3

Plastics Properties and Testing

3.1 Introduction

There are two stages in the process of becoming familiar with plastics. The first is rather general and involves an introduction to the unique molecular structures of polymers, their physical states, and transitions which have marked influence on their behavior. These have been dealt with in Chapter 1. The second stage, which will be treated in this chapter, is more specific in that it involves a study of the specific properties of plastics which dictate their applications. Besides the relative ease of molding and fabrication, many plastics offer a range of important advantages in terms of high strength/weight ratio, toughness, corrosion and abrasion resistance, low friction, and excellent electrical resistance. These qualities have made plastics acceptable as materials for a wide variety of engineering applications. It is important therefore that an engineer be aware of the performance characteristics and significant properties of plastics.

In this chapter plastics have been generally dealt with in respect to broad categories of properties, namely, mechanical, electrical, thermal, and optical. In this treatment the most characteristic features of plastic materials have been highlighted.

An important facet of materials development and proper materials selection is testing and standardization. The latter part of this chapter is therefore devoted to this aspect. It presents schematically (in simplified form) a number of standard test methods for plastics, highlighting the principles of the tests and the properties measured by them.

3.2 Mechanical Properties

Several unfamiliar aspects of material behavior of plastic need to be appreciated, the most important probably being that, in contrast to most metals at room temperature, the properties of plastics are time dependent [1–4]. Then superimposed on this aspect are the effects of the level of stress, the temperature of the material, and its structure (such as molecular weight, molecular orientation, and density). For example, with polypropylene an increase in temperature from 20 to 60°C may typically cause a 50% decrease in the allowable design stress. In addition, for each 0.001 g/cm³ change in density of this material there is a corresponding 4% change in design stress. The material, moreover, will have enhanced strength in the direction of molecular alignment (that is, in the direction of flow in the mold) and less in the transverse direction.

Because of the influence of so many additional factors on the behavior of plastics, properties (such as modulus) quoted as a single value will be applicable only for the conditions at which they are measured. Properties measured as single values following standard test procedures are therefore useful only as a means of quality control. They would be useless as far as design in concerned, because to design a plastic component it is necessary to have complete information, at the relevant service temperature, on the
time-dependent behavior (viscoelastic behavior) of the material over the whole range of stresses to be experienced by the component.

### 3.2.1 Stress and Strain

Any force or load acting on a body results in stress and strain in the body. Stress represents the intensity of the force at any point in the body and is measured as the force acting per unit area of a plane. The deformation or alteration in shape or dimensions of the body resulting from the stress is called **strain**. Strain is expressed in dimensionless units, such as \( \text{cm/cm} \), \( \text{in./in.} \), or in percentage.

Corresponding to the three main types of stress—tensile, compressive, and shear—three types of strain can be distinguished. Thus, **tensile strain** is expressed as elongation per unit length (Figure 3.1a),

\[
\varepsilon = \frac{\Delta \ell}{\ell_0} = \frac{(\ell - \ell_0)}{\ell_0}
\]

and **compressive strain** as contraction per unit length (Figure 3.1b),

\[
\varepsilon = \frac{\Delta \ell}{\ell_0} = \frac{(\ell_0 - \ell)}{\ell_0}
\]

If the applied force or load, \( F \), is tensile or compressive, the resulting tensile or compressive stress, \( \sigma \), is defined by

\[
\sigma = \frac{F}{A}
\]

where \( A \) is the cross-sectional area perpendicular to the direction in which the force acts (Figure 3.1a).

The shearing stress is defined by a similar equation

\[
\tau = \frac{F_s}{A}
\]

where \( F_s \) is the shearing force acting on an area \( A \), which is parallel to the direction of the applied force (Figure 3.1c).

**Shear strain** is measured by the magnitude of the angle representing the displacement of a certain plane relative to the other, due to the application of a pure shear stress, such as \( \alpha \) in Figure 3.1c. The corresponding shear strain \( \gamma \) may be taken equal to the ratio \( \frac{aa'}{ab} = \tan \alpha \). A shear strain is produced in torsion, when, for example, a circular rod is twisted by tangential forces, as shown in Figure 3.1d. For small deformations the shear strain, \( \gamma \), can be calculated from the triangle \( ABC \)

\[
\gamma = \frac{BC}{AB} = \frac{r\theta}{\ell}
\]

where \( r \) is the radius and \( \theta \) is the angle of twist.

An ideal elastic material is one which exhibits no time effects. When a stress is applied the body deforms immediately, and it recovers its original dimensions completely and instantaneously when the

---

**FIGURE 3.1** (a) Tensile or longitudinal strain, \( \varepsilon = \frac{(\ell - \ell_0)}{\ell_0} \). (b) Compressive strain, \( \varepsilon = \frac{(\ell_0 - \ell)}{\ell_0} \). (c) Shear strain, \( \gamma = \frac{aa'}{ab} \). (d) Shear strain in torsion \( \gamma = \frac{r\theta}{\ell} \).
stress is removed. When the ideal elastic body is subjected to tensile (or compressive) stress, the proportionality is expressed as

$$\sigma = E \cdot \varepsilon$$  \hspace{1cm} (3.6)

where $\sigma$ is the applied stress (tensile or compressive) in lbf/in.$^2$, kgf/cm$^2$ or other appropriate units of force per unit cross-sectional area (Equation 3.3), $\varepsilon$ is the axial strain (Equation 3.1 and Equation 3.2), and $E$ is the modulus of elasticity, commonly known as the Young’s modulus. The proportionality law as defined above is known as Hooke’s law.

Likewise, if the ideal solid is subjected to a shear stress ($\tau$), then the shear strain ($\gamma$) developed as a function of stress applied is given by the expression

$$\tau = G \cdot \gamma$$  \hspace{1cm} (3.7)

Here, the proportionality constant $G$ is known as the shear modulus, also called the modulus of rigidity.

The elastic constants in tensile deformation and shear deformation are summarized and compared below:

<table>
<thead>
<tr>
<th></th>
<th>Tensile (Figure 3.1a)</th>
<th>Shear (Figure 3.1c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stress</td>
<td>$\sigma = F/A$</td>
<td>$\tau = F/A$</td>
</tr>
<tr>
<td>Strain</td>
<td>$\varepsilon = (\ell - \ell_0)/\ell$</td>
<td>$\gamma = \tan \alpha$</td>
</tr>
<tr>
<td>Modulus</td>
<td>$E = \sigma/\varepsilon$</td>
<td>$G = \tau/\gamma$</td>
</tr>
<tr>
<td>Compliance</td>
<td>$D = \varepsilon/\sigma$</td>
<td>$J = \gamma/\tau$</td>
</tr>
</tbody>
</table>

It may be noted that for an ideal elastic body compliance is the inverse of modulus.

The modulus of elasticity, $E$, and the modulus of rigidity, $G$, as defined above, apply under longitudinal and shear forces, respectively. When a hydrostatic force is applied, a third elastic modulus, the modulus of compressibility or bulk modulus, $K$, is used. It is the reciprocal of compressibility, $\beta$, and is defined as the ratio of the hydrostatic pressure, $\sigma_h$, to the volumetric strain, $\Delta V/V_0$:

$$K = \frac{\sigma_h}{\Delta V/V_0} = \frac{1}{\beta}$$  \hspace{1cm} (3.8)

As indicated in Figure 3.1, an elongation (or compression) in one direction, due to an axial force, produces a contraction (or expansion) in the lateral direction, i.e., at right angles to the direction of the force. The ratio of the lateral strain to the longitudinal strain is called Poisson’s ratio $\nu$. It is an important elastic constant. For instance, a tensile stress, $\sigma_x$, which produces a tensile strain, $\varepsilon_x$, in the $x$-direction will also produce a contractive strain, $\varepsilon_y$, in the $y$-direction, the two being related by

$$\nu = -\frac{\varepsilon_y}{\varepsilon_x}$$  \hspace{1cm} (3.9)

Combining Equation 3.9 with Equation 3.6 and rearranging yields

$$\varepsilon_y = -(\nu/E)\sigma_x$$  \hspace{1cm} (3.10)

Equation 3.10 thus defines the contribution ($\varepsilon_y$) of the stress $\sigma_x$ in the $x$-direction to the total strain in the $y$-direction.

Poisson’s ratio, $\nu$, as defined above, is a fourth elastic constant. For small deformations, the bulk modulus and modulus of rigidity can be calculated from the modulus of elasticity and Poisson’s ratio by the following equations:

$$K = \frac{E}{3(1-2\nu)}$$  \hspace{1cm} (3.11)

$$G = \frac{E}{2(1+\nu)}$$  \hspace{1cm} (3.12)
The elastic modulus can also be calculated from the bulk modulus and the modulus of rigidity by the relation

\[
\frac{1}{E} = \frac{1}{9K} + \frac{1}{3G}
\] (3.13)

For soft materials such as gels, pastes, putties and many colloidal systems, which do not compress to the extent to which they are deformed under stress, \(K\) is very large compared to \(G\), and therefore from Equation 3.13, \(E = 3G\). For other materials as metals, fibers, and some plastics, however, \(K\) must be considered.

### 3.2.2 Stress–Strain Behavior

The stress–strain behavior of plastics measured at a constant rate of loading provides a basis for quality control and comparative evaluation of various plastics. The diagram shown in Figure 3.2a is most typical of that obtained in tension for a constant rate of loading. For compression and shear the behavior is quite similar except that the magnitude and the extent to which the curve is followed are different.

In the diagram, load per unit cross section (stress) is plotted against deformation expressed as a fraction of the original dimension (strain). Even for different materials the nature of the curves will be similar, but they will differ in (1) the numerical values obtained and (2) how far the course of the typical curve is followed before failure occurs. Cellulose acetate and many other thermoplastics may follow the typical curve for almost its entire course. Thermosets like phenolics, on the other hand, have cross-linked molecules, and only a limited amount of intermolecular slippage can occur. As a result, they undergo

![Nominal stress–strain diagram](image)

**FIGURE 3.2** (a) Nominal stress–strain diagram. (b) Typical moduli values quoted for plastics.
fracture at low strains, and the stress–strain curve is followed no further than to some point below the knee, such as point 1.

Ultimate strength, elongation, and elastic modulus (Young's modulus) can be obtained from the stress-strain study (Figure 3.2a). For determining the Young’s modulus ($E$) the slope of the initial tangent, i.e., the steepest portion of the curve, is measured. Other moduli values are also used for plastics (see Figure 3.2b).

The appearance of a permanent set is said to mark a yield point, which indicates the upper limit of usefulness for any material. Unlike some metals, in particular, the ferrous alloys, the drop-of-beam effect and a sharp knee in the stress–strain diagram are not exhibited by plastics. An arbitrary yield point is usually assigned to them. Typical of these arbitrary values is the 0.2% or the 1% offset yield stress (Figure 3.3a).

Alternatively, a yield stress can be defined as that at which the ratio of total stress to total strain is some selected amount, say 50% or 70% of the elastic modulus (Figure 3.3b). In the first case the yield stress is conveniently located graphically by offsetting to the right the stated amount of 0.2% (or 1%) and drawing a line paralleling that drawn for the elastic modulus. The point at which this line intersects the observed stress–strain line defined the yield stress. In the second case also the point of intersection of the line drawn with a slope of $0.7E$, for instance, with the observed stress–strain line determines the yield stress.

Up to point 1 in Figure 3.2a, the material behaves as an elastic solid, and the deformation is recoverable. This deformation, which is small, is associated with the bending or stretching of the inter-atomic bonds between atoms of the polymer molecules (see Figure 3.4a). This type of deformation is nearly instantaneous and recoverable. There is no permanent displacement of the molecules relative to each other.

**FIGURE 3.3** Location of a yield value.

**FIGURE 3.4** Deformation in plastics. (a) Stretching of polymer molecule. (b) Straightening out of a coiled molecular chain. (c) Intermolecular slippage.
Between points 1 and 2 in Figure 3.2a, deformations have been associated with a straightening out of a kinked or coiled portion of the molecular chains (see Figure 3.4b), if loaded in tension. (For compression the reverse is true.) This can occur without intermolecular slippage. The deformation is recoverable ultimately but not instantaneously and hence is analogous to that of a nonlinear spring. Although the deformation occurs at stresses exceeding the stress at the proportional limit, there is no permanent change in intermolecular arrangement. This kind of deformation, characterized by recoverability and nonlinearity, is very pronounced in the rubber state.

The greatest extension that is recoverable marks the elastic limit for the material. Beyond this point extensions occur by displacement of molecules with respect to each other (Figure 3.4c), as in Newtonian flow of a liquid. The displaced molecules have no tendency to slip back to their original positions, therefore these deformations are permanent and not recoverable.

Poisson’s ratio is a measure of the reduction in the cross section accompanying stretching and is the ratio of the transverse strain (a contraction for tensile stress) to longitudinal strain (elongation). Poisson’s ratio for many of the more brittle plastics such as polystyrene, the acrylics, and the thermoset materials is about 0.3; for the more flexible plasticized materials, such as cellulose acetate, the value is somewhat higher, about 0.45. Poisson’s ratio for rubber is 0.5 (characteristic of a liquid); it decrease to 0.4 for vulcanized rubber and to about 0.3 for ebonite. Poisson’s ratio varies not only with the nature of the material but also with the magnitude of the strain for a given material. All values cited here are for zero strain.

Strain energy per unit volume is represented as the area under the stress–strain curve. It is another property that measures the ability of a material to withstand rough treatment and is related to toughness of the material. The stress–strain diagram thus serves as a basis for classification of plastics. Strong materials have higher ultimate strength than weak materials. Hard or unyielding materials have a higher modulus of elasticity (steeper initial slope) than soft materials. Tough materials have high elongations with large strain energy per unit volume. Stress–strain curves for type cases are shown in Figure 3.5.

It must be emphasized that the type behavior shown in Figure 3.5 depends not only on the material but also very definitely on conditions under which the test is made. For example, the bouncing putty silicone is putty-like under slow rates of loading (type curve a) but behaves as an elastic solid under high rates of impact (type curve b or d).

Figure 3.6a shows that at high extension rates (>1 mm/sec) unplasticized PVC is almost brittle with a relatively high modulus and strength. At low extension rates (<0.05 mm/sec) the same material exhibits a lower modulus and a high ductility, because at low extension rates the polymer molecular chains have time to align themselves under the influence of the applied load. Thus the material is able to flow at the same rate as it is being strained. (This interesting phenomenon observed in some plastics is known as cold drawing.)

Further examples of the effect of conditions on the behavior of plastics are illustrated by the stress-strain curves for plasticized cellulose acetate when determined at different temperatures (Figure 3.6b). Thus the material is hard and strong at low temperatures, relatively tough at ordinary temperatures, and soft and weak at higher temperatures. This behavior may be attributed to variable molecular slippage effects associated with plasticizer action.

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**FIGURE 3.5** Classification of plastics on the basis of stress–strain diagram. (a) Soft and weak. (b) Weak and brittle. (c) Strong and tough. (d) Hard and strong.
3.2.3 Viscoelastic Behavior of Plastics

In a perfectly elastic (Hookean) material the stress, \( \sigma \), is directly proportional to the strain, \( \varepsilon \). For uniaxial stress and strain the relationship may be written as

\[
\sigma = \text{constant} \times \varepsilon
\]  
(3.14)

where the constant is referred to as the modulus of elasticity.

In a perfectly viscous (Newtonian) liquid the shear stress, \( \tau \), is directly proportional to the rate of strain, \( \dot{\gamma} \), and the relationship may be written as

\[
\tau = \text{constant} \times \dot{\gamma}
\]  
(3.15)

where the constant is referred to as the viscosity.

Polymeric materials exhibit stress–strain behavior which falls somewhere between these two ideal cases; hence, they are termed viscoelastic. In a viscoelastic material the stress is a function of both strain and time and so may be described by an equation of the form

\[
\sigma = f(\varepsilon, t)
\]  
(3.16)

This equation represents nonlinear viscoelastic behavior. For simplicity of analysis it is often reduced to the form

\[
\sigma = \varepsilon f(t)
\]  
(3.17)

which represents linear viscoelasticity. It means that in a tensile test on linear viscoelastic material, for a fixed value of elapsed time, the stress will be directly proportional to strain.

The most characteristics features of viscoelastic materials are that they exhibit time-dependent deformation or strain when subjected to a constant stress (creep) and a time-dependent stress when subjected to a constant strain (relaxation). Viscoelastic materials also have the ability to recover when the applied stress is removed. To a first approximation, this recovery can be considered as a reversal of creep.

3.2.3.1 Modulus and Compliance

Consider the tensile experiment of Figure 3.1a as a stress relaxation study in which the deformation is imposed suddenly and held fixed while the resulting stress, \( \sigma(t) \), is followed with time. The tensile relaxation modulus, \( E(t) \), is then obtained as

\[
E(t) = \frac{\sigma(t)}{\varepsilon_0}
\]  
(3.18)
with $\varepsilon_0$ being the constant strain and the parenthesis showing the functional dependence. Similarly a shear relaxation experiment measures the shear relaxation modulus $G(t)$:

$$G(t) = \tau(t)/\gamma_0$$

(3.19)

where $\gamma_0$ is the constant strain.

Consider now the tensile experiment of Figure 3.1a as a creep study in which a steady stress $\sigma_0$ is suddenly applied to the polymer specimen and held constant. In general, the resulting strain $\varepsilon(t)$ will be a function of time starting from the imposition of load. The results of creep experiments are often expressed in terms of compliances rather than moduli. The tensile creep compliance $D(t)$ is

$$D(t) = \varepsilon(t)/\sigma_0$$

(3.20)

The shear creep compliance $J(t)$ is similarly defined as

$$J(t) = \gamma(t)/\tau_0$$

(3.21)

where $\tau_0$ is the constant shear stress and $\gamma(t)$ is the resulting time-dependent strain.

A compliance is the inverse of a modulus for an ideal elastic body, but this is not true for viscoelastic materials. Consider, for example, two experiments carried out with identical samples of a viscoelastic material. In experiment (a) the sample is subjected to a tensile stress $\sigma_1$ for time $t$. The resulting tensile strain at $t$ is $\varepsilon_1$, and the creep compliance measured at that time is $D_1(t) = \varepsilon_1/\sigma_1$. In experiment (b) a sample is stressed to a level $\sigma_2$ such that strain $\varepsilon_1$ is achieved immediately. The stress is then gradually decreased so that the strain remains at $\varepsilon_1$ for time $t$ (i.e., the sample does not creep further). Let the stress on the material at time $t$ be $\sigma_3$; the corresponding relaxation modulus will be $E_2(t) = \sigma_3/\varepsilon_1$. In measurements of this type, it can be expected that $\sigma_2 > \sigma_1 > \sigma_3$ and $E(t)\neq 1/D(t)$.

$E(t)$ and $G(t)$ are obtained directly only from stress relaxation measurements, while $D(t)$ and $J(t)$ require creep experiments for their direct observation.

### 3.2.4 Stress–Strain–Time Behavior

When a mass of polymer is stressed the deformation produced may be considered as a sum of the following three deformations (see Figure 3.4):

1. A deformation due to bond bending and stretching which is instantaneous and independent of temperature (ordinary elastic deformation, $\varepsilon_{oe}$).
2. A deformation due to chain uncoiling which is not instantaneous and whose rate depends on temperature (high elastic deformation, $\varepsilon_{he}$).
3. A deformation due to slippage of polymer molecules past one another (viscous deformation $\varepsilon_v$). It is often assumed that the rates of such viscous deformation do not change with time if the applied stress is constant.

Figure 3.7 shows schematically the above types of deformational response as a result of a fixed stress imposed on a body showing ordinary elastic deformation only (Figure 3.7b), a second body showing high elastic deformation only (Figure 3.7c), and a third body showing viscous deformation only (Figure 3.7d). In each case, the stress is imposed at time $t_0$ and held at a constant value until time $t_1$, when it is removed. Real polymers exhibit deformation-time curves which are a combination of the three basic responses, and a simple relationship for a combined or total strain $\varepsilon$

$$\varepsilon = \varepsilon_{oe} + \varepsilon_{he} + \varepsilon_v$$

can be used to analyze the deformation under a given stress.
The combined response, however, differs widely among polymers. Figure 3.8 shows typical deformation-time curves. It will be noted that, given sufficient time, $\varepsilon_{he}$ will reach a constant value while $\varepsilon_v$ continues to increase with time. On release of stress, $\varepsilon_{he}$ will eventually disappear but $\varepsilon_v$ will remain constant. An important conclusion resulting from this is that since both the high elastic and the viscous components of strain depend on both time and temperature the total strain also will depend on time and temperature. This has been shown to be an important factor affecting many polymer properties. It is therefore proposed to consider the background to this fact in greater detail in the following section.

![Figure 3.8](image_url)

**FIGURE 3.8** Strain-time curves: (a) material showing substantial ordinary elastic, high elastic, and viscous components of strain; (b) material in which high elastic deformation predominates.
3.2.4.1 The WLF Equations

For a polymeric segment to move from its position to its adjacent site there must be some holes in the mass of the material into which the segment can move—and simultaneously leave a vacant space into which another segment may move. The important point is that molecular motion cannot take place without the presence of holes. These holes, collectively, are called free volume.

One interpretation of the glass transition temperature \( T_g \) is that it is a temperature below which the free volume is really too small for much molecular movement. However, at or above \( T_g \) the molecules have sufficient energy for movement, jostling occurs and the free volume increases quite sharply with an increase in temperature.

It is usual to express the temperature coefficient of the free volume as being the difference between the thermal expansion coefficients above and below \( T_g \). This may be expressed mathematically by the equation

\[
f = f_g + (\alpha_a - \alpha_b)(T - T_g) = f_g + \Delta\alpha(T - T_g)
\]  

(3.22)

where \( f \) is the fractional free volume at temperature \( T \), \( f_g \) is the fractional free volume at \( T_g \), and \( \alpha_a \) and \( \alpha_b \) are the coefficients of thermal expansion above and below the \( T_g \), respectively. The value of \( \Delta\alpha \) is simply \( (\alpha_a - \alpha_b) \).

Now it has been shown that the viscosity is related to the fractional free volume by an expression of the form

\[
\frac{1}{\eta_T} = Ke^{-A/\eta}
\]

(3.23)

so that

\[
\frac{1}{\eta_{T_g}} = Ke^{-A/\eta_g}
\]

(3.24)

where \( K \) and \( A \) are constants. Combining these one may write

\[
\log_e \left( \frac{\eta_T}{\eta_{T_g}} \right) = \frac{1}{f} - \frac{1}{f_g}
\]

(3.25)

Substituting for \( f \) from Equation 3.22, this expression yields

\[
\log_{10} \left( \frac{\eta_T}{\eta_{T_g}} \right) = \frac{-(T - T_g)}{2.303f_g(f_g/\Delta\alpha) + (T - T_g)}
\]

(3.26)

Experimental data on a large range of polymers have demonstrated the approximate general validity of the equation

\[
\log_{10} \left( \frac{\eta_T}{\eta_{T_g}} \right) = \frac{-17.44(T - T_g)}{51.6 + (T - T_g)}
\]

(3.27)

known as the Williams, Landel, and Ferry Equation (WLF equation). Solving Equation 3.26 and Equation 3.27 one obtains \( f_g = 0.025 \) and \( \Delta\alpha = 4.8 \times 10^{-4} \) deg\(^{-1}\).

Equation 3.27 implies that if we know the viscosity at some temperature \( T \) we can estimate the viscosity at \( T_g \), and from this estimate the viscosity at another temperature \( T_1 \). The WLF equation thus gives the effect of temperature on viscosity.

There are also other applications of the WLF equation. In essence, if the value of material property changes with temperature, and if this change arises from changes in the viscosity of the system, then it may well be possible to apply the WLF equation to the property change.
One example of this is in relation to stress relaxation. If a polymer is deformed to a fixed strain at constant temperature, the force required to maintain that strain will decay with time due to viscous slippage of molecules. One measure of this rate of decay or stress relaxation is the relaxation time $\lambda$, which may be defined as the time taken for the stress to decrease to $1/e$ of its initial value on application of strain (discussed later). In this case, it is found that

$$\log_{10} \left( \frac{\lambda_T}{\lambda_{T_g}} \right) = -\frac{17.44(T - T_g)}{51.6 + (T - T_g)}$$

(3.28)

which is of the same form as Equation 3.27.

For experiments performed in shear, there is a rather complicated relation between the time-dependent stress relaxation shear modulus $G(t)$ defined by Equation 3.19 and the time-dependent creep compliance $J(t)$ defined by Equation 3.21. But if the slope of log $G(t)$ versus log $t$ is $-m$, then, to a good approximation,

$$G(t) \cdot J(t) = \sin \frac{m\pi}{m\pi}$$

(3.29)

for $m < 0.8$. Not only are $G(t)$ and $J(t)$ related, but the former in turn is related to the tensile modulus which itself is related to the stress relaxation time $\lambda$. It is therefore possible in theory to predict creep-temperature relationships from WLF data, though in practice these are best determined by experiments.

### 3.2.5 Creep Behavior

Except for a few exceptions like lead, metals generally exhibit creep at higher temperatures. Plastics and rubbers, however, possess very temperature-sensitive creep behavior; they exhibit significant creep even at room temperature. In creep tests a constant load or stress is applied to the material, and the variation of deformation or strain with time is recorded. A typical creep curve plotted from such a creep test is shown in Figure 3.9a. The figure shows that there is typically an almost instantaneous elastic strain AB followed by a time-dependent strain, which occurs in three stages: primary or transient creep BC (stage I), secondary or steady-state creep CD (stage II), and tertiary or accelerated creep DE (stage III).

![Typical creep curve](image)

**FIGURE 3.9** Typical creep curve (a) with linear time scale and (b) with logarithmic time scale. (c) Family of creep curves for poly(methyl methacrylate) at 20°C ($1 \text{ kgf/cm}^2 = 0.098 \text{ MPa}$).
The primary creep has a rapidly decreasing strain rate. It is essentially similar in mechanism to retarded elasticity and, as such, is recoverable if the stress is removed. The secondary or steady-state creep is essentially viscous in character and is therefore nonrecoverable. The strain rate during this state is commonly referred to as the creep rate. It determines the useful life of the material. Tertiary creep occurs at an accelerated rate because of an increase in the true stress due to necking of the specimen.

Normally a logarithmic time scale is used to plot the creep curve, as shown in Figure 3.9b, so that the time dependence of strain after long periods can be included. If a material is linearly viscoelastic (Equation 3.17), then at any selected time each line in a family of creep curves (with equally spaced stress levels) should be offset along the strain axis by the same amount. Although this type of behavior may be observed for plastics at low strains and short times, in most cases the behavior is nonlinear, as indicated in Figure 3.9c.

Plastics generally exhibit high rates of creep under relatively low stresses and temperatures, which limits their use for structural purposes. Creep behavior varies widely from one polymer to another; thermoset polymers, in general, are much more creep resistant than thermoplastic polymers. The steady-state creep in plastics and rubbers (often referred to as cold flow) is due to viscous flow, and increases continuously. Clearly, the material cannot continue to get larger indefinitely, and eventually fracture will occur. This behavior is referred to as creep rupture. The creep strength of these materials is defined as the maximum stress which may be applied for a specified time without causing fracture. The creep strength of plastics is considerably increased by adding fillers and other reinforcing materials, such as glass fibers and glass cloth, since they reduce the rate of flow.

The creep and recovery of plastics can be simulated by an appropriate combination of elementary mechanical models for ideal elastic and ideal viscous deformations. Although there are no discrete molecular structures which behave like individual elements of the models, they nevertheless aid in understanding the response of plastic materials.

3.2.6 Maxwell Model

The Maxwell model consists of a spring and dashpot connected in series (Figure 3.10a). When a load is applied, the elastic displacement of the spring occurs immediately and is followed by the viscous flow of liquid in the dashpot which requires time. After the load is removed, the elastic displacement is recovered immediately, but the viscous displacement is not recovered.

3.2.6.1 Stress–Strain Relation

The spring is the elastic component of the response and obeys the relation

\[ \sigma_1 = E\varepsilon_1 \]  

(3.30)

\( \sigma_1 \) and \( \varepsilon_1 \) are the stress and strain, respectively, and \( E \) is a constant.

![Figure 3.10](a) The Maxwell model. (b), (c) Responses of the model under time-dependent modes of deformation.
The dashpot (consisting of a piston loosely fitting in a cylindrical vessel containing a liquid) accounts for the viscous component of the response. In this case the stress $\sigma_2$, is proportional to the rate of strain $\dot{\varepsilon}_2$; i.e.,

$$\sigma_2 = \eta \dot{\varepsilon}_2 \quad (3.31)$$

where $\eta$ is a material constant called the coefficient of viscous traction.

The total strain, $\varepsilon$, of the model under a given stress, $\sigma$, is distributed between the spring and the dashpot elements:

$$\varepsilon = \varepsilon_1 + \varepsilon_2 \quad (3.32)$$

From Equation 3.32 the rate of total displacement with time is

$$\dot{\varepsilon} = \dot{\varepsilon}_1 + \dot{\varepsilon}_2 \quad (3.33)$$

and from Equation 3.30 through Equation 3.32,

$$\dot{\varepsilon} = \frac{1}{E} \dot{\varepsilon}_1 + \frac{1}{\eta} \dot{\varepsilon}_2 \quad (3.34)$$

But both elements are subjected to the entire stress, $\sigma$,

$$\sigma = \sigma_1 = \sigma_2 \quad (3.35)$$

Therefore Equation 3.34 can be written as

$$\dot{\varepsilon} = \frac{1}{E} \dot{\sigma} + \frac{1}{\eta} \sigma \quad (3.36)$$

which is the governing equation of the Maxwell model. It is interesting to consider the responses that this model predicts under three common time-dependent modes of deformation.

Equation 3.36 is commonly rearranged as follows:

$$\dot{\sigma} = E \dot{\varepsilon} - \frac{1}{\lambda} \sigma \quad (3.37)$$

where $\lambda = \eta/E$ is the ratio of the viscosity $\eta$ of the dashpot and the tensile modulus $E$ of the spring.

Note that $\lambda$ has the units of time and that it characterizes the viscoelastic nature of the element very concisely, as the ratio of the viscous portion of the response to the elastic portion. This naturally occurring parameter is taken to be the response time or the relaxation time of the model.

Equation 3.37 is the governing equation of the Maxwell model. It is interesting to consider the responses that this model predicts under three common time-dependent modes of deformation.

1. **Creep.** If a constant stress $\sigma_0$ is applied, then Equation 3.37 becomes

$$\dot{\varepsilon} = \frac{\sigma_0}{E} \left( \frac{1}{\lambda} - \frac{1}{\lambda} \right) \quad (3.38)$$

Integration yields

$$\varepsilon = \varepsilon_0 (1 + t/\lambda) \quad (3.39)$$

which indicates a constant rate of increase of strain with time—i.e., steady-state creep (Figure 3.10b). Equation 3.39 describes the creep response of the Maxwell element.

2. **Relaxation.** If the strain is held constant, then Equation 3.37 becomes

$$\dot{\sigma} + \sigma/\lambda = 0 \quad (3.40)$$
Solving this differential equation with the initial condition \( \sigma = \sigma_0 \) at \( t = t_0 \) gives

\[
\sigma = \sigma_0 \exp(-t/\lambda) \tag{3.41}
\]

This indicates an exponential decay of stress with time (Figure 3.10c). The stress will relax and approach zero monotonically. The relaxation time \( \lambda \) is thus the time required for the stress to decay to \( 1/e \), or 0.37, of its initial value.

Since the strain remains constant in a relaxation experiment, Equation 3.41 can also be written as

\[
E(t) = E_0 \exp(-t/\lambda) \tag{3.42}
\]

where \( E(t) \) is the tensile modulus of the Maxwell element at time \( t \), and \( E_0 \) the modulus at the initial time of deformation.

The corresponding equation for the Maxwell element in shear is

\[
G(t) = G_0 \exp(-t/\lambda) \tag{3.43}
\]

where \( G(t) \) is the shear modulus of the Maxwell element at time \( t \), and \( G_0 \) is the modulus at \( t = 0 \); the relaxation time \( \lambda \) is now the ratio of the viscosity \( \eta \) of the viscous component and the shear modulus \( G \) of the elastic component of the model.

3. **Recovery.** When the initial stress, \( \sigma_0 \), is removed, there is an instantaneous recovery of the elastic strain, \( \varepsilon_0 \), and then, as shown by Equation 3.36, the strain rate is zero, so there is no further recovery (Figure 3.10b).

### 3.2.6.2 Generalized Maxwell Model

The behavior of a polymer system is so complicated that we cannot represent it with the response time of a single Maxwell element. In other words, the simple model described above cannot approach the behavior of a real system. In 1893, Weichert showed that stress–relaxation experiments could be represented as a generalization of Maxwell’s equation. The mechanical model according to Weichert’s formulation is shown in Figure 3.11; it consists of a large number of Maxwell elements coupled in parallel.

Since the strain in each element is common, we sum the forces acting on the individual elements to obtain the total stress as a function of time, i.e.,

\[
\sigma(t) = \sum \sigma_i \tag{3.44}
\]

For relaxation with constant strain \( \varepsilon_0 \) we combine Equation 3.41 and Equation 3.44 to obtain

\[
\sigma(t) = \varepsilon_0 \sum E_i \exp\left(-\frac{t}{\lambda_i}\right) \tag{3.45}
\]

where \( \lambda_i = \eta_i/E_i \) is the relaxation time of the \( i \)th element.

The overall modulus as a function of time, \( E(t) \), is thus

\[
E(t) = \frac{\sigma(t)}{\varepsilon_0} = \sum E_i \exp\left(-\frac{t}{\lambda_i}\right) \tag{3.46}
\]

The synthesis of \( E(t) \) from known values of \( E_i \) and \( \lambda_i \) is simplified by the use of semilog paper.

**FIGURE 3.11** Generalized Maxwell model (Weichert’s formulation).
Example 3.1: Derive the overall time-dependent modulus $E(t)$ for $0 < t < 200$ sec when

<table>
<thead>
<tr>
<th>$i$</th>
<th>$E_0$ [(dynes/cm$^2) \times 10^{-8}]]$</th>
<th>$\lambda_i$ (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.000</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>0.667</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>0.333</td>
<td>25</td>
</tr>
</tbody>
</table>

Answer: For each element, $E_i(t)$ is given by a straight line on semilog paper (Equation 3.42) with intercept $(E_i)_0$ and a negative slope of $\lambda_i$ (Figure 3.12). Adding the curves arithmetically gives $E(t)$ directly:

$$E_i(t) = (E_i)_0 \exp\left(-\frac{t}{\lambda_i}\right)$$

$$E(t) = \sum_{i=1}^{3} E_i(t)$$

Note that $E(t)$ is not a straight line in Figure 3.12.

As can be seen, the Maxwell–Weichert model possesses many relaxation times. For real materials we postulate the existence of a continuous spectrum of relaxation times ($\lambda_i$). A spectrum skewed toward lower times would be characteristic of a viscoelastic fluid, whereas a spectrum skewed toward longer times would be characteristic of a viscoelastic solid. For a real system containing crosslinks the spectrum would be skewed heavily toward very long or infinite relaxation times. In generalizing, $\lambda$ may thus be allowed to range from zero to infinity. The concept that a continuous distribution of relaxation times should be required to represent the behavior of real systems would seem to follow naturally from the fact that real polymeric systems also exhibit distributions in conformational size, molecular weight, and distance between crosslinks.

If the number of units is allowed to become infinite, the summation over the differential units of the model (Equation 3.44) can be explained by an integration over all relaxation times. Thus as $i \to \infty$ in Figure 3.11, the range of allowable relaxation times becomes zero to infinity. From the notion that the stresses in the individual elements, $\sigma_i$, are functions of time and relaxation times, $\sigma_i = \sigma_i(t, \lambda_i)$, we

![FIGURE 3.12 Time-dependent modulus for individual Maxwell elements and for the sum of three elements in parallel $\Sigma E_i(t)$](image-url)
define a continuous function $\sigma(t, \lambda)$ such that the total stress, $\sigma(t)$, is given by the following (compare Equation 3.44):

$$\sigma(t) = \int_{0}^{\infty} \sigma(t, \lambda) d\lambda$$  \hspace{1cm} (3.47)

and for relaxation with constant strain, $\epsilon_0$, it is given by the following (compare Equation 3.45):

$$\sigma(t) = \epsilon_0 \int_{0}^{\infty} E(\lambda) e^{-t/\lambda} d\lambda$$  \hspace{1cm} (3.48)

Since $E(t) = \sigma(t)/\epsilon_0$, we find that we have developed an expression suitable for representing the time dependence of the relaxation modulus, i.e.,

$$E(t) = \int_{0}^{\infty} E(\lambda) e^{-t/\lambda} d\lambda$$  \hspace{1cm} (3.49)

The function $E(\lambda)$ is referred to as the distribution of relaxation times or the relaxation spectrum. In principle, once $E(\lambda)$ is known, the result of any other type of mechanical experiment can be predicted. In practice $E(\lambda)$ is determined from experimental data on $E(t)$. Since the distribution of relaxation times is so broad, it is more convenient to consider $\ln \lambda$. Hence we introduce the function $H(\ln \lambda)$, where the parenthesis denotes functional dependence, to replace $E(\lambda)$ as

$$E(\lambda) = \frac{H(\ln \lambda)}{\lambda}$$  \hspace{1cm} (3.50)

Then Equation 3.49 becomes (note the change of limits):

$$E(t) = \int_{-\infty}^{+\infty} H(\ln \lambda) e^{-t/\lambda} d(\ln \lambda)$$  \hspace{1cm} (3.51)

and all relaxation times are considered as $\ln \lambda$.

What we desire now is a means to determine $H(\ln \lambda)$ from data obtained as $E(t)$ versus $\ln t$. This is virtually impossible to do directly, and a number of approximate methods have been devised. These approximations are discussed in the advanced reference works of Ferry [5] and Tobolsky [6].

3.2.7 Kelvin or Voigt Model

In the Kelvin or Voigt model the spring and dashpot elements are connected in parallel, as shown in Figure 3.13a. This model roughly approximates the behavior of rubber. When the load is applied at zero time, the elastic deformation cannot occur immediately because the rate of flow is limited by the dashpot. Displacements continue until the strain equals the elastic deformation of the spring and it resists further movement. On removal of the load the spring recovers the displacement by reversing the flow through the dashpot, and ultimately there is no strain. The mathematical relations are derived next.

3.2.7.1 Stress–Strain Relation

Since the two elements are connected in parallel, the total stress will be distributed between them, but any deformation will take place equally and simultaneously in both of them; that is,

$$\sigma = \sigma_1 + \sigma_2$$  \hspace{1cm} (3.52)

$$\epsilon = \epsilon_1 + \epsilon_2$$  \hspace{1cm} (3.53)
From Equation 3.30, Equation 3.31, and Equation 3.52,
\[ \sigma = E\varepsilon_1 + \eta\dot{\varepsilon}_2 \]
or, using Equation 3.53,
\[ \sigma = E\varepsilon + \eta\dot{\varepsilon} \]  
which is the governing equation for the Kelvin (or Voigt) model. Its predictions for the common time-dependent deformations are derived next.

1. **Creep.** If a constant stress, \( \sigma_0 \), is applied, Equation 3.54 becomes
\[ \sigma_0 = E\varepsilon + \eta\dot{\varepsilon} \]  
The differential equation may be solved for the total strain, \( \varepsilon \), to give
\[ \varepsilon = \sigma_0 \frac{1 - \exp\left(-\frac{E}{\eta} t\right)}{E} \]  
This equation indicates that the deformation does not appear instantaneously on application of stress, but it increases gradually, attaining asymptotically its maximum value \( \varepsilon = \sigma_0/E \) at infinite time (Figure 3.13b). The Voigt model is thus said to exhibit retarded elastic deformation in creep experiments. The quantity \( \eta/E = \lambda \) is called a retardation time. It is the time \( (t = \lambda) \) at which the deformation is retarded by \( 1/e \) of its maximum value. (The physical meaning of \( \eta/E \) for Maxwell and Voigt models should not be confused.)

By comparison with Equation 3.56 the creep equation under a constant shear stress \( \tau_0 \) may be written as
\[ \gamma = \frac{\tau_0}{G} \left[1 - \exp(-t/\lambda)\right] \]  
where \( \gamma \) is the time-dependent shear strain of the Voigt element and \( G \) is the shear modulus of its elastic component; \( \lambda \) is the retardation time \( (=\eta/G) \).
Equation 3.57 is conveniently written as

\[ J = J_0 [1 - \exp(-t/\lambda)] \]  \hspace{1cm} (3.58)

where \( J \) is the shear creep compliance \((=\gamma/\tau_0)\) at time \( t \), and \( J_0 \) is the shear creep compliance at the time of stress application.

2. \textit{Relaxation}. If the strain is held constant; then Equation 3.54 becomes

\[ \sigma = E \varepsilon \]

3. \textit{Recovery}. If the stress is removed, Equation 3.54 becomes

\[ 0 = E \varepsilon + \eta \dot{\varepsilon} \]

This differential equation may be solved with the initial condition \( \varepsilon = \varepsilon_0 \) at the time of stress removal to give

\[ \varepsilon = \varepsilon_0 \exp \left( -\frac{E}{\eta} t \right) \]  \hspace{1cm} (3.59)

This equation represents an exponential recovery of strain which, as a comparison with Equation 3.56 shows, is a reversal of the predicted creep.

The Kelvin (or Voigt) model therefore gives an acceptable first approximation to creep and recovery behavior but does not predict relaxation. By comparison, the previous model (Maxwell model) could account for relaxation but was poor in relation to creep and recovery. It is evident therefore that a better simulation of viscoelastic materials may be achieved by combining the two models.

### 3.2.8 Four-Element Model

A combination of the Maxwell and Kelvin models comprising four elements is shown in Figure 3.14a. The total strain is

\[ \varepsilon = \varepsilon_1 + \varepsilon_2 + \dot{\varepsilon}_k \]  \hspace{1cm} (3.60)

![FIGURE 3.14](image-url)  \hspace{1cm} (a) Four-element model. (b), (c) Responses of the model under time-dependent modes of deformation.
where $\varepsilon_k$ is the strain response of the Kelvin model. From Equation 3.30, Equation 3.31, and Equation 3.56,

$$
\varepsilon = \frac{\sigma_0}{E_1} + \frac{\sigma_0 t}{\eta_1} + \frac{\sigma_0}{E_2} \left[ 1 - \exp \left( -\frac{E_2}{\eta_2} t \right) \right]
$$

(3.61)

Thus the strain rate is

$$
\dot{\varepsilon} = \frac{\sigma_0}{\eta_1} + \frac{\sigma_0}{\eta_2} \exp \left( -\frac{E_2}{\eta_2} t \right)
$$

(3.62)

The response of this model to creep, relaxation, and recovery situations is thus the sum of the effects described previously for the Maxwell and Kelvin models and is illustrated in Figure 3.14b.

Though the model is not a true representation of the complex viscoelastic response of polymeric materials, it is nonetheless an acceptable approximation to the actual behavior. The simulation becomes better as more and more elements are added to the model, but the mathematics also becomes more complex.

### 3.2.9 Zener Model

Another model, attributed to Zener, consists of three elements connected in series and parallel, as illustrated in Figure 3.15, and known as the standard linear solid. Following the procedure already given, we derive the governing equation of this model:

$$
\eta_3 \ddot{\sigma} + E_1 \sigma = \eta_3 (E_1 + E_2) \dot{\varepsilon} + E_1 E_2 \varepsilon
$$

(3.63)

This equation may be written in the form

$$
a_1 \ddot{\sigma} + a_0 \sigma = b_1 \dot{\varepsilon} + b_0 \varepsilon
$$

(3.64)

where $a_1$, $a_0$, $b_1$, and $b_0$ are all material constants. A more general form of Equation 3.64 is

$$
a_n \frac{\partial^n \sigma}{\partial t^n} + a_{n-1} \frac{\partial^{n-1} \sigma}{\partial t^{n-1}} + \cdots + a_0 \sigma
$$

$$
= b_m \frac{\partial^m \varepsilon}{\partial t^m} + \cdots + b_0 \varepsilon
$$

(3.65)

The modern theory of viscoelasticity favors this type of equation. The models described earlier are special cases of this equation.

**Hookean body.** All constants $a$ and $b$ except $a_0$ and $b_0$ are zero. Equation 3.65 becomes

$$
a_0 \sigma = b_0 \varepsilon
$$

(3.65a)

**Maxwell element.** All constants $a$ and $b$ except $a_0$, $a_1$, and $b_1$ are zero. Equation 3.65 becomes

$$
a_0 \sigma + a_1 \frac{\partial \sigma}{\partial t} = b_1 \frac{\partial \varepsilon}{\partial t}
$$

(3.65b)
This is the spring and dashpot in series and applies to stress relaxation at constant strain. 

Voigt element. All constants \( a \) and \( b \) except \( a_0, b_0, \) and \( b_1 \) are zero. Equation 3.65 becomes

\[
a_0 \sigma = b_0 \varepsilon + b_1 \frac{\partial \varepsilon}{\partial t}
\]

(3.65c)

This is the spring and dashpot in parallel and applies to strain retardation at constant stress.

### 3.2.10 Superposition Principle

Each of the creep curves in Figure 3.9c depicts the strain response of a material under a constant stress. However, in service, materials are often subjected to a complex sequence of stresses or stress histories, and obviously it is not practical to obtain experimental creep data for all combinations of loading. In such cases a theoretical model can be very useful for describing the response of a material to a given loading pattern.

The most commonly used model is the Boltzmann superposition principle, which proposes that for a linear viscoelastic material the entire loading history contributes to the strain response, and the latter is simply given by the algebraic sum of the strains due to each step in the load. The principle may be expressed as follows. If an equation for the strain is obtained as a function of time under a constant stress, then the modulus as a function of time may be expressed as

\[
E(t) = \frac{\sigma}{\varepsilon(t)}
\]

(3.66)

Thus if the applied stress is \( \sigma_0 \) at zero time, the creep strain at any time, \( t \), will be given by

\[
\varepsilon(t) = \frac{1}{E(t)} \sigma_0
\]

(3.67)

On the other hand, if the stress, \( \sigma_0 \), was applied at zero time and an additional stress, \( \sigma_1 \), at time \( u \), the Boltzmann superposition principle says that the total strain at time \( t \) is the algebraic sum of two independent responses; that is,

\[
\varepsilon(t) = \frac{1}{E(t)} \sigma_0 + \frac{1}{E(t-u)} \sigma_1
\]

(3.68)

For any series of stress increments this equation can be generalized to

\[
\varepsilon(t) = \sum_{u=-\infty}^{u=t} \frac{1}{E(t-u)} \sigma_i
\]

(3.69)

The lower limit of the summation is taken as \(-\infty\) since the entire stress history contributes to the response.

As an illustration, for a series of step changes in stress as in Figure 3.16a, the strain response predicted by the model is shown schematically in Figure 3.16b. The time-dependent strain response (creep curve) due to the stress \( \sigma_0 \) applied at zero time is predicted by Equation 3.66 with \( \sigma = \sigma_0 \). When a second stress, \( \sigma_1 \), is added to \( \sigma_0 \), the new curve will be obtained, as illustrated in Figure 3.16b, by adding the creep due to \( \sigma_1 \) to the anticipated creep due to \( \sigma_0 \). Removal of all stress at a subsequent time \( u_2 \) is then equivalent to removing the creep stain due to \( \sigma_0 \) and \( \sigma_1 \), independently, as shown in Figure 3.16b. The procedure is repeated in a similar way for other stress changes.

To take into account a continuous loading cycle, we can further generalize Equation 3.69 to

\[
\varepsilon(t) = \int_{-\infty}^{t} \frac{1}{E(t-u)} \frac{d\sigma(u)}{du} \, du
\]

(3.70)
In the same way the stress response to a complex strain history may be derived as

\[ \sigma(t) = \int_{-\infty}^{t} E(t-u) \frac{d\varepsilon(u)}{du} \, du \]  

(3.71)

When the stress history has been defined mathematically, substitution in Equation 3.70 and integration within limits gives the strain at the given time. The stress at a given time is similarly obtained from Equation 3.71.

### 3.2.11 Isometric and Isochronous Curves

Isometric curves are obtained by plotting stress vs. time for a constant strain; *isochronous curves* are obtained by plotting stress vs. strain for a constant time of loading. These curves may be obtained from the creep curves by taking a constant-strain section and a constant-time section, respectively, through the creep curves and reploting the data, as shown in Figure 3.17.

An isometric curve provides an indication of the relaxation of stress in the material when the strain is kept constant. Since stress relaxation is a less common experimental procedure than creep testing, an isometric curve, derived like the preceding curves from creep curves, is often used as a good approximation of this property.

Isochronous curves, on the other hand, are more advantageously obtained by direct experiments because they are less time consuming and require less specimen preparation than creep testing. The experiments actually involve a series of mini creep and recovery tests on the material. Thus a stress is applied to a specimen of the material, and the strain is recorded after a time \( t \) (typically 100 sec). The stress
is then removed and the material is allowed to recover. This procedure is repeated until there are sufficient points to plot the isochronous curve.

Note that the isochronous test method is quite similar to that of a conventional incremental loading tensile test and differs only in that the presence of creep is recognized and the “memory” of the material for its stress history is overcome by the recovery periods. Isochronous data are often presented on log-log scales because this provides a more precise indication of the nonlinearity of the data by yielding a straight-line plot of slope less than unity.

### 3.2.12 Pseudoelastic Design Method

Due to the viscoelastic nature of plastics, deformations depend on such factors as the time under load and the temperature. Therefore the classical equations available for the design of structural components, such as springs, beams, plates, and cylinders, and derived under the assumptions that (1) the modulus is constant and (2) the strains are small and independent of loading rate or history and are immediately reversible, cannot be used indiscriminately. For example, classical equations are derived using the relation

\[ \text{Stress} = \text{constant} \times \text{strain} \]

where the constant is the modulus. From the nature of the creep curves shown in Figure 3.17a, it is clear that the modulus of a plastic is not constant. Several approaches have been developed to allow for this fact, and some of them also give very accurate results; but mathematically they are quite complex, and this has limited their use. However, one method that has been widely accepted is the pseudoelastic design method. In this method appropriate values are chosen for the time-dependent properties, such as modulus, and substituted into the classical equations.
The method has been found to give sufficiently accurate results, provided that the value of the modulus is chosen judiciously, taking into account the service life of the component and the limiting strain of the plastic. Unfortunately, however, there is no straightforward method for finding the limiting strain of a plastic. The value may differ for various plastics and even for the same plastic in different applications. The value is often arbitrarily chosen, although several methods have been suggested for arriving at an appropriate value.

One method is to draw a secant modulus which is 0.85 of the initial tangent modulus and to note the strain at which this intersects the stress–strain curve (see Figure 3.2b). But this method may be too restrictive for many plastics, particularly those which are highly crystalline. In most situations the maximum allowable strain is therefore decided in consultations between designer and product manufacturer.

Once an appropriate value for the maximum strain is chosen, design methods based on creep curves and the classical equations are quite straightforward, as shown in the following examples.

**Example 3.2:** A plastic beam, 200 mm long and simply supported at each end, is subjected to a point load of 10 kg at its mid-span. If the width of the beam is 14 mm, calculate a suitable depth so that the central deflection does not exceed 5 mm in a service life of 20,000 h. The creep curves for the material at the service temperature of 20°C are shown in Figure 3.18a. The maximum permissible strain in this material is assumed to be 1%.

**Answer:** The linear elastic equation for the central deflection, \( \delta \), of the beam is

\[
\delta = \frac{PL^3}{48EI}
\]

where \( P \), load at mid-span; \( L \), length of beam; \( E \), modulus of beam material; \( I \), second moment of area of beam cross section

The second moment of area is

\[
I = \frac{bd^3}{12} = \frac{14d^3}{12} \text{mm}^4
\]

![Figure 3.18](image-url)

**FIGURE 3.18** (a) Creep curves for material used in illustrative examples. (b) Isochronus curve at 20,000 h service life (1 kgf/cm\(^2\) = 0.098 MPa).
So from the expression for $\delta$,$$d^3 = \frac{PL^3}{56E}\delta$$

The only unknown on the right side is $E$. For plastic this is time dependent, but a suitable value corresponding to the maximum permissible strain may be obtained by referring to the creep curves in Figure 3.18a. A constant-time section across these curves at 20,000 h gives the isochronous curve shown in Figure 3.18b. Since the maximum strain is recommended as 1%, a secant modulus may be taken at this value. It is $9285$ kgf/cm$^2$ (=92.85 kgf/mm$^2$). Using this value in the above equation gives

$$d^3 = \frac{10(200)^3}{56 \times 92.85 \times 5}$$

$$d = 14.5 \text{ mm}$$

**Example 3.3:** A thin-wall plastic pipe of diameter 150 mm is subjected to an internal pressure of 8 kgf/cm$^2$ at 20°C. It is suggested that the service life of the pipe should be 20,000 h with a maximum strain of 2%. The creep curves for the plastic material are shown in Figure 3.18a. Calculate a suitable wall thickness for the pipe.

**Answer:** The hoop stress, $\sigma$, in a thin-wall pipe of diameter $d$ and thickness $h$, subjected to an internal pressure, $P$, is given by

$$\sigma = \frac{Pd}{2h} \text{ so } h = \frac{Pd}{2\sigma}$$

A suitable design stress may be obtained from the creep curves in Figure 3.18a. By referring to the 20,000-h isochronous curve (Figure 3.18b) derived from these curves, the design stress at 2% strain is obtained as 167.7 kg/cm$^2$. (Note that a similar result could have been obtained by plotting a 2% isometric curve from the creep curves and reading the design stress at a service life of 20,000 h.) Substituting the design stress into the equation for $h$ gives

$$h = \frac{8 \times 150}{2 \times 167.7} = 3.58 \text{ mm}$$

It may be seen from the creep curves (Figure 3.18a) that when the pipe is first pressurized, the strain is less than 1%. Then as the material creeps, the strain increases steadily to reach its limit of 2% at 20,000 h.

In both examples it has been assumed that the service temperature is 20°C. If this is not the case, then creep curves at the appropriate temperature should be used. However, if none are available, a linear extrapolation between available temperatures may be sufficient for most purposes.

Again, for some materials like nylon the moisture content of the material has a significant effect on its creep behavior. In such a case creep curves are normally available for the material in both wet and dry states, and appropriate data should be used, depending on the service conditions.

### 3.2.13 Effect of Temperature

Many attempts have been made to obtain mathematical expressions which describe the time and temperature dependence of the strength of plastics. Since for many plastics at constant temperature a plot of
stress, $\sigma$, against the logarithm of time to failure (creep rupture), $t$, is approximately linear, one of the expressions most commonly used is

$$t = Ae^{-B\sigma}$$  \hspace{1cm} (3.72)

where $A$ and $B$ are constants. In reality, however, they depend on factors such as material structure and on temperature.

The most successful attempts to include the effects of temperature in a relatively simple expression have been made by Zhurkov and Bueche, who used an equation of the form [7]

$$t = t_0 \exp \left( \frac{U_0 - \gamma \sigma}{RT} \right)$$  \hspace{1cm} (3.73)

where $t_0$ is a constant which has approximately the same value for most plastics, $U_0$ is the activation energy of the fracture process, $\gamma$ is a coefficient which depends on the structure of the material, $R$ is the molar gas constant, and $T$ is the absolute temperature.

A series of creep rupture tests on a given material at a fixed temperature would permit the values for $U_0$ and $\gamma$ for the material to be determined from this expression. The times to failure at other stresses and temperatures could then be predicted.

The relative effects of temperature rises on different plastic materials depend on the structure of each material and, particularly, whether it is crystalline or amorphous. If a plastic is largely amorphous (e.g., polymethyl methacrylate, polystyrene), then it is the glass transition temperature ($T_g$) which will determine the maximum service temperature, since above $T_g$ the material passes into the rubbery region (see Figure 1.19).

On the other hand, in plastics which have a high degree of crystallinity (e.g., polyethylene, polypropylene), the amorphous regions are small, so $T_g$ is only of secondary importance. For them it is the melting temperature which will limit the maximum service temperature. The lowest service temperatures which can be used are normally limited by the brittleness introduced into the material. The behavior of plastics materials at room temperature is related to their respective $T_g$ values. This aspect has been dealt with in Chapter 1.

### 3.2.14 Time–Temperature Superposition

In engineering practice, it is often necessary to design for the use of a material over a long period of time—many years, for example. A common parameter to use in design work is the elastic modulus. We know, however, that for polymers the modulus decreases with increasing time under load.

Accumulation of long-term data for design with plastics can be very inconvenient and expensive. A method is thus needed to extrapolate data from shorter time studies at higher temperature to longer times over several decades of time scale at the desired temperature so that a lower limit of the modulus can be determined for use in design. On the other hand, it is sometimes difficult to obtain data over a very short time scale. One must then extrapolate data obtained under practicable experimental conditions to these short time scales. An empirical method for such extrapolations is available for amorphous polymer systems and, in general, for polymer systems where structure does not change during the period of testing.

The aforesaid extrapolations make use of a time-temperature superposition principle which is based on the fact that time and temperature have essentially equivalent effects on the modulus values of amorphous polymers. Figure 3.19 shows modulus data taken at several temperatures for poly(methyl methacrylate) [8]. Because of the equivalent effect of time and temperature, data at different temperatures can be superposed on data taken at a specified reference temperature merely by shifting individual curves one at a time and consecutively along the log $t$ axis about the reference temperature.
This time–temperature superposition procedure has the effect of producing a single continuous curve of modulus values extending over many decades of log $t$ at the reference temperature. A curve constructed in this way, as shown in Figure 3.20 (with a reference temperature 115°C), is known as the master curve.

The time-temperature superposition can be expressed mathematically as

$$E(T_1, t) = E(T_2, t/a_T)$$

(3.74)

for a tensile stress relaxation experiment ($T_2 > T_1$). The procedure asserts that the effect of changing the test temperature on viscoelastic properties is the same as that of multiplying or dividing the time scale by a constant quantity ($a_T$) at each temperature. The quantity $a_T$ is called the shift factor, and it must be obtained directly from the experimental curve by measuring the amount of shift along the log $t$ scale.

**FIGURE 3.19** Logarithm of tensile relaxation modulus versus logarithm of time for unfractionated poly(methyl methacrylate) of $M_v = 3.6 \times 10^6$. (After McLoughlin, J. R. and Tobolsky, A. V. 1952. *J. Colloid Sci.*, 7, 555.)

**FIGURE 3.20** Modulus-time master curve based on time–temperature superposition of data in Figure 3.19. Times referred to temperature of 115°C.
necessary to match the curve. The parameter $a_T$ is chosen as unity at the reference temperature and is a function of the temperature alone, decreasing with increasing temperature.

It is common practice now to use the glass transition temperature ($T_g$) as the reference temperature for master curve construction. For most amorphous polymers, the shift factor at any other temperature $T$ is then given fairly well by

$$\log_{10} a_T = \log \left( \frac{t(T)}{t(T_g)} \right) = \frac{-17.44(T - T_g)}{51.6 + (T - T_g)}$$

Equation 3.75 is known as the WLF equation (see Equation 3.27) after the initials of the researchers who proposed it [9]. The expression given holds between $T_g$ and $T_g + 100^\circ C$. However, if a different reference temperature is chosen an equation with the same form as Equation 3.75 can be used, but the constants on the right hand side must be re-evaluated.

The significance of the WLF generalization (Equation 3.75) cannot be over-emphasized. Again and again, one finds in the literature methods of superposing time and temperature for mechanical and other properties in amorphous and partially amorphous materials. Whatever modifications are introduced usually reduce the behavior back in the direction of Equation 3.75.

### 3.2.15 Dynamic Mechanical Properties

A complete description of the viscoelastic properties of a material requires information over very long times. To supplement creep and stress relaxation measurements which are limited by experimental limitations, experiments are therefore performed in which an oscillating stress or strain is applied to the specimen. These constitute an important class of experiments for studying the viscoelastic behavior of polymeric solids. In addition to elastic modulus, it is possible to measure by these methods the viscous behavior of the material in terms of characteristic damping parameters.

Damping is an engineering material property and the observed response is much more sensitive to the polymer constitution than in step-function experiments. Oscillatory experiments (also referred to as dynamic mechanical experiments) thus offer a powerful technique to study molecular structure and morphology. A significant feature is the breadth of the time-scale spectrum available with these methods, e.g., $10^{-5} - 10^8$ cycles/sec.

In a dynamic experiment, the stress will be directly proportional to the strain if the magnitude of the strain is small enough. Then, if the stress is applied sinusoidally the resulting strain will also vary sinusoidally. (The same holds true if the strain is the input and the stress the output.) At sufficiently low frequencies, the strain will follow the stress in phase. However, in the general case the strain will be out of phase.

In the last instance, the strain can be factored into two components—one of which is in phase with the stress and the other which lags behind the stress by $\pi/2$ rad. Alternatively, the stress can be decomposed into a component in phase with the strain and one which leads the strain by $\pi/2$ rad. This is accomplished by use of a rotating vector scheme, as shown in Figure 3.21.

The magnitude of the stress at any time is represented by the projection OC of the vector OA on the vertical axis. Vector OA rotates with a frequency $\omega$ equal to that of the sinusoidally varying stress. The length of OA is the stress amplitude (maximum stress) involved in the experiment. The strain is represented by the projection OD of vector OB on the vertical axis. The strain vector OB rotates in the same direction as OA with frequency $\omega$ but it lags OA by an angle $\delta$. The loss tangent (discussed later) is defined as $\tan \delta$.

The strain vector OB can be resolved into vector OE along the direction of OA and OF perpendicular to OA. Then the projection OH of OE on the vertical axis is the magnitude of the strain which is in phase with the stress at any time. Similarly, projection OI of vector OF is the magnitude of the strain which is $\pi/2$ rad (one quarter cycle) out of phase with the stress.

The stress can be similarly resolved into two components with one along the direction of OB and one leading the strain vector by $\pi/2$ rad. The ratio of the in-phase stress to the strain amplitude (maximum
strain) is called the storage modulus. In a shear deformation experiment this quantity is labeled $G' (\omega)$. The ratio of the out-of-phase stress to the strain is the loss modulus $G'' (\omega)$.

If, on the other hand, the strain vector is resolved into its components, the ratio of the in-phase strain to stress amplitude (maximum stress) is the storage compliance $J' (\omega)$ and the ratio of the out-of-phase strain to the stress amplitude is the loss compliance $J'' (\omega)$.

It is evident from the above description that $G' (\omega)$ and $J' (\omega)$ are associated with the periodic storage and complete release of energy in the sinusoidal deformation process. The loss parameters $G'' (\omega)$ and $J'' (\omega)$, on the other hand, reflect the nonrecoverable use of applied mechanical energy to cause viscous flow in the material. At a specified frequency and temperature, the dynamic response of a polymer in shear deformation can be summarized by any one of the following pairs of parameters: $G' (\omega)$ and $G'' (\omega)$, $J' (\omega)$ and $J'' (\omega)$, or absolute modulus $|G|$ and $\tan \delta$.

### 3.2.16 Rheological Behavior

Rheology is the science of deformation and flow of matter. Essentially, all thermoplastic resins (and many thermosetting resins) are required to undergo flow in the molten state during the course of product manufacture. Important fabrication processes such as injection, extrusion, and calendering all involve the flow of molten polymers. In plastics fabrication, it is important to understand the effect, on melt viscosity, of such factors as temperature, pressure, rate of shear, molecular weight, and structure. It is also equally important to have reliable means of measuring viscous properties of materials.

The flow behavior of polymeric melts cannot be considered to be purely viscous in character. The response of such materials is more complex, involving characteristics that are both viscous and elastic. This is only to be expected when one is trying to deform variously entangled long-chain molecules with a distribution of molecular weights.

During flow, polymer molecules not only slide past each other, but also tend to uncoil—or at least they are deformed from their equilibrium, random coiled-up configuration. On release of the deforming stresses, these molecules tend to revert to random coiled-up forms. Since molecular entanglements cause the molecules to act in a cooperative manner, some recovery of shape corresponding to the recoiling
occurs. In phenomenological terms, we say that the melt shows elasticity in addition to viscous flow. The elastic—that is to say, time-dependent—effects play a most important part in die swell, extrusion defects, and melt fracture, which will be considered later in this section.

### 3.2.16.1 Classification of Fluid Behavior

Although one can measure deformation in a solid, one cannot normally do this in a liquid since it undergoes a continuously increasing amount of deformation when a shear stress is applied. But one can determine the deformation rate (the shear rate) caused by an applied shear stress, or vice versa, and fluid behavior can be classified on this basis.

We begin by making a reference to Figure 3.22, which schematically illustrates two parallel plates of very large area $A$ separated by a distance $r$ with the space in between filled with a liquid. The lower plate is fixed and a shear force $F_s$ is applied to the top plate of area $A$ producing a shear stress ($\tau = F_s/A$) that causes the plate to move at a uniform velocity $v$ in a direction parallel to the direction of the force.

It may be assumed that the liquid wets the plates and that the molecular layer of liquid adjacent to the stationary plate is stationary while the layer adjacent to the top plate moves at the same velocity as the plate. Intermediate layers of liquid move at intermediate velocities, and at steady state in laminar flow a velocity distribution is established as indicated by the arrows in the diagram. The velocity gradient between the two plates is $dv/dr$. It is defined as the shear rate and is commonly given the symbol $\dot{\gamma}$ i.e.,

$$\dot{\gamma} = \frac{dv}{dr} \tag{3.76}$$

If the liquid is ideal and it is maintained at a constant temperature, the shear stress is linearly and directly proportional to the shear rate such that one may write

$$\tau = \eta(\frac{dv}{dr}) = \eta \dot{\gamma} \quad \text{or} \quad \eta = \frac{\tau}{\dot{\gamma}} \tag{3.77}$$

where $\eta$ is the coefficient of viscosity or simply the viscosity or internal friction of the liquid. The linear relationship between $\tau$ and $\dot{\gamma}$ given by Equation 3.77 or Equation 3.78 is known as Newton’s law and liquids which behave in this manner are called Newtonian fluids or ideal fluids. Other fluids which deviate from Newton’s law are described as non-Newtonian. For such fluids, the viscosity defined by Equation 3.78 is also known as the apparent viscosity.

In practice, the Newtonian behavior is confined to low molecular weight liquids. Polymer melts obey Newton’s law only at shear rates close to zero and polymer solutions only at concentrations close to zero. The most general rheological equation is

$$\eta = f(\dot{\gamma}, T, t, P, c, \ldots \ldots) \tag{3.79}$$

where the variables are $\dot{\gamma}$ = shear rate (itself a function of the shear stress), $T$ = temperature, $t$ = time, $P$ = pressure (itself a function of volume), $c$ = concentration, and the multiple dots which follow include, for example, molecular parameters (such as molecular weight and molecular weight distribution), compositional variables (crystallinity and the presence of additives), and factors that relate to processing history. Such an equation is clearly unrealistic, so we shall consider here some of the principal variables, one at a time, assuming that the others remain constant.

Several common types of rheological behavior are shown in Figure 3.23 based upon $\tau$ vs. $\dot{\gamma}$ curves.
These flow phenotypes are named Newtonian, pseudoplastic, dilatant, and Bingham. In Newtonian liquids, the viscosity is constant and independent of shear rate.

In pseudoplastic and dilatant liquids the viscosity is no longer constant. In the former it decreases and in the latter it increases with increasing shear rate; that is to say, the shear stress increases with increasing shear rate less than proportionately in a pseudoplastic and more than proportionately in a dilatant. Pseudoplastics are thus described as shear-thinning and dilatants as shear-thickening fluid systems. These two flow phenotypes can be described by an Equation the “power law”:

\[ \tau = \eta_N \dot{\gamma}^n \]  

(3.80)

where \( \eta_N \) is the zero shear (Newtonian) viscosity. The exponent \( n \) is greater than unity for a dilatant and less than unity for a pseudoplastic. A Newtonian is then seen to be a special case, with \( n = 1 \).

Equation 3.80 gives a linear relationship between \( \log \tau \) and \( \log \dot{\gamma} \) and the slope of the experimental plot (Figure 3.24) gives the value of \( n \). For the analysis of flow behavior of many systems, the power law relationship has been useful as from a plot of data (Figure 3.24), and measuring the slope, one can readily get an idea of just how non-Newtonian the fluid is.

A Bingham body would be described by the equation

\[ \tau - \tau_y = \eta \dot{\gamma} \]  

(3.81)

where \( \tau_y \) is the yield stress or yield value. Below \( \tau_y \) the material will not flow at all (hence \( \dot{\gamma} = 0 \) and \( \eta = \infty \)) so that the material, to all intents and
purposes, is a solid. However, as soon as \( \tau \) exceeds \( \tau_y \), the material suddenly behaves like a liquid with a viscosity that remains constant with increasing shear rate. Materials which exhibit this type of behavior include drilling muds, sewage sludge, toothpaste, greases and fats, as well as the clay slurries originally observed by Bingham.

Lenk [10] has shown that the flow phenotypes form part of a general response pattern which may be summarized in a general flow curve. The generalized flow curve is shown in Figure 3.25 alongside a fully developed stress–strain curve for a typical tough solid in tension after conversion of the conventional stress (i.e., force per unit of original cross-sectional area) to true stress (i.e., force per unit of actual cross-sectional area after deformation). This conversion can be effected if a continuous record of the changes in cross-sectional area of the specimen under test is kept. It may be seen that the shapes of the two curves are absolutely identical and the regions into which the two curves divide have also analogous physical significance.

It is well known that at extremely low shear rates the slope of the \( \tau/\gamma \) curve (Figure 3.23) is constant and that there exists some very low but finite threshold shear rate beyond which deviation from linearity commences. The slope of the initial linear portion of the curve is known as the “limiting viscosity,” the zero shear viscosity, or the Newtonian viscosity. Beyond this low shear rate region (initial Newtonian regime) the material is shear-softened (i.e., becomes pseudoplastic), a phenomenon which has its counterpart in the solid state where it is known as strain-softening.

Continuing in the pseudoplastic region it is often found that an upper threshold can be reached beyond which no further reduction in viscosity occurs. The curve then enters a second linear region of proportionality the slope of which is the second Newtonian viscosity.

Polymer melts are almost invariably of the pseudoplastic type, and the existence of first and second Newtonian regions has long been recognized. The pseudoplastic behavior appears to arise from the elastic nature of the melt and from the fact that under shear, polymers tend to be oriented.

At low shear rates Brownian motion of the segments occurs so polymers can coil up (re-entangle) at a faster rate than they are oriented. At higher shear rates such re-entangling rates are slower than the orientation rates and the polymer is hence apparently less viscous. However at very high shear rates (beyond the range of usual interest in the polymer processing industries) the degree of orientation reaches a maximum and so a further decrease in effective viscosity cannot occur; the polymer is this range again becomes Newtonian.

Generally speaking, the larger the polymer molecule the longer the recoiling (re-entangling, relaxation) time so that high-molecular-weight materials tend to be more non-Newtonian at lower shear rates than lower-molecular-weight polymers.
The dilatant type is less common among plastics under ordinary conditions, but it can be found in heavily filled systems and in some PVC pastes. The dilatant type (Figure 3.23c) represents the entire generalized flow curve in which the initial Newtonian and pseudoplastic regions have degenerated to a vanishingly small portion of the curve as a whole. In some cases of dilatancy a linear region may be distinguished before the curvature appears. In other cases no distinctly linear portion can be seen at the low-shear-rate end. The Bingham type is not common among plastics.

3.2.16.2 Effect of Shear Rate on Viscosity

Most polymer melts exhibit non-Newtonian behavior with the apparent viscosity decreasing with increasing shear rate (shear thinning). Viscosity of polymer at high shear rates may be several orders of magnitude smaller than the viscosity at low shear rates. Typical shear rate vs. viscosity curves are shown in Figure 3.26. The polymer melt has a Newtonian viscosity which is high at very low shear rates. Viscosity decreases nearly linearly with shear rate when plotted on a log–log scale (Figure 3.26). In this linear range, the power law equation (Equation 3.80) with $n<1$ is applicable.

The reduction of viscosity with increasing rate of shear [11,12] is taken advantage of in achieving desirable and optimum viscosity for polymers in processing machines and equipment without raising the temperature to detrimental levels, simply by raising the shear rate to as high a level as economically and otherwise possible. A reduction in viscosity with increasing shear rate is also taken advantage of in brushing and spraying of paints which are polymer solutions/suspensions containing pigments.

3.2.16.3 Effect of Molecular Weight on Viscosity

The molecular weight of a polymer is the most important factor affecting rheology. For most polymers the zero-shear viscosity is approximately proportional to the weight-average molecular weight ($M_w$) below a critical value ($M_c$) and depends on $M_w$ to a power equal to 3.5 at molecular weights above $M_c$:

$$\eta = K_1 M_w \quad \text{for} \quad M_w < M_c$$

and

$$\eta = K_2 M_w^{3.5} \quad \text{for} \quad M_w > M_c$$

![Figure 3.26](image-url)  
**FIGURE 3.26** Typical log viscosity–log shear rate curves at five different temperatures. Curve 1 is for the highest temperature and curve 5 is for the lowest temperature. For a typical polymer, the temperature difference between each curve is approximately 10°C.
The relationship between viscosity and molecular weight shown by a graphical logarithmic plot in Figure 3.27 is characterized by a sharp change at the critical molecular weight ($M_c$). The value of $M_c$ varies from one polymer to another. For most polymers $M_c$ is between 5,000 and 15,000.

The critical molecular weight corresponding to the transition in the viscosity behavior at $M_c$ points to additional hindrance to flow from this point onwards due to chain entanglements. Below this point the molecules usually move independently as in low-molecular-weight liquids, but above this point mutual entanglements of chain molecules is so prominent that movement of one involves dragging of others along with it; as a consequence, increasing molecular weight is associated with a very high rate of viscosity increase.

Considering the fact that the viscosity is increasing logarithmically with molecular weight in Figure 3.27, it should be clear why molecular weight control is important in polymer processing. One needs a molecular weight high enough to attain good mechanical properties but not so high that the molten polymer is too viscous to be processed economically.

The distribution of molecular weights in a polymer also influences its rheology. In general, the broader the range, the lower the shear rate at which shear thinning (decrease in viscosity) develops. Thus polymers with broad molecular-weight distribution are easier to extrude than those with narrow distribution.

Chain branching is another factor that influences flow. The more highly branched a given polymer, the lower will be its hydrodynamic volume and the lower its degree of entanglement at a given molecular weight. One can make the general observation, therefore, that viscosity is higher with linear than with branched polymers at a given shear rate and molecular weight. This does not mean that chain branching is necessarily desirable. In fact, branching results in weaker secondary bonding forces and possibly poorer mechanical properties.

### 3.2.16.4 Effect of Temperature on Polymer Viscosity

The viscosity of most polymers changes with temperature. An Arrhenius equation of the form

$$\eta = Ae^{E/RT}$$

where $A$ is a constant and $E$ is the activation energy, has often been used to relate viscosity and temperature. Constants in the Arrhenius equation can be evaluated by plotting the logarithm of viscosity against the reciprocal of absolute temperature, using shear stress or shear rate as a parameter. The data for most materials give straight line over reasonably large range of temperature.

Whilst the Arrhenius equation can be made to fit experimental data quite well it does nothing to explain the difference between polymers. In this regard, the WLF equation (see Equation 3.27):

$$\log \left( \frac{\eta(T)}{\eta(T_g)} \right) = \frac{-17.44(T - T_g)}{51.6 + (T - T_g)}$$

is more useful. Melt viscosity, according to this equation, is a function of $(T - T_g)$. Thus, for example, a major cause of the difference between the viscosity of poly(methacrylate) at its processing temperature (where $T - T_g = 100^\circ C$) and the
viscosity of polyethylene at its processing temperature (where $T - T_g = 200^\circ\text{C}$) is explicable by this relationship. The WLF equation also explains why viscosity is more temperature sensitive with materials processed closer to their $T_g$, for example, poly(methyl methacrylate), compared with nylon 6.

3.2.16.5 Effect of Pressure on Viscosity

While temperature rises at constant pressure cause a decrease in viscosity, pressure rises at constant temperature cause an increase in viscosity since this causes a decrease in free volume. It is commonly found that

$$\left( \frac{\partial \eta}{\partial T} \right)_v = 0 \tag{3.85}$$

In other words, if the volume and hence free volume are made constant by increasing pressure as temperature is increased then the viscosity also remains constant. It is in fact found that within the normal processing temperature range for a polymer it is possible to consider an increase in pressure as equivalent, in its effect on viscosity, to a decrease in temperature.

For most polymers an increase in pressure of 100 atm is equivalent to a drop of temperature in the range 30–50°C. It is also found that those polymers most sensitive to temperature changes in their normal processing range are the most sensitive to pressure.

3.2.16.6 Weissenberg Effects

An elastic aftereffect is generally found in high-molecular-weight fluid materials after extrusion under high shear stress through an orifice or die, and this is seen to happen within a fraction of a second after extrusion. Herzog and Weissenberg [13] observed the existence of a “normal” force in polymers subjected to shear stress. In the polymeric melt systems, the entangled polymer chains get deformed elastically during flow and a different kind of force is generated within the flowing melt in addition to the force applied. The additional force generated is manifested as tensile force perpendicular to the shear plane.

This is visualized when a cone with vertical channels and with its axis normal to a plate is rotated with a viscous liquid placed between cone and plate. Liquid will climb into these channels (Figure 3.28a). The arrows in Figure 3.28a indicate that a force exists which acts on the liquid, normal to the shear plane. This force can be measured, without drilling channels into the cone, by placing pressure transducers in contact with the liquid at the cone face and by measuring the pressure exerted on the cone by the liquid.

The effect, known as the Weissenberg effect, is more easily demonstrated by subjecting a viscous liquid mass to shear in a coaxial cylinder system by rotating one while keeping the other fixed (Figure 3.28b). It is most easily demonstrated by rotating the inner cylinder. On rotation, the liquid climbs up the rotating inner rod or cylinder to a significant height.

The Weissenberg effect is clearly manifested in the increase in diameter of extruded profiles of a variety of molten polymers. The extrusion swelling (Figure 3.29), more commonly known as die swell, arises probably due to a combination of normal stress effects and a possible elastic recovery consequent to prior compression before the melt or liquid enters the die.

A practical aspect of the Weissenberg effect or die swell is that, on extrusion or calendaring, the melt coming out is larger than the die or nip size. The control of size is done by partly using a smaller aperture and by partly having an increased draw down. The extrusion, the swelling may be largely minimized by having a conical die design with the narrow end towards the interior and by lowering of melt temperatures, extrusion rates, or molecular weight of the polymer.

3.2.16.7 Irregular Flow or Melt Fracture

Above a certain shear stress considered as the critical shear stress, flow instabilities of many polymer melts exhibited by an abrupt change in the shape of the molten extrudate are found to occur. The irregularities
in flow may be due to Reynolds turbulence or structural turbulence and thermo-mechanical breakdown of the polymer [14].

Above the critical shear stress, the material near the wall relaxes very much faster than the core material leading to the flow irregularities, which, according to Tordella [15], is caused by a fracture of the melt before its entry into the die. Polymers that show flow irregularities at low output rates are those that have comparatively long relaxation times. The origin of flow irregularities and the site of melt fracture is near the entrance to the die since this is the zone of greatest shear stress. The stress enhancement is so great compared to the relaxation time that the polymer melt fractures much like a solid.

Melt fracture depends on die geometry, molecular weight, molecular-weight distribution, and chain branching. A linear polymer such as high-density polyethylene is characterized by a higher critical shear stress than the corresponding branched polymer (low-density polyethylene) of comparable molecular weight.

### 3.2.17 Measurement of Viscosity

Perhaps the most important factor to a process engineer in predicting extrusion or molding behavior is melt viscosity. Several methods are used to obtain the viscosity of polymer solutions and melts experimentally as a function of shear rate [16]. Instruments for making such measurements must necessarily accomplish two things: (1) the fluid must be sheared at measurable rates, and (2) the stress developed must be known. Two kinds of instruments having simple geometry and wide use a rotational viscometer and capillary or extrusion rheometer.
3.2.17.1 Rotational Viscometers

In a rotational viscometer (using cylinders, cones, spheres, and discs) the fluid is sheared at a given temperature in the fluid is sheared at a given temperature in the annular or enclosed space due to rotation of the inner cylinder or the like device while the outer cylinder or device is kept stationary or vice versa. In either case the torque required for the rotation is a measure of the shearing stress and the speed of rotation gives a measure of the rate of shear. Rotational viscometers using coaxial cylinders (Figure 3.30a) measure relatively low viscosity liquids. Typical is the Haake-Rotovisco. In this device, the cup is stationary and the bob is driven a through a torsion spring. In a cone-and-plate rotational viscometer (Figure 3.30b), the molten polymer is contained between the bottom plate and the cone, which is rotated at a constant velocity ($\Omega$). Shear stress ($\tau$) is defined as

$$\tau = \frac{3\Phi}{2\pi R_c^3}$$

(3.86)

where $\Phi$ is the torque in dynes per centimeter (CGS) or in Newtons per meter (SI), and $R_c$ is the cone radius in centimeters or meters. Shear rate ($\dot{\gamma}$) is given by

$$\dot{\gamma} = \frac{\Omega}{\alpha}$$

(3.87)

where $\Omega$ is the angular velocity in degrees per second (CGS) or in radians per second (SI) and $\alpha$ is the cone angle in degrees or radians. Viscosity is then

$$\eta = \tau/\dot{\gamma} = \frac{3\alpha\Phi}{2\pi R_c^2 \Omega} = \frac{k\Phi}{\Omega}$$

(3.88)

where ($K = \frac{3\alpha}{2\pi R_c^3}$) is a constant defined by viscometer design.

An analogous result is obtained if the plate rotates and the cone and plate viscometer is the Weissenberg Rheogoniometer. It consists of a plate that can be rotated at different speeds by means of a constant speed motor-cum-gear assembly (Figure 3.31). The speed or rotation is measured accurately by means of a transducer.

A cone is placed concentrically above the plate, the cone angle being around 1–5°. The cone is supported vertically by a frictionless air bearing and is attached to a firm support through a calibrated torsional spring. Any torque experienced by the cone leads to an equilibrium deflection of this spring which is measured by means of a transducer. The polymer sample is placed in the space between the cone and plate.

FIGURE 3.30 (a) Coaxial cylinder viscometer. (b) Cone and plate rheometer.
and plate and the torque experienced by the stationary cone is measured for different rotational speeds of
the plate.

Relating the shear stress at the cone surface to the measured torque and the shear rate to the angular
velocity of the plate, the expression for the viscosity ($\eta$) is obtained as

$$\eta = \frac{3K\theta\sin \alpha}{2\pi R_p^4 \omega}$$  \hspace{1cm} (3.89)

where $K$ is the torsional constant and $\theta$ is the deflection of the spring; $R_p$ is the radius and $\omega$ is the angular
velocity of the plate; and $\alpha$ is the angle of the cone. While $\theta$ and $\omega$ are experimentally determined
quantities, $K$ and $\alpha$ are obtained by calibration on other materials.

The cone and plate viscometer gives reliable experimental data over an extensive range of shear rates
($10^{-4}$–$10^4$ sec$^{-1}$). Not only can it be used to measure viscosities in simple shear, but it can also be used to
determine the dynamic properties of viscoelastic materials. The unit is also set up to measure the normal
stresses exhibited by viscoelastics, i.e., those perpendicular to the plane of shear.

### 3.2.17.2 Capillary Rheometers

These rheometers are widely used to study the rheological behavior of molten polymers. As shown in
Figure 3.32 the fluid is forced from a reservoir into and through a fine-bore tube, or capillary, by either
mechanical or pneumatic means. The fluid is maintained at isothermal conditions by electrical tem-
perature control methods. Either the extrusion pressure or volumetric flow rate can be controlled as the
independent variable with the other being the measured dependent variable.

Under steady flow and isothermal conditions for an incompressible fluid (assuming only axial flow and
no slip at the wall), the viscous force resisting the motion of a column of fluid in the capillary is equal to
the applied force tending to move the column in the direction of flow. Thus,

$$\tau = \frac{R\Delta P}{2L}$$  \hspace{1cm} (3.90)

where $R$ and $L$ are the radius and length of the column and $\Delta P$ is the pressure drop across the capillary. The
shear stress $\tau$ is therefore zero at the center of the capillary and increases to a maximum value at the capillary
wall. This maximum value is the one generally used for the shear stress in capillary flow.

In normal capillary rheometry for polymer melts, the flowing stream exits into the atmosphere, and the
driving static pressure in the reservoir is taken to be $\Delta P$. In such cases, end effects involving viscous and
elastic deformations at the entrance and exit of the capillary should be taken into account when calculating
the true shear stress at the capillary wall, particularly if the ratio of capillary length to radius ($L/R$) is small.
For a fluid showing Newtonian behavior the shear rate ($\dot{\gamma}$) at the wall is given by

$$\dot{\gamma} = \frac{4Q}{\pi R^3}$$  \hspace{1cm} (3.91)

where $Q$ is the volumetric flow rate through the capillary under a pressure drop $\Delta P$. Melt viscosity is expressed as

$$\eta = \frac{\tau}{\dot{\gamma}} = \frac{\pi R^4 \Delta P}{8LQ}$$  \hspace{1cm} (3.92)

The measured values of polymer flow taken by capillary rheometers are often presented as plots of shear stress versus shear rate at certain temperatures. These values are called apparent shear stress and apparent shear rate at the tube wall. Corrections must be applied to these values in order to obtain true values. The corrected value of shear stress is determined by the Bagley correction \[17\]

$$\tau_c = \frac{R \Delta P}{2(L + e)}$$  \hspace{1cm} (3.93)

where $\tau_c$ is the corrected value and $e$ is the length correction expressed as a function of radius.

Correction to the shear rate is necessitated by the fact that unlike in isothermal Newtonian flow where the velocity distribution from wall to wall in a tube is parabolic, nonparabolic velocity profile develops in non-Newtonian flow. The Rabinowitsch correction \[18\] is applied to shear rate to eliminate this error as follows:

$$\dot{\gamma}_c = \frac{3n + 1}{4n} \dot{\gamma}_a$$  \hspace{1cm} (3.94)

where the subscript $c$ stands for corrected value and subscript $a$ stands for apparent value of shear rate at tube wall; the correction term $n$ is given by $\frac{d \log \tau_a}{d \dot{\gamma}_a}$ and is 1 for Newtonian flow.

There are three main reasons why the capillary rheometer is widely used in the plastics industry: (1) shear rate and flow geometry in capillary rheometer are very similar to conditions actually encountered in extrusion and injection molding; (2) a capillary rheometer typically covers the widest shear rate ranges ($10^{-6}$ sec$^{-1}$ to $10^6$ sec$^{-1}$); and (3) a capillary rheometer provides good practical data and information on the die swell, melt instability, and extrudate defects.

### 3.2.18 Plastics Fractures

The principal causes of fracture of a plastic part are the prolonged action of a steady stress (creep rupture), the application of a stress in a very short period of time (impact), and the continuous application of a cyclically varying stress (fatigue). In all cases the process of failure will be accelerated if the plastic is in an aggressive environment.

Two basic types of fracture under mechanical stresses are recognized: brittle fracture and ductile fracture. These terms refer to the type of deformation that precedes fracture.

Brittle fractures and potentially more dangerous because there occurs no observable deformation of the material. In a ductile failure, on the other hand, large nonrecoverable deformations occur before rupture actually takes place and serve as a valuable warning. A material thus absorbs more energy when it fractures in a ductile fashion than in a brittle fashion.

In polymeric materials fracture may be ductile or brittle, depending on several variables, the most important of which are the straining rate, the stress system, and the temperature. Both types of failures may thus be observed in the one material, depending on the service conditions.
3.2.19 Impact Behavior of Plastics

Tests of brittleness make use of impact tests. The main causes of brittle failure in materials have been found to be (1) triaxiality of stress, (2) high strain rates, and (3) low temperatures. Test methods developed for determining the impact behavior of materials thus involve striking a notched bar with a pendulum. This is the most convenient way of subjecting the material to triaxiality of stress (at the notch tip) and a high strain rate so as to promote brittle failures.

The standard test methods are the Charpy and Izod tests, which employ the pendulum principle (Figure 3.33a). The test procedures are illustrated in Figure 3.33b and c. The specimen has a standard notch on the tension side.

In the Charpy test the specimen is supported as a simple beam and is loaded at the midpoint (Figure 3.33b). In the Izod test it is supported as a cantilever and is loaded at its end (Figure 3.33c). The standard energy absorbed in breaking the specimen is recorded.

The results of impact tests are often scattered, even with the most careful test procedure. A normal practice in such cases is to quote the median strength rather than the average strength, because the median is more representative of the bulk of the results if there is a wide scatter with a few very high or very low results. Impact strengths are normally expressed as

\[
\text{Impact} = \frac{\text{Energy absorbed to break}}{\text{Area at notch section}}
\]

(ft-lbf/in\(^2\), cm-kgf/cm\(^2\), or J/m\(^2\)). Occasionally, the less satisfactory term of energy to break per unit width may be quoted in units of ft-lbf/in, cm-kgf/cm or J/m.

The choice of notch depth and tip radius will affect the impact strength observed. A sharp notch is usually taken as a 0.25-mm radius, a blunt notch as a 2-mm radius. The typical variation of impact strength with notch-tip variation for several thermoplastics is presented in Figure 3.34. It is evident that the use of a sharp notch may even rank plastic materials in an order different from that obtained by using a blunt notch. This fact may be explained by considering the total energy absorbed to break the specimen as consisting of energy necessary for crack initiation and for crack propagation.

---

**FIGURE 3.33** Impact test. (a) Schematic diagram of Charpy impact testing machine. (b) Arrangement of Charpy impact specimen. (c) Mounting of Izod impact specimen.
When the sharp notch (0.25-mm radius) is used, it may be assumed that the energy necessary to initiate the crack is small, and the main contribution to the impact strength is the propagation energy. On this basis Figure 3.34 would suggest that high-density polyethylene and ABS have relatively high crack-propagation energies, whereas materials such as PVC, nylon, polystyrene, and acrylics have low values. The large improvement in impact strength observed for PVC and nylon when a blunt notch is used would imply that their crack-initiation energies are high. On the other hand, the smaller improvement in the impact strength of ABS with a blunt notch would suggest that the crack-initiation energy is low. Thus the benefit derived from using rounded corners would be much less for ABS than for materials such as nylon or PVC.

Temperature has a pronounced effect on the impact strength of plastics. In common with metals, many plastic materials exhibit a transition from ductile behavior to brittle as the temperature is reduced. The variation of impact strength with temperature for several common thermoplastics is shown in Figure 3.35. The ranking of the materials with regard to impact strength is seen to be influenced by the test temperature. Thus, at room temperature (approximately 20°C) polypropylene is superior to acetal; at subzero temperatures (e.g., −20°C) polypropylene does not perform as well as acetal. This comparison pertains to impact behavior measured with a sharp (0.25-mm) notch. Note that notch sharpness can influence the impact strength variation with temperature quite significantly. Figure 3.36 shows that when a blunt (2-mm) notch is used, there is indeed very little difference between acetal and polypropylene at 20°C, whereas at −20°C acetal is much superior to polypropylene.

It may be seen from Figure 3.35 and Figure 3.36 that some plastics undergo a change from ductile or tough (high impact strength) to brittle (low impact strength) behavior over a relatively narrow temperature change. This allows a temperature for ductile-brittle transition to be cited. In other plastic materials this transition is much more gradual, so it is not possible to cite a single value for transition temperature. It is common to quote in such cases a brittleness temperature, $T_B(1/4)$.
This temperature is defined as the value at which the impact strength of the material with a sharp notch (1/4-mm tip radius) is 10 kJ/m² (4.7 ft-lbf/in²). When quoted, it provides an indication of the temperature above which there should be no problem of brittle failure. However, it does not mean that a material should never be used below its $T_B (1/4)$, because this temperature, by definition, refers only to the impact behavior with a sharp notch. When the material is unnotched or has a blunt notch, it may still have satisfactory impact behavior well below $T_B (1/4)$.

Other environmental factors besides temperature may also affect impact behavior. For example, if the material is in the vicinity of a fluid which attacks it, then the crack-initiation energies may be reduced, resulting in lower impact strength. Some materials, particularly nylon, are significantly affected by water, as illustrated in Figure 3.37. The absorption of water produces a spectacular improvement in the impact behavior of nylon.

Note that the method of making the plastic sample and the test specimen can have significant effect on the measured values of the properties of the material. Test specimens may be molded directly or machined from samples which have been compression molded, injection molded, or extruded. Each processing method involves a range of variables, such as melt temperature, mold or die temperature, and shear rate, which influence the properties of the material.

Fabrication defects can affect impact behavior for example, internal voids, inclusion, and additives, such as pigments, which can produce stress concentrations within the material. The surface finish of the specimen may also affect impact behavior. All these account for the large variation usually observed in the results of testing one material processed and/or fabricated in different ways. It also emphasizes the point that if design data are needed for a particular application, then the test specimen must match as closely as possible the component to be designed.

In some applications impact properties of plastics may not be critical, and only a general knowledge of their impact behavior is needed. In these circumstances the information provided in Table 3.1 would be
adequate. The table lists the impact behavior of a number of commonly used thermoplastics over a range of temperatures in three broad categories [19].

3.2.20 Fatigue of Plastics

A material subject to alternating stresses over long periods may fracture at stresses much below its maximum strength under static loading (tensile strength) due to the phenomenon called fatigue. Fatigue has been recognized as one of the major causes of fracture in metals. Although plastics are susceptible to a wider range of failure mechanisms, it is likely that fatigue still plays an important part in plastics failure.

For metals the fatigue process is generally well understood and is divided into three stages crack initiation, crack growth, and fracture. Fatigue theory of metals is well developed, but the fatigue theory of polymers is not. The completely different molecular structure of polymers means that three is unlikely to be a similar type of crack initiation process as in metals, though it is possible that once a crack is initiated the subsequent phase of propagation and failure may be similar.

Fatigue cracks may develop in plastics in several ways. If the plastic article has been machined, surface flaws capable of propagation may be introduced. However, if the article has been molded, it is more probable that fatigue cracks will develop from within the bulk of the material. In a crystalline polymer the initiation of cracks capable of propagation may occur through slip of molecules. In addition to acting as a path for crack propagation, the boundaries of spherulites (see Chapter 1), being areas of weakness, may thus develop cracks during straining. In amorphous polymers cracks may develop at the voids formed during viscous flow.

**FIGURE 3.36** Variation of impact strength with temperature for several thermoplastics with blunt notch.
FIGURE 3.37 Effect of water content on impact strength of nylon.

TABLE 3.1 Impact Behavior of Common Thermoplastics over a Range of Temperatures

<table>
<thead>
<tr>
<th>Plastic Material</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>−20</td>
</tr>
<tr>
<td>Polyethylene (low density)</td>
<td>A</td>
</tr>
<tr>
<td>Polyethylene (high density)</td>
<td>B</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>C</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>C</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>C</td>
</tr>
<tr>
<td>ABS</td>
<td>B</td>
</tr>
<tr>
<td>Acetal</td>
<td>B</td>
</tr>
<tr>
<td>Teflon</td>
<td>B</td>
</tr>
<tr>
<td>PVC (rigid)</td>
<td>B</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>B</td>
</tr>
<tr>
<td>Poly(phenylene oxide)</td>
<td>B</td>
</tr>
<tr>
<td>Poly(ethylene terephthalate)</td>
<td>B</td>
</tr>
<tr>
<td>Nylon (dry)</td>
<td>B</td>
</tr>
<tr>
<td>Nylon (wet)</td>
<td>B</td>
</tr>
<tr>
<td>Glass-filled nylon (dry)</td>
<td>C</td>
</tr>
<tr>
<td>Polysulfone</td>
<td>B</td>
</tr>
</tbody>
</table>

Note: A, tough (specimens do not break completely even when sharply notched); B, notch brittle; C, brittle even when unnotched.
A number of features are peculiar to plastics, which make their fatigue behavior a complex subject not simply analyzed. Included are viscoelastic behavior, inherent damping, and low thermal conductivity. Consider, for example, a sample of plastic subjected to a cyclic stress of fixed amplitude. Because of the high damping and low thermal conductivity of the material, some of the input energy will be dissipated in each cycle and appear as heat. The temperature of the material will therefore rise, and eventually a stage will be reached when the heat transfer to the surroundings equals the heat generation in the material. The temperature of the material will stabilize at this point until a conventional metal-type fatigue failure occurs.

If, in the next test, the stress amplitude is increased to a higher value, the material temperature will rise further and stabilize, followed again by a metal-type fatigue failure. In Figure 3.38, where the stress amplitude has been plotted against the logarithm of the number of cycles to failure, failures of this type have been labeled as fatigue failures. This pattern will be repeated at higher stress amplitudes until a point is reached when the temperature rise no longer stabilizes but continues to rise, resulting in a short-term thermal softening failure in the material. At stress amplitudes above this crossover point there will be thermal failures in an even shorter time. Failures of this type have been labeled as thermal failures in Figure 3.38. The fatigue curves in Figure 3.38 thus have two distinct regimes—one for the long-term conventional fatigue failures, and one for the relatively short-term thermal softening failures.

The frequency of the cyclic stress would be expected to have a pronounced effect on the fatigue behavior of plastics, a lower frequency promoting the conventional-type fatigue failure rather than thermal softening failure. Thus it is evident from Figure 3.38 that if the frequency of cycling is reduced, then stress amplitudes which would have produced thermal softening failures at a higher frequency may now result in temperature stabilization and eventually fatigue failure. Therefore, if fatigue failures are required at relatively high stresses, the frequency of cycling must be reduced.

Normally, fatigue failures at one frequency on the extrapolated curve fall from the fatigue failures at the previous frequency (Figure 3.38). As the cyclic stress amplitude is further reduced in some plastics, the frequency remaining constant, the fatigue failure curve becomes almost horizontal at large values of the number of stress cycles (N). The stress amplitude at which this leveling off occurs is clearly important for design purposes and is known as the fatigue limit. For plastics in which fatigue failure continues to occur even at relatively low stress amplitudes, it is necessary to define an endurance limit—that is, the stress amplitude which would not cause fatigue failure up to an acceptably large value of N.

![Figure 3.38](image-url)  
**FIGURE 3.38** Typical fatigue behavior of a thermoplastic at several frequencies, F, fatigue failure; T, thermal failure, ○, 5.0 Hz; Δ, 1.67 Hz; □, 0.5 Hz. (Adapted from Crawford, R. J. 1981. *Plastics Engineering*, Pergamon, London.)
3.2.21 Hardness

Hardness of a material may be determined in several ways: (1) resistance to indentation, (2) rebound efficiency, and (3) resistance to scratching. The first method is the most commonly used technique for plastics. Numerous test methods are available for measuring the resistance of a material to indentation, but they differ only in detail. Basically they all use the size of an indent produced by a hardened steel or diamond indenter in the material as an indication of its hardness—the smaller the indent produced, the harder the material, and so the greater the hardness number. The measured hardness is defined as macro- or micro-hardness according to the load applied on the indenter, the load being more than 1 kg for macrohardness and 1 kg or less for microhardness tests. Hardness tests are simple, quick, and nondestructive, which account for their wide use for quality control purposes.

3.2.22 Indentation Hardness

The test methods used for plastics are similar to those used for metals. The main difference is that because plastics are viscoelastic allowance must be made for the creep and the time-dependent recovery which occurs as a result of the applied indentation load.

3.2.22.1 Brinell Hardness Number

A hardened steel ball 10 mm in diameter is pressed into the flat surface of the test specimen under load of 500 kg for 30 sec. The load is then removed, and the diameter of the indent produced is measured (Figure 3.39). The Brinell hardness number (BHN) for macrohardness is defined as

\[
BHN = \frac{\text{Load applied to indentor (kgf)}}{\text{Contact area of indentation (mm}^2\text{)}} = \frac{2P}{\pi D(D - \sqrt{D^2 - d^2})}
\]  

(3.95)

where \(D\) is the diameter of the ball and \(d\) is the diameter of the indent. Tables are available to convert the diameter of the indent into BHN.

Although the units of Brinell hardness are kgf/mm\(^2\), it is quoted only as a number. A disadvantage of the Brinell hardness test when used for plastics is that the edge of the indent is usually not well defined. This problem is overcome in the following test.

3.2.22.2 Vickers Hardness Number

The Vickers hardness test differs from the Brinell test in that the indenter is a diamond (square-based) pyramid (Figure 3.39) having an apex angle of 136°. If the average diagonal of the indent is \(d\), the hardness number is calculated from

\[
\text{Vickers hardness number} = \frac{\text{Load applied to indentor (kgf)}}{\text{Contact area of indentation (mm}^2\text{)}} = 1.854\left(\frac{P}{d^2}\right)
\]  

(3.96)

Tables are available to convert the average diagonal into Vickers number used for both macro- and microhardnesses.

\[
\text{Vickers hardness number} = \frac{\text{Load applied to indentor (kgf)}}{\text{Contact area of indentation (mm}^2\text{)}} = 1.854\left(\frac{P}{d^2}\right)
\]  

(3.96)

Tables are available to convert the average diagonal into Vickers number used for both macro- and microhardnesses.

![FIGURE 3.39 Indentation hardness tests. (a) Brinell test. (b) Vickers test. (c) Knoop test.](Downloaded By: 10.3.98.93 At: 05:34 14 Jan 2019; For: 9781315155876, chapter3, 10.1201/9781315155876-3)
3.2.22.3 Knoop Hardness Number

The indentor used in the Knoop hardness test for microhardness measurement is a diamond pyramid, but the lengths of the two diagonals, as shown in Figure 3.39, are different. If the long diagonal of the indent is measured as $D$, the hardness number is obtained from

$$\text{Knoop hardness number} = 14.23 \left( \frac{P}{D^2} \right)$$

(3.97)

Time-dependent recovery of the indentation in plastics is a problem common to all three tests. To overcome this problem, allow a fixed time before making measurements on the indent.

3.2.22.4 Rockwell Hardness Number

The Rockwell test used to measure macrohardness differs from the other three tests because the depth of the indent rather than its surface area is taken as a measure of hardness. A hardened steel ball is used as the indentor. A major advantage of the Rockwell test is that no visual measurement of the indentation is necessary, and the depth of the indent is read directly as a hardness value on the scale.

The test involves three steps, as shown in Figure 3.40. A minor load of 10 kg is applied on the steel ball, and the scale pointer is set to zero within 10 sec of applying the load. In addition to this minor load, a major load is applied for 15 sec. A further 15 sec after removal of the major load (with the minor load still on the ball), the hardness value is read off the scale. Since creep and recovery effects can influence readings, it is essential to follow a defined time cycle for the test.

Several Rockwell scales (Table 3.2) are used, depending on the hardness of the material under test (Table 3.3). The scale letter is quoted along with the hardness number e.g., Rockwell R60. Scales R and L are used for low-hardness number, e.g., Rockwell R60. Scales R and L are used for low-hardness materials, and scales M and E when the hardness value is high. When the hardness number exceeds 115 on any scale, the sensitivity is lost, so another scale should be used.

3.2.22.5 Barcol Hardness

The Barcol hardness tester is a hand-operated hardness measuring device. Its general construction is shown in Figure 3.41. With the back support leg placed on the surface, the instrument is gripped in the hand and its measuring head is pressed firmly and steadily onto the surface until the instrument rests on the stop ring. The depth of penetration of the spring-loaded indentor is transferred by a lever system to an indicating dial, which is calibrated from 0 to 100 to indicate increasing hardness. To allow for creep, one normally takes readings after 10 sec.

The indentor in the Barcol Tester Model No. 934-1 is a truncated steel cone having an included angle of 26° with a flat tip of 0.157 mm (0.0062 in.) in diameter. The values obtained using this instrument are

**FIGURE 3.40** Stages in Rockwell hardness test: 1, minor load; 2, minor and major loads; 3, minor load only.
found to correlate well to Rockwell values on the M scale. This instrument is used for metals and plastics. Two other models, No. 935 and No. 936, are used for plastics and very soft materials, respectively.

### 3.2.22.6 Durometer Hardness

A durometer is an instrument for measuring hardness by pressing a needle-like indentor into the specimen. Operationally, a durometer resembles the Barcol tester in that the instrument is pressed onto the sample surface until it reaches a stop ring. This forces the indentor into the material, and a system of levers transforms the depth of penetration into a pointer movement on an indicating dial, which is calibrated from 0–100.

<table>
<thead>
<tr>
<th>Scale</th>
<th>Major Load (kg)</th>
<th>Dia. of Indentor (in.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>60</td>
<td>1/2</td>
</tr>
<tr>
<td>L</td>
<td>60</td>
<td>1/4</td>
</tr>
<tr>
<td>M</td>
<td>100</td>
<td>1/4</td>
</tr>
<tr>
<td>E</td>
<td>100</td>
<td>1/8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Material</th>
<th>Test Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rubber</td>
<td>Shore A or BS 903</td>
</tr>
<tr>
<td>Plasticized PVC</td>
<td>Shore A or BS 2782</td>
</tr>
<tr>
<td>Low-density polyethylene</td>
<td>Shore D</td>
</tr>
<tr>
<td>Medium-density polyethylene</td>
<td>Shore D</td>
</tr>
<tr>
<td>High-density polyethylene</td>
<td>Shore D</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>Rockwell R</td>
</tr>
<tr>
<td>Toughened polystyrene</td>
<td>Rockwell R</td>
</tr>
<tr>
<td>ABS</td>
<td>Rockwell R</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>Rockwell M</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>Rockwell M</td>
</tr>
</tbody>
</table>

**TABLE 3.2** Rockwell Hardness Scales

**TABLE 3.3** Choice of Hardness Test Methods Based on Modulus Range of Plastics

**FIGURE 3.41** General construction of Barcol hardness tester.
The two most common types of durometers used for plastics are the Shore Type A and Shore Type D. They differ in the spring force and the geometry of the indentor, as shown in Figure 3.42. Due to creep, readings should be taken after a fixed time interval, often chosen as 10 sec. Typical hardness values of some of the common plastics measured by different test methods are shown in Table 3.4. The indentation-based techniques cannot be applied to soft, rubber-like polymers, for which, particularly when dealing with blends, copolymers, etc., one can use the Fakirov equation: \( H = 1.97T_g - 571 \) with \( H \) (microhardness) in MPa and \( T_g \) (glass transition temperature) in °K. Combining the rule of mixtures \( (H = \Sigma H_i \phi_i) \) and this equation, it is possible to calculate the \( H \)-value of materials comprising soft component and/or phase [20].

### 3.2.23 Rebound Hardness

The energy absorbed when an object strikes a surface is related to the hardness of the surface: the harder the surface, the less the energy absorbed, and the greater the rebound height of the object after impact. Several methods have been developed to measure hardness in this way. The most common method uses a Shore scleroscope, in which the hardness is determined from the rebound height after the impact of a diamond cone dropped onto the surface of the test piece. Typical values of Scleroscope hardness together with the Rockwell M values (in parentheses) for some common plastics are as follows: PMMA 99 (M 102), LDPE 45 (M 25), polystyrene 70 (M 83), and PVC 75 (M 60).
3.2.24 Scratch Hardness

Basically, scratch hardness is a measure of the resistance the test sample has to being scratched by other materials. The most common way of qualifying this property is by means of the Mohs scale. On this scale various materials are classified from 1 to 10. The materials used, as shown in Figure 3.43, range from talc (1) to diamond (10). Each material on the scale can scratch the materials that have a lower Mohs number; however, the Mohs scale is not of much value for classifying plastic materials, because most common plastics fall in the 2–3 Mohs range. However, the basic technique of scratch hardness may be used to establish the relative merits of different plastic materials from their ability to scratch one another.

![Comparison of hardness scales (approximate).](image-url)
Scratch hardness is particularly important in plastics used for their optical properties and is usually determined by some of mar-resistance test. In one type of test a specimen is subjected to an abrasive treatment by allowing exposure to a controlled stream of abrasive, and its gloss (specular reflection) is measured before and after the treatment. In some tests the light transmission property of the plastic is measured before and after marring.

### 3.2.25 Stress Corrosion Cracking of Polymers

Stress corrosion cracking of polymers occurs in a corrosive environment and also under stress [21,22]. This kind of crack starts at the surface and proceeds at right angles to the direction of stress. The amount of stress necessary to cause stress corrosion cracking is much lower than the normal fracture stress, although there is a minimum stress below which no stress corrosion cracking occurs.

The stress corrosion resistance of polymers depends on the magnitude of the stress, the nature of the environment, the temperature, and the molecular weight of the specimen. Ozone cracking is a typical example of stress corrosion cracking of polymers. The critical energy for crack propagation ($\tau_c$) in ozone cracking varies very little from one polymer to another and is about 100 erg/cm$^2$ (0.1 J/m$^2$). This value is much lower than the $\tau_c$ values for mechanical fracture, which are about $10^7$ erg/cm$^2$ ($10^4$ J/m$^2$).

In ozone cracking very little energy is dissipated in plastic or viscoelastic deformations at the propagating crack, and that is why $\tau_c$ is about the same as the true surface energy. The only energy supplied to the crack is that necessary to provide for the fresh surfaces due to propagation of the crack, because in ozone cracking chemical bonds at the crack tip are broken by chemical reaction, so no high stress is necessary at the tip.

The critical energy $\tau_c$ is about 4,000 erg/cm$^2$ for PMMA in methylated spirits at room temperature, but the value is lower in benzene and higher in petroleum ether. Thus $\tau_c$ in this case is much higher than the true surface energy but still much lower than that for mechanical crack propagation.

### 3.3 Reinforced Plastics

The modulus and strength of plastics can be increased significantly by means of reinforcement [23–25]. A reinforced plastic consists of two main components—a matrix, which may be either a thermoplastic or thermosetting resin, and a reinforcing filler, which is mostly used in the form of fibers (but particles, for example glass spheres, are also used).

The greater tensile strength and stiffness of fibers as compared with the polymer matrix is utilized in producing such composites. In general, the fibers are the load-carrying members, and the main role of the matrix is to transmit the load to the fibers, to protect their surface, and to raise the energy for crack propagation, thus preventing a brittle-type fracture. The strength of the fiber-reinforced plastics is determined by the strength of the fiber and by the nature and strength of the bond between the fibers and the matrix.

#### 3.3.1 Types of Reinforcement

The reinforcing filler usually takes the form of fibers, since it is in this form that the maximum strengthening of the composite is attained. A wide range of amorphous and crystalline materials can be used as reinforcing fibers, including glass, carbon, asbestos, boron, silicon carbide, and more recently, synthetic polymers (e.g., Kevlar fibers from aromatic polyamides). Some typical properties of these reinforcing fibers are given in Table 3.5.

Glass is relatively inexpensive, and in fiber form it is the principal form of reinforcement used in plastics. The earliest successful glass reinforcement had a low-alkali calcium–alumina borosilicate composition (E glass) developed specifically for electrical insulation systems. Although glasses of other compositions were developed subsequently for other applications, no commercial glass better than E glass...
has been found for plastics reinforcement. However, certain special glasses having extra high-strength properties or modulus have been produced in small quantities for specific applications (e.g., aerospace technology).

Glass fibers are usually treated with finishes. The function of a finish is to secure good wetting and to provide a bond between the inorganic glass and the organic resin. The most important finishes are based on silane compounds—e.g., vinyltrichlorosilane or vinyltriethoxysilane.

### 3.3.2 Types of Matrix

The matrix in reinforced plastics may be either a thermosetting or thermoplastic resin. The major thermosetting resins used in conjunction with glass-fiber reinforcement are unsaturated polyester resins and, to a lesser extent, epoxy resins. These resins have the advantage that they can be cured (cross-linked) at room temperature, and no volatiles are liberated during curing.

Among thermoplastic resins used as the matrix in reinforced plastics, the largest tonnage group is the polyolefins, followed by nylon, polystyrene, thermoplastic polyesters, acetal, polycarbonate, and polysulfone. The choice of any thermoplastic is dictated by the type of application, the service environment, and the cost.

### 3.3.3 Analysis of Reinforced Plastics

Fibers exert their effect by restraining the deformation of the matrix while the latter transfers the external loading to the fibers by shear at the interface. The resultant stress distributions in the fiber and the matrix tend to be complex. Theoretical analysis becomes further complicated because fiber length, diameter, and orientation are all factors. A simplified analysis follows for two types of fiber reinforcement commonly used, namely, (1) continuous fibers and (2) discontinuous fibers.

#### 3.3.3.1 Continuous Fibers

We will examine what happens when a load is applied to an ideal fiber composite in which the matrix material is reinforced by fibers which are uniform, continuous, and arranged uniaxially, as shown in Figure 3.44a.

Let us assume that the fibers are gripped firmly by the matrix so that there is no slippage at the fiber-matrix interface and both phases act as a unit. Under these conditions the strains in the matrix and in the fiber under a load are the same (Figure 3.44b), and the total load is shared by the fiber and the matrix:

\[ P_c = P_m + P_f \]  \hspace{1cm} (3.98)

where \( P \) is the load and the subscripts c, m, and f refer, respectively, to composite, matrix and fiber.

### TABLE 3.5 Typical Properties of Reinforcing Fibers

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Density (g/cm³)</th>
<th>Tensile Strength</th>
<th>Tensile Modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( 10^4 ) kgf/cm²</td>
<td>GPa</td>
</tr>
<tr>
<td>E Glass</td>
<td>2.54–2.56</td>
<td>3.5–3.7</td>
<td>3.4–3.6</td>
</tr>
<tr>
<td>Carbon</td>
<td>1.75–2.0</td>
<td>2.1–2.8</td>
<td>2.1–2.8</td>
</tr>
<tr>
<td>Asbestos</td>
<td>2.5–3.3</td>
<td>2.1–3.6</td>
<td>2.1–3.5</td>
</tr>
<tr>
<td>Boron</td>
<td>2.6</td>
<td>3.0–3.6</td>
<td>3.0–3.5</td>
</tr>
<tr>
<td>Silicon carbide</td>
<td>3.2–3.4</td>
<td>3.0–3.7</td>
<td>3.0–3.6</td>
</tr>
<tr>
<td>Kevlar-49</td>
<td>1.45</td>
<td>3.0–3.6</td>
<td>3.0–3.6</td>
</tr>
</tbody>
</table>

Since the load $P = \sigma A$, Equation 3.98, expressed in terms of stresses ($\sigma$) and cross-sectional areas ($A$), becomes

$$\sigma_c A_c = \sigma_m A_m + \sigma_f A_f$$  \hspace{1cm} (3.99)

Rearranging gives

$$\sigma_c = \sigma_m \left( \frac{A_m}{A_c} \right) + \sigma_f \left( \frac{A_f}{A_c} \right)$$  \hspace{1cm} (3.100)

Since the fibers run throughout the length of the specimen, the ratio $A_m/A_c$ can be replaced by the volume fraction $\Phi_m = V_m/V_c$, and similarly $A_f/A_c$ by $\Phi_f$. Equation 3.100 thus becomes

$$\sigma_c = \sigma_m \Phi_m + \sigma_f \Phi_f$$  \hspace{1cm} (3.101)

Equation 3.101 represents the rule of mixture for stresses. It is valid only for the linear elastic region of the stress–strain curve (see Figure 3.2). Since $\Phi_m + \Phi_f = 1$, we can write

$$\sigma_c = \sigma_m (1 - \Phi_f) + \sigma_f \Phi_f$$  \hspace{1cm} (3.102)

Since the strains on the components are equal,

$$\varepsilon_c = \varepsilon_m = \varepsilon_f$$  \hspace{1cm} (3.103)

Equation 3.101 can now be rewritten to give the rule of mixture for moduli

$$E_c \varepsilon_c = E_m \varepsilon_m \Phi_m + E_f \varepsilon_f \Phi_f$$

i.e.,

$$E_c = E_m \Phi_m + E_f \Phi_f$$  \hspace{1cm} (3.104)

Equation 3.103 also affords a comparison of loads carried by the fiber and the matrix. Thus for elastic deformation Equation 3.103 can be rewritten as

$$\frac{\sigma_c}{E_c} = \frac{\sigma_m}{E_m} = \frac{\sigma_f}{E_f}$$

or

$$\frac{P_f}{P_m} = \frac{E_f}{E_m} \left( \frac{A_f}{A_m} \right) = \frac{E_f}{E_m} \left( \frac{\Phi_f}{\Phi_m} \right)$$  \hspace{1cm} (3.105)

Because the modulus of fibers is usually much higher than that of the matrix, the load on a composite will therefore be carried mostly by its fiber component (see Example 3.4). However, a critical volume
fraction of fibers ($\Phi_{\text{crit}}$) is required to realize matrix reinforcement. Thus for Equation 3.102 and Equation 3.105 to be valid, $\Phi_f > \Phi_{\text{crit}}$.

The efficiency of reinforcement is related to the fiber direction in the composite and to the direction of the applied stress. The maximum strength and modulus are realized in a composite along the direction of the fiber. However, if the load is applied at 90° to the filament direction, tensile failure occurs at very low stresses, and this transverse strength is not much different than the matrix strength. To counteract this situation, one uses cross-plied laminates having alternate layers of unidirectional fibers rotated at 90°, as shown in Figure 3.44c. (A more isotropic composite results if 45° plies are also inserted.) The stress–strain behavior for several types of fiber reinforcement is compared in Figure 3.45.

As already noted, if the load is applied perpendicularly to the longitudinal direction of the fibers, the fibers exert a relatively small effect. The strains in the fibers and the matrix are then different, because they act independently, and the total deformation is thus equal to the sum of the deformations of the two phases.

$$V_c \varepsilon_c = V_m \varepsilon_m + V_f \varepsilon_f \quad (3.106)$$

Dividing Equation 3.106 by $V_c$ and applying Hooke’s law, since the stress is constant, give

$$\frac{\sigma}{E_c} = \frac{\sigma \Phi_m}{E_m} + \frac{\sigma \Phi_f}{E_f} \quad (3.107)$$

Dividing by $\sigma$ and rearranging, we get

$$E_c = \frac{E_m E_f}{E_m \Phi_f + E_f \Phi_m} \quad (3.108)$$

The fiber composite thus has a lower modulus in transverse loading than in longitudinal loading.
Example 4: A unidirectional fiber composite is made by using 75% by weight of E glass continuous fibers (sp. gr. 2.4) having a Young’s modulus of $7 \times 10^5$ kg/cm$^2$ (68.6 GPa), practical fracture strength of $2 \times 10^4$ kg/cm$^2$ (1.9 GPa), and an epoxy resin (sp. gr. 1.2) whose modulus and tensile strength, on curing, are found to be $10^5$ kg/cm$^2$ (9.8 GPa) and $6 \times 10^2$ kg/cm$^2$ (58.8 MPa), respectively. Estimate the modulus of the composite, its tensile strength, and the fractional load carried by the fiber under tensile loading. What will be the value of the modulus of the composite under transverse loading?

**Answer:** Volume fraction of glass fibers ($\Phi_f$)

$$\Phi_f = \frac{0.75/2.4}{0.75/2.4 + 0.25/1.2} = 0.60$$

$$\Phi_m = 1 - 0.6 = 0.4$$

From Equation 3.104,

$$E_c = 0.4(10^5) + 0.6(7 \times 10^5) = 4.6 \times 10^5$$ kg/cm$^2$ (45 GPa)

From Equation 3.101,

$$\sigma_c = 0.4(6 \times 10^2) + 0.6(2 \times 10^4) = 1.22 \times 10^4$$ kg/cm$^2$ (1.2 GPa)

Equation 3.105, on rearranging, gives

$$\frac{P_f}{P_c} = \frac{E_f \Phi_f}{E_c} = \frac{7 \times 10^5}{4.6 \times 10^5} \times 0.6 = 0.91$$

Thus, nearly 90% of the load is carried by the fiber, and the weakness of the plastic matrix is relatively unimportant.

For transverse loading, from Equation 3.108,

$$E_c = \frac{10^5(7 \times 10^7)}{0.6 \times 10^5 + 0.4(7 \times 10^5)} = 2 \times 10^5$$ kg/cm$^2$ (19.6 GPa)

Equation 3.102 and Equation 3.104 apply to ideal fiber composites having uni-axial arrangement of fibers. In practice, however, not all the fibers are aligned in the direction of the load. This practice reduces the efficiency of the reinforcement, so Equation 3.102 and Equation 3.104 are modified to the forms

$$\sigma_c = \sigma_m (1 - \Phi_f) + k_1 \sigma_f \Phi_f$$

$$E_c = E_m (1 - \Phi_f) + k_2 E_f \Phi_f$$

If the fibers are bi-directional (see Figure 3.45), then the strength and modulus factors, $k_1$ and $k_2$, are about 0.3 and 0.65, respectively.

### 3.3.3.2 Discontinuous Fibers

If the fibers are discontinuous, the bond between the fiber and the matrix is broken at the fibers ends, which thus carry less stress than the middle part of the fiber. The stress in a discontinuous fiber therefore varies along its length. A useful approximation pictures the stress as being zero at the end of the filler and as reaching the maximum stress in the fiber at a distance from the end (Figure 3.46a).
The length over which the load is transferred to the fiber is called the transfer length. As the stress on the composite is increased, the maximum fiber stress as well as the transfer length increase, as shown in Figure 3.46a, until a limit is reached, because the transfer regions from the two ends meet at the middle of the fiber (and so no further transfer of stress can take place), or because the fiber fractures. For the latter objective to be reached, so as to attain the maximum strength of the composite, the fiber length must be greater than a minimum value called the critical fiber length, $l_c$.

Consider a fiber of length $l$ embedded in a polymer matrix, as shown in Figure 3.46b. One can then write, equating the tensile load on the fiber with the shear load on the interface,

$$\frac{\sigma \pi d^2}{4} = \tau \pi d l$$

where $\sigma$ is the applied stress, $d$ is the fiber diameter, and $\tau$ is the shear stress at the interface.

The critical fiber length, $l_c$, can be derived from a similar force balance for an embedded length of $l_c/2$. Thus,

$$l_c = \frac{\sigma_{ff} d}{2\tau_i}$$

and

$$\frac{l_c}{d} = \frac{\sigma_{ff}}{2\tau_i}$$

where $\sigma_{ff}$ is the fiber strength and $\tau_i$ is the shear strength of the interface or the matrix, whichever is smaller.

So if the composite is to fail through tensile fracture of the fiber rather than shear failure due to matrix flow at the interface between the fiber and the matrix, the ratio $l_c/d$, known as the critical aspect ratio, must be exceeded, or, in other words, for a given diameter of fiber, $d$, the critical fiber length, $l_c$, must be exceeded.
If the fiber length is less than \( l_c \), the matrix will flow around the fiber, and maximum transfer of stress from matrix to fiber will not occur. Using Equation 3.112, we can estimate the value of \( l_c/d \) from the values of \( \sigma_{ff} \) and \( \tau \), and vice versa. Typical values of \( l_c/d \) for glass fiber and carbon fiber in an epoxy resin matrix are 30–100 and 70, respectively.

If the fibers are discontinuous, then, since the stress is zero at the end of the fiber, the average stress in the fibers will be less than the value \( \sigma_{f\max} \) which it would have achieved if the fibers had been continuous over the whole length of the matrix. The value of the average stress will depend on the stress distribution in the end portions of the fibers and also on their lengths. If the stress distributions are assumed to be as shown in Figure 3.46a, then the average stress in the fibers may be obtained as follows.

Considering a differential section of the fiber as shown in Figure 3.46a, we obtain

\[
F_1 = \sigma_f \frac{\pi d^2}{4}
\]

\[
F_2 = \left( \sigma_f + \frac{d\sigma_f}{dx} \right) \frac{\pi d^2}{4}
\]

\[
F_3 = \tau \pi d \, dx
\]

For equilibrium,

\[
F_1 = F_2 + F_3
\]

so

\[
\sigma_f \frac{\pi d^2}{4} = \left( \sigma_f + \frac{d\sigma_f}{dx} \right) \frac{\pi d^2}{4} + \tau \pi d \, dx
\]

(3.113)

Integrating gives

\[
\frac{d}{4} \int_0^\sigma d\sigma_f = -\int_{l/2}^x \tau \, dx
\]

\[
\sigma_f = \frac{4\tau (l/2 - x)}{d}
\]

(3.114)

Three cases may now be considered.

### 3.3.3.3 Fiber Length Less than \( l_c \)

In this case the peak stress occurs at \( x = 0 \) (Figure 3.47a). So from Equation 3.114,

\[
\sigma_f = \frac{2\tau l}{d}
\]

The average fiber stress is obtained by dividing the area of the stress-fiber length diagram by the fiber length; that is,

\[
\bar{\sigma}_f = \frac{(l/2)2\tau l/d}{l} = \frac{\tau l}{d}
\]

(3.115)

The stress, \( \sigma_c \), in the composite is now obtained from Equation 3.109

\[
\sigma_c = \sigma_m(1 - \Phi_f) + \frac{\tau l k_1}{d} \phi_f
\]
3.3.3.4 Fiber Length Equal to \( l_c \)

In this case the peak value of stress occurs at \( x = 0 \) and is equal to the maximum fiber stress (Figure 3.47b). So

\[
\sigma_f = \sigma_{f_{\text{max}}} = \frac{2\tau l_c}{d}
\]  

(3.116)

Average fiber stress \( \bar{\sigma}_f \) is

\[
\bar{\sigma}_f = \frac{1}{2} \frac{l_c (2\tau l_c / d)}{l_c}
\]

i.e.,

\[
\bar{\sigma}_f = \frac{\tau l_c}{d}
\]

(3.117)

So from Equation 3.109,

\[
\sigma_c = \sigma_m (1 - \phi_f) + k_1 \left( \frac{\tau l_c}{d} \right) \phi_f
\]

3.3.3.5 Fiber Length Greater than \( l_c \)

1. For \( l/2 > x > (l - l_c)/2 \) (Figure 3.47c),

\[
\sigma_f = \frac{4\tau}{d} \left( \frac{1}{2} l - x \right)
\]

2. For \( (l - l_c)/2 > x > 0 \) (Figure 3.47c),

\[
\sigma_f = \text{constant} = \sigma_{f_{\text{max}}} = \frac{2\tau l_c}{d}
\]

The average fiber stress, from the area under the stress-fiber length graph is

\[
\bar{\sigma}_f = \frac{(l_c/2)\sigma_{f_{\text{max}}} + (l - l_c)\sigma_{f_{\text{max}}}}{l} = \left( 1 - \frac{h}{2l} \right) \sigma_{f_{\text{max}}}
\]

(3.118)
So from Equation 3.109,

\[ \sigma_c = \sigma_m(1 - \phi_f) + k_f\phi_f \left(1 - \frac{l_c}{2l}\right)\phi_{f_{\text{max}}}. \]  

(3.119)

It is evident from Equation 3.118 that to get the average fiber stress as close as possible to the maximum fiber stress, the fibers must be considerably longer than the critical length. At the critical length the average fiber stress is only half of the maximum fiber stress, i.e., the value achieved in continuous fibers (Figure 3.47c).

Equations such as Equation 3.119 give satisfactory agreement with the measured values of strength and modulus for polyester composites reinforced with chopped strands of glass fibers. These strength and modulus values are only about 20%–25% of those achieved by reinforcement with continuous fibers.

**Example 5:** Calculate the maximum and average fiber stresses for glass fibers of diameter 15 μm and length 2 mm embedded in a polymer matrix. The matrix exerts a shear stress of 40 kgf/cm² (3.9 MPa) at the interface, and the critical aspect ratio of the fiber is 50.

**Answer:**

\[ l_c = 50 \times 15 \times 10^{-3} = 0.75 \text{ mm} \]

Since \( l > l_c \), then

\[ \sigma_{\text{max}} = \frac{2\tau_l}{d} = 2 \times 40 \times 50 = 4 \times 10^3 \text{ kgf/cm}^2 ( = 392 \text{ MPa}) \]

Also,

\[ \bar{\sigma}_f = \left(1 - \frac{l_c}{2l}\right)\sigma_{f_{\text{max}}} = \left(1 - \frac{0.75}{2 \times 2}\right)(4 \times 10^3) = 3.25 \times 10^3 \text{ kgf/cm}^2 ( = 318 \text{ MPa}) \]

### 3.3.4 Deformation Behavior of Fiber-Reinforced Plastic

As we have seen, the presence of fibers in the matrix has the effect of stiffening and strengthening it. The tensile deformation behavior of fiber-reinforced composites depends largely on the direction of the applied stress in relation to the orientation of the fibers, as illustrated in Figure 3.45. The maximum strength and modulus are achieved with unidirectional fiber reinforcement when the stress is aligned with the fibers (0°), but there is no enhancement of matrix properties when the stress is applied perpendicular to the fibers. With random orientation of fibers the properties of the composite are approximately the same in all directions, but the strength and modulus are somewhat less than for the continuous-fiber reinforcement.

In many applications the stiffness of a material is just as important as its strength. In tension the stiffness per unit length is given the product \( EA \), where \( E \) is the modulus and \( A \) is the cross-sectional area. When the material is subjected to flexure, the stiffness per unit length is a function of the product \( EI \), where \( l \) is the second moment of area of cross section (see Example 3.2). Therefore the stiffness in both tension and flexure increases as the modulus of the material increases, and the advantages of fiber reinforcement thus become immediately apparent, considering the very high modulus values for fibers.
3.3.5 Fracture of Fiber-Reinforced Plastics

Although the presence of the reinforcing fibers enhances the strength and modulus properties of the base material, they also cause a complex distribution of stress in the materials. For example, even under simple tensile loading, a triaxial stress system is set up since the presence of the fiber restricts the lateral contraction of the matrix. This system increases the possibility of brittle failure in the material. The type of fracture which occurs depends on the loading conditions and fiber matrix bonding.

3.3.5.1 Tension

With continuous-fiber reinforcement it is necessary to break the fibers before overall fracture can occur. The two different of fracture which can occur in tension are shown in Figure 3.48. It is interesting to note that when an individual fiber in a continuous-fiber composite breaks, it does not cease to contribute to the strength of the material, because the broken fiber then behaves like a long short fiber and will still be supporting part of the external load at sections remote from the broken end. In short-fiber composites, however, fiber breakage is not an essential prerequisite to complete composite fracture, especially when the interfacial bond is weak, because the fibers may then be simply pulled out of the matrix as the crack propagates through the latter.

3.3.5.2 Compression

In compression the strength of glass-fiber reinforced plastics is usually less than in tension. Under compressive loading, shear stresses are set up in the matrix parallel to the fibers. The fiber aligned in the loading direction thus promote shear deformation. Short-fiber reinforcement may therefore have advantages over continuous fibers in compressive loading because in the former not all the fibers can be aligned, so the fibers which are inclined to the loading plane will resist shear deformation. If the matrix-fiber bond is weak, debonding may occur, causing longitudinal cracks in the composite and buckling failure of the continuous fibers.

FIGURE 3.48 Typical fracture modes in fiber-reinforced plastics. (a) Fracture due to strong interfacial bond. (b) Jagged fracture due to weak interfacial bond.
3.3.5.3 Flexure or Shear

In flexure or shear, as in the previous case of compression, plastics reinforced with short fibers are probably better than those with continuous fibers, because in the former with random orientation of fibers at least some of the fibers will be correctly aligned to resist the shear deformation. However, with continuous-fiber reinforcement if the shear stresses are on planes perpendicular to the continuous fibers, then the fibers will offer resistance to shear deformation. Since high volume fraction ($\phi_0$) can be achieved with continuous fibers, this resistance can be substantial.

3.3.6 Fatigue Behavior of Reinforced Plastics

Like unreinforced plastics, reinforced plastics are also susceptible to fatigue. There is, however, no general rule concerning whether glass reinforcement enhances the fatigue endurance of the base material. In some cases the unreinforced plastic exhibits greater fatigue endurance than the reinforced material; in other cases, the converse is true.

In short-fiber glass-reinforced plastics, cracks may develop relatively easily at the interface close to the ends of the fibers. The cracks may then propagate through the matrix and destroy its integrity long before fracture of the composite takes place. In many glass-reinforced plastics subjected to cyclic tensile stresses, debonding many occur after a few cycles even at modes stress levels. Debonding may be followed by resin cracks at higher stresses, leading eventually to the separation of the component due to intensive localized damage. In other modes of loading, e.g., flexure or torsion, the fatigue endurance of glass-reinforced plastics is even worse than in tension. In most cases the fatigue endurance is reduced by the presence of moisture.

Plastics reinforced with carbon and boron, which have higher tensile moduli than glass, are stiffer than glass-reinforced plastics and are found to be less vulnerable to fatigue.

3.3.7 Impact Behavior of Reinforced Plastics

Although it might be expected that a combination of brittle reinforcing fibers and a brittle matrix (e.g., epoxy or polyester resins) would have low impact strength, this is not the case, and the impact strengths of the fibers or the matrix. For example, polyester composites with chopped-strand mat have impact strengths from 45 to 70 ft-lb/in$^2$ (94–147 kJ/m$^2$), whereas a typical impact strength for polyster resin is only about 1 ft-lb/in$^2$ (2.1 kJ/m$^2$).

The significant improvement in impact strength by reinforcement is explained by the energy required to cause debonding and to overcome friction in pulling the fibers out of the matrix. It follows from this that impact strengths would be higher if the bond between the fiber and the matrix is relatively weak, because if the interfacial bond is very strong, impact failure will occur by propagation of cracks across the matrix and fibers requiring very little energy.

It is also found that in short-fiber-reinforced plastics the impact strength is maximum when the fiber length has the critical value. The requirements for maximum impact strength (i.e., short fiber and relatively weak interfacial bond) are thus seen to be contrary to those for maximum tensile strength (long fibers and strong bond). The structure of a reinforced plastic material should therefore be tailored in accordance with the service conditions to be encountered by the material.

3.4 Electrical Properties

The usefulness of an insulator or dielectric ultimately depends on its ability to act as a separator for points across which a potential difference exists. This ability depends on the dielectric strength of the material, which is defined as the maximum voltage gradient that the material withstands before failure or loss of the material’s insulating properties occurs.
Besides permittivity (dielectric constant), dielectric losses, and dielectric strength, another property used to define the dielectric behavior of a material is the insulation resistance, i.e., the resistance offered by the material to the passage of electric current. This property may be important in almost all applications of insulators.

This resistivity (i.e., reciprocal of conductivity) of a plastic material with a perfect structure would tend to be infinite at low electric fields. However, the various types of defects which occur in plastics may act as sources of electrons or ions which are free to contribute to the conductivity or that can be thermally activated to do so. These defects may be impurities, discontinuities in the structure, and interfaces between crystallites and between crystalline and amorphous phases. Common plastics therefore have finite, though very high, resistivities from $10^8$ to $10^{20}$ ohm-cm. These resistivity values qualify them as electrical insulators.

Polymeric materials have also been produced which have relatively large conductivities and behave in some cases like semiconductors and even photoconductors [26]. For example, polyphenylacetylene, polyaminoquinones, and polycenequinone radical polymers have been reported with resistivities from $10^3$ to $10^8$ ohm-cm. It has been suggested that the conductivity in these organic semiconductors is due to the existence of large number of unpaired electrons, which are free within a given molecule and contribute to the conduction current by hopping (tunneling) from one molecule to an adjacent one (see "Electroactive Polymers" in Chapter 5).

### 3.4.1 Dielectric Strength

Dielectric strength is calculated as the maximum voltage gradient that an insulator can withstand before puncture or failure occurs. It is expressed as volts (V) per unit of thickness, usually per mil (1 mil = 1/1,000 in.).

Puncture of an insulator under an applied voltage gradient results from small electric leakage currents which pass through the insulator due to the presence of various types of defects in the material. (Note that only a perfect insulator would be completely free from such leakage currents.) The leakage currents warm the material locally, causing the passage of a greater current and greater localized warming of the material, eventually leading to the failure of the material. The failure may be a simple puncture in the area where material has volatilized and escaped, or it may be a conducting carbonized path (tracking) that short circuits the electrodes.

It is obvious from the cause of dielectric failure that the measured values of dielectric strength will depend on the magnitude of the applied electric field and on the time of exposure to the field. Since the probability of a flaw and a local leakage current leading ultimately to failure increases with the thickness of the sample, dielectric strength will also be expected to depend on the sample thickness.

The measurement of dielectric strength (Figure 3.49a) is usually carried out either by the short-time method or by the step-by-step method. In the former method the voltage is increased continuously at a uniform rate (500 V/sec) until failure occurs. Typically, a 1/8-in. thick specimen requiring a voltage of about 50,000 V for dielectric failure will thus involve a testing period of 100 sec or so.

In step-by-step testing, definite voltages are applied to the sample for a definite time (1 min), starting with a value that is half of that obtained by short-time testing, with equal increments of 2,000 V until failure occurs. Since step-by-step testing provides longer exposure to the electric field, dielectric strength values obtained by this method are lower than those obtained by the short-time test. Conditions to step-by-step testing correspond more nearly with those met in service. Even so, service failure almost invariably occurs at voltages below the measure dielectric strength. It is thus necessary to employ a proper safety factor to provide for the discrepancy between test and service conditions.

Increase in thickness increases the voltage required to give the same voltage gradient, but the probability of a flaw and a local leakage current leading ultimately to failure also increases. The breakdown voltage increases proportionally less than thickness increases, and as a result the dielectric strength of a material decreases with the thickness of specimen (Figure 3.49b). For this reason, testing of insulation plastic should be done with approximately the thickness in which it is to be used in service.
It is seen from Figure 3.49b that the dielectric strength increases rapidly with decreasing thickness of the sample. A rule of thumb is that the dielectric strength varies inversely with the 0.4 power of the thickness. For example, if the dielectric strength of poly(vinyl chloride) plastic is 375 V/mil in a thickness of 0.075 in., it would be $375(75/15)^{0.4}$ or about 700 V/mil in foils only 15 mils thick. The fact that thin foils may have proportionally higher dielectric strength is utilized in the insulation between layers of transformer turns.

The dielectric strength of an insulation material usually decreases with increase in temperature and is approximately inversely proportional to the absolute temperature. But the converse is not observed, and below room temperature dielectric strength is substantially independent of temperature change.

Mechanical loading has a pronounced effect on dielectric strength. Since a mechanical stress may introduce internal flaws which serve as leakage paths, mechanically loaded insulators may show substantially reduced values of dielectric strength. Reductions up to 90% have been observed.

Dielectric strength of an insulating material is influenced by the fabrication detail. For example, flow lines in a compression molding or weld lines in an injection molding may serve as paths of least resistance for leakage currents, thus reducing the dielectric strength. Even nearly invisible minute flaws in a plastic insulator may reduce the dielectric strength to one-third its normal value.

### 3.4.2 Insulation Resistance

The resistance offered by an insulating material to the electric current is the composite effect of volume and surface resistances, which always act in parallel. Volume resistance is the resistance to leakage of the electric current through the body of the material. It depends largely on the nature of the material. But surface resistance, which is the resistance to leakage along the surface of a material, is largely a function of surface finish and cleanliness. Surface resistance is reduced by oil or moisture on the surface and by surface roughness. On the other hand, a very smooth or polished surface gives greater surface resistance.

A three-electrode system, as shown in Figure 3.50, is used for measurement of insulation resistance. In this way the surface and volume leakage currents are separated. The applied voltage must be well below the dielectric strength of the material. Thus, in practice, a voltage gradient less than 30 V/mil is applied. From the applied voltage and the leakage current, the leakage resistance is computed. Since
the measured value depends, among other things, on the time during which the voltage is applied, it is essential to follow a standardized technique, including preconditioning of the specimen to obtain consistent results.

The insulation resistance of a dielectric is represented by its volume resistivity and surface resistivity. The volume resistivity (also known as specific volume resistance) is defined as the resistance between two electrodes covering opposite faces of a centimeter cube. The range of volume resistivities of different materials including plastics is shown in Figure 3.51. Values for plastics range from approximately $10^{10}$ ohm-cm for a typical cellulose acetate to about $10^{19}$ ohm-cm for a high-performance polystyrene.

The surface resistivity (also known as specific surface resistance) is defined as the resistance measured between the opposite edges of the surface of a material having an area of 1 cm$^2$. It ranges from $10^{10}$ ohm for cellulose acetate to $10^{14}$ ohm for polystyrene.

The insulation resistance of most plastic insulating materials is affected by temperature and the relative humidity of the atmosphere. The insulation resistance falls off appreciably with an increase in temperature or humidity. Even polystyrene, which has very high insulation resistance at room temperature, becomes generally unsatisfactory above 80°C (176°F). Under these conditions polymers like polytetrafluoroethylene and polychlorotrifluoroethylene are more suitable. Plastics that have high water resistance are relatively less affected by high humidities.

### 3.4.3 Arc Resistance

The arc resistance of a plastic is its ability to withstand the action of an electric arc tending to form a conducting path across the surface. In applications where the material is subject to arcing, such as switches, contact bushes, and circuit breakers, resistance to arc is an important requirement. Arcing tends to produce a conducting carbonized path on the surface.

The arc resistance of an insulator may be defined as the time in seconds that an arc may play across the surface without burning a conducting path. A schematic of an arc-resistance test is shown in Figure 3.52. Plastics that carbonize easily (such as phenolics) have relatively poor arc resistance. On the other hand, there are plastics (such as methacrylates) that do not carbonize, although they would decompose and give off combustible gases. There would thus be no failure in the usual sense. Special arc-resistant formulations involving noncarbonizing mineral fillers are useful for certain applications. But when service conditions are severe in this respect, ceramics ought to be used, because they generally have much better arc resistance than organic plastics.

Related to arc resistance is ozone resistance. This gas is found in the atmosphere around high-voltage equipment. Ignition cable insulation, for example, should be ozone resistant. Natural rubber is easily
attacked and deteriorated by ozone. Fortunately, most synthetic resins have good ozone resistance and are satisfactory from this point of view.

### 3.4.4 Dielectric Constant

The effect of a dielectric material in increasing the charge storing capacity of a capacitor can be understood by considering the parallel-plate type sketched in Figure 3.53. If a voltage $V$ is applied across two metal plates, each of area $A$ m², separated by a distance, $d$ m, and held parallel to each other in vacuum, the electric field established between the plates (Figure 3.53a) is

$$E = \frac{-V}{d} \quad (3.120)$$

The charge density, $Q_0/A$, where $Q_0$ is the total charge produced on the surface area $A$ of each plate, is directly proportional to the electric field.

$$\frac{Q_0}{A} = -\varepsilon_0 E = \varepsilon_0 \frac{V}{d} \quad (3.121)$$

or

$$Q_0 = A\varepsilon_0 \frac{V}{d} = C_0 V \quad (3.122)$$

![FIGURE 3.52](image_url) **Arc-resistance test.**

![FIGURE 3.53](image_url) **Schematic illustration of the effect of dielectric material in increasing the charge storing capacity of a capacitor.**
The proportionality constant, \( \varepsilon_0 \), is called the dielectric constant (or permittivity) of a vacuum. It has units of
\[
\varepsilon_0 = \frac{Q_0/A}{V/d} = \frac{\text{coul/m}^2}{\text{V/m}} = \frac{\text{coul/V}}{\text{m}} = \frac{\text{farad}}{\text{m}}
\]
and a value of \( 8.854 \times 10^{-12} \text{ farad/m} \).

The quantity \( C_0 \) in Equation 3.122 is the capacitance of a capacitor (condenser) with a vacuum between its plates. It can be defined as the ratio of the charge on either of the plates to the potential differences between the plates.

Now if a sheet of a dielectric material is inserted between the plates of a capacitor (Figure 3.53b), an increased charge appears on the plates for the same voltage, due to polarization of the dielectric. The applied field \( E \) causes polarization of the entire volume of the dielectric and thus gives rise to induced charges, or bound charges, \( Q' \), at its surface, represented by the ends of the dipole chains. These induced charges may be pictured as neutralizing equal charges of opposite signs on the metal plates. If one assumes, for instance, that the induced charge \( -Q' \) neutralizes an equal positive charge in the upper plate of the capacitor (Figure 3.53b), the total charge stored in the presence of the dielectric is \( Q = Q_0 + Q' \).

The ratio of the total charge \( Q \) to the free charge \( Q_0 \) (which is not neutralized by polarization) is called the relative dielectric constant or relative permittivity, \( \varepsilon_r \), and is characteristic of the dielectric material.

\[
\varepsilon_r = \frac{\text{Total charge}}{\text{Free charge}} = \frac{Q}{Q_0} \tag{3.123}
\]

Obviously, \( \varepsilon_r \) is always greater than unity and has no dimensions. For most materials \( \varepsilon_r \) exceeds 2 (Table 3.6).

Dividing both the numerator and denominator of Equation 3.123 by the applied voltage \( V \) and applying the definition of \( C \) from Equation 3.122, we obtain

\[
\varepsilon_r = \frac{\varepsilon}{\varepsilon_0} = \frac{C}{C_0} \tag{3.124}
\]

The relative dielectric constant or relative permittivity is thus defined as the ratio of the capacitance of a condenser with the given material as the dielectric to that of the same condenser without the dielectric.

### TABLE 3.6 Dielectric Properties of Electrical Insulators

<table>
<thead>
<tr>
<th>Material</th>
<th>( \varepsilon_r ) at 60 Hz</th>
<th>( \tan \delta ) at 60 Hz</th>
<th>( \tan \delta ) at 10^6 Hz</th>
<th>Dielectric Strength(^a) (V/mil)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ceramics</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Porcelain</td>
<td>6</td>
<td>0.010</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Alumina</td>
<td>9.6</td>
<td>–</td>
<td>&lt;0.0005</td>
<td>200–300</td>
</tr>
<tr>
<td>Zircon</td>
<td>9.2</td>
<td>0.035</td>
<td>0.001</td>
<td>60–290</td>
</tr>
<tr>
<td>Soda-lime</td>
<td>7</td>
<td>0.1</td>
<td>0.01</td>
<td>–</td>
</tr>
<tr>
<td>Fused silica</td>
<td>4</td>
<td>0.001</td>
<td>0.0001</td>
<td>–</td>
</tr>
<tr>
<td>Mica</td>
<td>7</td>
<td>–</td>
<td>0.0002</td>
<td>3,000–6,000 (1–3 mil specimen)</td>
</tr>
<tr>
<td><strong>Polymers</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyethylene</td>
<td>2.3</td>
<td>&lt;0.0005</td>
<td>–</td>
<td>450–1,000</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>2.5</td>
<td>0.0002</td>
<td>0.0003</td>
<td>300–1,000</td>
</tr>
<tr>
<td>Polyvinyl chloride</td>
<td>7</td>
<td>0.1</td>
<td>–</td>
<td>300–1,000</td>
</tr>
<tr>
<td>Nylon-6, 6</td>
<td>4</td>
<td>0.02</td>
<td>0.03</td>
<td>300–400</td>
</tr>
<tr>
<td>Teflon</td>
<td>2.1</td>
<td>&lt;0.0001</td>
<td>–</td>
<td>400</td>
</tr>
</tbody>
</table>

\(^a\) Specimen thickness 1/8 in.
(The dielectric constant for air is 1.0006. It is usually taken as unity—that is, the same as a vacuum—and the relative dielectric constant is referred to simply as the dielectric constant).

The dielectric susceptibility, \( \chi \), is defined as

\[
\chi = \varepsilon_r - 1 = \frac{\varepsilon - \varepsilon_0}{\varepsilon_0}
\]

(3.125)

It thus represents the part of the total dielectric constant which is a consequence of the material. From Equation 3.123,

\[
\chi = \frac{\text{Bound charge}}{\text{Free charge}}
\]

The magnitude of the induced or bound charge \( Q' \) per unit area is the polarization, \( P \), which has the same units as charge density.

Therefore,

\[
P = \frac{Q'}{A} = \frac{Q - Q_0}{A}
\]

(3.126)

Substituting from Equation 3.121, Equation 3.123, and Equation 3.125, we obtain

\[
P = \chi \varepsilon_0 E = \varepsilon_0 (\varepsilon_r - 1) E
\]

(3.127)

This equation, as we shall see later, provides a link between the permittivity, which is a macroscopic, measurable property of a dielectric, and the atomic or molecular mechanisms in the dielectric which give rise to this property.

### 3.4.4.1 Polarization and Dipole Moment

In terms of the wave-mechanical picture, an atom may be looked upon as consisting of a positively charged nucleus surrounded by a negatively charged cloud, which is made up of contribution from electrons in various orbitals. Since the centers of positive and negative charges are coincident (see Figure 3.54a), the net dipole moment of the atom is zero.

If an electric field is applied, however, the electron cloud will be attracted by the positive plate and the nucleus by the negative plate, with the result that there will occur a small displacement of the center of gravity of the negative charge relative to that of the positive charge (Figure 3.54a). The phenomenon is described by the statement that the field has induced an electric dipole in the atom; and the atom is said to have suffered electronic polarization—electronic because it arises from the displacement of the electron cloud relative to the nucleus.

The electric dipole moment of two equal but opposite charges, \(+q\) and \(-q\), at a distance \( r \) apart is defined as \( qr \). For the atomic model of Figure 3.54a, it can be shown by balancing the opposite forces of the electric field and the coulombic attraction between the nucleus and the center of the electron cloud that the dipole moment, \( \mu \), induced in an atom by the field \( E \) is

\[
\mu = (4\pi\varepsilon_0 R^3)E = \alpha_e E
\]

(3.128)

where \( \alpha_e \) is a constant, called the electronic polarizability of the atom. It is proportional to the volume of the electron cloud, \( R^3 \). Thus the polarizability increases as the atoms become larger.

On the macroscopic scale we have earlier defined the polarization, \( P \), to represent the bound charges induced per unit area on the surface of the material. Therefore, if we take unit areas on opposite faces of a cube separated by a distance \( d \), the dipole moment due to unit area will be

\[
\mu = Pd
\]
For \( d = 1 \) (i.e., for unit volume) \( \mu = P \). The polarization \( P \) is thus identical with the dipole moment per unit volume (check the units: \( \text{coul/m}^2 = \text{coul m/m}^3 \)).

A dipole moment may rise through a variety of mechanisms, any or all of which may thus contribute to the value of \( P \). The total polarization may be represented as a sum of individual polarizations, each arising from one particular mechanism (Figure 3.54) or, more appropriately, as an integrated sum of all the individual dipole moments per unit volume.

\[
P = P_e + P_i + P_0 + P_s = \sum \frac{\mu_e + \sum \mu_i + \sum \mu_0 + \sum \mu_s}{V}
\]  

(3.129)

Electronic polarization, \( P_e \), as discussed previously, arises from electron displacement within atoms or ions in an electric field; it occurs in all dielectrics. Similarly, displacements of ions and atoms within molecules and crystal structures (Figure 3.54b) under an applied electric field give rise to ionic (or atomic) polarization, \( P_i \). Orientation polarization, \( P_0 \), arises when asymmetric (polar) molecules having permanent dipole moments are present, since they become preferentially oriented by an electric field (Figure 3.54c). Interfacial (or space charge) polarization, \( P_s \), is the result of the presence of higher conductivity phases in the insulating matrix of a dielectric, causing localized accumulation of charge under the influence of an electric field (Figure 3.54d).

Any or all of these mechanisms may be operative in any material to contribute to its polarization. A question to be discussed now is, which of the mechanisms are important in any given dielectric? The answer lies in studying the frequency dependence of the dielectric constant.

**FIGURE 3.54** Schematic illustrations of polarization mechanisms. (a) Electronic displacement. (b) Ionic displacement. (c) Dipole orientation. (d) Space charge.
3.4.4.2 Dielectric Constant versus Frequency

Let us consider first a single dipole in an electric field. Given time, the dipole will line up with its axis parallel to the field (Figure 3.54c). If now the field is reversed, the dipole will turn 180° to again lie parallel to the field, but it will take a finite time; so if the frequency of the field reversal increases, a point will be reached when the dipole cannot keep up with the field, and the alteration of the dipole direction lags behind that of the field. For an assembly of dipoles in a dielectric, this condition results in an apparent reduction in the dielectric constant of the material. As the frequency of the field continues to increase, at some stage the dipoles will barely have started to move before the field reverses. Beyond this frequency, called the relaxation frequency, the dipoles make virtually no contribution to the polarization of the dielectric.

We may now consider the various mechanisms and predict, in a general way, the relaxation frequency for each one. Electrons with their extremely small mass have little inertia and can follow alterations of the electric field up to very high frequencies. Relaxation of electronic polarization is thus not observed until about $10^6$ Hz (ultraviolet region). Atoms or ions vibrate with thermal energy, and the frequencies of these vibrations correspond to the infrared frequencies of the electromagnetic spectrum. The relaxation frequencies for ionic polarization are thus in the infrared range.

Molecules or groups of atoms (ions) behaving as permanent dipoles may have considerable inertia, so relaxation frequencies for orientation polarization may be expected to occur at relatively smaller frequencies, as in the radio-frequency range. Since the alternation of interfacial polarization requires a whole body of charge to be moved through a resistive material, the process may be slow. The relaxation frequency for this mechanism is thus low, occurring at about $10^3$ Hz.

Figure 3.55 shows a curve of the variation of the dielectric constant (relative permittivity) with frequency for a hypothetical solid dielectric having all four mechanisms of polarization. Note that except at high frequencies the electronic mechanism makes a relatively low contribution to permittivity. However, in the optical range of frequencies, only this mechanism and the ionic mechanism operate; they therefore strongly influence the optical properties of materials.

3.4.4.3 Dielectric Constant versus Temperature

Liquids have higher dielectric constants than solids because dipole orientation is easier in the former. The effect is shown schematically in Figure 3.56a. After the abrupt change due to melting, the dielectric constant decreases as the temperature is increased, which is due to the higher atomic or molecular mobility and thermal collisions tending to destroy the orientation of dipoles.

![Figure 3.55 Dielectric constant versus frequency.](image-url)
Figure 3.56 shows the schematic variations of dielectric constants with temperature for amorphous solids, such as glasses and many polymers. Above the glass transition temperature ($T_g$), atoms and molecules have some freedom of movement, which allows orientation of permanent dipoles with the field, thereby increasing the dielectric constant. Since the polar groups which contribute to orientation polarization are not identically situated in an amorphous matrix, the dielectric constant changes over a temperature range rather than abruptly at a single temperature as in a crystalline material (cf. Figure 3.56a). The decrease in the dielectric constant after melting is again due to greater molecular mobility and thermal collisions.

3.4.4.4 Dielectric Losses

The behavior of a dielectric under an applied field has much in common with that of a material subjected to mechanical loading. The displacements of atoms and molecules within a material, when a mechanical force is applied, do not occur instantaneously but lag behind the force, resulting in elastic aftereffect and energy dissipation by mechanical hysteresis under an alternating force. Similarly, in dielectrics the lag of polarization behind the applied field produces energy dissipation by electrical hysteresis in an alternating field (Figure 3.57b). Such energy losses are related to the internal dipole friction. The rotation of dipoles with the field is opposed by the internal friction of the material, and the energy required to maintain this rotation contributes to the power loss in dielectrics.

Figure 3.57 Charge density versus electric field. (a) Loss-free cycle. (b) High-loss cycle. (c) Phase shift in a perfect capacitor. (d) Phase shift in a real capacitor.
Besides electrical hysteresis, leakage currents also contribute to dielectric losses. Leakage currents occur mainly by ionic conduction through the dielectric material and are usually negligible except at high temperatures. There are various ways of measuring energy losses by a dielectric.

A fundamental property of a capacitor is that if an alternating voltage is applied across it in a vacuum, the current that flows to and from it due to its successive charging and discharging is 90° out of phase with the voltage (Figure 3.57c), and no energy is lost. However, in real capacitors containing a dielectric, the lag of polarization causes a phase shift of the current (Figure 3.57d). The phase shift angle, $\delta$, is called the loss angle, and its tangent ($\tan \delta$) is referred to as the loss tangent or dissipation factor. (An ideal dielectric would have a phase angle of 90°, and hence the loss angle would be zero.)

The sine of the loss angle ($\sin \delta$) or the cosine of the phase angle ($\cos \theta$) is termed the power factor. In electrical applications the power loss ($PL$) is defined as the rate of energy loss per unit volume and is derived to be

$$PL = \frac{\omega E^2 \varepsilon_0}{2} \tan \delta$$

(3.130)

where $E$ is the electric field and $\omega$ is the angular velocity; $\varepsilon$, $\tan \delta$ is called the loss factor.

For most materials $\delta$ is very small; consequently, the three measures of energy dissipation—$\delta$, $\tan \delta$, and $\sin \delta (= \cos \theta)$—are all approximately the same. Since these values vary somewhat with frequency, the frequency must be specified (see Table 3.6).

It is evident from this discussion that the power loss and heat dissipation in a dielectric will be aided by a high dielectric constant, high dissipation factor, and high frequency. Therefore, for satisfactory performance electrical insulating materials should have a low dielectric constant and a low dissipation factor but a high dielectric strength (Table 3.6) and a high insulation resistance.

Polyethylene and polystyrene with their exceptionally low dissipation factors (<0.0005) and low dielectric constant (2.3–2.5) are the most suitable for high-frequency applications, as in television and radar. For dielectrics used in capacitors, however, a high dielectric constant is desirable.

### 3.4.4.5 Dielectric Losses of Polar Polymers

When a polymer having polar groups (e.g., polymethyl methacrylate, polyvinyl chloride) is placed in an electric field, the polar groups behaving as dipoles tend to orient themselves in response to the field (Figure 3.58a). In an alternating field the friction of the dipoles rotating with the field contributes to the dielectric loss. This loss is small at low frequencies where the polar groups are able to respond easily to the field, and also at high frequencies where the polar groups are unable to change their alignment with

![FIGURE 3.58](image-url)
the field. The loss is maximum in the transitional region where the polymer is passing from high response at low frequency to low response at high frequency (Figure 3.58b).

Since the friction of dipoles in an alternating field produces heat, polar polymers can be heated by the application of radio-frequency field in fabrication processes (see high-frequency welding, Chapter 2).

### 3.5 Optical Properties

Optical characteristics of plastics include color, clarity, general appearance, and more directly measurable properties, such as index of refraction [27]. For optical applications, however, other properties, including dimensional stability, scratch resistance, temperature limitation, weatherability, and water absorption, must be considered.

#### 3.5.1 Optical Clarity

Most resins by nature are clear and transparent. They can be colored by dyes and will become opaque as pigments or fillers are added. Polystyrene and poly (methyl methacrylate) are well known for their optical clarity, which even exceeds that of most glass. Optical clarity is a measure of the light transmitting ability of the material. It depends, among other things, on the length of the light path, which can be quantitatively expressed by the Lambert–Beer law, or

\[
\log \left( \frac{I}{I_0} \right) = -AL,
\]

where \( I/I_0 \) is the fraction of light transmitted, \( L \) is the path length, and \( A \) is the absorptivity of the material at that wavelength. The absorptivity describes the effect of path length and has the dimension of reciprocal length.

Transparent colored materials are obtained by adding a dye to a water white resin. A color results when a dye removes part of the visible light traveling through the piece. The red color, for example, is produced by a dye which absorbs the blue, green, and yellow components of the light and transmits the red unchanged (Figure 3.59). However, for any dye to be effective it must be soluble in the plastic, and it is best incorporated in the plastic before molding. Fluorescent dyes absorb radiant energy at one wavelength, perhaps in the ultraviolet, and emit it as less energetic but more visible radiation.

Cast phenolics, allyls, cellulosics, and many other clear plastics show a natural tendency to absorb in the blue and to be yellowish. Ultraviolet photodecomposition is largely responsible for the development of yellowish color in plastics exposed to sunlight. Incorporation of an invisible ultraviolet-absorbing material such as phenyl salicylate or dihydroxybenzophenone in the plastic greatly reduces photodecomposition.

Addition of a blue or green tint into the plastic can also mask the yellow color. In addition to yellowing, plastics show darkening due to outdoor exposure as the transmission curve shifts downward, and there is pronounced absorption at wavelengths shorter than about 5,000 Å (Figure 3.60).

![Figure 3.59](image-url) Light transmission diagram for plastic.
The optical clarity of a plastics specimen is measured by the lack of optical haze. Haze is arbitrarily defined as the fraction of transmitted light which is deviated $2\frac{1}{2}^\circ$ or more from an incident beam by forward scattering. When the haze value is greater than 30%, the material is considered to be translucent. The forward scattering of the light beam, which is responsible for haze, occurs at internal interfaces such as caused by a dust particle, bubble, particles of a filler or pigment, or by density changes.

Due to scattering at interfaces, a crystalline plastic with myriads of crystallite regions bounded by interfaces is translucent. Crystalline polyethylene is thus translucent at room temperature, but, on warming, the crystallites disappear and the material becomes transparent. It can thus be inferred that plastics which are transparent at room temperature, such as polystyrene or poly(methyl methacrylate), are of the noncrystalline type and without fillers.

The effect of interfaces due to fillers depends to a large extent on the difference in the indices of refraction of plastic and filler. Thus transparent glass-filled polyester panels are obtained if the indices of refraction of glass and resin are identical and the glass is surface treated to enable the resin to wet the glass completely.

### 3.5.2 Index of Refraction

The index of refraction for any transparent material is the ratio of the sine of the angle of an incident ray to the sine of the angle of refraction (Figure 3.61). It also corresponds to the ration of the speed of light in a vacuum (or air, closely) to its speed in the material. The refractive index values of several common plastics are compared with those of other materials in Table 3.7.

The refraction property makes possible the focusing action of a lens. Plastic lenses have the advantage that they are light in weight (about half as heavy as glass) and practically nonshattering. But they have the disadvantage of low scratch resistance and comparatively poor dimensional stability for temperature changes.

When tolerances are less critical, plastic lenses can be mass produced by virtue of the moldability of plastics; these lenses are quite satisfactory for inexpensive camera view finders, for example, but in applications where exacting tolerances are required, such as cameras, periscopes, or similar high-resolution devices, molded plastic lenses have not been suitable. If plastic lenses are to be used in

![Figure 3.60 Yelowing of plastics on exposure.](image)

![Figure 3.61 Refraction of light. Index of refraction: $n = (\sin i)/(\sin r)$.](image)
these applications, they should be ground and polished in much the same manner as in glass, though, of course, it is easier to do so (Figure 3.62).

The refractive index, \( n \), of an isotropic material is given by the Lorentz–Lorenz relation

\[
\frac{n^2 - 1}{n^2 + 2} = \frac{4}{3} \pi P
\]

where \( P \) is the optical polarizability per unit volume of material. For a pure substance it is more convenient to write this equation in the form

\[
\frac{(n^2 - 1)M}{(n^2 + 2)p} = \frac{4}{3} \pi N_A \alpha = R
\]

where \( M \) is the molecular weight of the substance, \( p \) is the density, \( N_A \) is Avogadro’s number, \( \alpha \) is the optical polarizability of a single molecule of the substance, and \( R \) is the molar refraction.

The quantity \( \alpha \) represents the amount of polarization of the molecule per unit electric field caused by the alternating electric field associated with the light ray passing through the material. The polarization may be regarded as due to the shift of the center of charge of the more loosely bound electrons relative to the nucleus (see Figure 3.54).

The refractive index varies with wavelength of light and is measured by the optical dispersion—that is, the difference in the refractive indexes for different wavelengths. It is responsible for the spectrum-separating ability of a prism in a spectroscope. Most plastics have relatively low optical dispersion. This property makes them more suitable for eyeglasses and large lenses for projection television.

---

**TABLE 3.7 Index of Refraction**

<table>
<thead>
<tr>
<th>Material</th>
<th>Index of Refraction (( n ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>1.00</td>
</tr>
<tr>
<td>Water</td>
<td>1.33</td>
</tr>
<tr>
<td>Cellulose acetate</td>
<td>1.48</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>1.49</td>
</tr>
<tr>
<td>Common glass</td>
<td>1.52</td>
</tr>
<tr>
<td>Poly(vinyl chloride) copolymer</td>
<td>1.53</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>1.59</td>
</tr>
<tr>
<td>Flint glass</td>
<td>1.65</td>
</tr>
<tr>
<td>Diamond</td>
<td>2.42</td>
</tr>
</tbody>
</table>

FIGURE 3.62 Principle of piped light.
3.5.3 Piped Lighting Effect

The difference in indexes of refraction for air and for a transparent solid (plastic or glass) is responsible for the ability of the latter, used as a rod or plate, to bend or pipe light around a curve. Bending can be explained as follows. It is evident from Figure 3.61 that a light beam in air cannot enter a material with \( i > 90^\circ \). Since \( \sin 90^\circ = 1 \), the maximum angle of refraction is that for which the sine is \( 1/n \), where \( n \) is the index of refraction. For poly(methyl methacrylate) \( n = 1.49 \), and the maximum angle of refraction becomes \( \sin^{-1} (1/1.49) \) or \( 42^\circ \) approximately. Obviously a light beam refracted at a greater angle cannot have come from the air, but it must have been reflected internally. A plastic plate with small curvature therefore gives internal reflections and can thus bend a light beam, as shown in Figure 3.62. Consideration of geometric optics shows the minimum radius of curvature for this piping of light to correspond to \( 1/(n - 1) \) times the thickness.

Polymer has numerous advantages over glass [28]. First and foremost, it is more pliable. It is also nonshattering, lightweight, and easy to fabricate. Polymer optical fiber (POF) has a shorter bend radius (i.e., more flexibility) and is more resilient to damage and abuse than glass due to its intrinsic material characteristics. The bending radius depends largely on the diameter of the fiber, large fiber giving a larger bend radius. Thus, for an outside diameter of one millimeter (1,000 \( \mu \text{m} \)), the bend radius (damage threshold) is approximately one centimeter, while for single-mode POF with outside diameter of 125 \( \mu \text{m} \), the bend radius is as low as 0.125 cm. The level of intensity loss from bending depends on the individual characteristics of the fiber, but intensity loss values have been observed at 10%-15% for bends close to the minimum (damage threshold) radius.

Attenuation is a measurement, in decibels (dB) per unit length, of how much reduction in light (due to absorption) is experienced per unit length of the fiber. Absorption varies largely with the wavelength of light. The attenuation of PMMA, generally used as POF core material, is approximately 100 dB/km in the visible region and increases rapidly at higher wavelength (Figure 3.63). This high attenuation of POF compared to the silica-based fiber limits the data link length. However, the field witnessed real progress in 1980s when low loss polymers were developed and drawn into fibers (see Chapter 5).

The light bending ability of POF is made use of in a wide variety of applications ranging from lighting scheme for pools and fountains to telecommunications and consumer electronics. In these applications (see more details in Chapter 5), the POF serves as a medium for transmitting light for illumination or imaging, or for transporting and/or controlling information that is encoded on a beam of light [29].

3.5.4 Stress-Optical Characteristics

An important phenomenon observed in amorphous plastics (also observed in optical glass) is the development of optical anisotropy due to stress. The stress-optical characteristic of transparent plastics is the basis of the important technique of photoelasticity by which stress and strain in complicated shapes, for which no analytical solution is readily available, can be determined experimentally and simply.

The amount of strain in various parts of a transparent plastic model of a machine part, subjected to loads simulating those in actual operation, is determined by measuring the anisotropy with polarized light; therefore from this measurement the distribution of stress and strain in the actual metal part can be deduced. Very complicated
shapes, including complete structures such as bridges or aircraft wings, have been successfully analyzed in this manner, employing plastic models.

The same stress-optical characteristic also permits examination of locked-in stresses in a molded plastic part. The part is examined under polarized light, and the amount of stress is indicated by the number of fringes or rings that become visible. Illumination with white light gives colorful patterns involving all the colors of the spectrum. Monochromatic light is, however, used for stress analysis because it permits more precise measurements.

In general, a single ray of light entering an anisotropic transparent material, such as crystals of sufficiently low symmetry and strained or drawn polymers, is propagated as two separate rays which travel with different velocities and are polarized differently. Both the velocities and the state of polarization vary with the direction of propagation. This phenomenon is known as birefringence or double refraction, and the material is said to be birefringent.

The stress-optical characteristic of plastics arises from this phenomenon of birefringence, induced by strains due to applied stress. The applied stress produces different densities along different axes. The stress-optical coefficient of most plastics is about 1,000 psi (70 kgf/cm² or 6.9 Mpa) per inch (2.54 cm) thickness per fringe. This means that a 1-in. thick part when illuminated with monochromatic light and viewed through a polarizing filter will show a dark fringe or ring for a stress of 1,000 psi. This sensitivity is many times higher than that shown by glass and makes transparent plastics useful in photoelastic stress analysis.

In one variation of the process the deforming stress is applied to a warm, soft plastic model which is then quenched to room temperature. The resulting locked-in stress may then be analyzed at leisure or, perhaps more conveniently, by cutting sections from the model and examining them separately. For this application, however, the plastic should have stress-optical stability. In this regard, unplasticized transparent plastics such as poly(methyl methacrylate), polystyrene, and cast poly(allyl phthalate) are superior to plasticized materials such as cellulose acetate.

### 3.6 Thermal Properties

The useful thermal properties of plastics include specific heat, thermal expansion, thermal conductivity, and thermal softening [30].

#### 3.6.1 Specific Heat

For most plastics the specific heat value (calories per gram per °C) lies between 0.3 and 0.4. On a weight basis this value is much higher than that of most metals. Both iron and copper, for example, have specific heats of about 0.1 at ordinary temperatures. However, along a volume basis, the specific heats of plastics are lower than those of common metals, because of the substantially lower density of plastics.

Knowledge of specific heat of a material helps to determine the energy requirement for increasing its temperature. In compression molding and injection molding the theoretical heat requirement can be calculated as the sum of this direct heat and any latent heat of melting minus any energy released by chemical reaction. But this heat requirement is not large compared to the heat loss by radiation and conduction from the press. The proportion of losses is substantially lower for injection molding than for compression molding. It is nevertheless customary in both cases to establish the heating requirements as well as mold cooling requirements by a process of trial and error.

In dielectric preheating, however, the specific heat of a molding powder is of more direct concern; this knowledge along with the amount of material and time enables one to calculate the required amount of radio-frequency power. For example, to raise the temperature of a 1-kg perform of specific heat 0.35 through 80°C in 1 min requires $1 \times 0.35 \times 80$ or 28 kcal/min or about 2 kW.
3.6.2 Thermal Expansion

Linear (thermoplastic) polymers have very high thermal expansion coefficients since they are weakly bonded materials and need less input of thermal energy to expand the structure. This applies to all polymers of the vinyl type which have expansion coefficients of about $90 \times 10^{-6}/^\circ C$. Network (thermosetting) polymers having a three-dimensional framework of strong covalent bonds exhibit less thermal expansion and have expansion coefficients in the range of $30 - 70 \times 10^{-6}/^\circ C$. These may be compared with values of $11 \times 10^{-6}/^\circ C$ for mild steel, $17 \times 10^{-6}/^\circ C$ for ordinary brass, and less than $10 \times 10^{-6}/^\circ C$ for ceramics. In spite of high thermal expansion, plastics do not easily undergo thermal cracking, because they also have very low elastic moduli and large strains do not induce high stresses.

One area where the high expansion of polymers plays a significant role is the molded dimensions of plastic parts. The linear mold shrinkage due to thermal contraction from molding to room temperature is usually about 1/2%–1%. Polyethylene and certain other materials exhibit even a higher shrinkage. As a result, plastic parts with close tolerances are difficult to make. It is also possible during the molding operation that different parts are not all at a uniform temperature. This may lead to differential shrinkage during cooling and produce warping, locked-up internal stresses, and weakening of the part.

Warping may be prevented by a suitable mounting. Internal stresses in plastics that are more subject to creep and cold flow tend to relieve themselves slowly; warming the part accelerates the process. Internal stresses in polystyrene and other brittle plastics can be removed by an annealing process similar to the one used in glass manufacture. It involves a controlled heating-cooling cycle, and for plastics it is obtained by immersing the parts in a liquid held at the proper temperature, followed by very slow cooling. Polystyrene for example can be heated in water at 80°C and then slowly cooled to 65°C. It is then cooled in undisturbed air.

The relatively high thermal expansion of plastics poses a problem in the use of molded metal inserts which are sometimes required for electrical contacts, screw thread mountings, or increased strength. To minimize stresses due to inserts, manufacturers usually use plastics with low coefficient of expansion. Phenolics and ureas are commonly used because their coefficient of expansion are among the lowest of the common plastics.

For many plastics the use of molded metal inserts is not satisfactory because of the excessive stress produced. As an example, polystyrene with brass inserts on cooling from the molding temperature of 160 to 20°C produces a strain of $(70 - 17) \times 10^{-6} \times (160 - 20)$ or 0.0074. For an elastic modulus of $0.46 \times 10^6$ psi (3.2 Gpa), the internal stresses become 3,400 psi (23 Mpa). The presence of this much internal stress renders the part useless, since the tensile strength of polystyrene is only 3,600 psi (25 Mpa).

However, by use of an appropriate filler the thermal expansion of plastics and, hence, the internal stresses can be reduced. Addition of 11% by weight of aluminum oxides in polystyrene gives a mixture whose thermal expansion is identical to that of brass. Brass inserts in this alumina-polystyrene composite show no evidence of internal stresses and are quite satisfactory.

When synthetic resins are used as cements, the thermal expansion needs to be matched; this matching is done by judiciously choosing the filler. In the production of panels of aluminum alloy overlaid on phenolic laminate, a filler consisting of a glass fiber–starch mixture is used to reduce the expansion characteristic of the resin and to match its expansion exactly with that of aluminum. The aluminum panel then adheres completely and cannot be removed without tearing the metal or rupturing the phenolic core.

There are cases where the high thermal expansion of plastics is used to advantage. One example is the shrink fitting of handles of cellulose nitrate on screwdrivers. Another example is in mold design where the shrinkage on cooling is sufficient to permit a small undercut.

3.6.3 Thermal Conductivity

Thermal conductivities of plastics are relatively low and approximate $0.0004$ $(\text{cal-cm})/(^\circ \text{C-cm}^2\text{-sec})$. The corresponding values are 0.95 for copper, 0.12 for cast iron, 0.002 for asbestos, 0.0008 for wood, and 0.0001 for cork (SI values in $\text{J/s-m-k}$ are obtained by multiplying by 418.7). Because of their low thermal
conductivities, plastics are used for handles to cooking utensils and for automobile steering wheels. The low thermal conductivity is also responsible for the pleasant feel of plastic parts. Quite hot or quite cold objects can be handled with less difficulty if they are made of plastic, since the thermal insulation afforded by the plastic prevents a continuous rush of heat energy to (or from) the hand.

Both thermal conductivity and temperature resistance of plastics have to be considered for their use at high temperatures. As an example consider a teapot handle; it must not deform even at 100°C. Therefore, common thermoplastics such as cellulose acetate are ruled out, but both a wood-flour-filled and an asbestos-filled phenolic might be considered.

The thermal conductivity of a mixture is nearly proportional to the volume percentage of each component. Wood-flour-filled phenolic has a higher thermal conductivity than the pure resin, but the conductivity of this composite is still low enough to justify its use as the handle to a teapot. This composite can also withstand temperatures up to 100°C sufficiently well to give the handle a reasonable service life. For parts subjected to higher temperatures, asbestos-filled phenolic is a better choice. It can be used as the insulating connection to an electric iron, for example.

Design of a handle determines to a great extent its service life. Quite often handles are found fastened directly to the hot object without regard for any temperature limitation; at the junction the plastic becomes brittle because of high temperature, and failure occurs. If the handle can be separated from the heated part and some cooling arrangement is included as part of the design, improved performance is to be expected.

3.6.4 Transition Temperatures and Temperature Limitations

Both first- and second-order transitions are observed in polymers. Melting and allotrophic transformations are accompanied by latent-heat effects and are known as first-order transitions. During second-order transitions, changes in properties occur without any latent-heat effects. Below the second-order-transition temperature (glass transition temperature) a rubberlike material acts like a true solid (see Chapter 1). Above this temperature the fixed molecular structure is broken down partially by a combination of thermal expansion and thermal agitation. The glass transition temperature of polystyrene is 100°C; below 100°C polystyrene is hard and brittle, and above 100°C it is rubberlike and becomes easily deformed.

The design engineer often requires to know the maximum temperature for which a polymer can be used in a given application. This depends largely on two independent factors: (1) the thermal stability of the polymer, particularly in air; and (2) the softening behavior of the polymer.

Thermal stability testing requires the study of the change in properties on aging at various service temperatures. The relationship between structure and stability was considered briefly in Chapter 1 and will be considered again in Chapter 5. The use of additives for improving such stability is discussed in Chapter 1.

The rigidity of a polymer is determined by the ease with which polymer molecules are deformed under load. Young’s modulus is a fundamental measure of the rigidity or stiffness of a material. It is thus clear from Figure 1.52 that the softening point is associated with the $T_g$ for amorphous polymers and with the $T_m$ for highly crystalline polymers. In addition, there are many polymers that soften progressively between $T_g$ and $T_m$ and the value determined for the softening point can depend significantly on the test method used.

Two particular test methods have become very widely used. These are the Vicat softening point test and the test widely known as the heat distortion temperature test (also called the deflection temperature under load test). In the Vicat softening point test a sample of polymer is heated at a specified rate temperature increase and the temperature is noted at which a needle of specified dimensions indents into the polymer a specified distance under a specified load.

The heat-distortion temperature is defined as the temperature at which the midpoint of a beam 1/2 by 1/2 by 5 in. supported 1/2-in. from each end, shows a net deflection of 0.01 in. when loaded centrally with 2.5 kg and heated at the specified rate of 2°C/min. Testing is also done at one-quarter of this load. For most materials the two heat-distortion temperatures are within 10°.
A large difference in these two heat distortion temperature indicates a material sensitive to temperature change, and for such materials at any elevated temperature stress should be minimum up to the heat-distortion temperature. A plastic is expected to maintain its shape under load, and hence this temperature represents an upper limiting point at which a plastic may be used.

Recommendations of upper temperature limits for plastics are usually based on general experience, although some consideration is given to high-load and low-load heat-distortion temperatures. The size and shape of the part as well as its molding conditions govern to a certain extent the maximum permissible temperature; service conditions such as temperature variations and humidity are also important.

### 3.6.5 Standard Properties of Plastics

Figure 3.64 through Figure 3.90 illustrate schematically (in simplified form) the bases of some of the standard properties of plastics [31]. Where standard test methods have been developed, these have been included. The principles of the different tests are shown, and the properties measured are indicated.

Note that the property values of plastics are highly dependent on the specimen preparation, equipment, and testing techniques used. For this reason it is essential to refer to the appropriate official standard test method when executing the work.

### 3.7 Identification of Common Plastics

The first step in the identification of polymers is a critical visual examination. While the appearance of the sample may indicate whether it is essentially a raw polymer or a compounded and processed item, learning about its form, feel, odor, color, transparency or opacity, softness, stiffness, brittleness, bounce, and surface texture may be important in the process of the identification of the polymer. For example, polystyrene, the general purpose polymer, is transparent and brittle, and produces a characteristic metallic tinkle when objects molded from it are dropped or struck.

Identification of plastics [32] is carried out by a systematic procedure: preliminary test, detection of elements, determination of characteristic values, and, finally, specific tests. For an exact identification, however, the test sample should first be purified so that it contains no additives (plasticizers, fillers, pigments, etc.) that may affect the results of an analysis. Purification is achieved by solvent extraction;

![Diagram](image)

**FIGURE 3.64** Tests for tensile strength (stress at fracture of the specimen) and elongation (extension of materials under load) of plastics. The first provides a measure of the breaking strength of the material but is radically affected by the rate of loading and the ambient temperature. Tensile strength in lbf/in.² or kgf/cm² = load (lbf or kgf)/a × b (in.² or cm²). Standard test methods: BS 2782 method 301, ASTM D638, ISO R527. Elongation % = (L₂ − L₁) × 100/L₁. Standard test methods: BS 2782 method 301, ASTM D638.
FIGURE 3.65  Test for tangent and secant moduli of plastics. For tangent modulus, load on tangent to load-extension curve at specified extension is used for calculating the stress value, while for secant modulus load on secant to load-extension curve is used. The modulus is given by stress/strain. Standard test methods: BS 2782 method 302, ASTM D638, ISO R527.


FIGURE 3.67  Test for compressive strength of plastics. Compressive strength (lbf/in.² or kgf/cm²) = load (lbf or kgf)/$a \cdot b$ (in.² or cm²). Standard test methods: ASTM D795, BS 2782 method 303, ISO R604.
FIGURE 3.68 Test for tenacity of filaments, cords, twines, etc. Tenacity (gf/denier) = breaking load (gf)/denier of specimen. (Denier of filaments, cords, twines, etc., is equal to the weight in grams of 9,000 meters of the sample).

FIGURE 3.69 Test for tear propagation resistance of plastic film and thin sheeting. Tear resistance (gf/cm/mil) = force required to tear sample (gf/cm)/thickness of film (mil). Standard test methods: ASTM D1922, BS 2782 method 308B.

FIGURE 3.70 Tests for blocking of plastic film. Blocking force (lbf/in.² or kgf/cm²) = load (lbf or kgf)/initial area of films in contact (in.² or cm²). Standard test method: ASTM D1893.
FIGURE 3.71  Tests for impact resistance of plastics. Izod impact strength = \((E_1 - E_2)/D\) ft-lbf/in. of notch or cm-kgf/cm of notch. Standard test methods: ASTM D256; BS 2782 method 306A, ISO R180. Falling weight impact strength = \(W \cdot H\) ft-lbf or m-kgf. \(F_{50}\) is the energy required to fracture 50% of the specimens.) Standard test method: BS 2782 method 306 B.

FIGURE 3.72  Test for fracture toughness of plastics. Specimen in three-point bending configuration, as shown, is loaded in a testing machine that has provision for autographic recording of load applied to the specimen. Specimen dimensions: \(L\), length (mm); \(W\), width (mm); \(B\), thickness (mm); \(S\), span length (mm); \(a\), initial crack length (mm). Plane strain fracture toughness, \(K_{lc} = PSf (a/W)BW^{3/2}\), where \(P = load (N)\) determined from load displacement record; \(f (a/W)\) = geometric factor. Example: \(L = 64\) mm, \(W = 10\) mm \(B = 3\) mm, \(S = 40\) mm, \(a = 3.2\) mm, \(P = 50.88\) N, \(f (a/W) = 1.61\) (from ASTM standard), \(K_{lc} = 34.3\) N mm\(^{-3/2}\) = 1.09 MPa m\(^{1/2}\). Standard test method: ASTM E399-74.
1.6 mm Adhesive

Area in test grips

25.4 mm

63.5 mm 63.5 mm

127 + L mm

177.8 + L mm

FIGURE 3.73 Form and dimensions of test specimen for single-lap-joint shear test to determine shear strengths of adhesives for bonding metals (standard test method: ASTM D1002-94). Recommended length of overlap (L) for most metals of 1.62 mm in thickness is 12.7 mm. Specimen is placed in grips of a testing machine so that outer 25.4 mm (1 in.) of each end is in contact with the jaws. Load is applied at the rate of 80–100 kg/cm² (1,200–1,400 psi) of shear area per min and continued till failure occurs.

T-peel test panel

25 mm

241 mm (bonded)

152 mm

241 mm (unbonded)

Pull

76 mm

Pull

FIGURE 3.74 Test panel and T-type test (T-peel test) specimen for peel resistance of adhesives (standard test method: ASTM D1876-95). The bent, unbonded ends of test specimen are clamped in test grips of tensile testing machine and load applied at a constant head speed of 254 mm (10 in.). Average peeling load (in pounds per inch of specimen width) is determined for the first 127 mm (5 in.) of peeling after the initial peak.

Balance

Wire

Water (23 ± 2°C)

Specimen (Tied to a sinker for plastics lighter than water)

FIGURE 3.75 Test for specific gravity and density of plastics. Sp. gr. = a/(a−w−b) where a = wt. of specimen without wire, b = wt. of specimen completely immersed and of the wire partially immersed in water, and w = wt. of partially immersed wire. Standard test method: ASTM D792.
Heat transfer to raise the temperature at constant rate, i.e., 1°C/min for polystyrene

Heater to raise the temperature at constant rate, i.e., 50°C/h for polyethylene

Standard weight i.e., 20 g for polystyrene

Standard weight i.e., 1 kgf for polyethylene

Heat transfer liquid

FIGURE 3.76 Tests for softening temperatures of plastics. Cantilever softening point is the temperature at which the sample bends through 30°. Standard test method: BS 2782 method 102 C. Vicat softening point is the temperature at which the needle penetrates 1 mm into the sample. Standard test methods: ASTM D1525, BS 2782 method 102D, ISO R306.

Heat transfer liquid

Heater to raise the temperature at a constant rate, i.e., 2°C/min for polyethylene

Standard weight

Standard needle

Sample

Supports

FIGURE 3.77 Test for deflection temperature of plastics under flexural load. Heat distortion temperature is the temperature at which a sample deflects by 0.1 in. (2.5 mm). Two measurements are made and quoted: (a) with a stress of 66 lbf/in.² (4.6 kgf/cm²) and (b) with a stress of 264 lbf/in.² (18.5 kgf/cm²). Standard test methods: ASTM D648, BS 2782 method 102, ISO R75.

FIGURE 3.79  Measurement of swelling of die extrudate. Die swell ratio = $B/A$.

FIGURE 3.80  Determination of oxygen index. Oxygen index, $n\% = 100 \times O_2/(O_2 + N_2)$, where $O_2$, volumetric flow rate of oxygen, cm$^3$/sec, at the minimum concentration necessary to support flaming combustion of a material initially at room temperature and $N_2$, corresponding flow rate of nitrogen, cm$^3$/sec. Standard test method: ASTM D2863.
FIGURE 3.81  Test for rate of burning. Burning rate $= 38 \text{ (cm)/t (min)}$. Standard test method: ASTM D568.

FIGURE 3.82  Test for index of refraction of transparent plastics. Refractive index $= \text{real depth (measured with vernier)/apparent depth} (D_2 - D_1)$. Standard test method: ASTM D542, ISO R489.
FIGURE 3.83 Test for haze of transparent plastics. Haze, % = 100 × \( \frac{T_2}{T_1} \). A low haze value is important for good short distance vision. Standard test method: ASTM D1003.

FIGURE 3.84 Measurement of narrow-angle light-scattering property of plastic film. Clarity, % = 100 × \( \frac{T_1}{T_1 + T_2} \).

FIGURE 3.86 Test for permittivity (dielectric constant) of insulating materials. (a) Position of maximum voltage obtained with sample by adjusting variable capacitor. Electrode gap = specimen thickness = $D_1$; (b) position of maximum voltage obtained with air by adjusting electrode gap to $D_2$ [variable capacitor remains as set in (a)]. Dielectric constant = $D_1$ (in. or mm)$/D_2$ (in. or mm). Standard test methods: ASTM D150, BS 2782 method 207A.

FIGURE 3.87 Test for DC resistance of insulating materials. Electrical resistance of specimen (ohm) = applied voltage (V)/current measured (A). Volume resistivity (ohm-cm) = resistance of specimen (ohm) × arc of upper electrode (cm²)/specimen thickness (cm). Standard test methods: ASTM D257, BS 2782 method 202.
either the material is dissolved out and polymer is obtained by reprecipitation or evaporation of the solvent, or the pure polymer remains as the insoluble residue. The solvent varies, and a general method cannot be given. However, for many materials particularly for those in which additives do not interfere, the unpurified material can be investigated and qualitative preliminary tests used.

In general, the following series of investigations should be carried out for preliminary tests of the material: (1) behavior on heating in an ignition tube and in the flame; (2) qualitative detection of heteroelements such as N, S, and halogens; (3) determination of properties such as density, refractive index, and melting point or range; (4) determination of solubility as an aid to polymer identification; and (5) ash or sulfated ash determination as a test for inorganic additives (fillers, pigments, stabilizers).

### 3.7.1 Behaviors on Heating and Ignition

Many polymers can be roughly identified by their behavior when carefully heated and ignited. Nitrocellulose and plastics containing this (e.g., celluloid) burn with explosive violence and other materials such as
poly(vinyl chloride) or fluoro-hydrocarbons decompose with the evolution of poisonous or irritating vapors. Only small quantities of material should therefore be taken for heating tests. The heating should be done gently, because if the heating is too rapid or intense, the characteristic changes may not be observed.

In a typical procedure, a small piece or amount (0.1 g) of the test sample is placed on a cleaned glass or stainless steel spatula, previously heated to remove any traces of combustible or volatile materials, and then warmed gently over a small colorless Bunsen flame until the sample begins to fume. The decomposing sample is removed from the flame and the nature of the fume or gas is examined with respect to color, odor, inflammability, and chemical identity including acidity, alkalinity, etc.

The sample is next moved to the hottest zone of the small Bunsen flame and note is taken of the following: (1) if the material burns and if so, how readily; (2) the nature and color of the flame as the material burns; (3) whether the material is self-extinguishing or continues to burn after removal from the flame, and (4) the nature of the residue.

Observations on heating and ignition of some common polymers are listed in Table 3.8.

3.7.2 Tests for Characteristic Elements

The results of tests for characteristic elements such as nitrogen, sulfur and halogens may serve to roughly indicate the nature of the unknown material, including the nature of the base polymer and additives, if present. The following tests may be performed for qualitative detection of N, S, and halogens.

1. **Nitrogen.** Above 50 mg of the test material is heated carefully in an ignition tube with twice the amount of freshly cut sodium, until the sodium melts. A further small amount of material is added and the tube is heated to red heat. It is then dropped carefully into water (20 ml) in a mortar. The solid is powdered and the solution filtered.

   A little freshly prepared ferrous sulfate is added to the filtrate and the latter boiled for 1 min. It is acidified with dilute hydrochloric acid, and 1–2 drops of ferric chloride solution added. A deep blue coloration or precipitate (Prussian blue) indicates nitrogen (if very little nitrogen is present, a green–blue color is formed initially). This test sometimes fails with substances containing nitro-groups and with nitrogen-containing heterocyclic compounds.

2. **Sulfur.** The fusion is carried out as for nitrogen. The filtrate (2 ml) is acidified with acetic acid and a few drops of an aqueous solution of lead acetate is added. A black precipitate of lead sulfide indicates the presence of sulfur.

**FIGURE 3.90** Determination of open cell content of rigid cellular plastics. Open cell content (approx.) = 100 \((V - V_1)/V\), where \(V_1\), displacement volume of specimen, cm\(^3\) and \(V\), geometric volume of specimen, cm\(^3\). Standard test method: ASTM D2856.
### TABLE 3.8 Heating Tests of Some Common Polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Color of Flame</th>
<th>Odor of Vapor</th>
<th>Other Notable Points</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>The material burns but self-extinguishes on removal from flame</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poly(vinyl chloride)</td>
<td>Yellow–orange, green bordered</td>
<td>Resembles hydrochloric acid and plasticizer (usually ester like)</td>
<td>Strongly acidic fumes (HCl), black residue</td>
</tr>
<tr>
<td>Poly(vinylidene chloride)</td>
<td>As above</td>
<td>Resembles hydrochloric acid</td>
<td>As above</td>
</tr>
<tr>
<td>Polychloroprene</td>
<td>Yellow, smoky</td>
<td>As above</td>
<td>As above</td>
</tr>
<tr>
<td>Phenol-formaldehyde resin</td>
<td>Yellow, smoky</td>
<td>Phenol, formaldehyde</td>
<td>Very difficult to ignite, vapor reaction neutral</td>
</tr>
<tr>
<td>Melamine-formaldehyde resin</td>
<td>Pale yellow, light</td>
<td>Ammonia, amines (typically fish like), formaldehyde</td>
<td>Very difficult to ignite, vapor reaction alkaline</td>
</tr>
<tr>
<td>Urea-formaldehyde resin</td>
<td>As above</td>
<td>As above</td>
<td>Melts sharply to clear, flowing liquid; melt can be drawn into a fiber; vapor reaction alkaline</td>
</tr>
<tr>
<td>Nylons</td>
<td>Yellow–orange, blue edge</td>
<td>Resembling burnt hair</td>
<td>Melts and chars</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>Luminous, sooty</td>
<td>Phenolic</td>
<td>Melts and chars</td>
</tr>
<tr>
<td>Chlorinated rubber</td>
<td>Yellow, green bordered</td>
<td>Acrid</td>
<td>Strongly acidic fumes, liberation of HCl; swollen, black residue</td>
</tr>
<tr>
<td><strong>The material burns and continues burning on removal from flame</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polybutadiene (BR)</td>
<td>Yellow, blue base, smoky</td>
<td>Disagreeable, sweet</td>
<td>Chars readily; vapor reaction neutral</td>
</tr>
<tr>
<td>Polyisoprene (NR, gutta percha, synthetic)</td>
<td>Yellow, sooty</td>
<td>Pungent, disagreeable, like burnt rubber</td>
<td>As above</td>
</tr>
<tr>
<td>Styrene–butadiene rubber (SBR)</td>
<td>Yellow, sooty</td>
<td>Pungent, fruity smell of styrene</td>
<td>As above</td>
</tr>
<tr>
<td>Nitrile rubber (NBR)</td>
<td>Yellow, sooty</td>
<td>Like burnt rubber/burnt hair</td>
<td>As above</td>
</tr>
<tr>
<td>Butyl rubber (IIR)</td>
<td>Practically smoke free candle like</td>
<td>Slightly like burnt paper</td>
<td>Melt does not char readily</td>
</tr>
<tr>
<td>Polysulfide rubber (polymer itself emits unpleasant, mercaptan like odor)</td>
<td>Smoke-free, bluish</td>
<td>Pungent; smell of H₂S</td>
<td>Yellow, acidic (SO₂) fumes</td>
</tr>
<tr>
<td>Cellulose (cotton, cellophane, viscose rayon, etc.)</td>
<td>Yellow</td>
<td>Burnt paper</td>
<td>Chars, burns without melting</td>
</tr>
<tr>
<td>Cellulose acetate</td>
<td>Yellow–green, sparks</td>
<td>Acetic acid, burnt paper</td>
<td>Melts, drips, burns rapidly, chars, acidic fumes</td>
</tr>
<tr>
<td>Cellulose acetate butyrate</td>
<td>Dark yellow (edges slightly blue), somewhat sooty, sparks</td>
<td>Acetic acid/butyric acid, burnt paper</td>
<td>Melts and forms drops which continue burning</td>
</tr>
<tr>
<td>Cellulose nitrate (plasticized with camphor)</td>
<td>Yellow</td>
<td>Camphor</td>
<td>Burns very fast, often with explosion</td>
</tr>
<tr>
<td>Methyl cellulose</td>
<td>Yellow, luminous</td>
<td>Burnt paper</td>
<td>Melts and chars</td>
</tr>
<tr>
<td>Ethyl cellulose</td>
<td>Pale yellow with blue–green base</td>
<td>Slightly sweet, burnt paper</td>
<td>Melts and chars</td>
</tr>
<tr>
<td>Polyacrylonitrile</td>
<td>Yellow</td>
<td>Resembling burnt hair</td>
<td>Dark residue; vapor reaction alkaline</td>
</tr>
<tr>
<td>Poly(vinyl acetate)</td>
<td>Yellow, luminous, sooty</td>
<td>Acetic acid</td>
<td>Sticky residue, acidic vapor</td>
</tr>
</tbody>
</table>

(Continued)
3. **Halogens.** The fusion is carried out as for nitrogen. The filtrate (2 ml) is acidified with dilute nitric acid, boiled in the fume cupboard to remove H₂S and HCN, and then a few drops of silver nitrate solution is added. A while precipitate, turning grey–blue, indicates chlorine, a yellowish precipitate indicates bromine and a yellow precipitate indicates iodine.

In Beilstein’s test, which provides a simple means of detecting halogens, a minute quantity of the test material is placed on a copper wire (initially heated in a nonluminous bunsen flame until the flame appears colorless and then cooled) and heated in the outer part of the flame. Carbon burns first with a luminous flame. A subsequent green to blue–green color, produced by volatilized copper halide, indicates halogen (chlorine, bromine, iodine).

The different polymers may be classified into several groups according to the element present as shown in Table 3.9. The focus of identification may be further narrowed down on the basis of other preliminary observations, e.g., fusibility or otherwise, melting point or range, heat distortion temperature, flame tests and tests for thermal degradation, and solubility or extractability in water or different organic solvents. The solubility behaviors of common polymers are compared in Table 3.10.

### 3.7.3 Specific Tests

When the observations and results of preliminary tests have been considered and most of the possible structures for the polymer base eliminated, an exact identification can be made by carrying out specific tests [33]. Some specific tests for ready identification of specific polymers are described below.

1. **Tests for polystyrene and styrenic copolymers.** The test depends on the aromatic rings of the styrene units in the polymer chain. The polymer sample (0.1 g) is heated under reflux in concentrated nitric acid and the clear mixture is poured into water (25 ml) to yield a pale yellow precipitate which is then extracted with ether (2 × 25 ml). The ether extracts are combined and washed thoroughly with water (2 × 5 ml), then extracted with dilute sodium hydroxide solution (2 × 5 ml) and finally with water (5 ml).

   The alkaline extracts and the aqueous extract are combined and the nitro compounds present in the mixture are reduced by adding granulated zinc (1 g) and concentrated hydrochloric acid and warming gently. The solution is cooled, filtered and then diazotized with a dilute solution (5 ml) of sodium nitrite under ice-cooled condition. The solution is finally poured into excess of alkaline β-naphthol solution producing a deep red color.

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**TABLE 3.8 (CONTINUED) Heating Tests of Some Common Polymers**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Color of Flame</th>
<th>Odor of Vapor</th>
<th>Other Notable Points</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(vinyl alcohol)</td>
<td>Luminous, limited smoky</td>
<td>Unpleasant, charry smell</td>
<td>Burns in flame, self extinguishing slowly on removal; black residue</td>
</tr>
<tr>
<td>Poly(vinyl butyral)</td>
<td>Bluish (yellow edge)</td>
<td>Like rancid butter</td>
<td>Melts, forms drops</td>
</tr>
<tr>
<td>Poly(vinyl acetal)</td>
<td>Purple edge</td>
<td>Acetic acid</td>
<td>Does not drip like poly (vinyl butyral)</td>
</tr>
<tr>
<td>Poly(vinyl formal)</td>
<td>Yellow–white</td>
<td>Slightly sweet</td>
<td>Does not drip like poly(vinyl butyral)</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>Luminous (blue center)</td>
<td>Like paraffin wax</td>
<td>Melts, forms drops; droplets continue burning</td>
</tr>
<tr>
<td>Poly(α-olefins)(PP, EPR, etc.)</td>
<td>As above</td>
<td>As above</td>
<td>As above</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>Luminous, very sooty</td>
<td>Sweet (styrne)</td>
<td>Softens, easily ignited</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>Luminous, yellow (blue, edge), slightly sooty, cracking</td>
<td>Sweet, fruity</td>
<td>Softens, chars slightly</td>
</tr>
</tbody>
</table>

2. Test for poly(vinyl chloride). Specific tests for chlorine containing polymers are performed only when the presence of chlorine is confirmed by preliminary test. The simplest method of chlorine determination is the Beilstein test, described previously. Plasticizers are removed from the test material by ether extraction and the Beilstein test for chlorine is repeated to make certain that chlorine is still present. The material is then dissolved in tetrahydrofuran, filtered and the polymeric product reprecipitated by adding methanol.

On addition of a few drops of a ∼10% methanolic solution of sodium hydroxide to 2–5 ml of ∼5% solution of the plasticizer free material, the mixture changes with time from colorless to light yellow–brown, dark brown, and finally to black.

In another test, poly(vinyl chloride) and vinyl chloride polymers readily form brown coloration and eventually dark brown precipitates when their pyridine solutions are boiled and treated with a few drops of methanolic sodium hydroxide (5%).

3. Test for poly(vinylidene chloride). Poly(vinylidene chloride), when immersed in morpholine, develops a brown color both in the liquid and the partially swollen polymer. The change takes place faster if the mixture is warmed in a water bath.

4. Test for poly(vinyl alcohol) and poly(vinyl acetate). When a small volume of iodine solution (0.2 g iodine and 1.0 g KI dissolved in 20 ml of a 1:1 alcohol–water mixture and diluted to 100 ml using 2N hydrochloric acid solution) is added to an equal volume of 0.25% neutral or acidic solution of poly(vinyl alcohol), a blue color develops almost immediately or on addition of a pinch of borax into the solution. Poly(vinyl acetate), however, turns deep brown on contact with the dilute iodine solution.

5. Test for polyacrylonitrile and acrylonitrile copolymers. When a strip of cupric acetate paper that is freshly moistened with a dilute solution of benzidine in dilute acetic acid is held in the pyrolytic vapors of polyacrylonitrile or its copolymers, a bright blue color develops readily. In another test, if the condensed pyrolyzate of polyacrylonitrile or its copolymers is made alkaline, boiled with a trace of ferrous sulfate, and then acidified, Prussian blue precipitate is readily produced.

6. Test for phenolic resins. The test material (dry) is heated in an ignition tube over a small flame. The mouth of the tube is covered with a filter paper, prepared by soaking it in an ethereal solution of 2,6-dibromoquione-4-chloro-imide and then drying it in air. After the material has been pyrolyzed for about a minute, the paper is removed and moistened with 1–2 drops of dilute ammonia solution. A blue color indicates phenols (care must be taken with plastics that contain

<p>| Table 3.9 Classification of Most Common Polymers According to Elements Present |
|-----------------------------------------------|---------------------------------|-----------------------------------------------|</p>
<table>
<thead>
<tr>
<th>Group</th>
<th>Element Found</th>
<th>Rubbers*</th>
<th>Plastics/Fibers</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N</td>
<td>Nitrile (NBR), polyurethane (ester/ether urethanes)</td>
<td>Cellulose nitrate, silk, polyamides, polymides, polyurethanes, polyacrylonitrile, SAN and ABS resins, urea-formaldehyde resins, melamine-formaldehyde resins, etc.</td>
</tr>
<tr>
<td>2</td>
<td>S</td>
<td>S-vulcanized diene rubbers (NR, IR, SBR, BR, CR, IIR, EPDM, NBR), polysulfide rubbers and chlorosulfonated polyethylenes</td>
<td>Wool, polysulfones, ebonite, etc.</td>
</tr>
<tr>
<td>3</td>
<td>Cl</td>
<td>Polychloroprene, chlorosulfonated polyethylenes, etc.</td>
<td>Poly(vinyl chloride), poly(vinylidene chloride) and related copolymers, polychlorotrifluoroethylene, chlorinated or hydrochlorinated rubber, etc.</td>
</tr>
<tr>
<td>4</td>
<td>Absence of N, S, Cl, etc.</td>
<td>Peroxide cross-linked or unvulcanized hydrocarbon rubbers (NR, IR, SBR, BR, IIR, EPDM, EPR, etc.)</td>
<td>Petroleum resins, coumaroneindene resins, cellulose and cellulosics other than cellulose nitrate, polyesters, polyethers or acetals, polyolefins, polystyrene, poly(methyl methacrylate), poly(vinyl acetate/alcohol), etc.</td>
</tr>
</tbody>
</table>

* See Appendix A3 for abbreviations.
<table>
<thead>
<tr>
<th>Resin</th>
<th>Soluble In</th>
<th>Insoluble In</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Polyolefins</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyethylene</td>
<td>Dichloroethylene, xylene, tetralin, decalin (boiling)</td>
<td>Alcohols, esters, halogenated hydrocarbons</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>Chloroform, trichloroethylene, xylene, tetralin, decalin (boiling)</td>
<td>Alcohols, esters</td>
</tr>
<tr>
<td>Polyisobutylene</td>
<td>Ethers, petroleum ether</td>
<td>Alcohols, esters</td>
</tr>
<tr>
<td>Poly(vinyl chloride)</td>
<td>Dimethyl formamide, tetrahydrofuran, cyclohexanone</td>
<td>Alcohols, hydrocarbons, butyl acetate</td>
</tr>
<tr>
<td>Poly(vinylidene chloride)</td>
<td>Butyl acetate, dioxane, ketones, tetrahydrofuran</td>
<td>Alcohols, hydrocarbons</td>
</tr>
<tr>
<td>Polytetrafluoroethylene</td>
<td>Insoluble</td>
<td>All solvents</td>
</tr>
<tr>
<td>Polychlorotrifluoroethylene</td>
<td>o-Chlorobenzotrifluoride (above 120°C)</td>
<td>All solvents</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>Benzene, methylene chloride, ethyl acetate</td>
<td>Alcohols, water</td>
</tr>
<tr>
<td>ABS</td>
<td>Chlorinated hydrocarbons, eg., p-dichlorobenzene</td>
<td>Aliphatic hydrocarbons, alcohols, esters, ketones</td>
</tr>
<tr>
<td>Polybutadiene</td>
<td>Benzene</td>
<td>Alcohols, esters, ketones</td>
</tr>
<tr>
<td>Polyisoprene</td>
<td>Benzene</td>
<td>Alcohols, esters, ketones</td>
</tr>
<tr>
<td><strong>Acrylics</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyacrylonitrile</td>
<td>Dimethylformamide and nitrophenol</td>
<td>Alcohols, esters, ketones, hydrocarbons</td>
</tr>
<tr>
<td>Polyacrylamide</td>
<td>Water</td>
<td>Alcohols, esters, ketones, hydrocarbons</td>
</tr>
<tr>
<td>Esters of polyacrylic acid</td>
<td>Aromatic hydrocarbons, esters, chlorinated hydrocarbons, ketones, tetrahydrofuran</td>
<td>Aliphatic hydrocarbons</td>
</tr>
<tr>
<td>Esters of polymethacrylic acid</td>
<td>Aromatic hydrocarbons, chlorinated hydrocarbons, esters, ketones, dioxane</td>
<td>Aliphatic hydrocarbons, alcohols, ethers</td>
</tr>
<tr>
<td>Poly(vinyl acetal)</td>
<td>Aromatic hydrocarbons, chlorinated hydrocarbons, ketones, methanol</td>
<td>Aliphatic hydrocarbons</td>
</tr>
<tr>
<td>Poly(vinyl alcohol)</td>
<td>Formamide, water</td>
<td>Aliphatic and aromatic hydrocarbons, alcohols, ethers, esters, ketones</td>
</tr>
<tr>
<td>Poly(vinyl acetals)</td>
<td>Esters, ketones, tetrahydrofuran, (butyrals in 9:1 chloroform-methanol mixture)</td>
<td>Aliphatic hydrocarbons, methanol</td>
</tr>
<tr>
<td>Poly(vinyl ethers)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methyl ether</td>
<td>Water, alcohol, benzene, chlorinated hydrocarbons, ethers, esters</td>
<td>Petroleum ether</td>
</tr>
<tr>
<td>Ethyl ether</td>
<td>Petroleum ether, benzene, chlorinated hydrocarbons, alcohols, ethers, esters, ketones</td>
<td>Water</td>
</tr>
<tr>
<td>Polyesters</td>
<td>Benzyl alcohol, nitrated hydrocarbons, phenols</td>
<td>Alcohols, esters, hydrocarbons</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>Chlorinated hydrocarbons, cyclohexanone, dimethyl formamide, cresol</td>
<td>(Only swelling in usual solvents)</td>
</tr>
<tr>
<td>Nylon</td>
<td>Formic acid, phenols, trifluoroethanol</td>
<td>Alcohols, esters, hydrocarbons</td>
</tr>
<tr>
<td>Molded phenolic resins</td>
<td></td>
<td>All common solvents</td>
</tr>
<tr>
<td>Molded amino resins</td>
<td></td>
<td>All common solvents</td>
</tr>
<tr>
<td>(urea, melamine)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(Continued)
substances yielding phenols on pyrolysis, e.g., phenyl and cresyl phosphate, cross-linked epoxide resins, etc.).

7. **Test for formaldehyde condensate resins.** Formaldehyde enters into the composition of several resins and polymers. Common examples are phenol-, urea-, and melamine-formaldehyde resins, polyoxymethylene and poly(vinyl formal). Formaldehyde is evolved when these are thermally treated or boiled with water in the presence of an acid (H₂SO₄).

The aqueous extracts or acid distillates are treated with chromotropic acid (1,8-dihydroxynaphthalene-3, 6-disulfonic acid). A few drops of 5% aqueous chromotropic acid is added to the aqueous test solution and then an excess of concentrated sulfuric acid is added, and the mixture preferably warmed to nearly 100°C for a few minutes. In the presence of formaldehyde, the solution turns violet/dark violet.

Phenol, urea, and melamine are also obtained as intermediates on acid hydrolysis of the corresponding formaldehyde condensate resins and appropriate tests for phenol, urea, and melamine may be employed for identification purposes.

**a. Phenol.** On addition to the extract (10 ml), approximately 0.5N potassium hydroxide (8–10 ml) and 2 ml of diazotized p-nitroaniline (5% sodium nitrite solution added to an ice-cold solution of 2–5 mg of p-nitroaniline dissolved in 500 ml of approximately 3% hydrochloric acid, until the

<table>
<thead>
<tr>
<th>TABLE 3.10 (CONTINUED) Solubility Behavior of Some Common Plastics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin</td>
</tr>
<tr>
<td>Polyurethanes</td>
</tr>
<tr>
<td>Noncross-linked</td>
</tr>
<tr>
<td>Cross-linked</td>
</tr>
<tr>
<td>Polyoxymethylene</td>
</tr>
<tr>
<td>Poly(ethylene oxide)</td>
</tr>
<tr>
<td>Epoxy resins</td>
</tr>
<tr>
<td>Uncured</td>
</tr>
<tr>
<td>Cured</td>
</tr>
<tr>
<td>Cellulose, regenerated</td>
</tr>
<tr>
<td>Cellulose ethers</td>
</tr>
<tr>
<td>Methyl</td>
</tr>
<tr>
<td>Ethyl</td>
</tr>
<tr>
<td>Cellulose esters (acetate, propionate)</td>
</tr>
<tr>
<td>Cellulose nitrate</td>
</tr>
<tr>
<td>Natural rubber</td>
</tr>
<tr>
<td>Chlorinated rubber</td>
</tr>
<tr>
<td>Styrene–butadiene rubber</td>
</tr>
</tbody>
</table>

solution becomes just colorless), a red or violet color develops indicating phenol. No differentiation between phenol and its homologs is possible by this test.

b. Urea and melamine. The aqueous extract is divided into two parts. (solutions 1 and 2). Solution 1 is made alkaline with dilute sodium hydroxide, and 1 ml of sodium hypochlorite solution is added. Solution 2 is treated with freshly prepared furfural reagent (5 drops of pure, freshly distilled furfural, 2 ml of acetone, 1 ml of concentrated hydrochloric acid, and 2 ml of water).

For urea, solution 1 remains colorless and solution 2 becomes orange to red after 3–5 h. For melamine, solution 1 slowly becomes orange and solution 2 remains colorless.

Detection of urea with urease also provides a useful differentiation between urea and melamine resins. For this test, the powdered sample (0.25 g) is placed in a 100 ml Erlenmeyer flask and boiled with 5% sulphuric acid until the smell of formaldehyde has disappeared. The mixture is neutralized with sodium hydroxide (phenolphthalein as indicator). Then 1 drop of 1 N sulphuric acid and 10 ml of 10% urease solution is added, a strip of red litmus paper is placed in the vapors and the flask is stoppered. The appearance of a blue color in the litmus paper after a short time indicates urea and thus the presence of urea resin.

8. Test for cellulose esters. Cellulose esters respond to the Molisch test for carbohydrates. The sample is dissolved in acetone and treated with 2–3 drops of 2% ethanolic solution of α-naphthol; a volume of 2–2.5 ml of concentrated H₂SO₄ is so added as to form a lower layer. A red to red-brown ring at the interface of the liquids indicates cellulose (glucose). A green ring at the interface indicates nitrocellulose and differentiates it from other cellulose esters.

A more sensitive test for nitrocellulose is provided by an intense blue color reaction when a drop of a solution of diphenylamine in concentrated H₂SO₄ (5% w/v) is added to the sample in the absence of other oxidizing agents.

9. Test for polyamides. When a strip of filter paper soaked in a fresh saturated solution of o-nitrobenzaldehyde in dilute sodium hydroxide is held over the pyrolytic vapors of polyamides containing adipic acid, a mauve-black color is readily developed. Pyrolytic vapors of polyamides from dicarboxylic acids other than adipic acid produce a grey color when tested similarly.

10. Tests for natural rubber and synthetic rubbers. Rubbers may be identified by testing the pyrolytic vapors from test samples. A strip of filter paper soaked in an ethereal solution containing p-dimethylaminobenzaldehyde (3%) and hydroquinone (0.05%) and then moistened with a 30% solution of trichloroacetic acid in isopropanol produces different color reactions in the presence of pyrolytic vapors of different rubbers.

Vapors from natural rubber (NR) produce a deep blue or blue–violet color, and those from styrene-butadiene rubber (SBR) pyrolysis turn the paper green or blue with a distinct green tinge. Polyisobutyl and butyl rubber resemble NR, and silicone rubbers resemble SBR, in this color reaction. Pyrolytic vapors from nitrile rubbers, on the other hand, give a brown or brown–yellow color and those from polychloroprenes (neoprene) turn the test paper grey with a yellow tinge.

In another test, pyrolytic vapors from polyisobutyl and butyl rubbers produce a bright yellow color on filter paper freshly soaked in a solution obtained by dissolving yellow mercuric oxide (5 g) in concentrated sulfuric acid (15 ml) and water (85 ml) on boiling. Other rubbers may either produce little change or give an uncharacteristic brown color.

Chromic acid oxidation provides a simple test for polychloroprenes. About 0.1 g of sample is gently heated in a test tube in the presence of chromic acid solution (5 ml) prepared by dissolving chromium trioxide (2 g) in water (5 ml) and adding concentrated sulfuric acid (1.5 ml). 1,4-Polychloroprene (the synthetic equivalent of natural rubber) yield acetic acid, which can be readily identified by its odor.

If the above test is positive, the sample may be further subjected to a modified Weber color test for polychloroprenes. For this test, an acetone-extracted polymer (0.05 g) is dissolved or suspended in carbon tetrachloride, treated with a little solution of bromine in carbon tetrachloride and heated in a water bath to remove excess bromine. The residue is then warmed with a little phenol. In the presence of polychloroprenes,
the solid or the solution turns violet or purple and gives a purple solution with chloroform. The test is also positive for natural rubber and butyl rubber.

### 3.8 Plastics Analysis by Instrumental Methods

Plastics analysis is used for many purposes, such as quality control, property prediction, determination of causes of failure, and reverse engineering or deformulation. However, plastics analysis usually poses a difficult challenge to the analyst. This is because plastics may be made of more than one polymer as blends or copolymers and, moreover, may contain a host of additives (to enhance or impart specific properties), such as inorganic fillers, plasticizers, antioxidants, fire retardants, antistatic agents, cross-linkers, and so on. In fact, a plastic compound may contain more than 10 different ingredients, and some at very low levels, making it unlikely that more than 90%–95% of the plastics formulation can be determined by analysis alone. For a plastics analyst to succeed in this scenario, he should have a good working knowledge of plastics technology.

A wide variety of instrumental techniques can be used for plastics analysis. These can be categorized as spectroscopic techniques, chromatographic techniques, and thermal techniques. The spectroscopic techniques include infrared (IR) spectroscopy, ultraviolet (UV) light spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, atomic absorption spectroscopy, x-ray fluorescence spectroscopy, Raman spectroscopy, and energy dispersive analysis. The chromatographic techniques include gas chromatography–mass spectrometry (GC–MS), liquid chromatography–mass spectrometry (LC–MS), gel permeation chromatography (GPC), and thin-layer chromatography (TLC). The thermal techniques include differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), and thermogravimetric analysis (TGA). In the present section, however, only two spectroscopic techniques, namely, IR spectroscopy and NMR spectroscopy, which are simple, rapid, convenient, and most widely used for characterization of polymers, will be presented, in fair detail, highlighting their theoretical basis, instrumental aspects, methods of operation, and various applications, with specific examples, for both qualitative and quantitative analyses of different types of polymers.

#### 3.8.1 IR Spectroscopy

The basis of IR spectroscopy [34] rests on the interaction of electromagnetic radiation with mass in the IR region, which ranges from 0.7 to 1000 μm in wavelength, that is, 14,000 to 10 cm⁻¹ in wavenumber. [The wavenumber (cm⁻¹), represented by the symbol “nu bar” (ν), is the number of waves per centimeter and is equal to 10⁴/λ, where λ is the wavelength in micrometers (μm) with 1 μm = 10⁻⁶ cm. Note, however, that the wavelength unit is also cited often simply as micron (μ). On the other hand, ν is related to frequency, ν (s⁻¹), by ν = cν, where c is the velocity of light in cm/s.] According to quantum mechanics, atoms and molecules can hold only certain definite quantities of energy, or exist in specific states. If E₁ and E₂ are discrete values of energy corresponding to two states, radiation of wavenumber ν is absorbed only when Equation 3.132 holds, where h is Planck’s constant:

\[ \nu = (E_2 - E_1)/hc \]  

(3.132)

The absorbed energy of the radiation changes the state of the atom or molecule from an initial state (E₁) to a final state (E₂). This is related to an absorption band, which may be defined as a range of wavelengths or frequencies in the electromagnetic spectrum that are characteristic of a particular transition from an initial to a final state in a substance.

The energy of IR radiation is small to cause transitions between electron energy levels. It can only bring about changes in vibrational and rotational states of a molecule, which are closely related to the molecular structure.
Bond vibrations are the physical basis of IR spectroscopy. Two atoms joined by a covalent bond may move back and forth along the bond axis, producing a bond stretch, as shown in Figure 3.91, where arrows indicate the directions of atom movement and relative motions of the atoms.

Though polymer molecules contain a large number of atoms, their IR spectra are relatively simple. The reason for this lies in the fact that each linear or branched polymer molecule contains end groups joined by a large sequence(s) of repeat units. A regular repetition of a series of identical units in the chain would mean that the actual number of spectroscopically active vibrational modes is relatively small. This concept of group frequencies is very useful for practical interpretation of IR spectra. For a large molecular weight polymer, moreover, the concentration of the end groups is relatively small, and so their absorption bands also are weak. The main contribution to the absorption spectrum then comes usually from vibrations of atoms or groups in the repeating units. This simplifies greatly the analysis of polymers by IR spectroscopy.

For simple qualitative work, a double-beam spectrometer, operating between 2.5 and 15 μm, is adequate, since the region between the visible and 2.5 μm is of little use for qualitative identification work, while very few characteristic bands are observed beyond 15 μm.

3.8.1.1 Methods of Measurement

IR spectra can be obtained by two methods—the transmission (or absorption) method and the reflection method. In the first method, the fraction of the incident light that is transmitted (or absorbed) is measured, yielding an absorption spectrum, while in the second method, known as attenuated total reflection (ATR), a reflection spectrum is obtained, which is superficially very similar to an absorption spectrum. In the ATR method [35], the incident radiation beam is passed through a small prism of a material of high refractive index (e.g., silver chloride or thallium bromoiodide) in such a way that the beam suffers total internal reflection at one face of the prism. When a sample whose spectrum is to be recorded is pressed into contact with this prism surface (at which the internal reflection occurs), the sample attenuates the reflection from this surface in such a manner that a spectrum is obtained. This ATR spectrum shows a remarkable similarity to a transmission spectrum, provided there is good contact between the prism surface and the sample. Since a beam penetrates only a few microns into the sample in the ATR method, the thickness of the sample beyond the depth of penetration is of no significance and the spectral absorbance is independent of the sample thickness. It is thus found that with samples over about 0.001 in (0.02 mm) thick, the ATR spectrum is independent of the sample thickness and laborious sample
preparation procedures can be avoided. A particularly important application of the ATR method is thus in the examination of surface coatings and laminates.

More common among the two IR methods described above is the transmission method in which the numerical values of percentage transmission, which depend on the sample thickness, are recorded. There are several methods of presenting these spectral data. A common method is to plot percentage transmission or fractional transmission (i.e., percentage transmission divided by 100) on the vertical axis (increasing upward) and to plot wavelength (µm or, simply, µ) or wavenumber (cm⁻¹) on the horizontal axis, increasing to the right for wavelength and decreasing to the right for wavenumber. Sometimes, the vertical axis is plotted in reverse with zero transmission (assumed, incorrectly, as 100% absorption) at the top of the ordinate, thus producing an absorption spectrum as a mirror image of the transmission spectrum. The effect is simply to reverse the direction of the vertical scale, but the presentation is not affected. Precalibrated charts are also often used on which the vertical axis is marked “Absorbance,” defined as

\[
\text{Absorbance} = \log_{10} \frac{100}{\text{Percentage transmission}}
\]  

(3.133)

The absorbance scale is nonlinear but since the horizontal scale is not affected, qualitative identification of the spectrum is easily done (see Figures 3.91 and 3.92).

### 3.8.1.2 Instruments

The construction principles of conventional IR spectrophotometers (based on dispersive technique) do not differ a great deal from one another. They consist of source of radiation, monochromator, and radiation detector with recording equipment. Common sources of radiation are Globar (i.e., a rod of silicon carbide fired to 1000–1200°C) and the Nernst lamp (the filament of which is composed of rare earth metal oxides) heated to about 2000°C. The emitted energy of both sources is maximum in the near-IR region (5000–10,000 cm⁻¹) and then decreases rapidly. The beam emanating from the source is split into two paths, that is, the sample beam and the reference beam. The sample beam passes through the sample to be analyzed, while the reference beam passes through the reference cell containing solvent that has been used for making the sample solution. The monochromator disperses both the sample and reference beams according to the wavelength for which prisms and diffraction gratings are used. The intensity of the beam that is passed through the sample and that of the reference beam are compared in the photometric part of the instrument. The recording assembly presents the ratio of the two intensities or the logarithm of the reciprocal of this ratio (i.e., absorbance) as a function of wavelength or wavenumber. Thermocouples, bolometers, or pneumatic Golay cells serve as radiation detectors.

### 3.8.1.3 Sample Preparation

Sample preparation is the first important step in IR analysis of polymers. Samples for IR analysis by transmission may be prepared in the form of solution, as films and, if insoluble, in pellet or disk form with alkali halide (e.g., potassium bromide), or in nujol mulls. The use of solutions is limited by the large number of absorption bands of most solvents and by the necessity of using at least two solvents if the whole range of spectrum is to be recorded.

**Pelletization** with potassium bromide powder is advantageous for insoluble samples. (The concentration of the sample in KBr should be in the range of 0.2% to 1%.) Instead of potassium bromide, other suitable materials such as thallium bromide, silver chloride, or polyethylene can be used as the basis of sample pellets. Mulls in nujol placed between AgCl, NaCl, KBr, or CsI plates or KBr pellets are also suitable for insoluble samples. (Nujol is a heavy paraffin oil with essentially alkane formula CₙH₂₄ₙ₊₂, where n is very large.) The halides are ionic and usually do not have any absorption peaks in the range normally covered in the IR spectrum. However, the presence of absorption bands attributed to CH₂ in nujols makes the analysis of vibrations of methylene groups impossible. Polymer samples can also be prepared as very thin platelets by cutting with a microtome, or in the form of fibers if special microscopic equipment is available.
For the examination of polyethylene and \( \alpha \)-olefin resins, such as polypropylene, and generally for thermoplastic resins that do not dissolve rapidly, hot pressing can be a most convenient and quick method of preparing films. The polymer is pressed between polished stainless steel plates (using a temperature at which plastic flow occurs readily) in a small hydraulic press (which generates a ram pressure of about 2 kN/cm\(^2\)) and cut to the same size as platens. To assist in stripping the pressed film, the plates are coated with polytetrafluoroethylene (PTFE). For films with thicknesses greater than about 0.05 mm, feeler gauges may be used as spacers, but for thinner films, the sample thickness is adjusted by altering the amount of material used. (Feeler gauges are small lengths of steel leaves or blades of different thicknesses used to check the parallelism and measure the clearance between two parts, typically in thousandths of an inch or hundredths of a millimeter.)

[Note: If thin films are used, thicknesses differing by an order of magnitude may be required for different polymers or special regions. Thus, for a saturated hydrocarbon polymer, such as polyethylene,
0.3 mm may be satisfactory, whereas for materials containing oxygenated groups, e.g., poly(methyl methacrylate), a reduction to 0.03 mm (which represents the lower limit obtainable by hot pressing) or less is necessary.

Casting films from solvents is often preferred for latices and soluble resins, as it requires no special apparatus and very thin samples are easily prepared. Moreover, if the resin can be taken into solution, fillers can be removed by filtering or centrifuging before casting the film. Films may be cast on a glass plate and subsequently stripped off, or cast directly on a sodium chloride or potassium bromide plate. Aqueous latices may be cast on silver chloride or thallium bromoiodide plates. Solvent may be removed from the film by the use of an IR lamp and vacuum oven. Very volatile solvents (e.g., ether, acetone, methylene chloride) should be avoided as they evaporate very rapidly, causing moisture condensation on the sample surface. If nothing is known of the nature of a resin, the following solvents may be tried in the order stated [35]:

1. Ethylene dichloride or 1,2-dichloroethane (dissolves a wide range of thermoplastic resins, including a majority of vinyls and acrylics)
2. Toluene (particularly useful for polyethylene and α-olefin polymers and copolymers)
3. Methyl ethyl ketone (particularly suitable for butadiene copolymers, but more difficult to remove than the aforesaid solvents)
4. Water (dissolves a number of resins rich in –OH, –CO₂H, or amine groups)
5. Formic acid (very suitable for polyamides and linear polyurethanes)
6. Dimethyl formamide (suitable for polyacrylonitrile, polyvinyl fluoride, polyvinylidene chloride, and some other resins)

For rubbers, and especially for carbon black-filled compositions, a useful method [36] is a prior extraction with acetone-chloroform mixture followed by refluxing with p-cymene-xylene mixture to dissolve the polymer.

Though the alkali halide (e.g., KBr) pellet or disk method is probably the most widely used procedure for preparing samples from simple (non-polymeric) solids, the majority of resins are very difficult to disperse in alkali halides and the spectra obtained by this method are inferior to those measured on solid films. Hence, in polymer work, the halide disk method is applied only to those insoluble resins and rubbers that do not respond to the various methods of film preparation. In some cases, it is advantageous to pre-grind the polymer before adding the halide powder. It is worth noting, moreover, that some polymers in powder form, especially PTFE and some linear polythenes, will sinter into disks without the addition of alkali halide powder in the usual disk-making procedure.

A modification of the disk method, which is often successful with rubbers, depends on cooling the rubber below its brittle point (in liquid nitrogen) and grinding it, while in this condition, with KBr, before pelletization. The disk may then be dried by heating in an oven at 140°C for a few minutes.

**3.8.1.4 Fourier Transform IR Spectroscopy**

In the dispersive spectroscopy technique, described above, a monochromatic light beam is shone at the sample, the amount of light absorbed is measured, and the process is repeated for each different wavelength or frequency. The spectrometer is set to start reading at one end and the frequency is swept smoothly across the whole span of the spectrum. The method is thus inherently slow. The inefficiency of such a method becomes obvious when one considers taking a spectrum with only one or two sorption peaks in it—with the spectrometer set to sweep from one end to the other, most of the time in this case is spent recording nothing but background noise! A solution to this problem is to adopt a method for measuring all of the aforesaid frequencies simultaneously, rather than individually. This is done in Fourier transform infrared (FT-IR) spectroscopy.

FT-IR spectroscopy employs a very simple optical device called an interferometer. The interferometer produces a unique type of signal that has all of the IR frequencies “encoded” into it. In the normal instrumental process, IR radiation is emitted from a glowing black-body source. This beam containing the full spectrum of wavelengths passes through an aperture (which controls the amount of energy) and enters
the interferometer where the spectral encoding takes place. The resulting interferogram signal then exits the interferometer and enters the sample compartment where it is transmitted through or reflected off the surface, depending on the type of analysis (transmission spectroscopy or ATR) being accomplished. Specific frequencies of energy, which are uniquely characteristic of the sample, are absorbed and the beam then passes to a detector that is capable of measuring the special interferogram signal. The measured signal is sent to a computer, which “decodes” that information to produce a conventional-type IR spectrum of transmittance (or absorbance) versus wavelength (or wavenumber). Since the signal can be measured very quickly, usually on the order of 1 s or so, the time element per sample is reduced to a matter of a few seconds rather than several minutes of the conventional dispersive method, thus increasing the overall speed, typically by a factor of 10 to 1000. The decoding is accomplished via a well-known mathematical technique called the Fourier transformation (hence the name “Fourier transform infrared spectroscopy”).

The FT-IR spectroscopy is preferred over dispersive or filter methods of IR spectral analysis for several reasons: (i) it is a precise measurement method that requires no external calibration; (ii) it can increase speed, collecting a scan every second or so; (iii) it can increase sensitivity, for example, by adding 1-s scans together to ratio out random noise; (iv) it has greater optical throughput; and (v) it is mechanically simple with only one moving part.

### 3.8.1.5 Qualitative Analysis

With an increase in the number of atoms in a molecule, the number of normal modes increases rather rapidly and a detailed analysis of the vibrational spectrum becomes impossible. One is therefore content to assign the strongest bands and to identify some of the weaker ones as overtones or combinations. For practical purposes, however, a number of very useful generalizations can be made, as shown below.

A particularly important spectral region is 1430–910 cm\(^{-1}\). This region contains many absorptions caused by bending vibrations and also the absorptions caused by several stretching vibrations (see Table 3.11). Since bending vibrations in a molecule are in general more numerous than stretching vibrations, this region of the spectrum is particularly rich in absorption bands. It is seldom possible to assign these bands to particular modes of vibration but the complex of bands as a whole is highly typical of the given molecular structure and is ascribed to skeletal vibrations, which involve all the atoms to much the same extent. Thus, these bands are often referred to as the fingerprint bands, because a molecule or structural moiety may often be recognized merely from the appearance of this part of spectrum. This frequency region, frequently called fingerprint region, is extremely useful in establishing conclusively the identity of two samples. Similar molecules, for instance, may show very similar spectra at frequencies higher than 1430 cm\(^{-1}\), but in the fingerprint region, there will usually be discernible differences.

Many commonly occurring functional groups such as \(-\text{CH}_3\), \(>\text{C}=\text{O}\), \(-\text{NH}_2\), and so on give rise to one or more characteristic absorption bands when they are present in a molecule. These bands (group frequencies) are, to a considerable extent, independent of the structure of the molecule as a whole and can be used for analysis. For example, all compounds containing a \(-\text{CH}_3\) group possess absorption bands in the region of 3000 and 1400 cm\(^{-1}\). Similarly, all compounds with a \(>\text{C}=\text{O}\) group have a strong band in the region of 1700 cm\(^{-1}\). With a few exceptions, these characteristic group frequencies fall in the regions well above or well below the fingerprint region. Table 3.11 contains some of the more important group frequencies along with a qualitative indication of their intensities.

A close look at Table 3.11 reveals some logical trends in group frequencies. We see, for instance, that the stretching vibration frequency decreases in the series \(\text{C}–\text{H}\), \(\text{C}–\text{F}\), \(\text{C}–\text{Cl}\), \(\text{C}–\text{Br}\), and \(\text{C}–\text{I}\). This trend is attributed to increasing mass of the atom within the group in the same sequence. This also accounts for the fact that the stretching frequency of \(\text{C}–\text{S}\) is less than that of \(\text{C}–\text{O}\). On the other hand, an increase in the strength of the bond should increase the vibration frequency. This trend is observed in the series \(\text{C}–\text{X}\), \(\text{C}–\text{X}\), \(\equiv\text{X}\), where \(\text{X}\) is \(\text{C}\) or \(\text{N}\), and also in \(\text{C}–\text{O}\) and \(\text{C}–\text{O}\).

When studying the spectrum of an unknown polymer, it is desirable to have the results of the qualitative elements test available (see Section 3.7.2) on the same polymer. As there is considerable overlapping of the
wavelength ranges in which different groups absorb, much time could be saved by immediately rejecting those groups excluded by the elements test.

Polymers consisting of carbon and hydrogen, and carbon, hydrogen, and oxygen are usually not separated in the simple elements test. But, in most cases, they can be distinguished without difficulty from their characteristic bands in the IR spectrum. Also for polymers that show the presence of additional elements, such as chlorine and sulfur, in the elements test, the characteristic bands arising directly from groups containing these additional elements must be considered along with characteristic bands for hydrocarbons and various oxygen-containing groups. It should be noted that, in some cases, the presence of additional elements may shift the position of these latter groups.

Common types of groups occurring in polymers and IR absorption bands associated with them are discussed below.

### TABLE 3.11 Characteristic IR Absorption Frequencies of Organic Functional Groups

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Type of Vibration</th>
<th>Frequency Range (cm⁻¹)</th>
<th>Intensity of Peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–H (alkane)</td>
<td>Stretch</td>
<td>2850–3000</td>
<td>Strong</td>
</tr>
<tr>
<td>–C–H (alkane)</td>
<td>Bending</td>
<td>1350–1480</td>
<td>Variable</td>
</tr>
<tr>
<td>=C–H (alkene)</td>
<td>Stretch</td>
<td>3010–3100</td>
<td>Medium</td>
</tr>
<tr>
<td>=C–H (alkene)</td>
<td>Bending</td>
<td>675–1000</td>
<td>Strong</td>
</tr>
<tr>
<td>C–H (alkyne)</td>
<td>Stretch</td>
<td>3300</td>
<td>Strong, sharp</td>
</tr>
<tr>
<td>C–H (aromatic)</td>
<td>Stretch</td>
<td>3000–3100</td>
<td>Medium</td>
</tr>
<tr>
<td>=C=C (alkene)</td>
<td>Stretch</td>
<td>1620–1680</td>
<td>Variable</td>
</tr>
<tr>
<td>–C≡C– (alkyne)</td>
<td>Stretch</td>
<td>2100–2260</td>
<td>Variable</td>
</tr>
<tr>
<td>=C=C (aromatic)</td>
<td>Stretch</td>
<td>1400–1600</td>
<td>Medium-weak, multiple</td>
</tr>
<tr>
<td>C–F</td>
<td>Stretch</td>
<td>1000–1400</td>
<td>Strong</td>
</tr>
<tr>
<td>C–Cl</td>
<td>Stretch</td>
<td>600–800</td>
<td>Strong</td>
</tr>
<tr>
<td>C–Br</td>
<td>Stretch</td>
<td>500–600</td>
<td>Strong</td>
</tr>
<tr>
<td>C–I</td>
<td>Stretch</td>
<td>500</td>
<td>Strong</td>
</tr>
<tr>
<td>O–H (alcohol)</td>
<td>Stretch (H-bonded)</td>
<td>3200–3600</td>
<td>Strong, broad</td>
</tr>
<tr>
<td>O–H (alcohol)</td>
<td>Stretch (free)</td>
<td>3500–3700</td>
<td>Strong, sharp</td>
</tr>
<tr>
<td>O–H (acid)</td>
<td>Stretch</td>
<td>2500–3300</td>
<td>Strong, very broad</td>
</tr>
<tr>
<td>C–O (alcohol)</td>
<td>Stretch</td>
<td>1050–1150</td>
<td>Strong</td>
</tr>
<tr>
<td>C–O (acid)</td>
<td>Stretch</td>
<td>1210–1320</td>
<td>Strong</td>
</tr>
<tr>
<td>C–O (ester)</td>
<td>Stretch</td>
<td>1000–1300</td>
<td>Two bands or more</td>
</tr>
<tr>
<td>C=O (carbonyl)</td>
<td>Stretch</td>
<td>1670–1820</td>
<td>Strong</td>
</tr>
<tr>
<td>C=O (acid)</td>
<td>Stretch</td>
<td>1700–1725</td>
<td>Strong</td>
</tr>
<tr>
<td>C=O (anhydride)</td>
<td>Stretch</td>
<td>1800–1830 and 1740–1775</td>
<td>Two bands</td>
</tr>
<tr>
<td>C=O (ester)</td>
<td>Stretch</td>
<td>1735–1750</td>
<td>Strong</td>
</tr>
<tr>
<td>C=O (amide)</td>
<td>Stretch</td>
<td>1640–1690</td>
<td>Strong</td>
</tr>
<tr>
<td>N–H (amine)</td>
<td>Stretch</td>
<td>3300–3500</td>
<td>Medium (primary amines have two bands; secondary have one band, often very weak)</td>
</tr>
<tr>
<td>N–H (amide)</td>
<td>Bending</td>
<td>1600</td>
<td>Medium</td>
</tr>
<tr>
<td>N–H (amide)</td>
<td>Stretch</td>
<td>3100–3500</td>
<td>Two bands</td>
</tr>
<tr>
<td>N–H (amide)</td>
<td>Bending</td>
<td>1550–1640</td>
<td>Two bands</td>
</tr>
<tr>
<td>C–N (amine)</td>
<td>Stretch</td>
<td>1080–1360</td>
<td>Medium-weak</td>
</tr>
<tr>
<td>CN (nitrile)</td>
<td>Stretch</td>
<td>2210–2260</td>
<td>Medium</td>
</tr>
</tbody>
</table>

**Hydrocarbon Groups.** A hydrocarbon-type polymer is indicated if the elements test proves to be negative for all elements except carbon and hydrogen. An IR analysis can then be undertaken. All hydrocarbon compounds, composed of only carbon and hydrogen, exhibit an IR band, usually with multiplicity of absorption peaks, near 3000 cm⁻¹ and another between 1470 and 1430 cm⁻¹. Saturated, unsaturated, or aromatic hydrocarbons are distinguished by the absorption bands beyond 1000 cm⁻¹. Unsaturated hydrocarbon groups produce highly characteristic bands between 1000 and 600 cm⁻¹. These bands thus represent a simple method of determining the structure of polythene and of diene polymers.

Aromatic structures produce relatively intense absorption bands in the 830 to 600 cm⁻¹ region depending on the type of substitution on the benzene ring. Most aromatic compounds also have one or more sharp bands of weak intensity between 1700 and 1430 cm⁻¹.

Figure 3.92, for example, shows the IR absorbance spectra of three common hydrocarbon-type polymers composed of only carbon and hydrogen—polyethylene, polypropylene, and polystyrene. Both polyethylene (Figure 3.92a) and polypropylene (Figure 3.92b) are marked by characteristic absorbance peaks at around 3000, 1500, and between 700 and 750 cm⁻¹. These three peaks result from C–H and C–C absorptions (see Table 3.11) in the IR region. The IR spectrum of polystyrene (mostly atactic and amorphous), however, shows absorbance bands at 3026 and 2849 cm⁻¹, corresponding to aromatic and aliphatic C–H stretches (see Table 3.11), respectively. The peaks at 1601 and 1493 cm⁻¹ are assigned to aromatic C=C– stretching. The C–H deformation vibration band of the five adjacent hydrogens of the benzene ring appears at 758 cm⁻¹, while the ring deformation vibration is observed at 700 cm⁻¹. The peaks at 3000 and 3100 cm⁻¹ are attributed to the C–H stretching vibrations [37] of ring hydrogens (see Table 3.11).

**Halide Groups.** Once the presence of halogens in a given polymer is confirmed by preliminary elements test, further confirmation can be obtained by conducting an IR spectral run on the polymer and comparing with available spectra. Teflon or polytetrafluoroethylene (PTFE) with the general formula [–CF₂–CF₂–], for example, exhibits a strong and distinctive absorption band near 1200 cm⁻¹ owing to the >CF₂ stretching vibration. This band is a multiplet and consists of three peaks at 1240, 1215, and 1150 cm⁻¹. Other major bands are located at 641, 554, and 515 cm⁻¹, and these are assigned to the >CF bending modes.

In the IR spectrum of poly(vinyl chloride) (PVC), another common polymer with halide groups and having the general formula [–CH₂–CHCl–], the peaks found in a range of 2800–3000 cm⁻¹ (Figure 3.93a) correspond to C–H stretch. The peak at higher wavenumber is assigned to the asymmetric stretching and the lower peak is assigned to the symmetric stretching vibration of C–H. The peaks around 1400 cm⁻¹ are assigned to C–H aliphatic bending vibration, while the peak at 1250 cm⁻¹ is attributed to the bending vibration of C–H near Cl. The C–C stretching vibration of the PVC backbone chain occurs in a range of 1000–1100 cm⁻¹. Finally, the peaks in a range of 600–650 cm⁻¹ correspond to the C–Cl bond.

**Hydroxyl Groups.** A careful examination of the hydroxyl stretching region (Table 3.11) can often be valuable in the determination of structure of unknown polymeric compounds. Thus, the presence of a band in the 3700–3150 cm⁻¹ (2.7–3.2 μm) region is a very reliable indication of the presence of hydroxyl groups. [Note, however, the following two exceptions. Since water shows strong absorption in this region, the sample must be fully dry for hydroxyl observation. Halide powders being rarely dry, halide disks for sample preparation are thus best avoided for measurement of hydroxyl groups. Also, N–H groups, if present, can cause interfering absorptions in the hydroxyl region (see Table 3.11).]

For illustration, Figure 3.93b shows the IR absorption spectrum of poly(vinyl alcohol) (PVA) with the general formula [–CH₂–CH(OH)–]. While strong hydroxyl bands of free alcohol, that is, non-bonded O–H stretching bands, usually occur at 3600–3650 cm⁻¹, PVA exhibits a bonded O–H stretching band at 3200–3570 cm⁻¹, which would be attributed to the formation of intramolecular and intermolecular hydrogen bonds among PVA chains owing to high hydrophilic forces. The band at 2940 cm⁻¹ is assigned to C–H stretching, whereas the bands (doublet) at 1330–1440 cm⁻¹ are likely to arise from mixed C–H and O–H in-plane bending vibrations [38].

**Carbonyl Groups.** For compounds containing carbonyl (C=O) groups, the precise range of absorption frequency 1700–1850 cm⁻¹ is often sufficient to determine their presence. [However, the carbonyl group
may bond so strongly to an existing hydroxyl group in its vicinity that the band of the latter in the usual range 3150–3700 cm$^{-1}$ could become difficult, or impossible, to observe. For example, in carboxylic acids, it is evident only as a broadening of the C–H band at 2870 cm$^{-1}$.

For illustration, the IR spectrum of poly (vinyl acetate) (PVAc), with the general formula \[\text{–CH}–\text{CH(OOCCH$_3$)}–\], is shown in Figure 3.93c. The most prominent band in this spectrum is seen at 1736 cm$^{-1}$, which may be assigned to the carbonyl (–C=O) stretching vibration (see Table 3.11). The adjacent region from 1700 to 500 cm$^{-1}$ is complex. It is composed of stretching –C–O vibration, rocking, wagging, and twisting vibrations of –CH$_2$ groups, out-of-plane bending vibrations of the –C–H chain, and one or more stretching vibrations of the polymer chain [39].

**Nitrogen-Containing Groups.** If the elements test on an unknown polymeric compound reveals the presence of nitrogen, it then becomes imperative to conduct IR spectral runs to determine the type of
nitrogen-containing group in the polymer. Nitrogen-containing groups commonly found in synthetic polymers are amines, amides, imide, nitrile, and urethane.

In IR spectra, primary amines (–NH₂) exhibit two N–H peaks, one near 3350 and one near 3180 cm⁻¹, from asymmetric and symmetric stretching vibrations, respectively. Secondary amines (–NHR), however, give rise to one –N–H stretch peak at 3300.

All amides produce a very strong –C=O peak at 1680–1630 cm⁻¹ (usually with the frequency lowered due to hydrogen bonding, if present). In addition, primary amides (–CONH₂) and secondary amides (–CONH–) exhibit IR absorptions owing to –N–H bending at 1640–1550 cm⁻¹, with primary amides showing two spikes, as in the case of amines, and secondary amides showing only one spike. Figure 3.94a, for example, shows the IR spectrum of nylon-6, which is a secondary polyamide with the general formula –[(CH₂)₅–CONH–]–. The spectrum features, as expected, three strong absorption bands at about
3294 cm\(^{-1}\) (hydrogen bonded >N–H stretch), 1645 cm\(^{-1}\) (C=O), and 1545 cm\(^{-1}\) (CONH). The two moderate peaks at 2932 and 2862 cm\(^{-1}\) are attributed to CH\(_2\) asymmetric stretching and CH\(_2\) symmetric stretching, respectively. In addition, a number of small peaks appear in the 1400–500 cm\(^{-1}\) region. These are attributed to NH, CO, CONH, CN, methylene sequences, and crystalline forms.

It may be mentioned that the major bands of nylon IR spectra are characteristic for polyamides and make identification of the generic class a simple task. However, the features distinguishing the subgeneric classes, such as nylon-6 and nylon-6,6, are more subtle. For example, nylon-6 and nylon-6,6 have similar IR spectra and are differentiated by the presence of a weak crystalline band near 935 cm\(^{-1}\) in the nylon-6,6 spectrum.

For polyimides, the main bands in the IR spectrum are those attributed to the carbonyl (C=O) groups in the imide [\(\text{–(–CONRCO–)}\)] ring, which appear as a doublet at 1780 and 1720 cm\(^{-1}\). The band at 1780 cm\(^{-1}\) is sharp, while that at 1720 cm\(^{-1}\) is broader and stronger. The spectra of polyamides–imides show the characteristic bands of the carbonyl groups of both the amide and imide structure. One can thus see a series of four bands of relatively high intensity in the 1600–1800 cm\(^{-1}\) region, which is a clear indication that the unknown resin sample is a polyamide–imide.

The nitrile (–C≡N) group produces an absorption band at 2240–2280 cm\(^{-1}\), a region that is relatively free of other well-known absorption bands and the band can therefore be easily observed. The major characteristic of the IR spectrum of polyacrylonitrile with the general formula \([\text{–(–CH\(_2\)–CH(CN)–)}\]– is thus the nitrile band at 2240 cm\(^{-1}\).

Polyurethanes containing the urethane linkage \([\text{–NH–CO–O–)}\) exhibit the prominent band pair noted earlier for the secondary amide structure, but the pair now occurs at about 1540 and 1700 cm\(^{-1}\). These bands are easily recognized in simple urethanes and in polyether and polyester urethane rubbers. Figure 3.94b, for example, shows a typical polyurethane IR spectrum. The characteristic band at 1730 cm\(^{-1}\) in this spectrum is associated with the C=O group in polyurethane, while other bands are assigned as follows. The absorption band at 3320 cm\(^{-1}\) corresponds to >NH stretching and the sharp peaks at 2860 and 2940 cm\(^{-1}\) are associated with \(-\text{CH}_2\) stretching, while other modes of \(-\text{CH}_2\) vibrations give rise to the bands in the region 1500–1300 cm\(^{-1}\). The bands at 1540 cm\(^{-1}\) are attributed to the group of \(-\text{NH}\) vibrations.

**Silicon-Containing Groups.** Polymeric organosilicon compounds are commonly referred to as silicones, the most widely used silicone resin being polydimethylsiloxane, with the general formula \([\text{–(–Si(CH}_3\text{)}_2\text{–O–)}\]. Methyl groups attached to a silicon atom undergo the same \(\text{C–H}\) stretching and bending vibrations as a CH\(_3\) attached to a carbon atom, but the positions of the bands for a Si–CH\(_3\) group are different from those for a C–CH\(_3\) group, because of electronic effects. The absorption attributed to the umbrella mode (symmetric bend) vibration of the Si–CH\(_3\) group produces a very intense band at 1260 ± 5 cm\(^{-1}\), and when a silicon atom has two methyl groups attached to it, denoted as Si(CH\(_3\))\(_2\), there appears a strong methyl rocking mode band at 800 ± 10 cm\(^{-1}\). The pattern of bands in the spectrum of polydimethylsiloxane is very characteristic—a series of four intense bands between 1200 and 800 cm\(^{-1}\) (see Figure 3.94c). Few other materials give rise to this pattern. The band attributed to the Si–H group occurs at about 2200 cm\(^{-1}\) and is exceedingly prominent. The absorption owing to the Si–O linkage, which forms the backbone of silicone resins, occurs between 1100 and 1000 cm\(^{-1}\), producing a broad, complex, and intense band.

Sharp bands arise near 1250 and 1430 cm\(^{-1}\) owing to Si–Me (as noted above) and Si–Phenyl groups, respectively. The group most frequently encountered, however, is the Si–Me group at 1250 cm\(^{-1}\). This band is particularly easy to observe, even in the presence of other materials absorbing in this region of the spectrum. Silicones containing the Si–H group are also easily recognized in mixtures, since few other substances have significant absorption in the region where the strong Si–H band appears (2100–2220 cm\(^{-1}\)). The absorption band attributed to the OH group attached to Si is, however, similar to that of the alcoholic OH group.

**Applications.** An IR spectrum may be looked upon as a “fingerprint” of a sample in the form of absorption peaks that correspond to the frequencies of vibrations of the bonds between the atoms making up the material. Because each different material is a unique combination of atoms, no two compounds
produce exactly the same IR spectrum. Therefore, IR spectroscopy can provide a positive identification of every different kind of material, though it can be reasonably expected that unambiguous identification of hydrocarbon polymers by IR spectral comparison alone will be difficult because of the similarity of spectra of various possible isomers. However, polymers containing various groups with special elements such as O, S, N, and so on are analyzed relatively easily because they may be analyzed via functional groups.

Since the IR spectrum can be looked upon as the molecular fingerprint of a sample, IR spectral analysis can be used in many cases to identify unknown materials and check the quality or consistency of a sample. Moreover, since the size of the peaks in the spectrum is a direct indication of the amount of material present, IR spectroscopy can also be used for quantitative analysis (explained later).

Since many functional groups can be easily detected and quantified by IR spectroscopy, this technique can be conveniently used in many cases to monitor the quality and state of polymeric materials exposed to environmental and other conditions. For example, many polymers easily undergo oxidation, which is indicated by the appearance of an absorption band of the C=O group near 1720 cm\(^{-1}\). Thermal and photo-chemical (UV-induced) oxidations of polyethylene plastics and fabrics may lead to the formation of hydroxyl (of hydroperoxide/alcohol) and carbonyl (of carboxyl and anhydride) groups, which are easily identified and measured by IR spectroscopy.

Since the quality and performance of plastic products depend on the quality of polymer components used in their manufacture, proper identification and quality testing are critically important for the plastics industry. IR spectral data can be used for identification of polymer samples, qualitative analysis of polymer starting materials, or analysis of in-process samples and product quality control. Comparison of measured spectral data with spectral reference databases provides a rapid and effective identification tool for all types of polymer materials, and all sizes and forms including pellets, parts, opaque samples, fibers, powders, wire coatings, and liquids. In appropriate cases, chemical reactions, such as analysis of esterification of cellulose by carboxylic acids, can be monitored by IR spectroscopy.

The aim of qualitative analysis of polymer mixtures is to determine the presence of individual components and, in the case of copolymers, to determine the presence of individual monomer units. This can be accomplished by considering that the spectrum of a mixture is additively composed of the spectra of the individual components and that all absorption bands of the spectrum should be ascribed to individual components, no band being in surplus and none missing. This is exemplified in Figure 3.95, which presents the IR spectra of butadiene-styrene, butadiene-acrylonitrile, and butadiene-styrene-acrylonitrile copolymers. In the first and the third spectra, the characteristic absorption bands of styrene units can be seen at about 700, 760, and 1500 cm\(^{-1}\), while in the second and third spectra, the absorption band at 2250 cm\(^{-1}\) shows the presence of the acrylonitrile unit.

The most reliable evidence for the identity of two compounds can be obtained from differential spectrophotometry. In this method, the compound under investigation is inserted into the path of the sample beam and a known compound into the path of the reference beam. If the two compounds are identical, the spectrum will be free of absorption bands. However, if there is a different content of the same group in the two compounds, the spectrum obtained will contain only the bands of this group.

Polymer blends are a mixture of chemically different polymers or copolymers with no covalent bonding between them. The IR spectrum will thus be expected to contain absorption bands of all the individual polymers of the blends, the relative intensities of the peaks being dependent on the relative proportions of the constituent polymers. However, if there is a chemical interaction between the polymers, this leads to a considerable difference (shift in peak position) in the blend spectrum. As an illustration, Figure 3.96 shows the FT-IR spectra of two neat resins, polystyrene (PS) and poly(methyl methacrylate) (PMMA), while the FT-IR spectra of their blends in various proportions are shown in Figure 3.97. There are no shifts of the peaks of any group in the blend spectra, which signifies that there is no chemical interaction between the constituent polymers and they remain as a physical mixture. A careful analysis of the IR spectra of the PS/PMMA blends (Figure 3.97) shows that there is a decrease in the transmittance of carbonyl (C=O) and methoxyl (–OCH\(_3\)) stretchings (at 1732 and 1149 cm\(^{-1}\), respectively) with an increase of PS content, while
**FIGURE 3.95** IR spectra of (a) a butadiene-styrene copolymer; (b) a butadiene-acrylonitrile copolymer, and (c) a butadiene-styrene-acrylonitrile terpolymer.

**FIGURE 3.96** IR spectra of (a) polystyrene and (b) poly(methyl methacrylate).
there is an increase in transmittance of these peaks with an increase of PMMA content, clearly indicating the formation of polymer blends.

### 3.8.1.6 Quantitative Analysis

IR spectroscopy is widely used for quantitative analysis in the field of synthetic resins. The analysis is based on Lambert–Beer’s law. If an absorption band in the IR spectrum arises from a particular component in the sample, the concentration of the component is related to the absorbance (A) or percentage transmission at the band maximum by this law, written as

\[
A = \log_{10}\left(\frac{100}{\text{Percentage transmission}}\right) = kcl \tag{3.134}
\]

where \(c\) is the concentration of the absorbing component, \(l\) is the thickness of the sample, and \(k\) is a constant. The sample can be prepared by hot pressing the resin between Teflon-coated stainless steel plates into sheets of thickness ranging, typically, from 0.2 to 3 mm or solvent casting films (typically 0.03 mm thick). The value of \(k\) can be determined by measuring the IR absorbance of samples containing a known concentration of the absorbing component.

For the determination of absorbance, a base-line calibration is normally used, the base line being drawn tangentially between the minima occurring at each side of the absorption peak. Considering, for example, the absorption band of the acetate group of PVAc at 2.15 \(\mu\)m, shown in Figure 3.98, the absorbance is measured by drawing the straight line background CD above the band and calculating \(\log_{10}(EG/EF)\). Plotting this absorbance against the thickness of PVAc calibration sample, the graph obtained should be linear and pass through the zero point. From the slope of the linear plot, the constant \(k\) in Equation 3.134 can be evaluated using the measured or calculated value of the acetate content of the resin. Using this value of \(k\) and the measured absorbance of the band at 2.15 \(\mu\)m, quantitative determination of vinyl acetate in a copolymer, such as vinyl chloride/vinyl acetate copolymer, can be performed. For copolymers containing up to 20% acetate, a sample of about 10 mm thickness gives a band of suitable intensity for measurement.

An alternative (and simpler) method for determining the acetate content in vinyl chloride/vinyl acetate copolymer is based on the measurement of the absorbance ratio at 5.8 \(\mu\)m/7.0 \(\mu\)m (i.e., \(-\text{C}=\text{O}\) to \(-\text{CH}_2-\))
ratio). In this method, the sample thickness need not be measured as the acetate content can be determined simply by referring to a calibration curve of 5.8 μm/7.0 μm absorbance ratio versus acetate content.

In many cases, some free vinyl acetate (residual monomer) may be present in vinyl acetate polymers or copolymers. Since the band at 2.15 μm is attributed to the acetate group, both free and combined vinyl acetate will absorb at this wavelength. For free vinyl acetate, however, the spectrum can be measured at 1.63 μm (using a relatively thick specimen), where the band is only attributed to the vinyl double bond (–CH=CH₂), and hence the monomer content of the sample can be determined.

Copolymers of vinyl chloride with acrylates (most commonly, methyl acrylate and ethyl acrylate) produce an ester carbonyl band at 5.8 μm, but the C–O band near 8.5 μm is different in the two cases. Moreover, ethyl acrylate even at low concentrations shows a band at 9.75 μm, which is not present in the methyl acrylate system. IR spectra of the blends of PVC and poly(methyl methacrylate) are similar to those of vinyl chloride/acrylate copolymers.

The presence of aliphatic ether in vinyl chloride polymers becomes evident from the appearance of a relatively strong ether band near 9.0 μm. The spectra of vinyl chloride/vinyl isobutyl ether copolymers (containing more than 10% vinyl isobutyl ether), for example, show a prominent, though rather broad, ether band near 9.0 μm, but also a doublet band owing to –CH(CH₃)₂ at 7.3 μm. The latter is, however, not a conclusive proof for the isobutyl group.

IR spectroscopy may provide a simple means of analyzing the composition of polymer blends in many cases. With well-homogenized and unfilled blends, the IR spectroscopic measurement can be performed directly on the sample. On the other hand, if the blend is inhomogeneous and/or filled, an indirect method may be used in which the polymer blend component is separated from the filler by solvent extraction and IR spectroscopy is then applied to the extracted polymer mixture.

Considering, as an example, the analysis of polyethylene–polyisobutene (unfilled) blend composition by IR spectroscopy using the direct method, a series of standard samples are prepared by blending known amounts of polyethylene and polyisobutene by milling and then hot-pressing the blend into films of about
0.3 mm thickness, which is suitable for polyisobutene contents between 5% and 25% (w/w). The IR spectra of all standard and unknown samples are measured over 9.0–12.5 μm and 2.1–2.8 μm wavelength ranges. The absorbances at the band maxima (~10.5 and ~2.4 μm) are measured by the base-line method. With straight line backgrounds XX’ and YY’ drawn as shown in Figure 3.99, the absorbances are calculated as $\log_{10}(AC/AB)$ and $\log_{10}(DF/DE)$. Denoting the latter as $A_{10.5}$ and $A_{2.4}$, respectively, the ratio $A_{10.5}/A_{2.4}$ is plotted against wt% polyisobutene contents of the blend standards to obtain a straight line passing through the origin. This calibration curve can be used to determine the polyisobutene content in an unknown polyethylene–polyisobutene blend from the absorbance ratio $A_{10.5}/A_{2.4}$ measured with a film of the blend.

The above method uses a reference band (2.4 μm) as a substitute for film thickness. The method proves useful when the film thickness is difficult to measure (e.g., for rubbery samples). However, if the samples are sufficiently rigid for thickness measurement (such as with a micrometer gauge), the measurement of the reference band absorbance may be omitted and the $A_{10.5}$/sample thickness ratio is used in a similar type of procedure.

If films of controlled thickness can be prepared by hot-pressing with, say, 0.05 mm feeler gauges as spacers between stainless steel plates (preferably coated with Teflon) and spectra are recorded over the wavelength range 9.5–15 μm, absorbances can then be measured at 10.5 and 13.9 μm band maxima by drawing base lines XX’ and YY’, as shown in Figure 3.100 and applied to Equation 3.134, leading to the following relation:

$$\frac{\text{Absorbance at 10.5 μm}}{\text{Absorbance at 13.9 μm}} = \frac{\log_{10} AC/BC}{\log_{10} DF/EF} = K \frac{\text{wt% polyisobutene in blend}}{\text{wt% polyethylene in blend}}$$

(3.135)

The value of $K$ can be determined from this relation using the known proportions of polyisobutene and polyethylene of the standard blend. Using the determined value of $K$ and the measured absorbances on the spectrum of an unknown sample, the ratio of the wt% contents of polyisobutene and polyethylene in the blend can be determined.

### 3.8.2 NMR Spectroscopy

NMR spectroscopy [34] is now established as an important technique for characterization and testing of polymers. NMR spectra can be observed from a number of atomic nuclei, but for the organic chemist, the spectra of the $^1$H nucleus, that is, the $^1$H NMR spectra or proton resonance spectra, are of the greatest practical importance, the reason being that most polymers are organic compounds containing hydrogen and a great deal can be learned about their structure if the relative positions and chemical environment of the hydrogen atoms in the molecule can be established. This information can be derived from proton...
resonance spectra. Though, in principle, complementary information would be obtained from carbon NMR spectra, for the majority of organic compounds, the naturally abundant isotope $^{12}$C is inactive, while the $^{13}$C nucleus, which is magnetically active, has low natural abundance and gives only weak resonance signals. The NMR spectroscopy of organic compounds is thus confined mainly to proton resonance spectra. Unless otherwise mentioned, NMR spectroscopy/spectra in this book will always mean proton NMR (or $^1$H NMR) spectroscopy/spectra.

3.8.2.1 General Principles

Certain atomic nuclei like H, D, $^{13}$C, F, and so on possess an intrinsic mechanical spin. Since a charged particle spinning about its axis is equivalent to a circular electric current, which, in turn, gives rise to a magnetic field, a spinning nucleus behaves as a tiny bar magnet whose axis is coincident with the axis of the spin, and its potential energy ($U_n$) in a magnetic field of strength $H$ is

$$U_n = -H\mu \cos \theta$$

where $\mu$ is the magnetic moment of the nucleus (i.e., the strength of the nuclear dipole) and $\theta$ is the angle between the magnetic moment vector and the direction of the magnetic field. According to quantum mechanics, the angle $\theta$ is not a continuous variable but can have only certain discrete values; in other words, in an applied magnetic field, the spin angular momentum vector for a nucleus cannot point in any arbitrary direction, but can have only a discrete set of orientations. This is the result of a phenomenon, known as space quantization. The angular momentum vector can point only such that its components along the direction of the magnetic field are given by $m_I(h/2\pi)$, where the quantum number $m_I$ can have any of the values $I, I-1, \ldots, -(I-1), -I$, with $I$ representing the spin of the nucleus. Thus, for $I = 1$, the possible values of $m_I$ are 1, 0, and $-1$, and the nucleus can have three spin orientations. For proton, however, $I = 1/2$ and $m_I$ can be only $+1/2$ and $-1/2$, and so proton can have only two spin orientations. Each orientation represents a spin state and transition of a nucleus from one spin state to an adjacent one may occur by absorption or emission of an appropriate quantum of energy.

From a classical point of view, the behavior of a spinning proton (pictured as a tiny bar magnet rotating about its axis) is analogous to that of a gyroscope spinning in frictionless bearings. It is a known fact that

![FIGURE 3.100 Measurement of absorbance of the absorption bands of a polyethylene–polyisobutene blend at 10.5 and 13.9 μm by the base-line calibration method.](image-url)
when a force (torque) is applied to a spinning gyroscope, its axis does not tilt but merely precesses about the direction of the force. Similarly, a spinning proton, behaving as a magnetic gyroscope, will precess about the direction of the applied field (see Figure 3.101), keeping the angle \( \theta \) constant. The expression for the precessional frequency (\( \omega \)) of such a spinning proton has the same form as the frequency of the precessional motion of an orbiting electron (known as Larmor frequency), namely,

\[
\omega = \frac{\text{Magnetic moment}}{\text{Angular moment}} \times H \text{ radian/s}
\]

\[
= \frac{\mu H}{2\pi p_n} \text{ cycles/s}
\]

where \( p_n \) is the spin angular momentum of the nucleus given by

\[
p_n = \frac{h}{2\pi} \sqrt{I(I+1)}
\]

So long as the angle \( \theta \) between its spinning axis and the field direction is constant, the potential energy of the proton in the field, given by Equation 3.136, will also be constant and no energy will be absorbed from the field.

In order to cause a change of the angle \( \theta \), a second magnetic field is to be applied perpendicular to the main field. The secondary magnetic field must not be a stationary one, however, as otherwise its effect in one half-cycle of the precessional motion will be cancelled by the effect in the other half-cycle. To produce a net effect, the secondary field must also rotate about the direction of the main field with a frequency equal to that of the precessing proton. The secondary magnetic field can then interact with the precessing proton and energy can be exchanged; if the frequencies differ, there will be no interaction. Thus, when the frequency of the rotating secondary field and the frequency of the precessing nucleus are equal, they are said to be in resonance, since in this condition, transition from one nuclear spin state to another can readily occur, giving rise to absorption or emission of energy.

A rotating magnetic field can be produced in a simple way by sending the output current of a radio-frequency crystal oscillator through a helical coil (solenoid) of wire. In NMR spectroscopy, the sample under investigation is taken in a small glass tube placed between the pole faces of a dc electromagnet (Figure 3.102). The coil that transmits the radio-frequency field is placed with its axis perpendicular to the direction of the main field produced by the electromagnet. The coil is made in two halves to allow

FIGURE 3.101 A spinning proton, behaving as a magnetic gyroscope, precesses about the direction of the applied magnetic field \( H \), with a constant angle \( \theta \).
the insertion of the sample holder. The electric current passing through the coil produces in it a magnetic field directed along its axis, and this field reverses its direction with the same frequency as the current.

It is a general property of vectors that the resultant of two identical vectors rotating with the same frequency in opposite directions is equivalent to a vector having constant direction and periodic change to magnitude, which, in fact, represents an alternating motion. The alternating magnetic field along the axis of the coil, described above, is thus equivalent to two magnetic fields rotating with the same frequency but in opposite directions. Of these two rotating magnetic fields, the one whose direction of rotation is the same as the direction of the precessional motion of the nucleus will act as the secondary magnetic field. The other field rotating in the opposite direction can be ignored, since its average effect is zero. To obtain a condition of resonance (absorption or emission of energy), the magnetic field at the proton and the frequency of the alternating current supplied to the coil from the oscillator must be such that Equation 3.137 is satisfied. The nuclei can then absorb energy from the secondary field. Coils located within the pole gap or wound about the poles of the magnet allow a sweep to be made through the applied magnetic field to bring about this condition of resonance.

When resonance absorption of energy takes place, it can be thought of as producing nuclei in the excited state, which will then tend to return to the lower level in order to approach the Boltzmann distribution ratio. The radiation emitted in this process is picked up by the receiver coil, which is a separate radio-frequency coil consisting of a few turns of wire wound tightly around the sample tube. The receiver coil is perpendicular to both the magnetic field and the radio-frequency transmitter coil in order to minimize pickup from these fields. It is the sample that provides this coupling between the receiver and the transmitter. The signal from the receiver coil can be displayed on an oscilloscope or a recorder chart.

Experimentally, the resonance condition may be obtained in two alternative ways. We might vary either the field strength of the electromagnet or the frequency of the oscillator, keeping the other fixed. Suppose we apply a fixed magnetic field and the Larmor frequency produced by it is, say, 60 Mc/s; if the frequency of the oscillator is then varied over a range including 60 Mc/s, resonance absorption will occur exactly at that frequency. On the other hand, we can fix the oscillator frequency at 60 Mc/s and vary the applied field over a range until absorption occurs. The latter arrangement is simple and widely used in practice. Most NMR spectrometers in use today employ a fixed oscillator frequency of either 60 Mc/s, 100 Mc/s or 220 Mc/s.
3.8.2.2 Chemical Shift

A very important characteristic of the NMR technique is that it can distinguish protons in different molecular environments. If the resonance frequencies of all protons in a molecule were the same, as given by Equation 3.137, then the NMR spectrum would show only one peak for the compound, and as such would be of little use to the organic chemist. However, we must consider the fact that the field strength represented in Equation 3.137 is the field strength experienced by the protons in the sample and is not the same as the strength of the applied magnetic field. Protons whether in hydrogen atoms or molecules are surrounded by an electromagnetic charge cloud having approximately spherical symmetry. A magnetic field induces electronic circulations in the charge cloud in a plane perpendicular to the applied field and in such a direction as to produce a field opposing the applied field, as shown in Figure 3.103. The induced field is directly proportional to the applied field \( H \) and so can be represented by \( \sigma H \), where \( \sigma \) is a constant. The effective magnetic field experienced by the proton is therefore

\[
H_{\text{eff}} = (H - \sigma H) = H(1 - \sigma) \quad (3.139)
\]

We can thus say that proton is shielded from the external field by diamagnetic electron circulation and \( \sigma \) represents the shielding constant. The extent of shielding of a proton depends on the electron density around it in a molecule.

A molecule may contain protons in different chemical environments. The average electron concentrations in these environments are different and so are the shielding effects on the protons. Consider, for example, the C–H and O–H bonds. Since oxygen is more electronegative than carbon, the electron density around the CH proton (i.e., proton in C–H bonds) should be considerably higher than that around the OH proton. We should thus expect that the shielding constant of the CH proton is greater than that of the OH proton. It then follows from Equation 3.139 that, for a given applied field, the effective field at the OH proton is greater than that of the CH proton. Consequently, as the applied magnetic field is increased, the OH proton will come into resonance before the CH proton. The separation between the resonances (absorption peaks) for the same nucleus in different chemical environments (causing different degrees of shielding) is known as the chemical shift. It is easy to see that the magnitude of the chemical shift will be proportional to the strength of the applied field.

From the chemical shifts, we should be able to know how many different types of protons there are in a molecule. It has, however, no effect on the signal or peak intensity. The intensity of absorption at a given field strength will be proportional to the number of protons in a given environment in the molecule and a spectrum will thus tell us how many of each type of protons are present. These are the two important facets

![Figure 3.103](image)
of NMR spectroscopy that make it a qualitative and quantitative analytical technique. As an illustration, we consider below the NMR spectrum of ethanol obtained under low resolution (Figure 3.104a). The spectrum shows three absorption peaks of intensity (area) ratio 1:2:3. The smallest peak is assigned to the single proton in the OH group, the next peak is assigned to the two protons in the CH$_2$ group, and the largest peak is assigned to the three protons in the CH$_3$ group.

That the absorption peak for the OH proton occurs at the lowest value of the applied field accords with the fact that the OH bond is polar with the bonding electrons being, on the average, closer to the oxygen atom, and as a result, the OH proton is relatively bare and unshielded from the applied field. On the other hand, the C–H bond being almost nonpolar, the bonding electrons in the CH$_3$ group are nearly equally distributed between the carbon atom and the three protons. The CH$_3$ protons are thus well shielded and a larger applied field is required to bring them into resonance. The CH$_2$ peak occurs in between OH and CH$_3$ peaks, because the electron withdrawal by the oxygen of the OH group also has some effect on the electron distribution in the adjacent CH$_2$ group and reduces the degree of shielding for the CH$_2$ protons. It is interesting to note that dimethyl ether (CH$_3$OCH$_3$), which is an isomer of ethanol, has six equivalent protons, and accordingly, the spectrum shows a single absorption peak.

Chemical shifts are very small compared to the strength of the applied field; their magnitude being a few milligauss at a field strength of about 10,000 gauss. Moreover, since electronic shielding ($\sigma_H$) is directly proportional to the strength of the applied field, the chemical shift value also varies with the field strength. Therefore, in NMR analysis, chemical shifts are usually expressed on a relative basis, in a form independent of field strength. For a proton in a given environment, the chemical shift is defined by

$$\delta = \frac{H_s - H_r}{H_r} \times 10^6 \text{ppm} \quad (3.140)$$

where $H_s$ and $H_r$ are the applied field strengths at which resonance occurs in a given substance and a reference substance, respectively. The reference substance is dissolved in the same solution as the sample (internal reference) so that both experience the same magnetic field. The chemical shift parameter $\delta$ is dimensionless; the factor $10^6$ is included to express it as parts per million (ppm).

The substance now almost universally selected as reference for proton resonances is tetramethyl silane, Si(CH$_3$)$_4$, or TMS in short. Its chief advantages are as follows: (i) it gives a single sharp peak (since all 12 protons in it are equivalent); (ii) its resonance peak occurs at an exceptionally high field, which is on the higher side of almost all other proton resonances in organic molecules, and (iii) it is chemically inert,
magnetically isotropic, and low boiling (boiling point, 27°C), so that it can be readily recovered from most samples after use.

Resonance positions are indicated on the δ-scale or the τ-scale. On the δ-scale (Equation 3.140), δ is zero for TMS and it increases downfield. On the τ-scale, τ is given a value of 10 at the resonance peak of TMS and it decreases downfield, being related to δ by τ = 10 − δ. The δ-scale has the disadvantage that a large numerical value of δ implies a low-field resonance and hence a small shielding of the nucleus from the applied field. In this respect, the τ-scale is more convenient, a larger value of τ implying a greater shielding of the nucleus.

### 3.8.2.3 Shielding Mechanisms

As illustrated in Figure 3.103, the magnetic field generated by the induced circulation opposes the applied magnetic field (H) and is called diamagnetic shielding. For protons, three main kinds of diamagnetic shielding can be recognized, which arise from three kinds of induced electron circulation, namely, local diamagnetic shielding, neighboring diamagnetic shielding by anisotropic groups, and interatomic diamagnetic circulation in aromatic rings.

The origin of local diamagnetic shielding has been explained in Section 3.8.2.2. It should be noted that the charge distribution surrounding protons has approximately spherical symmetry irrespective of the presence of magnetic field or chemical bonding. Thus, even if a molecule, of which the proton is a part, changes its orientation with respect to the applied field direction owing to incessant rotation and vibration, mainly diamagnetic currents will flow around the proton because of the almost axial symmetry of the charge cloud with respect to the field direction. The degree of shielding of a proton is, however, dependent on the electron density around it—the higher the electron density, the higher the shielding and hence the higher the field at which the proton absorbs (as reflected in a lower δ and a higher τ).

The circulation of electrons about neighboring atoms can be effective at a proton only if the generated secondary magnetic fields are anisotropic. As shown in Figure 3.105, the diamagnetic anisotropy of the triple bond in acetylene serves to decrease the external magnetic field (i.e., increase the shielding) of the acetylenic protons. In contrast, the diamagnetic anisotropy of the carbonyl group in an aldehyde causes

![FIGURE 3.105](image-url)
deshielding, that is, decreases shielding at the aldehydic proton (see Figure 3.106), while protons attached to a single-bonded carbon actually experience slight deshielding (Figure 3.107).

The third type of diamagnetic shielding is associated with aromatic and pseudo-aromatic rings, having cyclically delocalized \( \pi \) electrons, which are readily induced into circulation in the plane of the ring by an applied magnetic field. This generates a secondary magnetic field that causes pronounced shielding at the center of the ring but deshielding outside in the plane of the ring where the protons lie (Figure 3.108). This accounts for the relatively low value of \( \tau \) for aromatic protons, as shown in Table 3.12.

Substitution of benzene shifts the \( \tau \) value for the absorption of the aromatic protons (Table 3.12). Electron-withdrawing groups (e.g., \(-\mathrm{NO}_2\), \(-\mathrm{CO}_2\mathrm{H}\)) lower the \( \tau \) value, while electron-donating groups (\(-\mathrm{OH}\), \(-\mathrm{NH}_2\)) raise the \( \tau \) value relative to benzene (2.73\( \tau \)), because of the local diamagnetic shielding effect.

Because of the \( \pi \)-electron circulation (Figure 3.108), aromatic rings provide a strong source of long-range shielding and deshielding. Long-range shielding applies to shielding that operates through space rather than directly through chemical bonds; the latter is short-range shielding. Thus, of the three main kinds of diamagnetic shielding, the first is short-range and the last two are long-range.

**FIGURE 3.106** Deshielding of an aldehydic proton owing to diamagnetic anisotropic effects.

**FIGURE 3.107** Diamagnetic shielding by the carbon–carbon single bond.
Secondary field generated by electron circulation

Induced circulation of π electrons

Applied field $H$

**FIGURE 3.108** The magnetic field generated by the induced circulation of electrons in benzene.

**TABLE 3.12** Typical Chemical Shifts for Various Types of Protons

<table>
<thead>
<tr>
<th>Type of Proton</th>
<th>$\Delta$</th>
<th>$\tau$</th>
<th>Type of Proton</th>
<th>$\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Protons on saturated carbons</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RCH$_3$</td>
<td>0.9</td>
<td>9.1</td>
<td>RCH$_3$</td>
<td>1.5</td>
</tr>
<tr>
<td>RCH$_2$R</td>
<td>1.3</td>
<td>8.7</td>
<td>$\text{C}_6\text{H}_5\text{NH}_2$</td>
<td>3.4</td>
</tr>
<tr>
<td>R$_3$CH</td>
<td>1.5</td>
<td>8.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_3$CN</td>
<td>1.97</td>
<td>8.03</td>
<td>RCHO</td>
<td>9.7</td>
</tr>
<tr>
<td>CH$_3$COCH$_3$</td>
<td>2.09</td>
<td>7.91</td>
<td>RCOOH</td>
<td>11.0–12.0</td>
</tr>
<tr>
<td>CH$_3$CHO</td>
<td>2.15</td>
<td>7.85</td>
<td>ROH</td>
<td>High variable</td>
</tr>
<tr>
<td>C$_6$H$_5$CH$_3$</td>
<td>2.54</td>
<td>7.66</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_3$OR</td>
<td>3.4</td>
<td>6.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RCH$_2$OR</td>
<td>3.7</td>
<td>6.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RCH$_3$Cl</td>
<td>3.7</td>
<td>6.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Protons on unsaturated carbons</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RC≡CH</td>
<td>2.4</td>
<td>7.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R$_2$C=CH$_2$</td>
<td>4.5–5.0</td>
<td>5.0–5.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R$_2$C=CHR</td>
<td>5.0–5.5</td>
<td>4.5–5.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Protons on aromatic rings</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_6$H$_6$</td>
<td>7.27</td>
<td>2.73</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_4$H$_5$NO$_2$$_a$</td>
<td>8.22</td>
<td>1.78</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.48</td>
<td>2.52</td>
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<tr>
<td></td>
<td>7.60</td>
<td>2.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_6$H$_5$NH$_2$$_a$</td>
<td>6.52</td>
<td>3.48</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.07</td>
<td>2.93</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.65</td>
<td>3.35</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* The three values given refer to ortho-, meta-, and para-protons, respectively.
3.8.2.4 Spin–Spin Coupling

The NMR spectrum of a substance is usually much more complex than would be expected solely on the basis of chemical shift effect. Thus, the resonance absorptions are often split into a number of components and may appear as doublets, triplets, quartets, or more complex patterns. The phenomenon, observed only with spectrometers of high resolution, is attributed to the effect on a nucleus (responsible for absorption peak) of other magnetic nuclei in the same molecule. This effect is referred to as spin–spin coupling. It may be heteronuclear, for example, between protons and adjacent fluorine nuclei, but the most important effect is homonuclear coupling between protons that are very close together in the same molecule but are in different chemical environments.

As an illustration, we consider the high-resolution spectrum of a common sample of ethanol represented in Figure 3.104b. By comparing it with Figure 3.104a, we see that the methyl (CH₃) absorption is now split into a triplet with areas of the three components in the approximate ratios of 1:2:1 and methylene (CH₂) absorption is split into a quartet, having relative areas of approximately 1:3:3:1. The separation between the components of the triplet is the same and equal to the separation between the components of the quartet. This separation, quoted in hertz (Hz, cycles per second), is known as the coupling constant J between the nuclei that interact. If the difference (in terms of frequency) between the absorption resonances of the interacting protons is large compared with J, then a simple rule of peak multiplicity is

The number of components into which a resonance absorption peak is split = \( n + 1 \),

(3.141)

where \( n \) = number of identical nuclei involved in the interaction.

In accordance with this rule, the methyl proton resonance peak is split into three components because two identical nuclei (i.e., the two methylene protons) are adjacent to it (i.e., on the next carbon atom). Similarly, the methylene proton resonance peak is split into four by interaction with the three identical methyl protons. [Note: The proton of the adjacent OH group does not partake in spin–spin coupling; otherwise, the methylene peak would split further. This is attributed to a rapid chemical exchange (proton transfer) of the hydroxyl proton among different ethyl alcohol molecules over a period of time, with the result that the methylene protons experience simply an average, nonsplitting field from the hydroxyl proton. The hydroxyl proton also experiences an averaged effect of the spin orientations of the methylene protons and its absorption peak therefore shows only a singlet.]

In simple cases of interacting nuclei, the component peaks of a multiplet are symmetrical about a midpoint and their relative areas are numerically proportional to the coefficients of the binomial expansion \((1 + r)^n\), where \( n \) is the number of protons on adjacent atoms. To illustrate, the following multiplicities will be predicted for the following compounds—n–propyl iodide (CH₃CH₂CH₂I): a three-proton triplet (relative areas 1:2:1), a two-proton sextet (1:5:10:5:1), and a two-proton triplet (1:2:1); isopropyl iodide [(CH₃)₂CHI]: a six-proton doublet (1:1) and a one-proton septet (1:6:15:20:15:6:1); methyl ethyl ether (CH₃OCH₂CH₃): a three-proton singlet, a two-proton quartet (1:3:3:1), and a three-proton triplet (1:2:1).

Observing the aforesaid patterns of relative intensities (i.e., relative areas) of the component peaks, doublets, triplets, quartets, and so on may sometimes be recognized in NMR spectra, even though they are partially overlapped by other bands. When plotted on a δ- or τ-scale, a spin–spin coupling pattern is compressed in the higher field strength spectrum. Thus, spectra recorded at, say, 60 MHz frequency and 100 MHz frequency will usually show differences. In principle, such differences may be used to differentiate spin–spin coupling from chemical shift.

3.8.2.5 Applications in Polymer Analysis

The NMR spectrum is presented as a plot of δ or τ shift on the horizontal axis against resonance energy as a vertical axis, usually on precalibrated paper. Field strength conventionally increases to the right. Unless otherwise indicated, it is presumed that the resonance of TMS is coincident with the zero of the δ (ppm) scale, which is on the right edge of the recorder chart. Most spectrometers have provision for integration
of areas under resonances. The integral is presented, using an arbitrary vertical scale, on the same chart as the resonance spectrum and in alignment with the latter on the horizontal axis.

To obtain sharp and well-defined NMR spectra, it is necessary to ensure that chemically equivalent nuclei in each molecule in the sample experience effectively the same magnetic environment. For this reason, samples are used in the liquid state and preferably in solution, as molecules then having higher mobility can assume all possible orientations with respect to the magnetic field. Each nucleus experiencing the same average magnetic environment ensures that the resonances are sharp. This condition can be achieved with monomeric substances in solution, but not with polymers. In practice, however, if rapid segmental motion of the polymer chain can be achieved, comparatively sharp resonances with substantially reduced width may be observed. Polymers are therefore examined in solution and often at 100°C to 150°C. Even under these conditions, resonances obtained for polymers are usually broader and the fine detail characteristic of monomeric substances is rarely achieved.

The NMR spectroscopy has been used for the analysis of polymers. Qualitative analysis and identification of polymers, quantitative analysis such as polymer end-group analysis and molecular weight determination, copolymer composition and sequence distribution analysis, polymer branching, structural isomerism, and polymer tacticity measurement may be mentioned as some of the applications. These are often done in combination with IR spectroscopic studies and elemental analysis as they may provide helpful leads and confirmation. Some examples of such applications are given below.

**Polymer Molecular Weights.** NMR analysis offers an easy method for determination of molecular weight of relatively low-molecular-weight polymers by end-group analysis. The method can be applied if the polymer has identifiable end-group protons that are distinguishable from protons of repeating monomer units by NMR and if accurate integration of resonance absorptions of different types of protons is provided by the instrument. Considering, for example, poly(ethylene glycol) diacrylate represented by the formula

\[
\text{H}_2\text{C}=-\text{CH}_2-\text{O}-(\text{O}--\text{CH}_2-\text{CH}_2-)_n-\text{O}--\text{CO}--\text{CH}={\text{CH}_2}.
\]

The end groups have formula weights (FW) 55 and 71, while the repeat unit has FW 44. Adding the area integrals of all the end-group proton resonances and dividing by the total number of end-group protons (i.e., 6) yields the value (say X) of the integral per end-group proton. Thereafter, dividing the sum of the integrals of all the repeat unit protons by the number of protons of one repeat unit (i.e., 4) gives the value (say Y) of the integral per proton of one repeat unit. Therefore, the number of repeat units in the polymer molecule is \( n = Y/X \) and polymer molecular weight \( = (55 + 71) + 44n \).

**Branching in Polyethylene.** Branching in polyethylene occurs in two forms—short-chain branching, which results from copolymerization of ethylene with another olefin (e.g., butene or octene), and long chain branching, where the length of the branches is on the same scale as that of the backbone. To detect and quantify these different types of branching, \(^{13}\text{C}\) NMR, instead of \(^1\text{H}\) NMR, is used based on the differences of the chemical shifts of the backbone chain carbon atoms attached or adjacent to the branch. The chemical shift depends on the length of the branch for branches up to 6 carbons in length, but is independent of branch length for all branches six carbons long or longer. On \(^{13}\text{C}\) NMR spectra of branched polyethylene, carbons can be classified as methylene carbon (C atom bonded to two other C atoms) on backbone and long-chain branches, methine carbon (C atom bonded to three other C atoms), \(\alpha C\) (C atom immediately adjacent to a methine carbon), \(\beta C\) (C atom immediately adjacent to an \(\alpha C\)), \(\gamma C\) (C atom immediately adjacent to a \(\beta C\)), \(2C\) (second C atom from end) on short branches, and chain-end methyl C.

**Tacticity in Polymers.** NMR spectroscopy is very useful for observation of stereoisomerism in polymers. Considering, for example, poly(methyl methacrylate) (PMMA) (Figure 3.109a), the two methylene protons are not magnetically equivalent in isotactic PMMA and so have different (though close) chemical shift values, forming an AB set, and there are two such sets, thus giving an appearance of four lines (Figure 3.109b). In syndiotactic PMMA (Figure 3.109b), the two methylene protons are magnetically equivalent and produce a single resonance in the center of the four preceding ones, while in atactic PMMA, the two methylene protons exhibit a combination of the above two resonance patterns. The three protons of the backbone methyl group are, however, sensitive to triad arrangements (Figure 3.109c). The isotactic,
syndiotactic, and atactic triads are resolved at different chemical shifts and a line appears at different locations for the three arrangements, the atactic line being between the iso and syndio lines (Figure 3.109b). Figure 3.110 compares the proton NMR spectra of a predominantly syndiotactic PMMA and a predominantly isotactic PMMA recorded by an NMR spectrometer employing fixed oscillator frequency of 60 Mc/s.

![FIGURE 3.109 Observation of tacticity in poly(methyl methacrylate) by $^1$H NMR spectroscopy. (a) Repeating unit of PMMA. (b) Proton NMR spectra of isotactic, syndiotactic, and atactic PMMA. (c) Arrangements of substituents in isotactic, syndiotactic, and atactic triads.](image)

**FIGURE 3.110** $^1$H NMR spectra of (a) predominantly syndiotactic PMMA and (b) predominantly isotactic PMMA with a 60-MHz NMR spectrometer. (Adapted from Bovey, F. A. 1972. *High Resolution NMR of Macromolecules*, Academic Press, New York.)
Copolymer Composition and Sequence Distribution. NMR spectroscopy can offer an easy method for the determination of composition of copolymers. The method is based on identifying the resonance absorption of a suitable proton in the comonomer units and recording their resonance absorption integrals. Considering, for example, a typical proton NMR spectrum of a copolymer of methyl methacrylate (MMA) and hexyl methacrylate (HMA), the resonance absorptions of O–CH$_3$ and O–CH$_2$ protons are identified at $\delta = 3.6$ and 3.9 ppm, respectively (Figure 3.111). The content of MMA in the copolymer is then calculated

![NMR spectrum of a copolymer of methyl methacrylate and hexyl methacrylate](image)

**FIGURE 3.111** $^1$H NMR spectrum of a copolymer of methyl methacrylate and hexyl methacrylate. (Adapted from Bovey, F. A. 1972. *High Resolution NMR of Macromolecules*, Academic Press, New York.)

![NMR spectra of polymers](image)

**FIGURE 3.112** $^1$H NMR spectra of (a) a poly(vinylidene chloride) homopolymer, (b) a polyisobutylene homopolymer, and (c) a copolymer of vinylidene chloride (VDC) and isobutylene (IB). Tetrad sequences in the copolymer associated with the resonance peaks are—1: VDC-VDC-VDC-VDC, 2: VDC-VDC-VDC-IB, 3: IB-VDC-VDC-IB, 4: VDC-VDC-IB-VDC, 5: IB-VDC-IB-VDC, 6: VDC-VDC-IB-IB, 7: IB-VDC-IB-IB. (Adapted from Bovey, F. A. 1972. *High Resolution NMR of Macromolecules*, Academic Press, New York.)
from the respective area integrals \((A)\), using the following equation:

\[
\%\text{MMA} = \frac{A_{3.6 \text{ ppm}}/3}{A_{3.6 \text{ ppm}}/3 + A_{3.9 \text{ ppm}}/2} \times 100
\]

Proton NMR spectroscopy has been used for observing sequence distribution of monomer units in copolymers. As a typical example, Figure 3.112a and b shows simple resonance peaks in poly(vinylidene chloride) and polyisobutylene homopolymers, respectively. In comparison, the spectrum of a copolymer of vinylidene chloride (VDC) and isobutylene (IB), shown in Figure 3.112c, exhibits a multiplicity of peaks, which are attributed to various tetrad sequences as noted.

References
