

Introduction to Polymers and their Important Properties for Electronic Applications

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1.1 INTRODUCTION TO POLYMERS AND THEIR PROPERTIES

The word plastic has its origins in the Greek language where 'plastikos' meant to form or shape. Today plastic has a number of meanings but the one which best fits the description of materials detailed in this work is that referring to any of various substances which harden and retain their shape after being moulded or formed by heat and pressure. This description is still rather broad, covering a large number of materials including many such as tar, clay and even mud which do not really agree with our current perception of a plastic. In order to qualify the word plastic, a more accurate description would be synthetic plastic, since this eliminates the naturally occurring materials that have plastic properties and only includes those derived by chemical means from relatively simple raw materials. Plastics are thus man-made polymers where the word polymer is an abbreviation of the two words poly and monomer and literally means many monomers. It should also be noted, however, that the word plastic is generally taken to refer to thermoplastic materials and therefore does not include thermosetting materials. Consequently, in this revision of the original chapter the word polymer will generally be used unless the reference is specifically to a thermoplastic material.

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During the nineteenth century much interesting work was performed on polymeric materials beginning with the vulcanization of rubber in 1839 and also including the development of nitrated cellulose (celluloid) in 1868. It was not until after the turn of the century that the first commercially successful fully synthetic polymer was produced. This was Bakelite made from phenol and formaldehyde by Leo Baekeland in 1909. Before the end of the 1920s a large number of other synthetic polymers had been created, notable examples being the development of polyvinyl chloride in 1927 and urea formaldehyde in 1929. Today there are literally hundreds of synthetic polymers commercially available with ranges of properties making them suitable for applications in many industries including the electrical and electronics industries. For every material commercially available, many more have been synthesized, examined and discarded as of no present use for various technical or economic reasons. The year of introduction and typical electronics applications for various polymers are shown in Table 1.1.

Much of the driving force behind the development of many modern polymeric materials came from the electrical and electronics industries, largely because of the numerous areas for application in electrical and

Table 1.1 Year of introduction and uses for various plastics

<i>Year</i>	<i>Material</i>	<i>Application</i>
1909	Phenol-formaldehyde	Equipment cases
1927	Polyvinyl chloride	Wire and cable insulation
1938	Polystyrene	Capacitor dielectrics
1942	Polyethylene	Capacitor dielectrics, wire insulation
1947	Epoxides	Adhesives, potting and moulding compounds, printed circuit boards
1957	Polypropylene	Capacitor dielectrics, wire insulation
1964	Polyimide	Dielectrics, die attach adhesives, printed circuit boards
1965	Polyxylylenes	Insulation, conformal coatings
1975	Polymethyl pentene	Microwave components, cable dielectrics
1982	Polyether imide	High reliability chip carriers, moulded interconnect devices (MIDs)
1984	Liquid crystal polymers	Connectors, switches, fibre optics
1988	Polyetherketoneketone	Injection moulded substrates
1990s	Polypyrrole (ICP)	Direct plate processes

Table 1.2 Typical applications for polymers in the electronics and electrical industries

Integrated circuits, transistors, diodes and other discrete devices	Transfer moulding compounds, injection moulding compounds, casting, potting, dip and powder coating compounds, die attach adhesives, photoresists, intermetal dielectrics, junction coatings.
Wires and cables	Sleeving, coatings, varnishes.
Connectors	Transfer moulding, injection moulding, compression moulding compounds.
Hybrids	Conductive and non-conductive adhesives, sealants, conformal coatings.
Transformers, coils, bushings	Transfer moulding compounds, coatings, potting compounds, coil impregnants, wire insulation.
Printed circuit boards	Laminates, conformal coatings, solder masks, masking tapes, component attachment adhesives, vibration dampers, photoresists and direct plate processes. Moulded interconnect devices.

electronic components. Typical applications for polymers in the electronics and electrical industries are shown in Table 1.2.

The principal reasons for this popularity are that polymers are generally inexpensive, readily shaped dielectric materials with easily controlled physical, mechanical and electrical properties. A typical radio manufactured 50 years ago would almost certainly have had a case made from a dark brown 'Bakelite' type phenolic resin and inside this would be components covered in a variety of strong-smelling sticky waxes or bituminous materials. Since then steady improvements in technology have paved the way for a huge selection of materials to be manufactured that are used in electronics applications unimaginable in the 1950s. Today, polymers are used throughout all parts of the electronics industry from the manufacturing processes to the final packaging as well as in the individual microcircuits themselves. Some further applications for polymers in electronic and electrical component manufacture are shown in Table 1.3.

Polymeric materials are used as the basis of photoresists for making metallization patterns on printed circuit boards, and also on the individual integrated circuit devices themselves. The circuit boards are typically made of various glass-fibre or paper filled epoxides and phenolics, and are usually coated with other polymeric materials such as photoresists and solder masks to facilitate the final stages of board manufacture and subsequently to protect the assembled board in service. One major recent innovation is the use of intrinsically conducting polymers as the conductive species in so-

Table 1.3 Uses for polymers in electronics and suitable materials

<i>Use</i>	<i>Suitable materials</i>
Transfer moulding	Epoxides, silicones, phenolics, polyimides.
Injection moulding	Polyethylene, polypropylene, polyphenylene sulphide. ABS, ABS/polycarbonate, polyetherimide.
Encapsulation/casting	Epoxides, polyurethanes, silicones.
Adhesives	Epoxides, polyimides, cyanoacrylates, polyesters, polyurethanes.
Coatings	Silicones, fluorocarbons, epoxides, polyxylylenes, polyurethanes, polyimides.
Films	Polyesters, polypropylene, polystyrene, polyimides.
Sealants	Silicones, polysulphides, polyurethanes, epoxide-polyamides, fluoro-silicones.
Substrates	Epoxides, polyimides, cyanate esters, engineering thermoplastics.
Photoresists	Epoxides, novolacs, butadienes, acrylates.

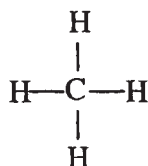
called direct plate processes which enable electroplating of through holes in multilayer printed circuit boards. The devices that are mounted on the completed printed circuit boards may have been manufactured using polymeric photoresists or have polymers such as polypropylene and polyester films in capacitors or epoxide resins in integrated circuits and transistors. The completed boards containing various devices are often then coated in another protective polymer if a harsh service environment is likely to be encountered.

Finally, electrical connections are made with wires coated in one of several polymers and the finished circuitry is often housed in an attractive case. Polymers can thus be seen to play an important role throughout all parts of the electronics and electrical industries' manufacturing process from the initial fabrication of devices to their final packaging.

1.2 CHEMISTRY OF POLYMERS

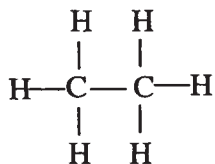
Polymers are different from the majority of simple inorganic and organic molecules commonly encountered in that they typically have very large molecules with molecular weights sometimes exceeding one million. Even though these molecules are big, they can be defined by the basic repeat unit that forms the polymer chain. Many of the overall properties of a particular type of polymer will be a direct result of the individual atoms and the way they are arranged in the repeat unit. One of the most important atoms in

polymer chemistry and indeed in all organic chemistry is the carbon atom. In polymer chemistry carbon is the atom that forms the basis of the main structural chains found in most polymer molecules. Carbon has a valency of four, which simply means that it has four sites at which it can combine with other elements. If a single atom of carbon combines with four atoms of hydrogen the gas methane is formed:

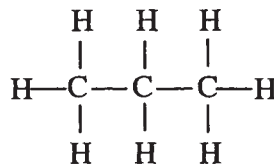


Methane (CH_4)

Carbon can combine with many other elements besides hydrogen and importantly can also form bonds with itself. Examples of carbon atoms combined with other carbon atoms and hydrogen atoms are the alkanes, such as ethane and propane, where two and three carbon atoms are joined together, respectively, and the rest of the unoccupied sites are used to combine with hydrogen atoms:

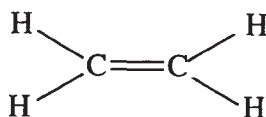


Ethane (C_2H_6)



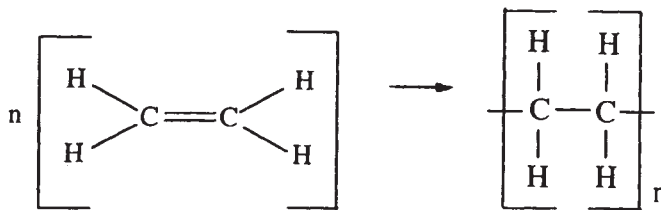
Propane (C_3H_8)

One of the key features of carbon which can ultimately lead to the formation of polymers is its ability to form multiple bonds with itself. For example, in the molecule ethylene (C_2H_4) there are not enough hydrogen atoms to occupy all of the available bonding sites and so the carbon atoms form a double bond between themselves



Ethylene (C_2H_4)

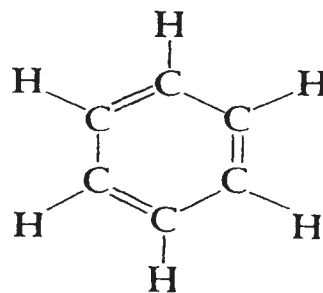
These double bonds are very reactive and under the right conditions ethylene molecules can polymerize in a chain reaction to form a long linear molecule of ethylene:



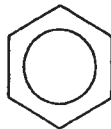
Ethylene

Polyethylene

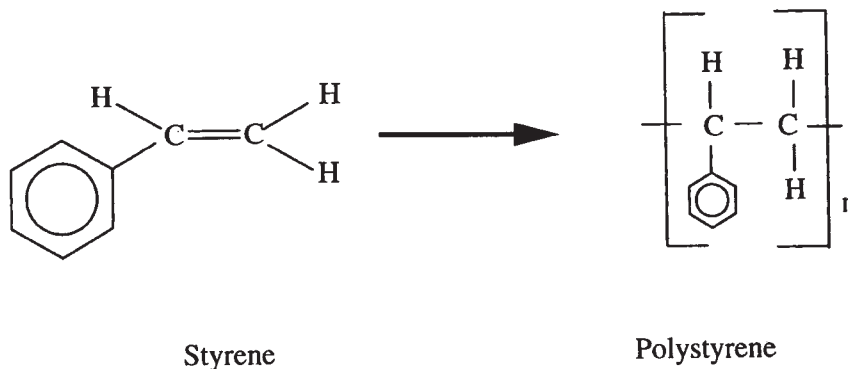
Carbon also has the capability of forming ring structures containing various numbers of carbon atoms; the simplest molecule containing six carbon atoms in a ring structure is benzene:

Benzene (C_6H_6)

For simplicity, the benzene molecule is drawn as a hexagon with a circle representing the double bonds between the carbon atoms:



If one of the hydrogen atoms of an ethylene molecule is replaced by a benzene ring the compound styrene is formed. Styrene can also be polymerized by reacting the carbon-carbon double bond of the ethylene part of the molecule to give polystyrene:



In addition to the substitution of one of the hydrogen atoms of ethylene with a benzene ring there are several other substituents that can be used and these lead to the formation of various well-known polymers:

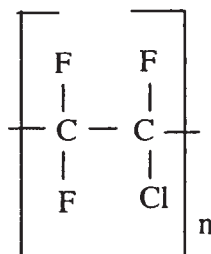
<i>Substituent</i>	<i>Resulting polymer</i>
-H	Polyethylene
-CH ₃	Polypropylene
-Cl	Polyvinyl chloride
-CH ₂ -CH ₃	Polybutylene
-OH	Polyvinyl alcohol
-C≡N	Polyacrylonitrile
-OOC-CH ₃	Polyvinyl acetate

These are known as polymers derived from vinyl monomers and the word vinyl refers to an ethylene molecule with one of its hydrogen atoms replaced with another atom or molecule. There is no reason why only one of the four hydrogen atoms can be replaced and it is quite normal to replace more than one of these atoms. When two atoms are replaced the resultant polymers are said to be derived from vinylidene monomers, where vinylidene refers to an ethylene molecule with two of its hydrogen atoms replaced with other atoms or molecules. When two hydrogen atoms are replaced they are both from the same carbon atom of the ethylene molecule. Some examples of linear polymers based on vinylidene monomers are shown below with their substituents.

<i>Substituent A</i>	<i>Substituent B</i>	<i>Resulting polymer</i>
-Cl	-Cl	Polyvinylidene chloride
-F	-F	Polyvinylidene fluoride

$-\text{CH}_3$		Poly α methyl styrene
$-\text{CH}_3$	$\begin{array}{c} -\text{C}-\text{O}-\text{CH}_3 \\ \\ \text{O} \end{array}$	Poly methyl methacrylate

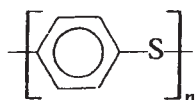
One further group of polymers based on ethene is possible and these have all four hydrogen atoms of the ethylene molecule replaced. When the substituent is fluorine the resultant polymer is polytetrafluoroethylene; alternatively, the hydrogen atoms may be replaced by three fluorine atoms and one chlorine atom in which case the resultant polymer is polychlorotrifluoroethylene.



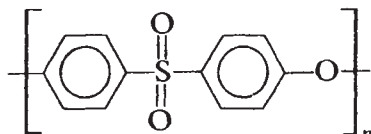
The above examples have been based upon ethylene and its derivative monomers, all of which have led to the formation of polymer backbones containing chains of linked carbon atoms. Carbon may join with other atoms and molecules such that they can also be incorporated into the polymer backbone. The previous examples have all been formed by the addition polymerization process in which carbon-carbon double bonds have been changed to single bonds in order that further carbon atoms could join together. In many of the polymers containing different atoms in their backbones polymerization may have occurred by another means such as condensation polymerization. Typical examples of linear polymers containing other atoms in addition to carbon in their backbones are shown below:

Structural unit

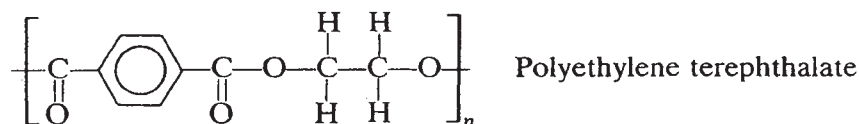
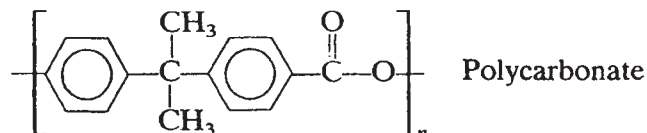
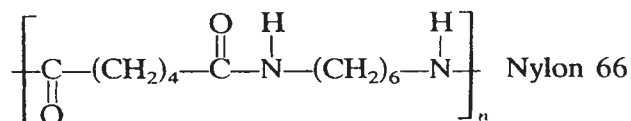
Polymer



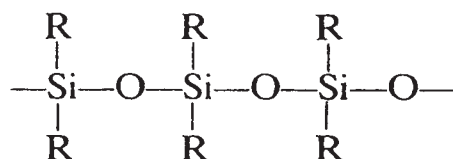
Polyphenylene sulphide



Polyether sulphone



Although carbon has the ability to form very large long chain molecules it is not completely unique in this characteristic. Nitrogen and oxygen can also form long chain molecules with carbon atoms. Sulphur can be incorporated either as an individual sulphur atom as in polyphenylene sulphide or it may form short chains of sulphur atoms. Perhaps the main examples of long chain polymers not requiring carbon atoms to form their backbones are the silicones. In these materials the main chain is composed of alternating silicon and oxygen atoms;



These materials are covered in detail in Chapter 2.

1.3 IMPORTANT ELECTRICAL PROPERTIES OF POLYMERS

One of the main reasons why polymers have become so widely used in electronics and electrical applications is that they are good dielectric materials with readily controllable electrical properties. However, the fact that polymers are good insulators does not mean that they are inert in an electrical field and the intrinsic properties of a material can usually be related to performance under specific test conditions. The electrical properties that have to be considered when selecting a material include dielectric constant,

volume resistivity, surface resistivity, dissipation, power and loss factors, arc resistance and dielectric strength. When selecting a polymer for a specific application the variation of these properties with changes in the likely service environment has to be taken into account since many of them are temperature, frequency, voltage and environmentally variable.

Most polymers serve as electrical insulators and may be required to operate in conditions of varying voltage with both direct current and alternating current at frequencies up to and above the GHz region. The voltage a polymer is exposed to may be as little as a few microvolts in communications equipment or up to several million volts in power distribution systems. Similarly, currents can vary from a few picoamps to many thousands of amps.

All of these variations may be encountered over a wide range of temperatures, humidities and operating environments. The selection of a material capable of operating under such variable conditions is obviously important and thus an understanding of the electrical properties of polymers and how they vary under these conditions is essential. Some of the more important electrical properties are now discussed.

1.3.1 Resistance and Resistivity

Most polymers, unless purposely modified, are excellent insulators having very high resistivities and conduct little electrical current. The insulation resistance of a material is the ratio of the applied voltage to the total current passing between two electrodes contacting the material. This resistance is measured in ohms and is directly proportional to the length and inversely proportional to the area of the specimen according to the equation

$$R = \rho l / A$$

where R = insulation resistance (Ω), l = length (m), A = area (m^2), ρ = specific resistivity ($\Omega \text{ m}$).

In order to compare different materials, it is usually more convenient to compare their resistivities because these values reduce resistance measurements to a common denominator. Volume resistivity is the ohmic resistance of a cube of dielectric material with sides of length 1 cm or 1 m, and is expressed in $\Omega \text{ cm}$ or $\Omega \text{ m}$, respectively.

All materials may be classified by their resistivities and they range from the metals which are extremely good conductors to the polymers which are very good insulators. Between these two extremes are the semiconductors such as germanium, silicon and gallium arsenide. Most materials can thus be conveniently placed into one of three groups: those that are good conductors, those that are good insulators and those in between which may be semiconductors. The resistivities of a number of materials are given in Table 1.4. Polymers generally have resistivities of $10^{12} \Omega \text{ cm}$ or greater

Table 1.4 Comparative electrical resistivities of materials

<i>Resistivity (Ω cm)</i>	<i>Material</i>	<i>Classification</i>
10^{18}	Polytetrafluoroethylene	Insulators
10^{17}	Polystyrene, polypropylene	
10^{16}	Polyethylene, silicone rubber	
10^{15}	Amine-cured epoxides	
10^{14}	Diamond	
10^{13}	Polyamides	
10^{12}		
10^{11}		Semiconductors
10^{10}	Glass	
10^9		
10^8	Silver bromide	
10^7		
10^6		
10^5		
10^4	Silicon	Conductors
10^3		
10^2	Germanium	
10^1		
10^0		
10^{-1}		
10^{-2}	Quinolinium salts	
10^{-3}		
10^{-4}	Bismuth, mercury, graphite	
10^{-5}	Polypyrrole and polythiophene	
10^{-6}	Silver, copper	
10^{-7}		

and some fluorinated polymers have resistivities in excess of $10^{18} \Omega$ cm. It should be noted, however, that intrinsically conducting polymers such as polyaniline and polypyrrole have been the subject of much study and development over the last decade or so and it is now possible to produce these materials with conductivities approaching those of the metals.

Various factors influence the resistivity of a polymer and these have to be taken into account when formulating or selecting materials for use in electronics. The chemical structure of the polymer itself will play an important role in determining the resistivity, as will the concentration of any impurities remaining in the material such as by-products of manufacture. The addition of flexibilizing and plasticizing agents is also known to reduce the resistivity of plastics and the degree of cure or crosslinking density of thermosetting materials must also be considered.

Resistivity varies with temperature and, in an opposite manner to metals, the resistivity of polymers decreases with temperature. There is thus the possibility that a material that has adequate insulative properties at room

temperature may be too conducting at elevated temperatures. The temperature dependence of resistivity is given by the equation

$$\rho = \rho_o \exp (\Delta E/2kT)$$

where ρ = resistivity at temperature T , ρ_o = limiting low temperature resistivity, k = Boltzmann's constant, ΔE = energy, T = absolute temperature.

Other factors influencing the resistivity of a polymer include voltage, frequency, pressure and the conditioning of the sample. In particular, environmental conditions are very important since relative humidity changes alter the resistivity. If a polymer absorbs a significant amount of moisture, the resistivity may drop to an unacceptably low value. Whilst this increase in conductivity is generally due to the direct presence of sorbed moisture within the polymer matrix and is reversible if the material is dried, some polymers may actually be degraded by the presence of moisture and high potential gradients. One example of this behaviour can occur with the polyester materials which, when exposed to high humidities in the presence of an electric field, may be hydrolysed to the acid and alcohol constituents from which they were made. In the presence of moisture these then form a conductive solution which can lead to corrosion or short-circuiting. The surface resistivities of plastics are also important because moisture and contaminants affect surface resistivity more than volume resistivity.

Large mouldings may take several weeks or months to register any changes in volume resistivity due to varying humidity conditions, but under the same humidity conditions or in contaminated environments the surface resistivity may change almost immediately. The surface resistivity of a material is the ratio of the potential gradient parallel to the current along its surface to the current per unit width of surface and is numerically equal to the surface resistance between two electrodes forming opposite sides of a square. The size of the square is immaterial and the units are Ω/square . It is measured as the resistance when a direct voltage is applied between the surface mounted electrodes of unit width and unit spacing (see IEC93 and ASTM D257).

For some special applications conductivity may be more important than resistivity, as is the case with conductive adhesives. The conductance of a polymer is the reciprocal of its resistance and likewise its conductivity is the reciprocal of its resistivity. The units of specific conductivity are mhos per centimetre or preferably Siemens per metre. As most polymers are normally good insulators, conductivity is often imparted by the incorporation of finely divided metals such as silver, gold and copper. Conductive polymers find important uses as electromagnetic and radio frequency shielding, as well as die attach materials for semiconductors. The newly emerging intrinsically conducting polymers offer conductivity without the need for the addition of metallic fillers. These are already being used commercially in

electronics applications such as the direct plate processes that form part of printed circuit board manufacturing.

1.3.2 Relative Permittivity (Dielectric Constant)

IEC 250 states that the relative permittivity of an insulating material is the ratio of capacitance of a capacitor, in which the space between and around the electrodes is entirely and exclusively filled with the insulating material in question, to the capacitance of the same configuration of electrodes in vacuum.

$$K = C_m / C_v$$

where K = relative permittivity, C_m = capacitance with material m as the dielectric and C_v = capacitance with a vacuum as the dielectric.

The relative permittivities of materials vary from just above one to several thousands for some inorganic materials, and typical examples are shown in Table 1.5.

The relative permittivities of materials are due to their electronic polarizability and compounds with polar groups in their molecular structure have large dielectric constants because their dipoles are able to orient in an electric field and have large dipole moments. Polar polymers absorb moisture from the atmosphere and for these reasons non-polar polymers are normally preferred over polar polymers for insulative applications. For general insulating or protective coatings dielectric constants up to 8 may be acceptable but the maximum relative permittivity specified by MIL-I-16923 for materials used in electronic and electrical assemblies is 4.5 at 1 kHz.

Table 1.5 Relative permittivities of various materials at 25°C

<i>Material</i>	<i>Relative permittivities</i>
Air	1.00053
Fluoropolymers	1.9–2.6
Polypropylene	2.2–2.3
Polystyrene	2.45–2.65
Benzocyclobutenes	2.6–2.8
Epoxides	2.8–5.5
Polyetherimide (Ultem)	3.15
Polyimide (Pyralin)	3.50
Epoxy-glass laminates	4.4–5.2
Phenolics	5.0–6.5
Ceramic filled PTFE	6.0–10.2
Nitrobenzene	34.9
Water	79.5
Lead titanate	200
Lead zirconate titanate (PZT)	3400

Relative permittivities of polymers vary with frequency and can either increase or decrease depending upon molecular structure, and the presence of any additives or fillers. In order to be of use in electrical and electronic applications a polymer should have reasonably constant dielectric properties over a broad range of temperatures, frequencies and humidities. It is for these reasons that materials such as polyethylene, polystyrene and the fluorocarbons find such extensive usage as electrical insulators.

1.3.3 Dissipation, Power and Loss Factors

The dissipation factor (D) is the ratio of the current of the resistive component (I_r) to the current of the capacitive component (I_c) and is also equal to the tangent of the dielectric loss angle δ , i.e.

$$D = I_r/I_c = \tan \delta$$

Typical values of the dissipation factor vary from 0.1 to less than 0.0005.

The power factor (PF) is the ratio of power dissipated to the product of the effective power output (volts $\times$ amps) and is a measure of the dielectric loss in the insulating plastic (which is effectively acting as a capacitor). The power factor and dissipation factor are related by the equation

$$D = \frac{\text{PF}}{\sqrt{1-(\text{PF})^2}}$$

Power factors for most plastics are fairly low and so the $(\text{PF})^2$ term in the equation can be ignored, making the power factor approximately equal to the dissipation factor. These two terms are often used interchangeably for dielectric materials.

The loss factor is a measure of the energy absorption of a material and is given by the product of the dielectric constant and the power factor, i.e.

$$\text{Loss factor} \cong K \tan \delta \cong KD$$

It is desirable for all of the above parameters to have as low values as possible and this is particularly important in the case of high-speed, high-frequency devices and circuitry working at frequencies up to 100 GHz. Low values are indicative of minimum conversion of electrical energy to heat and little overall power loss in the system. These factors are again generally functions of frequency, temperature, humidity and the purity of the polymer. Both relative permittivity and dissipation factor are measured using the same test equipment and the test method is detailed in IEC250.

1.3.4 Arc Resistance

The arc resistance of a material is the time (in seconds) that its surface may be exposed to an arc before electrical breakdown occurs. A high-voltage,

low-current arc is used to simulate the conditions likely to be found in service. Standard test procedures used in the United States are UL746A and ASTM-D-495, whilst in Europe the test is to DIN 53484 VDE 0303. A number of arc testers are commercially available that comply with these specifications. The specimen to be examined is placed between the electrodes and an arc generated at specified intervals and currents.

Failure due to arcing can occur in three different ways:

1. By the formation of a thin conductive line between the electrodes known as tracking.
2. By the formation of a conductive path of carbonaceous material due to surface heating.
3. By self-ignition of the material without the formation of any visible conductive path.

The arc resistance of a plastic is very dependent upon its molecular structure and the presence and amount of any additives in the formulation. Fillers have a significant effect upon the arc resistance and materials such as alumina and silica can give considerable improvements. Arc resistance is also very dependent on the condition of the surface and is easily reduced by moisture, salts or even grease from skin contact.

1.3.5 Comparative Tracking Index (CTI)

The tracking index is the relative resistance of insulating materials to tracking when the surface is exposed under electrical stress to water containing ionic contaminants. This is an important test because it evaluates the safety of actual components with insulation between live parts. Insulating materials must obviously be resistant to tracking and the CTI is defined as the maximum voltage at which no failure occurs when contaminant-containing water e.g. a 0.1% solution of ammonium chloride in distilled water, is applied to the surface. It is desirable to have as high a CTI as possible and materials meeting the CTI requirements at 600 V are known as 'high tracking' resins. The test itself is somewhat complex and is detailed in IEC 112 and ASTM D3638. CTI values for polymers are influenced by the presence of additives used in their formulation. They can be lowered by pigments, especially carbon blacks, flame retardants and glass fibres and can be raised by the addition of minerals such as titania.

1.3.6 Dielectric Strength and Breakdown Voltage

The dielectric strength of a polymer is a measure of its ability to withstand voltage without breakdown or the passage of considerable amounts of current. It is defined as the minimum voltage at or below which no breakdown occurs. Rather similarly, the breakdown voltage is the voltage

above which actual failure occurs and the two items are often used interchangeably.

The dielectric strength of a material is, like the properties reported above, very dependent upon molecular structure, the level of impurities and the relative humidity to which the sample has been exposed. Consequently, the dielectric strength of a material should be measured under carefully specified conditions. There are several standardized procedures for measuring dielectric strength; in the United States ASTM-D-149 is commonly used whilst the ISO and DIN standards are IEC 243 and 53981 VDE 0303 respectively.

1.4 IMPORTANT MECHANICAL, CHEMICAL AND PHYSICAL PROPERTIES OF POLYMERS

In addition to having excellent electrical properties for electronic and electrical applications, polymers also have desirable mechanical, chemical and physical properties that enhance their capabilities in these fields. Polymers are available with very high purity and can be easily moulded to form rigid protective packages for delicate microcircuits, whilst others are available that are extremely flexible making them useful as wire coatings and sleeveings. These properties are determined largely by the chemical composition and subsequent formulation of the given material but the way in which a plastic is manufactured and used sometimes also has a bearing on the final properties. In this section some of the more important mechanical, chemical and physical properties of polymers are discussed.

1.4.1 Mechanical Properties

Unlike many metals, polymers are not perfectly elastic, possessing characteristics of both elastic and viscous materials. Consequently, they are often regarded as being viscoelastic. In order to select the best material for a given application it is usually important to know how its properties vary with time, temperature and environmental changes. A number of the more important physical capabilities of a polymer can be defined by examining the following properties: elasticity, stiffness, strength, toughness and resilience.

The elasticity of a polymer is its ability to carry stress without suffering a permanent deformation. The stiffness of a material is a measure of its ability to carry a stress without changing its dimensions, and strength determines its ability to carry a dead load. Toughness represents the ability to absorb energy and undergo permanent changes without rupturing whilst resilience is a measure of the work required to deform a material to its elastic limit and determines the energy that it can absorb without undergoing a permanent deformation.

All of these properties can be determined from the stress/strain characteristics of a plastic by plotting its stress/strain curve. Stress is defined as the intensity (measured per unit area) of the internal distributed forces, or components of force, which resist a change in the form of a body. Strain is the change per unit length in a linear dimension of a body accompanying a stress and is measured in metres per metre or in percent. When under tension or compression, strain is measured along the dimension under consideration. Many plastics have stress/strain characteristics that can be represented by a curve with the general shape shown in Fig. 1.1.

The slope of the curve where stress and strain are almost proportional represents a measure of the material's stiffness. In this region the ratio of stress to strain is known as the modulus of elasticity or Young's modulus. At the first bend in the curve (1) the stress value represents the yield point and is a measure of the strength of the material and its resistance to permanent deformation. Before the yield point is reached strains are largely recoverable and are a measure of elastic deformation. From the yield point (1) to the break point (2) the strains are no longer immediately recoverable and they determine the degree of plastic deformation. The area under the curve represents the work required to fracture the polymer sample and is an approximate measure of its toughness. The resilience of a material can be determined from the area under the curve up to the yield point. The various shapes of stress/strain curve allow polymers to be classified according to five main types of behaviour:

1. Soft and weak polymers having low moduli of elasticity, yield points and low elongations at break.
2. Hard and brittle polymers having high moduli of elasticity, no well-defined yield points and low strain at break.

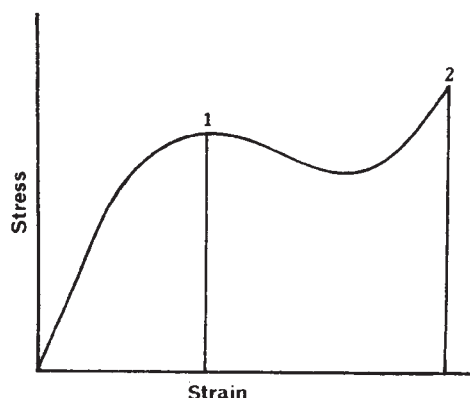


Fig. 1.1. A typical stress/strain curve for a polymer.

3. Soft, tough polymers having low moduli of elasticity, low yield points and high strain at break.
4. Hard, strong polymers having high moduli of elasticity and yield points with moderate stress at break.
5. Hard, tough polymers having high moduli of elasticity and yield points and also high stress and strain at break.

In addition to mechanical failure under conditions of high stress, failure can also occur at relatively low stress levels under some conditions and this must again be taken into account when selecting materials for a specific application. The failure of a polymer at relatively low stress levels can occur under the following circumstances:

- fatigue
- stress relaxation
- creep
- chemical exposure

Fatigue is the term used to describe the behaviour of a polymer under repeated cycles of stress or strain which cause a deterioration of the material and result in progressive fracture. Fatigue is dependent upon frequency, amplitude, temperature, stress and mode of stressing.

Stress relaxation occurs in a polymer when it has been deformed to a predetermined shape and then restrained in that shape so that total deformation neither increases nor decreases. Under these conditions the phenomenon of stress relaxation can then occur and the initial stress in the plastic gradually decreases. It can be defined as the time-dependent change in stress which results from the application of a constant total strain to the material at constant temperature. Creep is defined as the time-dependent part of the strain which results from the application of a constant stress to a plastic. By comparing the definitions of creep and stress relaxation it can be seen that the two phenomena are closely related. Creep occurs when a constant stress is applied for an extended period whilst stress relaxation occurs during long-term exposure to a constant strain.

The loss of mechanical properties during exposure of a polymer to certain environments may also be important in electrical and electronic applications. Whilst some chemicals may have little effect upon the strength of an unstressed part there may be a totally different behaviour with the same part under stressed conditions. Contact with water, acids, alkalis and solvents can cause a number of undesirable effects in a polymer such as swelling, shrinkage, distortion, crazing, cracking, softening, weight loss or gain, and loss of strength or stiffness. All of these factors must be taken into account when selecting a material for use in electrical and electronic components, particularly where mechanical and physical properties are likely to be important.

A number of other mechanical properties are also often considered important. The hardness, abrasion resistance and machinability may need to be considered where some reworking of a compound is needed or where machining into a particular shape is required. Depending upon the final usage of the material the tensile, shear and compressive strengths of a polymer can be important. Such properties would need to be considered where the polymer was used as a structural component or where it is likely to be exposed to forces that could cause mechanical failure. The flexibility of a polymer and, more particularly, maintenance of flexibility over a likely operating temperature range need to be characterized since wire coatings must stay flexible at low temperatures and junction coatings used to protect semiconductors must not become rigid if the equipment in which they are used happens to be exposed to low temperatures. Shrinkage can be important when attempting to mould parts to strict tolerances since thermosetting materials experience shrinkage during moulding because of the curing reaction which takes place. Another property that is important with plastic moulding compounds is viscosity. This must be controlled so that moulds fill properly yet the resinous components do not bleed out of the mould, and, in the case of wire-bonded semiconductors, so that wire bonds are not swept off contacts causing shorting or open circuits.

1.4.2 Chemical Properties

The resistance of a polymer to various chemicals is largely determined by its molecular composition and varies widely from type to type. Some polymers such as polytetrafluoroethylene are inert even in aggressive chemicals and solvents whilst others are easily decomposed in the mildest solvents or are soluble in water. Although exceptions are frequently discovered, it is quite possible to make predictions of a material's likely behaviour in various environments by studying its molecular structure. Polymers that have a backbone made up entirely of carbon-carbon bonds with hydrophobic groups attached usually have good oxidation resistance and low moisture absorption. Low moisture sorption obviously helps to minimize attack by aggressive aqueous solutions. If a degree of double bonding (unsaturation) is introduced into the chain the oxidation resistance will tend to decrease although the water absorption characteristics may change only slightly. A typical example is butyl rubber that contains few double bonds. This is much more resistant to oxidation than natural rubber which has a larger number of double bonds in the chain.

Where the polymer backbone contains groups such as the ester or amide linkages found in polyesters and polyamides, the degree of moisture sorption is usually high and they are readily attacked by chemicals with hydrolysing capabilities. They are thus rather unstable in both moderately strong acids and alkalis. The absolute structure of the material concerned

will play a part in determining the actual degree of hydrolysis that occurs and the moisture sorption characteristics will also be important. If the molecular structure dictates a low moisture permeability, transport of aggressive solutions into the bulk of the material may be retarded with attack predominantly limited to the material surface.

The introduction of hydrophilic groups onto the main chain of the polymer results in the enhanced sensitivity of the material to both moisture and aqueous solutions. The classic example of such a material is polyvinyl alcohol which is soluble in both water and some other polar solvents. Interestingly, however, polyvinyl alcohol is not affected by hydrophobic solvents such as the hydrocarbons. The presence of a hydroxyl group on every second carbon atom in the main chain of polyvinyl alcohol not only provides high polarity to the molecule but also allows it to exhibit strong adhesion to certain substrates. In general the introduction of polar groups both in the main chain and in the side groups leads to very high surface energies and surface tensions resulting in good adhesive properties. The amide linkage in polyamides, whilst being largely responsible for their moisture sorption, also leads to powerful hydrogen bonding and their good adhesive properties.

The molecular weight of a polymer molecule also has a significant effect in determining the chemical properties. A typical example is a polymer's solubility in a solvent which is usually inversely proportional to its molecular weight. The swelling, absorption and permeability of polymers to gases and liquids is also related to molecular weight although the relationship is not clearly defined and it has been stated that molecular weight does not affect diffusion and permeation by liquids and gases. The general chemical reactivity of polymers is known to decrease with increasing molecular weight. This is thought to be due to the reactivity of the end groups of the polymer molecule which are usually the most reactive parts of the whole molecule. Since the number of end groups is inversely proportional to the number average molecular weight, it is expected that polymer reactivity will decrease with increasing molecular weight. As ageing processes are chemical degradation reactions that occur in polymers, their resistance to this type of deterioration should also be related to molecular weight. The ageing of polymers by oxygen, ozone, moisture and ultra-violet light is found to decrease with increasing molecular weight and again this is because the number of reactive end groups is reduced. The lower mobility of the higher molecular weight molecules also reduces reactivity and degradation of very high molecular weight polymers may only degrade them to medium molecular weight polymers with almost equivalent properties.

The presence of impurities or monomeric additives in a polymer also has an important bearing upon its final properties and the applications for which it will be suitable. No organic chemical reactions give absolutely

100% yields of the desired products and polymerization reactions are no exception. In addition to by-products, residual monomers may be present which can degrade the mechanical and thermal properties of the plastic. Residual solvents can cause softening and degradation of electrical properties in polymers, particularly where coatings from solution are being applied or where polymerization is carried out in solution. Moisture and other small molecules can be generated during condensation polymerizations or they can be absorbed from unsuitable storage environments. The presence of moisture, whilst not only causing degraded mechanical and electrical properties, can lead to difficulties in moulding a polymer and may even be the source of hydrolytic instability. Contamination can also occur in the form of ions which are residual impurities from the synthesis of the polymer's starting materials. Chloride and sodium ions are sometimes found in epoxide resins as by-products of the synthesis and these can lead to malfunctioning of epoxide encapsulated semiconductors and early corrosion of certain conductors such as aluminium. In addition, ions can lead to reductions in the insulative properties of a polymer. Catalysts used to promote a polymerization reaction may leave residues that have a deleterious effect upon thermal stability and electrical properties of a polymer. Effective post-cures are required with epoxide moulding compounds in order to decompose these catalyst residues and to improve the bulk resistivity of the cured materials.

In order to evaluate a material for its chemical stability it is necessary to test it under conditions which as nearly as possible replicate those likely to be encountered in service. One fairly simple test that can be applied to most plastic materials as part of an initial screening process, involves immersing moulded discs or bars for seven days in a variety of liquids at room temperature. This test uses a number of acids, alkalis and salt solutions of varying concentrations and a series of solvents with a range of polarities. At the end of the test, the samples are examined for changes in dimensions, weight, colour and other physical properties.

Before selecting a polymer for an electrical or electronic application its chemical properties should be considered just as the electrical, mechanical and physical properties are taken into account. The final operating environment and conditions of service will often dictate the type of material to be used and the required purity.

1.4.3 Physical Properties

A number of other important properties have to be considered when selecting a polymer for electronic and electrical usage. There may be restrictions on the amount of material that can be used or perhaps it must have a certain degree of thermal conductivity to impart heat dissipation to a circuit. Some of these other physical properties are now briefly discussed.

Polymers have distinct advantages over the majority of other materials in terms of weight of material used. Most have densities that are considerably lower than the metals they often replace in structural applications with values normally between 0.9 and 2.0 (a good number lie between 1.0 and 1.4). Density considerations become important in applications where overall weight must be minimized such as in aerospace electronics. Since the approval of a polymer used is normally based on volume rather than weight and yet the polymer is sold by weight, a reduction in density of the material will also allow more parts to be made per unit weight and this factor should be considered where material costs must be carefully controlled.

There are several thermal properties of a polymer that are considered important, such as its thermal expansion coefficient, thermal conductivity, thermal stability, melting point and glass transition temperature. The thermal expansion coefficient of a polymer needs to be taken into account when it is in intimate contact with another material with a different thermal expansion coefficient. Polymers have much higher thermal expansion coefficients than most other materials especially metals, ceramics and the silicon substrates found in electrical and electronic components. The thermal expansion coefficient depends partly upon molecular weight and this is largely because the polymer end groups are one of the major contributing factors. Increasing the effective molecular weight by crosslinking also assists in reducing the expansion coefficient of a polymer. Where lower thermal expansion coefficients are required, fillers and fibres are often added to reduce them as is the case with most moulding compounds and printed circuit board laminates.

The thermal conductivities of polymers are much lower than those of other materials and because of this they often find use as thermal insulators. The thermal conductivity coefficient is the time rate of heat flow under steady-state conditions through a unit area and unit thickness per unit temperature gradient. Polymers used with electrical and electronic assemblies usually require high thermal conductivities because of the need to dissipate heat from circuitry. For many applications the polymers are formulated with high thermal conductivity fillers such as crystalline silica or alumina. Other high thermal conductivity electrically insulating inorganic materials include beryllia (BeO), aluminium nitride (AlN), boron nitride (BN) and silicon carbide (SiC). The use of diamond in high thermal conductivity applications has also progressed significantly in recent years. Where possible the thermal conductivity of, for example, an adhesive layer, can also be improved by using as thin a coating as possible. Thermal management issues are becoming increasingly important as device, e.g. microprocessor, operating speeds and power consumptions increase. It is already common practice to employ chip mounted cooling fans and the predictions are that thermal dissipations will continue to grow; there is clearly an opportunity for new high thermal conductivity materials.

The thermal stability or heat resistance of polymers is obviously of particular importance when products have to withstand exposure to heat under a wide variety of service conditions. As polymers are organic materials they are susceptible to the undesirable reactions of these materials such as thermal degradation, oxidation and hydrolysis. Thermal stability is another parameter that is directly related to molecular weight and the polymer's molecular structure. Much of the instability at high temperatures is due to the nature of the end groups of the polymer molecules, which are sites for reactivity. The thermal stability of a polymer can be enhanced by reducing the number of reactive impurities that can take part in thermal degradation. Crosslinking a polymer increases its molecular weight and decreases its volatility leading to increased thermal stability. Molecular structure also plays a significant part in determining thermal stability and the presence of aromatic and highly electronegative elements tends to enhance both the thermal and the oxidative stability. The hydrogen atoms of polyethylene can be replaced with electronegative fluorine atoms to give the high thermal stability polymer polytetrafluoroethylene.

The melting point and/or the glass transition temperature (T_g) of a polymer will also have an important part in the choice of materials for an application. Both of these thermal characteristics play a large part in determining many of the mechanical properties of a polymer. The glass transition temperature of a material represents the point above which it behaves as a viscous liquid or a rubber. Below the glass transition temperature the polymer behaves as a hard, brittle, glass-like compound. Silicone rubbers are examples of materials that have T_g values below room temperature and Perspex is an example of a material that has a T_g above room temperature. The T_g of a material is determined by its molecular structure with factors such as flexibility, symmetry and the bulkiness of the molecules playing a major part. Obviously, the melting point of a thermoplastic polymer also determines the acceptable temperature range over which it can be used and for thermoplastic materials will limit the maximum service temperature of, for instance, coated wires. The glass

Table 1.6 Glass transition temperatures (T_g) and melting points (T_m) of some common polymers

<i>Polymer</i>	$T_g(^{\circ}C)$	$T_m(^{\circ}C)$
Polyethylene	-120	137
Polypropylene	-18	176
Polystyrene	100	240
Polyethylene terephthalate	69	267
Polymethyl methacrylate	105	160
Polyvinyl chloride	87	212
FR4 epoxy laminate	130-140	n/a

transition temperatures and melting points of several thermoplastic materials are given in Table 1.6.

1.5 SUMMARY

This chapter has given a brief introduction to polymers, their fundamental chemistries and the key properties that make them useful in electrical and electronic applications. There are normally many other factors which have to be taken into account when selecting polymeric materials for a specific application. Quite often it is not possible to satisfy all application requirements with one material and some form of compromise has to be made. For further details of the properties of polymers for electronic applications the reader is referred to Chapter 2 of the previous edition of this book.