°C	-	-
Heat distortion temperature (HDT)/°C	154	151
Tensile strength, MPa	207	152
Tensile elongation, %	-	10
Flexural modulus, GPa	8.3	6.0
Notched Izod (J/m)	43	59
Unnotched Izod (J/m)	1100	1600
CTE, $10^{-6}$ m/m/°C	30	31
LOI, %	49	55
Density $g/cm^3$	1.21	1.19

The material has a fairly low HDT and loss of properties above the glass transition temperature ( $T_g$ ; 158/168 °C) is a disadvantage. With reinforcement, other high-performance engineering plastics can match and exceed many of the properties of polyphenylenes. However, the disadvantages of such reinforcement with fibres can include:

- Anisotropy, tolerances and dimensional stability
- Inferior surface finish
- Contamination by reinforcement wear particles (key in medical applications and telecommunications and electronics)
- Abrasion due to fibres (especially glass)
- Magnetic resonance imaging (MRI) and X-ray imaging artefacts
- Lower elongation and impact performance
- Increased density (which might be critical in aerospace applications)
- Electromagnetic shielding effects

Despite the rigid rod character, these materials are not liquid crystalline. The typical weaknesses of liquid crystalline polyesters (LCP) (poor weld lines, poor transverse properties, poor compressive strength, fibrillated morphology) do not apply. Unfortunately, they also lack the low viscosity characteristics of LCP. However, grades are available for extrusion and injection moulding. For Primospire PR250, melt temperatures of ~350 °C are combined with mould temperatures of 130–145 °C. Slow-to-moderate injection speeds are recommended. The material is not subject to hydrolysis, but should be dried before use to avoid cosmetic defects. Primospire is readily machined.

## **10.4 Applications**

In electronics, high dimensional tolerance back end test sockets and probe cards can be machined from extruded plate to replace components made from ceramics. They have extreme dimensional stability and accuracy, wear resistance and moisture stability. Wafer handling components benefit from acid resistance, flatness and dimensional stability. Particle generation (helped by lack of fillers) is exceptionally low. Other applications include chemical mechanical polishing rings, etch chamber components, and transport devices.

Low density is an advantage for aerospace applications. Components can be injection-moulded or thermoformed. Radomes combine stiffness and rain erosion resistance while allowing optimum radio transparency and low weight. Ablative properties are used in rocket nozzles and missile shields. Other applications include lightweight fasteners and brackets.

Medical-grade polyphenylenes have been tested to International Organization for Standardization ISO 10993 and US Pharmacopeia USP Class VI, and can be sterilised with electron beams, ethylene oxide, gamma radiation and steam. The unfilled modulus is high, closer to bone than for many materials. Dimensional stability and stiffness mean that polyphenylenes are used in MRI scanner components and orthopaedic support and target devices. The excellent surface finish is a further advantage in medical environments. Catheters and laparoscopic tubes benefit from stiffness; longer, thinner catheters can operate without problems due to kinking.

Transparent film can be thermoformed and laminated, and offer excellent wear and scratch resistance. It can act as a fire barrier or be used to improve the scratch resistance of materials such as polycarbonate. The low CTE and high stiffness offer advantages in the development of circuits. Films can be oriented. There are several patents relating to the use of polyphenylene in fuel cell membranes.

Military armour applications benefit from high-speed impact resistance, low weight, stiffness and thermoformability.

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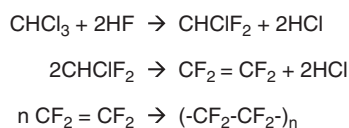
# 11 Perfluoropolymers

## 11.1 Introduction [1, 2]

Fluoropolymers are polyolefins in which some or all of the hydrogen atoms have been replaced by fluorine. Fully fluorinated structures (perfluoropolymers) can offer high-temperature performance combined with nearly universal chemical resistance. They are used extensively in chemical process and mechanical engineering equipment as well as specialist electrical applications. However, relative to the other materials described in this book, they are soft and tend to creep under mild conditions. The introduction of hydrogen into the backbone can improve mechanical properties but at the expense of continuous-use temperature (CUT), temperature performance and chemical resistance. Accordingly, only fully fluorinated polymers are considered in this chapter.

## 11.2 Chemistry and Manufacturing

Suppliers of perfluoropolymers include AGC, Arkema, Daikin, DuPont, Dyneon, and Solvay Solexis. Polytetrafluoroethylene (PTFE) was the earliest commercially available fluoropolymer. The monomer (tetrafluoroethylene (TFE)) is highly explosive. It is made by the thermal cracking of chlorodifluoromethane (itself made by the reaction of chloroform and hydrofluoric acid) at 800–1000°C. It is then scrubbed, dried, liquefied and purified by distillation. TFE is polymerised in an aqueous medium in the presence of free-radical initiators and surfactant-dispersing agents. The reaction takes place at relatively moderate temperatures but is extremely exothermic. The resulting size of the PTFE particle depends on the polymerisation conditions. With agitation but very small amounts of dispersing agents, a granular product is formed. Larger amounts of dispersing agents create aqueous dispersions which can produce agglomerates of fine PTFE powder or be concentrated to form aqueous dispersion products. The overall reaction is shown in **Figure 11.1**.

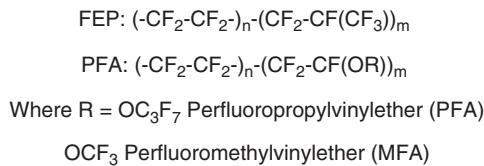


**Figure 11.1** Synthesis of PTFE

Many potential contaminants will degrade at PTFE processing temperatures. Isolation of the polymer is carried out under extremely clean conditions to develop optimum properties. Processes include washing, drying, granulating (for granular grades) and compounding (for filled grades). The polymer may be mixed with fillers such as short glass fibre, carbon fibre, powdered metal (e.g., bronze), graphite and molybdenum disulfide. Fine powder compounds can be produced by adding fillers to the aqueous dispersion followed by coagulation.

Low levels of comonomer are used to create improved 'second generation' PTFE [3, 4]. For example, <0.2 mol% of perfluoropropylvinylether can be used to reduce melt viscosity, improve fusion characteristics, weldability and mechanical properties as well as to reduce voids and creep.

Fluorinated ethylene propylene (FEP) and perfluoroalkoxy (PFA) are well-known melt processable copolymers of TFE with hexafluoropropylene and perfluoropropylvinylether, respectively [5]. However there are other important copolymers such as tetrafluoroethylene/perfluoromethylvinylether copolymer (MFA) which has a lower melting point ( $T_m$ ) than PFA. General structures are shown in **Figure 11.2**. Polymerisations can be undertaken in aqueous or organic media. There has been considerable interest in the use of supercritical carbon dioxide as a more economic and environmentally friendly alternative.



**Figure 11.2** Structures of FEP and PFA

### 11.3 Structure–property Relationships in Perfluoropolymers

Melting point, CUT, strength and modulus (including for some partially fluorinated systems) are summarised in **Table 11.1**. It is useful to understand why the different perfluoropolymers have specific properties.

Fluorine is a larger atom than hydrogen. In PTFE, the fluorine atoms form a close-packed 'protective spiral' around the carbon backbone. The result is a rigid, non-polar, highly crystalline structure with very weak interchain interactions. Accordingly, PTFE has a low coefficient of friction and is markedly weak and soft. A very high molecular weight (~1,000,000 g/mol) is required to develop sufficient chain entanglement for optimum mechanical properties; this limits melt

Table 11.1 Thermal properties of fluoropolymers

	$T_m/^\circ\text{C}$	CUT/ $^\circ\text{C}$	Heat distortion temperature (HDT)/ $^\circ\text{C}$	Density $\text{g}/\text{cm}^3$
Fully fluorinated				
PTFE	327	260	49	2.13–2.19
FEP	277	204	-	2.12–2.17
PFA	310	260	-	2.12–2.17
Partially fluorinated				
Ethylenetetrafluoroethylene (ETFE)	271	150–180	71	1.7
Ethylenechlorotrifluoroethylene (ECTFE)	238	150–180	63	1.68
Polyvinylidene fluoride (PVDF)	138–160	130	38–115	1.76–1.78
<i>Reproduced with permission from D. Kemmish, High Performance Engineering Plastics, Rapra Review Report 86, Smithers Rapra Technology Ltd, Shawbury, Shrewsbury, UK, 1995. ©1995, Smithers Rapra Technology Ltd</i>				

processability. The  $T_m$  is high and even melt-processed material can approach 70% crystallinity. Chemical resistance is excellent because it is very difficult to disrupt the highly crystalline, non-polar structure. The C-F bond is very strong and oxidative stability is excellent.

It is temperature performance and chemical resistance that qualify perfluoropolymers to be counted among the high-performance engineering plastics. The relatively poor mechanical properties can be improved by the introduction of hydrogen atoms. The chains are now polar and interchain electrostatic interactions improve mechanical performance. However, this is at the expense of the CUT,  $T_m$ , and chemical resistance.

FEP typically contains a  $\text{CF}_3$  side chain at 10–12%. This allows chains to lock together and develop mechanical properties at lower molecular weight, thereby improving melt processability. The  $T_m$  is lowered because the side groups disrupt the crystalline structure and reduce the size and perfection of crystals. Unfortunately, the steric stress introduced by bulky  $\text{CF}_3$  side groups also facilitates oxidative degradation processes, and the CUT is lowered.

The PFA comonomer is used at a lower level than the FEP comonomer, so the reduction in  $T_m$  is less. This is possible because the side chains are longer and therefore lock together more effectively than in FEP. Steric stress is reduced by the presence of an oxygen spacer, so the CUT is equivalent to that for PTFE.

## 11.4 Properties and Processing

**Table 11.2** summarises the properties of PTFE, FEP and PFA. PTFE melts at 327°C and has a CUT of 260°C. At lower temperatures, density changes associated with other transitions need to be considered. Transitions are reported at 19, 30 and 90°C.

Table 11.2 Properties of perfluoropolymers				
Material	PTFE	PTFE and glass fibre	FEP	PFA
Tensile strength/MPa	20–35	25	23	25
Tensile elongation %	300–500	300	300	300
Flexural modulus/GPa	0.5	1	0.6	0.6
Hardness (shore D)	60	70	55	60
Coefficient of expansion 10 <sup>-6</sup> m/m/°C	100	100	90	-
Limiting oxygen index %	>95	>95	>95	>95
Density g/cc	2.13–2.22	2.25	2.15	2.15
CUT/°C[en]Tm/°C	260 327	260 327	204 260	260 310

*Note: The properties of fluoropolymers can vary widely according to grade, composition and processing methods. The numbers in this table are indicative only. Specific grades can have numbers outside these ranges.*

The mechanical properties of PTFE are poor for an engineering polymer, closer to what might be expected of polyethylene. Creep (perhaps more aptly described as ‘cold flow’) occurs at room temperature and at fairly low loads. The HDT is not often quoted, but is ~85°C for even glass-filled PTFE. Fillers can reduce creep and improve impact performance and wear resistance. At >200°C, the effect of reinforcement almost disappears. The difficulties associated with PTFE processing mean that mechanical and permeation properties are very much a function of process conditions and variations in the resultant product features (e.g., microporosity). Accordingly, ranges may be quoted for many mechanical performance and permeation values.

The chemical resistance of PTFE is superb, often described as ‘almost universal’. However, according to literature from WL Gore, it is attacked by metallic alkali metals, fluorine, metal hydrides (at high concentration) and amines and imines at high temperatures. Swelling may be an issue in certain environments (e.g., fluorinated hydrocarbons). Ultraviolet resistance is excellent but resistance to hard radiation is



poor. Indeed, irradiation is used to reduce molecular weight and to create grades which can be ground to fine powders. Such low-molecular-weight fine powders are often produced from recycled PTFE and used as additives in other engineering thermoplastics to improve friction and wear properties. If a minor percentage (typically 10%) of fine powder is added to engineering plastics, there is a marked improvement in wear characteristics because of reduction in interfacial friction. This is because PTFE forms a continuous coating at the sliding interface, dramatically reducing friction and heat build-up. As would be expected for a weak and soft material, the abrasion resistance of PTFE is poor. It can be improved by fillers (including harder engineering plastics such as polyphenylenesulfide and polyetheretherketone).

FEP and PFA have generally similar environmental resistance to PTFE. FEP has a lower  $T_m$  ( $\sim 277^\circ\text{C}$ ) and CUT ( $\sim 204^\circ\text{C}$ ); the exact values will depend on the copolymer composition. PFA has a  $T_m$  of  $310^\circ\text{C}$  and a CUT of  $260^\circ\text{C}$ . They are stiffer with a lower tendency to creep. Both materials exhibit generally low permeability. Conventional melt processing means porosity is often much lower than in PTFE, leading to further relative improvements in mechanical performance and permeability.

Dielectric and insulating properties are generally excellent. Perfluoropolymers do not support combustion but will degrade in fire situations to produce toxic and corrosive products.

Unlike FEP and PFA, PTFE is not melt-processable using conventional thermoplastic techniques (although some recent patents have described melt-processable forms) [6]. When PTFE melts, it becomes gel-like and retains its shape because of its exceptionally high molecular weight. Even at  $380^\circ\text{C}$  the viscosity is orders of magnitude higher than that for other high-temperature plastics.

The methods used to process PTFE are similar to those used in powder metallurgy. The polymer is shaped into a preform at room temperature, sintered at  $340\text{--}380^\circ\text{C}$ , and then cooled under strictly defined conditions. In ‘pressure sintering’, pressure is applied during sintering. In ‘free sintering’, sintering is undertaken after the initial application of pressure. Free sintering is cheaper but produces a more porous product. In solid phase forming preforms in the gel state are shaped under pressure in a mould. Film and sheet can be produced by using a sharp knife to cut (‘skive’) a continuous film or sheet from a rotating PTFE billet. Ram extrusion can be used to produce profiles. In paste extrusion, PTFE powder is mixed with lubricants and then forced through a cold die. The lubricant is then evaporated and the product sintered. Typical paste-extrusion product forms include wire insulation, tubes and tape. Aqueous dispersions can be used for coating and impregnation (e.g., to produce PTFE-impregnated fabrics). Unfortunately, PTFE degrades at processing temperatures to produce toxic products, and appropriate containment and extraction equipment is required.

FEP is quite viscous and processing temperatures are limited by thermal stability. It is more often extruded than injection moulded. PFA can be processed by extrusion, compression, blow, transfer and injection moulding. MFA has a lower  $T_m$  than PFA, and some types can be used as a cost-effective replacement for FEP.

## **11.5 Applications**

PTFE is used because of its high temperature performance and excellent environmental resistance. It is weak and much more frequently used in compressive applications than those that involve tensile or flexural loads.

PTFE is used extensively in chemical process equipment. Applications include tank and pump linings, gaskets, valve and pump components, seals, bellows, hoses, expansion joints, pipes, and pipe linings. Under heavy loads, gaskets will usually be recessed in a groove to prevent creep. 'Second generation' modified PTFE offers lower creep and permeability.

A remarkable range of PTFE fibres is available. WL Gore have developed PTFE fibres with a very wide range of stiffness and strength properties. Applications include hot gas and chemical filtration, bearings, gaskets, marine awnings, conveyor belts, release fabrics and dental floss. The fibres can contain reactive ingredients such as catalysts. Fibres can also be used to increase the bending fatigue life of high-performance ropes.

In mechanical engineering, PTFE is used in seals, bearings and piston rings. Bearings and piston rings take advantage of the low coefficient of friction and the absence of a stick-slip effect (the static and dynamic coefficients are equal). PTFE film can be inserted into recesses in bushings and shafts to provide a film bearing. However, temperature performance is limited by creep regardless of the high  $T_m$  and CUT. Composite bearings can make use of PTFE. For example, the polymer may be embedded in a porous layer of steel-backed sintered bronze. Some bearings can be extremely large (e.g., bearing plates for bridges).

PTFE has various specialised electrical applications which make use of properties such as the CUT,  $T_m$ , chemical resistance, low water absorption, dielectric strength, low polarisability and low coefficient of friction. Examples include measurement probes, cables for safety systems and switchgear. High-voltage circuit breakers combine insulation with resistance to thermal erosion and high voltage arcing. High-dielectric strength, low-dissipation factor, low-flammability PTFE films are used as insulation in motors, transformers, relays and switches. PTFE is used as insulation for electronic equipment in computers and aircraft, and for wrapping coaxial cables.

Two famous consumer applications of PTFE are non-stick coatings and the expanded microporous PTFE made by WL Gore. Coatings applied with aqueous

dispersions tend not to be used for corrosion protection because of the presence of micro voids.

FEP is extensively used in extruded wire insulation. Low dielectric loss is especially important for data transmission, and this can be further improved by foaming. It is used in the chemical process industry in a similar manner to PTFE, including pipe linings, heat exchangers, tower packing and components for valves and pumps. Injection mouldings and extruded shapes make use of toughness, relatively high use temperature and chemical resistance. MFA can be used as a cost-effective replacement for FEP in some applications.

PFA is used to produce injection-moulded silicon wafer carriers and other equipment for the production of silicon-based devices. As a perfluoropolymer, it can survive in environments where other wafer carrier materials (e.g., polyaryletherketone) would fail. High-purity grades are available, and this increases the device yield, easily justifying the use of expensive materials. Other applications in the semiconductor industry include pumps, pipes, fittings, filtration and tubing. PFA can also be extruded, blow-moulded and compression-moulded. It is used for the insulation of wire and cable, including sensor wiring for use in extreme environments such as chemical process plants or oil wells. PFA tubes used in power plant flue gas heat exchangers have shown remarkable lifetime and ageing performance. Chemical process applications include column packing, pumps, pipes and tanks. Over-braided hose constructions have replaced rigid metal pipes in fuel, lubrication and cooling systems. In film form, its resistance to weathering, optical clarity and moisture barrier properties mean that it finds use as a photovoltaic front sheet.

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# A bbreviations

BPADA	Bisphenol A dianhydride
BPDA	Biphenyldianhydride
CT	Computed tomography
CTE	Coefficient of thermal expansion
CUT	Continuous use temperature
DCDPS	Dichlorodiphenylsulfone
DMAC	Dimethylacetamide
DMTA	Dynamic mechanical thermal analysis
DSC	Differential scanning calorimetry
ESC	Environmental stress cracking
FAA	US Federal Aviation Administration
FDA	US Food and Drug Administration
FEP	Fluorinated ethylene propylene
FTIR	Fourier transform infrared spectroscopy
GPC	Gel permeation chromatography
HBA	Hydroxybenzoic acid
HDT	Heat distortion temperature
HNA	Hydroxynaphthoic acid
ISO	International Organization for Standardization
LED	Light-emitting diode
LOI	Limiting oxygen index
LCP	Liquid crystalline polyester
MFA	Tetrafluoroethylene/perfluoromethylvinylether copolymer
MFI	Melt flow index
MPD	Metaphenylene diamine
MRI	Magnetic resonance imaging
MS	Mass spectrometry

## Abbreviations

NMP	N-methylpyrrolidone
NMR	Nuclear magnetic resonance
ODA	Oxydianiline
OSU	Ohio State University
PA	Polyamide
PAEK	Polyaryletherketone
PAES	Polyarylethersulphone
PAI	Polyamideimide
PBI	Polybenzimidazole
PEEK	Polyetheretherketone
PEI	Polyetherimide
PEK	Polyetherketone
PEKEKK	Polyetherketoneetherketoneketone
PEKK	Polyetherketoneketone
PES	Polyethersulfone
PFA	Perfluoroalkoxy
PI	Polyimide
PMDA	Pyromellitic dianhydride
PPA	Polyphthalamide
PPD	Paraphenylenediamine
PPS	Polyphenylenesulfide
PPSU	Polyphenylsulfone
PSU	Polysulfone
PTFE	Polytetrafluoroethylene
RTI	Relative thermal index
TFE	Tetrafluoroethylene
T <sub>g</sub>	Glass transition temperature
TLCP	Thermotropic liquid crystalline polyester/polymer
T <sub>m</sub>	Melting point
TMA	Trimellitic anhydride acid
UL	Underwriters Laboratories
USP	United States Pharmacopeia
USPTO	United States Patent and Trademark Office
UV	Ultraviolet

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High performance engineering plastics are used in a vast range of applications and environments. They are becoming increasingly important because of trends towards more reliable and higher performance machines and devices.

This book aims at the development of a working knowledge and understanding of high performance engineering plastics. It starts with a simple, practical overview of key properties and principles. In each of the chapters there are sections on production chemistry, product forms, properties, processing and applications. There is a strong bias towards materials and concepts which are used in practice. The materials covered include high performance polyethersulfones, polyetherimides, polyphthalamides, polyphenylene sulfide, polyaryletherketones, polyamideimides, polyimides, polybenzimidazole, liquid crystalline polyesters and perfluoropolymers.

The reader will develop the ability to understand why materials are chosen for certain applications, why those materials have particular properties and how those properties can be modified. This will facilitate conversations with both materials suppliers and end users. It will help to identify the best and most cost effective solutions.



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