

Polymer

Chapter 4

Thermal Transitions in Polymers

I. INTRODUCTION

When a block of ice is heated, its temperature increases until at a certain temperature (depending on the pressure) it starts to melt. No further increase in temperature will be observed until all the ice has melted (solid becomes liquid). If heating is continued, the same phenomenon is observed as before and as the liquid starts to boil (liquid turns to vapor). It is pertinent to make two observations here:

- Water exists in three distinct physical states — solid, liquid, and gas (vapor).
- Transitions between these states occur sharply at constant, well-defined temperatures.

The thermal behavior of all simple compounds, such as ethanol or toluene, is analogous to that of water. However, the transitions in polymers are somewhat different and certainly more complex. In the first place, those molecules large enough to be appropriately termed polymers do not exist in the gaseous state. At high temperatures, they decompose rather than boil since what we would consider conventionally as their "boiling points" are generally higher than their decomposition temperatures. Second, a given polymeric sample is composed of a mixture of molecules having different chain lengths (molecular weights). In contrast to simple molecules, therefore, the transition between the solid and liquid forms of a polymer is rather diffuse and occurs over a temperature range whose magnitude (of the order of 2 to 10°C) depends on the polydispersity of the polymer (Figure 4.1). On melting, polymers become very viscous (viscoelastic) fluids, not freely flowing as in the case of low-molecular-weight materials.

In addition, there is a still more fundamental difference between the thermal behavior of polymers and simple molecules. To understand, first recall that molecular motion in a polymer sample is promoted by its thermal energy. It is opposed by the cohesive forces between structural segments (groups of atoms) along the chain and between neighboring chains. These cohesive forces and, consequently, thermal transitions in polymers depend on the structure of the polymer. In this regard, two important temperatures at which certain physical properties of polymers undergo drastic changes have been identified:

- • The glass transition temperature, T_g ✓
- • The crystalline melting point, T_m ✓

If a polymer is amorphous, the solid-to-liquid transition occurs very gradually, going through an intermediate "rubbery" state without a phase transformation. The transition from the hard and brittle glass into a softer, rubbery state occurs over a narrow temperature range referred to as the glass transition temperature. In the case of a partially crystalline polymer, the above transformation occurs only in the amorphous regions. The crystalline zones remain unchanged and act as reinforcing elements thus making the sample hard and tough. If heating is continued, a temperature is reached at which the crystalline zones begin to melt. The equilibrium crystalline melting point, T_m , for polymers corresponds to the temperature at which the last crystallite starts melting. Again, in contrast to simple materials, the value of T_m depends on the degree of crystallinity and size distribution of crystallites. The general changes in physical state due to changes in temperature and molecular weight are shown in Figure 4.2 for amorphous and crystalline polymers.

The thermal behavior of polymers is of considerable technological importance. Knowledge of thermal transitions is important in the selection of proper processing and fabrication conditions, the characterization of the physical and mechanical properties of a material, and hence the determination of appropriate end uses. For example, the glass transition temperature of rubber determines the lower limit of the use of rubber and the upper limit of the use of an amorphous thermoplastic. We take up discussion of these transition temperatures in succeeding sections.

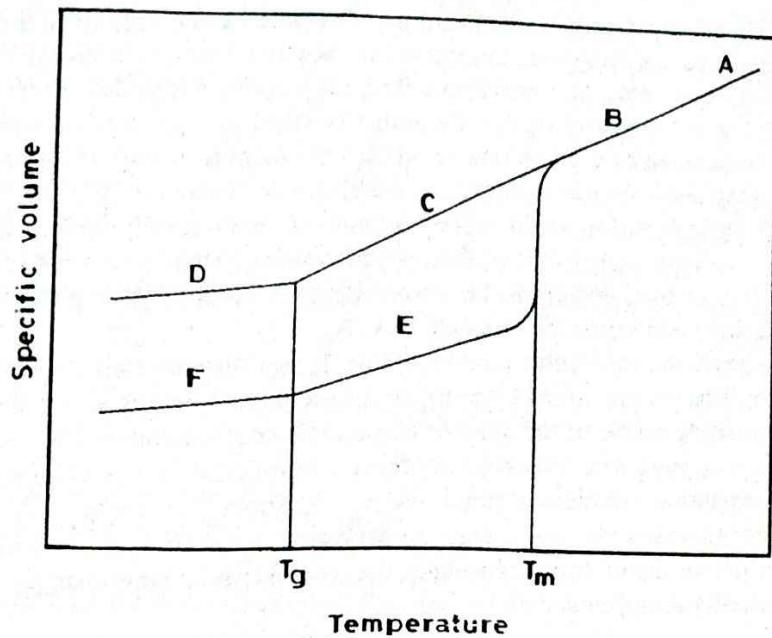


Figure 4.3 Specific volume-temperature curves for a semicrystalline polymer. (A) Liquid region; (B) viscous liquid with some elastic response; (C) rubbery region; (D) glassy region; (E) crystallites in a rubbery matrix; (F) crystallites in a glassy matrix.

constant rate. At a characteristic temperature, T_g , the rate of volume expansion increases suddenly to a higher constant level, i.e., there is a change in the slope of the volume-temperature curve from a lower to a higher volume coefficient of expansion. At the same time, there is an abrupt change in physical behavior from a hard, brittle, glassy solid below T_g (region D) to a soft, rubbery material above T_g (region C). On further heating, the polymer changes gradually from the rubbery state to a viscous liquid (region B) whose viscosity decreases with increasing temperature until decomposition sets in.

For a crystalline polymer, the changes at T_g are less drastic. This is because these changes are restricted mainly to the amorphous domains while the crystalline zones remain relatively unaffected. Between the glass transition (T_g) and the melting temperature (T_m) (region E) the semicrystalline polymer is composed of rigid crystallites immersed (dispersed) in a rubbery amorphous matrix. In terms of mechanical behavior, the polymer remains rigid, pliable, and tough. At the melting temperature, the crystallites melt, leading to a viscous state (region B). Above T_m the crystalline polymer, like the amorphous polymer, exists as a viscous liquid.

A. MOLECULAR MOTION AND GLASS TRANSITION

In polymers, *intramolecular* bonds are due to primary valence bonds (covalent) while the *intermolecular* attractions usually are due to secondary bonding forces. The intermolecular forces are opposed by thermal agitation, which induces vibration, rotation, and translation of a molecular system. Atomic vibrations exist at all temperature levels. The stability of the molecular system depends on the vibration energy of the chemical bonds. In polymers, thermal degradation occurs when the energy of vibration exceeds the primary bonding between atoms, while the transitional phenomena associated with crystalline melting point, the glass transition temperature, and the polymer deformations are related to rotation and vibration of molecular chains.

Bearing this in mind, let us consider what happens on a molecular scale when an amorphous polymer is heated from below its glass transition temperature. At very low temperatures — i.e., in the glassy state — chain segments are frozen in fixed positions; atoms undergo only low-amplitude vibratory motion about these positions. As the temperature is increased, the amplitude of these vibrations becomes greater, thereby reducing the effectiveness of the secondary intermolecular bonding forces. Consequently, the cooperative nature of the vibrations between neighboring atoms is enhanced. At the glass transition temperature, chain ends and a substantial number of chain segments have acquired sufficient energy to overcome intermolecular restraints and undergo rotational and translational motion. Therefore, the glass transition temperature is referred to as the onset of large-scale cooperative motion of chain segments.

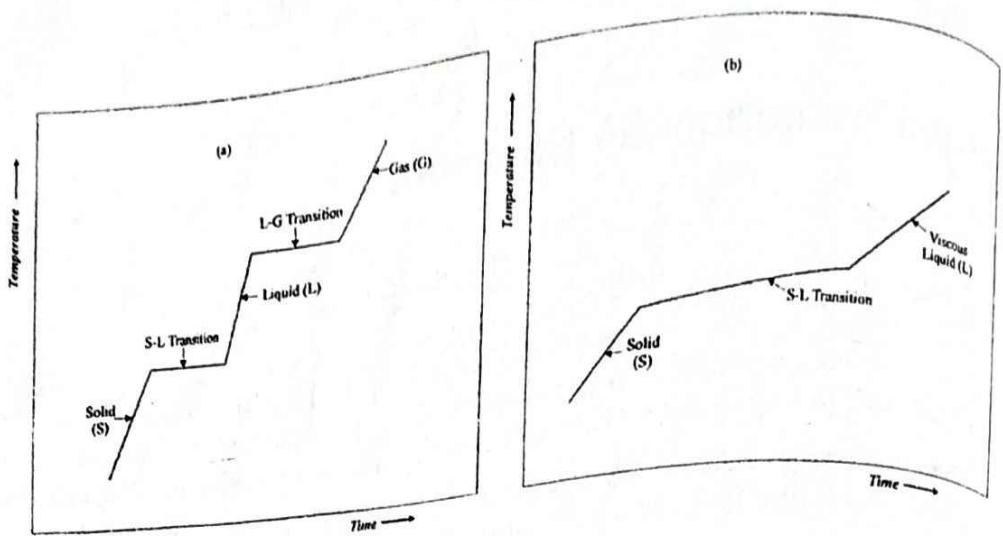


Figure 4.1 Relative thermal responses of simple molecules (a) and polymers (b).

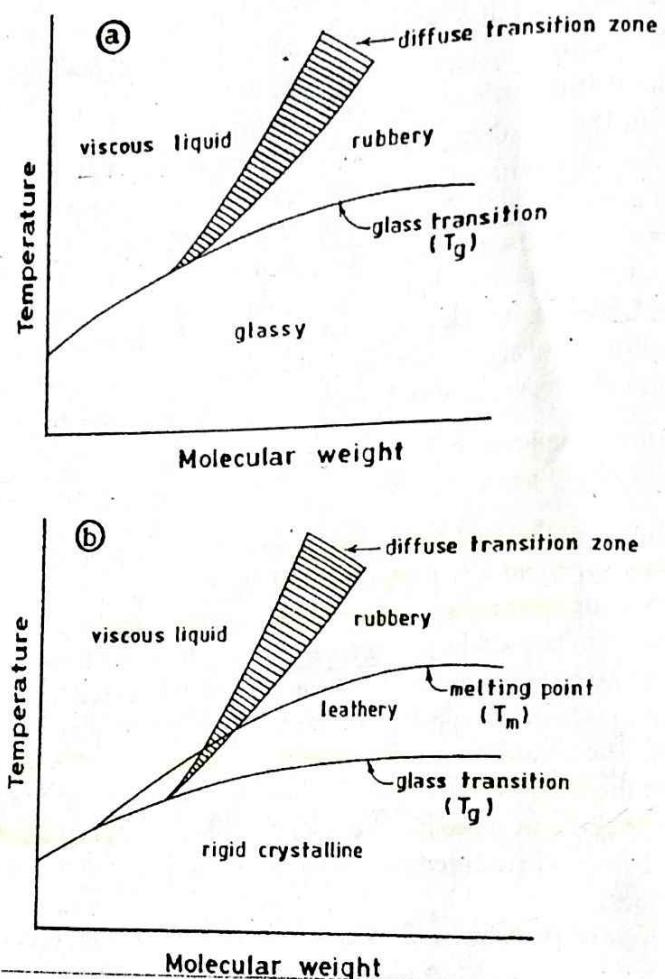


Figure 4.2 Temperature-molecular weight diagram. (a) For amorphous polymer; (b) for crystalline polymer.

H. THE GLASS TRANSITION

To illustrate the concept of glass transition, let us consider the specific volume-temperature behavior for both amorphous (ABCD) and crystalline (ABEF) polymers, as shown in Figure 4.3. As the amorphous polymer (line ABCD) is heated from the low-temperature region (region D), the volume expands at a

(of the order of 20 to 50 consecutive carbon atoms). Rotational and translational modes of motion provide important mechanisms for energy absorption. This accounts for glassy-to-rubbery transition and the tough nature of an amorphous polymer above its glass transition temperature.

Below the T_g , or in the glassy state, only atoms or small groups of atoms such as short sections of the main chain or pendant/side groups move against the local restraints of intermolecular interactions. This movement may result in other transitions, which are designated α , β , γ , etc., in order of decreasing temperature. The fully extended chain, which is the conformation of minimum energy, is the preferred conformation at low temperatures. Therefore, as the molecules straighten out, the free volume, as we shall see in the next section, decreases. Consequently, flow becomes difficult and the polymer assumes the characteristic hard and brittle behavior of glasses.

As we said above, the molecular motion of the T_g is restricted only to segmental motion; entire molecular motion is as yet precluded by chain entanglements. However, above the T_g , or in the rubbery state, there is a sharp increase in the number of possible conformations. The molecular motion in the rubbery state requires more free volume, and this rise in the relative free volume leads to the observed higher volume expansion coefficient above the T_g . As heating is continued into the liquid region, molecules acquire increased thermal energy, and the amplitudes of associated molecular motions also increase. Translation, or slip of entire molecules, becomes possible; large changes in conformation occur and elasticity virtually disappears.

B. THEORIES OF GLASS TRANSITION AND MEASUREMENT OF THE GLASS TRANSITION TEMPERATURE

The fundamental nature of the glass transition is still unclear. It is a complex process that involves equilibrium, thermodynamic and kinetic factors. The various theories of the glass transition, however, have used either the thermodynamic or the kinetic approach. The thermodynamic approach is based on entropy considerations of the glassy state, while the kinetic theory of the glass transition considers the relaxation phenomena associated with the glass transition. Each approach gives only a partial explanation to the observed behavior of polymers. We now briefly discuss these theories along with the free volume theory.

1. Kinetic Theory

The kinetic concept of glass transition considers the glass transition as a dynamic phenomenon since the position of the T_g depends on the rate of heating or cooling. It predicts that the value of T_g measured depends on the time scale of the experiment in relation to that of the molecular motions arising from the perturbation of the polymer system by temperature changes. A number of models have been proposed to correlate these molecular motions with changes in macroscopic properties observed in the experiment. One approach considers the process of vitrification (glassification) as a reaction involving the movement of chain segments (kinetic units) between energy states. For the movement of a chain segment from one energy state to another to occur, a critical "hole" or empty space must be available. To create this hole sufficient energy must be available to overcome both the cohesive forces of the surrounding molecules and the potential energy barrier associated with the rearrangement. The temperature at which the number of holes of sufficient size is great enough to permit flow is regarded as the T_g . This theory permits a description of the approach to thermodynamic equilibrium. When a polymeric material above T_g is cooled, there is sufficient molecular motion for equilibrium to be achieved. However, the rate of approach to equilibrium, and hence the T_g , depends on the cooling rate employed in the experiment.

2. Equilibrium Theory

The equilibrium concept treats the ideal glass transition as a true second-order thermodynamic transition, which has equilibrium properties. The ideal state, of course, cannot be obtained experimentally since its realization would require an infinite time. According to the theory of Gibbs and DiMarzio,¹ the glass transition process is a consequence of the changes in conformational entropy with changes in temperature. The reduced level in molecular reorganization observed near the transition temperature is attributed to the reduction in the number of available conformations as the temperature is lowered. The equilibrium conformational entropy becomes zero when a thermodynamic second-order transition is reached ultimately. Thereupon, the conformations are essentially "frozen in" since the time required for conformational changes becomes virtually infinite. The glass transition temperature, T_g , therefore approaches the

true transition temperature as the time scale of experiment becomes longer. Based on this reasoning and using a statistical thermodynamics treatment that utilizes a quasi-lattice theory, Gibbs and DiMarzio¹ developed quantitative predictions of the second-order phase transition that are in agreement with experiment.

3. Free Volume Theory

A most useful and popular theory of glass transition is the "free volume" model of Fox and Ferry and, later, of Williams, Landell, and Ferry.² This theory considers the free volume, V_f , of a substance as the difference between its specific volume, \bar{V} , and the space actually occupied by the molecules, V_0 , where V_0 is expressed as:

$$V_0 = V' + \alpha_g T \quad (4.1)$$

where V' = the extrapolated volume of glass at absolute zero

α_g = thermal expansion coefficient of the glass

This model further defines the free volume fraction, f , at temperature T as

$$\begin{aligned} f &= V_f / \bar{V} \\ &= f_g + \alpha_f (T - T_g) \end{aligned} \quad (4.2)$$

and

$$\alpha_f = \alpha_i - \alpha_g = \frac{df}{dT} = \frac{1}{V_f} \frac{dV_f}{dT} \quad (4.3)$$

where f_g = free volume fraction at T_g

α_i = thermal expansion coefficient above T_g

α_g = thermal expansion coefficient below T_g

For most amorphous polymers, the free volume fraction at the glass transition temperature is found to be a constant, with a value of 0.025. Amorphous polymers, when cooled, are therefore supposed to become glassy when the free volume fraction attains this value. Thereupon no significant further change in the free volume will be observed.

Many important physical properties of polymers (particularly amorphous polymers) change drastically at the glass transition temperature. The variations of these properties with temperature form a convenient method for determining T_g . Some of the test methods include the temperature variation of specific volume (dilatometry) as discussed in Section II, refractive index (refractometry), and specific heat (calorimetry, DSC or DTA). Others include temperature-induced changes in vibrational energy level (infrared spectroscopy), proton environment (nuclear magnetic resonance or NMR), dipole moment (dielectric constant and loss), elastic modulus (creep or stress relaxation), and mechanical energy absorption (dynamic mechanical analysis or DMA). Discussion of details of these test methods is beyond the scope of this volume.

C. FACTORS AFFECTING GLASS TRANSITION TEMPERATURE

We have seen from the previous discussion that at the glass transition temperature there is a large-scale cooperative movement of chain segments. It is therefore to be expected that any structural features or externally imposed conditions that influence chain mobility will also affect the value of T_g . Some of these structural factors include chain flexibility; stiffness, including steric hindrance, polarity, or inter-chain attractive forces; geometric factors; copolymerization; molecular weight, branching; cross-linking; and crystallinity. External variables are plasticization, pressure, and rate of testing.

Table 4.1 Effect of Chain Flexibility on T_g

Polymer	Repeat Unit	T_h (°C)
Polychethylene	$\text{--CH}_2\text{--CH}_2\text{--}$	-120
Polydimethylsiloxane	$\begin{array}{c} \text{CH}_3 \\ \\ \text{--Si--O--} \\ \\ \text{CH}_3 \end{array}$	-123
Polycarbonate	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{O}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)-\text{C}_6\text{H}_4-\text{O}-\text{C}(=\text{O})- \end{array}$	150
Polysulfone	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{O}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{S}(=\text{O})_2-\text{C}_6\text{H}_4- \end{array}$	190
Poly(2,6-dimethyl-1,4-phenylene oxide)	$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{--C}_6\text{H}_3(\text{O})-\text{C}_6\text{H}_4-\text{O}-- \end{array} \right]$	220

1. Chain Flexibility

Chain flexibility is determined by the ease with which rotation occurs about primary valence bonds. Polymers with low hindrance to internal rotation have low T_g values. Long-chain aliphatic groups — ether and ester linkages — enhance chain flexibility, while rigid groups like cyclic structures stiffen the backbone. These effects are illustrated in Table 4.1. Bulky side groups that are stiff and close to the backbone cause steric hindrance, decrease chain mobility, and hence raise T_g (Table 4.2).

The influence of the side group in enhancing chain stiffness depends on the flexibility of the group and not its size. In fact, side groups that are fairly flexible have little effect within each series; instead polymer chains are forced further apart. This increases the free volume, and consequently T_g drops. This is illustrated by the polymethacrylate series (Table 4.3).

2. Geometric Factors

Geometric factors, such as the symmetry of the backbone and the presence of double bonds on the main chain, affect T_g . Polymers that have symmetrical structure have lower T_g than those with asymmetric structures. This is illustrated by two pairs of polymers: polypropylene vs. polyisobutylene and poly(vinyl chloride) vs. poly(vinylidene chloride) in Table 4.4. Given our discussion above on chain stiffness, one would have expected that additional groups near the backbone for the symmetrical polymer would enhance steric hindrance and consequently raise T_g . This, however, is not the case. This "discrepancy" is due to conformational requirements. The additional groups can only be accommodated in a conformation with a "loose" structure. The increased free volume results in a lower T_g .

Another geometric factor affecting T_g is *cis-trans* configuration. Double bonds in the *cis* form reduce the energy barrier for rotation of adjacent bonds, "soften" the chain, and hence reduce T_g (Table 4.5).

3. Interchain Attractive Forces

Recall from our earlier discussion that intermolecular bonding in polymers is due to secondary attractive forces. Consequently, it is to be expected that the presence of strong intermolecular bonds in a polymer chain, i.e., a high value of cohesive energy density, will significantly increase T_g . The effect of polarity, for example, can be seen from Table 4.6. The steric effects of the pendant groups in series (CH_3 , $-\text{Cl}$,

Table 4.2 Enhancement of T_g by Steric Hindrance

Polymer	Repeat Unit	T_g (°C)
Polyethylene	$-\text{CH}_2-\text{CH}_2-$	-120
Polypropylene	$-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-$	-10
Polystyrene	$-\text{CH}_2-\underset{\text{C}_6\text{H}_5}{\text{CH}}-$	100
Poly(α -methylstyrene)	$-\text{CH}_2-\underset{\text{C}_6\text{H}_5}{\underset{\text{CH}_3}{\text{C}}}-$	192
Poly(o -methylstyrene)	$-\text{CH}_2-\underset{\text{C}_6\text{H}_4\text{CH}_3}{\text{CH}}-$	119
Poly(m -methylstyrene)	$-\text{CH}_2-\underset{\text{C}_6\text{H}_3\text{CH}_3}{\text{CH}}-$	72
Poly(α -vinyl naphthalene)	$-\text{CH}_2-\underset{\text{C}_1\text{C}_2\text{H}_2}{\text{CH}}-$	135
Poly(vinyl carbazole)	$-\text{CH}_2-\underset{\text{C}_1\text{C}_2\text{N}}{\text{CH}}-$	208

and $-\text{CN}$) are similar, but the polarity increases. Consequently, T_g is increased in the order shown in the table. The same effect of increased T_g with increasing CED can be observed when one considers going from the intermolecular forces in poly(methyl acrylate), an ester, through the strong hydrogen bonds in poly(acrylic acid) to primary ionic bonds in poly(zinc acrylate) (Table 4.7).

Recall again that secondary bonding forces are effective only over short molecular distances. Therefore, any structural feature that tends to increase the distance between polymer chains decreases the cohesive energy density and hence reduces T_g . This effect has already been clearly demonstrated in the polyacrylate series where the increased distance between chains due to the size of the alkyl group, R, reduced T_g .

Table 4.3 Decrease of T_g with Increasing Flexibility of Side Chains for Polymethacrylate Series

Generalized Formula	R	T_g ($^{\circ}\text{C}$)
$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{C}=\text{O} \\ \\ \text{O} \\ \\ \text{R} \end{array}$	methyl	105
	ethyl	65
	<i>n</i> -propyl	35
	<i>n</i> -butyl	21
	<i>n</i> -hexyl	-5
	<i>n</i> -octyl	-20
	<i>n</i> -dodecyl	-65

Table 4.4 Effect of Symmetry of T_g

Polymer	Repeat Unit	T_g ($^{\circ}\text{C}$)
Polypropylene	$-\text{CH}_2-\underset{\substack{ \\ \text{CH}_3}}{\text{CH}}-$	-10
Polyisobutylene	$-\text{CH}_2-\underset{\substack{ \\ \text{CH}_3}}{\text{CH}}-$	-70
Poly(vinyl chloride)	$-\text{CH}_2-\underset{\substack{ \\ \text{Cl}}}{\text{Cii}}-$	87
Poly(vinylidene chloride)	$-\text{CH}-\underset{\substack{ \\ \text{Cl}}}{\text{C}}-$	-17

Table 4.5 Relative Effects of *cis-trans* Configuration on T_g

Polymer	Repeat Unit	T_g ($^{\circ}\text{C}$)
Poly(1,4- <i>cis</i> -butadiene)	$\begin{array}{ccccc} & & \text{CH}_2 & & \\ & \diagdown & & \diagup & \\ -\text{CH}_2 & & \text{CH}=\text{CH} & & \text{CH}_2- \\ & \diagup & & \diagdown & \\ & & & & \end{array}$	-108
Poly(1,4- <i>trans</i> -butadiene)	$\begin{array}{ccccc} & & \text{CH}_2 & & \\ & \diagdown & & \diagup & \\ -\text{CH}_2 & & \text{CH}=\text{CH} & & \text{CH}_2- \\ & \diagup & & \diagdown & \\ & & & & \end{array}$	-83

Table 4.6 Effect of Polarity on T_g

Polymer	Repeat Unit	Dielectric Constant at 1kHz	$T_g(^{\circ}\text{C})$
Polypropylene	$\text{--CH}_2\text{--CH}(\text{CH}_3)\text{--}$	2.2–2.3	-10
Poly(vinyl chloride)	$\text{--CH}_2\text{--CH}(\text{Cl})\text{--}$	3.39	87
Polyacrylonitrile	$\text{--CH}_2\text{--CH}(\text{CN})\text{--}$	5.5	103

Table 4.7 Effect of Polarity on the T_g of Some Acrylic Polymers

Polymer	Repeat Value	$T_g(^{\circ}\text{C})$
Polymethylacrylate	$\text{--CH}_2\text{--CH}(\text{C=O})\text{--O--CH}_3$	3
Poly(acrylic acid)	$\text{--CH}_2\text{--CH}(\text{C=O})\text{--O--H}$	106
Poly(zinc acrylate)	$\text{--CH}_2\text{--CH}(\text{C=O})\text{--O--Zn}^{++}\text{--O--C(=O)--CH}_2\text{--CH}(\text{C=O})\text{--}$	>400

4. Copolymerization

The transition temperatures T_g and T_m are important technological characteristics of polymers. It is desirable — in fact, valuable — to be able to control either T_g or T_m independent of each other. This, however, is often impossible. Polymer chemists have circumvented this problem to some extent by polymer modification via copolymerization and polyblending. These procedures have become powerful tools for tailoring polymer systems for specific end uses.

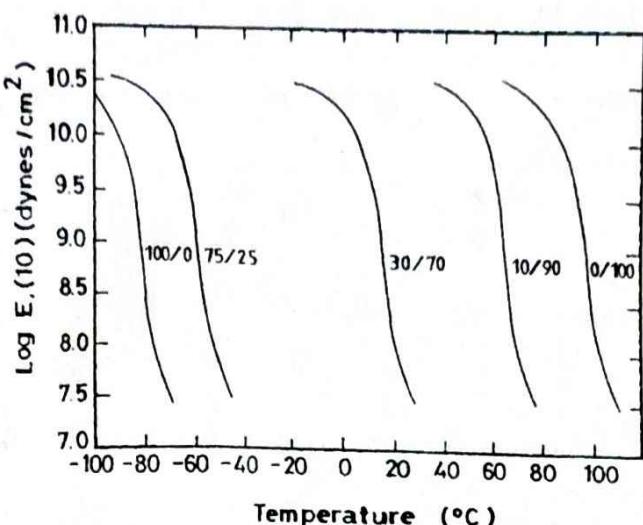


Figure 4.4 E , vs. fraction ratios of butadiene-styrene copolymers. (From Tobolsky, A.V., *Properties and Structure of Polymers*, John Wiley & Sons, New York, 1960. With permission of Dorothy Tobolsky.)

A copolymer system may be characterized either by the geometry of the resulting polymer — that is, the arrangement of the different monomers (random, alternating, graft, or block) — or by the compatibility (miscibility) of the two monomers.

a. Isomorphous Systems (Homogeneous Copolymers or Compatible Polyblends)

In isomorphous systems, the component monomers occupy similar volumes and are capable of replacing each other in the crystal system. The resulting copolymer, irrespective of its geometry, is necessarily homogeneous, and polyblends of the individual homopolymers or copolymers have similar transition properties. Copolymerization merely shifts the T_g to the position intermediate between those of the two homopolymers; it does not alter the temperature range or the modulus within the transition region (Figure 4.4). This shift is illustrated in Figure 4.4, which shows the modulus temperature curves for polybutadiene (100/0) and polystyrene (0/100) and for various compositions of butadiene-styrene copolymer.

For this system, if the glass transitions (T_{g1} and T_{g2}) of the individual homopolymers (1 and 2) are known, it is possible to estimate the T_g of the copolymer (or polyblend) using the relation

$$T_g = V_1 T_{g1} + V_2 T_{g2} \quad (4.4)$$

where V_1 and V_2 are the volume fractions of components 1 and 2, respectively. This is shown schematically in Figure 4.5 (line 1).

b. Nonisomorphous Systems

In nonisomorphous systems, the specific volumes of the monomers are different. In this case, the geometry of the resulting polymer becomes important.

Random or alternating — For these copolymers, the composition is necessarily homogeneous (no phase separation) and, as discussed above, the glass transitions are intermediate between those of the two homopolymers. The increased disorder resulting from the random or alternating distribution of monomers enhances the free volume and consequently reduces T_g below that predicted by Equation 4.4 (line 2, Figure 4.5). The T_g of the copolymer whose components have weight fractions W_1 and W_2 and glass transitions T_{g1} and T_{g2} , respectively, can be calculated from the relation

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \quad (4.5)$$

Examples of this type are methyl methacrylate-acrylonitrile, styrene-methyl methacrylate, and acrylonitrile-acrylamide copolymers. It is also possible that monomers involved in the copolymerization process

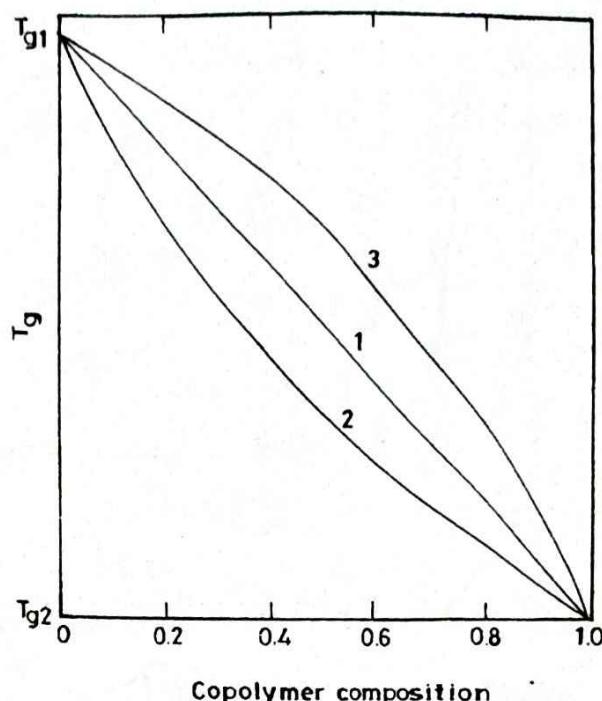


Figure 4.5 Variation in glass transition temperature with copolymer composition (schematic).

(as in the copolymers methylacrylate-methylmethacrylate and vinylidene chloride-methylacrylate) introduce significant interaction between chains. In this case the T_g will be enhanced relative to the predicted value (Figure 4.5, line 3).

Block and graft copolymers (incompatible copolymers) — For block or graft copolymers in which the component monomers are incompatible, phase separation will occur. Depending on a number of factors — for example, the method of preparation — one phase will be dispersed in a continuous matrix of the other. In this case, two separate glass transition values will be observed, each corresponding to the T_g of the homopolymer. Figure 4.6 shows this behavior for polyblends of polystyrene (100) and 30/70 butadiene-styrene copolymer (0).

Example 4.1: What is the T_g of butadiene-styrene copolymer containing 10 vol% styrene?

Solution: Butadiene and styrene form a completely compatible random copolymer. Therefore the following relation is applicable: $T_g = V_1 T_{g1} + V_2 T_{g2}$.

Assume 1 = polybutadiene

2 = polystyrene

$$T_{g1} = -80^\circ\text{C}, T_{g2} = 100^\circ\text{C}$$

$$T_g = 0.90(-80) + 0.10(100)$$

$$= -62^\circ\text{C}$$

5. Molecular Weight

Since chain end segments are restricted only at one end, they have relatively higher mobility than the internal segments, which are constrained at both ends. At a given temperature, therefore, chain ends provide a higher free volume for molecular motion. As the number of chain ends increases (which means a decrease in M_n), the available free volume increases, and consequently there is a depression of T_g . The effect is more pronounced at low molecular weight, but as M_n increases, T_g approaches an asymptotic value. An empirical expression relating the inverse relations between T_g and M_n is given by Equation 4.6.

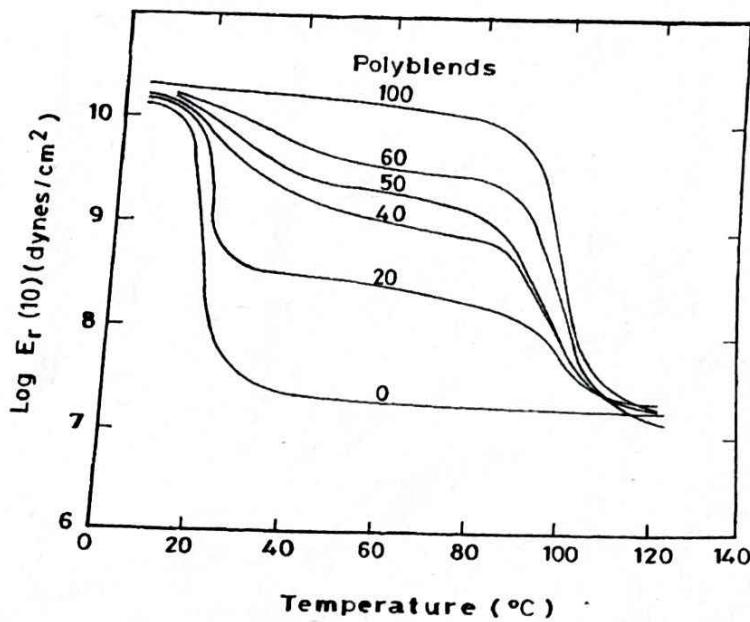


Figure 4.6 $E_r(10)$ vs. temperature for polyblends of polystyrene and a 30/70 butadiene-styrene copolymer. Numbers on the curves are the weight percent of polystyrene in the blend. (From Tobolsky, A.V., *Properties and Structure of Polymers*, John Wiley & Sons, New York, 1960. With permission of Dorothy Tobolsky.)

$$T_g = T_g^\infty = K/\bar{M}_n \quad (4.6)$$

where $T_g^\infty = T_g$ of an infinite molecular weight
 K = a constant

For polystyrene it has been found that $T_g^\infty = 100^\circ\text{C}$ while K is about 2×10^5 .

Example 4.2: What is the T_g of polystyrene of $\bar{M}_n = 3000$?

Solution: From above, $T_g^\infty = 100$, $K = 2 \times 10^5$.

$$T_g = 100 - \frac{2 \times 10^5}{3000} \\ = 33^\circ\text{C}$$

6 / Cross-Linking and Branching

By definition, cross-linking involves the formation intermolecular connections through chemical bonds. This process necessarily results in reduction in chain mobility. Consequently, T_g increases. For lightly cross-linked systems like vulcanized rubber, T_g shows a moderate increase over the uncross-linked polymer. In this case, T_g and the degree of cross-linking have a linear dependence, as shown by the following approximate empirical equation.

$$T_g - T^0 = \frac{3.9 \times 10^4}{M_c} \quad (4.7)$$

where T_g = the glass transition temperature of the uncross-linked polymer having the same chemical composition as the cross-linked polymer

M_c = the number-average molecular weight between cross-linked points

For highly cross-linked systems like phenolics and epoxy resins, the glass transition is virtually infinite. This is because the molecular chain length between cross-links becomes smaller than that required for cooperative segmental motion.

Like long and flexible side chains, branching increases the separation between chains, enhances the free volume, and therefore decreases T_g .

7. Crystallinity

In semicrystalline polymers, the crystallites may be regarded as physical cross-links that tend to reinforce or stiffen the structure. Viewed this way, it is easy to visualize that T_g will increase with increasing degree of crystallinity. This is certainly not surprising since the cohesive energy factors operative in the amorphous and crystalline regions are the same and exercise similar influence on transitions. It has been found that the following empirical relationship exists between T_g and T_m :

$$\frac{T_g}{T_m} = \begin{cases} 1/2 & \text{for symmetrical polymers} \\ 2/3 & \text{for unsymmetrical polymers} \end{cases} \quad (4.8)$$

where T_g and T_m are in degrees Kelvin.

8. Plasticization

Plasticity is the ability of a material to undergo plastic or permanent deformation. Consequently, plasticization is the process of inducing plastic flow in a material. In polymers, this can be achieved in part by the addition of low-molecular-weight organic compounds referred to as plasticizers (see Chapter 9). Plasticizers are usually nonpolymeric, organic liquids of high boiling points. Plasticizers are miscible with polymers and, in principle, should remain within the polymer. Addition of plasticizers to a polymer, even in very small quantities, drastically reduces the T_g of the polymer. This is exemplified by the versatility of poly(vinyl chloride) which, if unmodified, is rigid, but can be altered into a flexible material by the addition of plasticizers such as diethylphthalate (DOP).

The effect of plasticizer in reducing T_g can be interpreted in several ways. Plasticizers function through a solvating action by increasing intermolecular distance, thereby decreasing intermolecular bonding forces. Alternatively, the addition of plasticizers results in a rapid increase in chain ends and hence an increase in free volume. A plasticized system may also be considered as a polyblend, with the plasticizer acting as the second component. In this case, our earlier relations for polyblends would apply (Equations 4.1 and 4.2). Since plasticizers generally have very low T_g , between -50°C and -160°C , addition of small amounts of the plasticizer would be expected to result in a substantial decrease in the T_g of a polymer. This is illustrated in Figure 4.7 for a poly(vinyl chloride)-diethylhexyl succinate system.

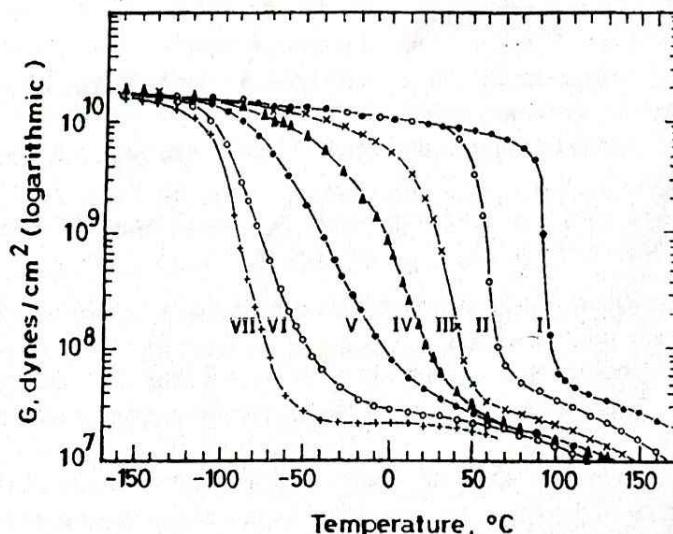


Figure 4.7 Shear modulus, G vs. temperature, measured for a time scale of approximately 1 s, poly(vinyl chloride) plasticized with diethylhexyl succinate. I, 100% monomer; II, 91%; III, 79%; IV, 70.5%; V, 60.7%; VI, 51.8%; VII, 40.8%. (From Schneider, K. and Wolf, K., *Kolloid Z.*, 127, 65, 1952.)

$$\bar{X}_n = \frac{\sum_{i=1}^N n_i M_r}{N}$$

where N = total number of molecules in the polymer mass

M_r = molecular weight of repeating unit

n_i = DP of molecule i.

Now $\bar{M}_n = \bar{X}_n M_r = 100 (15 + 14 \times 10 + 28)$
 $= 18,300$

$$\text{Polydispersity} = \frac{\bar{M}_w}{\bar{M}_n} = \frac{120,000}{18,300} = 6.56$$

III. CLASSIFICATION OF POLYMERS

Polymers can be classified in many different ways. The most obvious classification is based on the origin of the polymer, i.e., natural vs. synthetic. Other classifications are based on the polymer structure, polymerization mechanism, preparative techniques, or thermal behavior.

A. NATURAL VS. SYNTHETIC

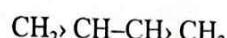
Polymers may either be naturally occurring or purely synthetic. All the conversion processes occurring in our body (e.g., generation of energy from our food intake) are due to the presence of enzymes. Life itself may cease if there is a deficiency of these enzymes. Enzymes, nucleic acids, and proteins are polymers of biological origin. Their structures, which are normally very complex, were not understood until very recently. Starch — a staple food in most cultures — cellulose, and natural rubber, on the other hand, are examples of polymers of plant origin and have relatively simpler structures than those of enzymes or proteins. There are a large number of synthetic (man-made) polymers consisting of various families: fibers, elastomers, plastics, adhesives, etc. Each family itself has subgroups.

B. POLYMER STRUCTURE

1. Linear, Branched or Cross-linked, Ladder vs. Functionality

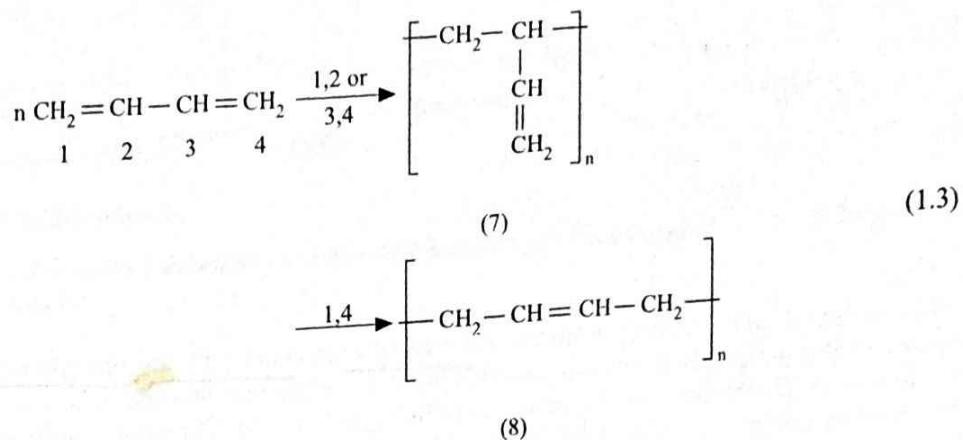
As we stated earlier, a polymer is formed when a very large number of structural units (repeating units, monomers) are made to link up by covalent bonds under appropriate conditions. Certainly even if the conditions are "right" not all simple (small) organic molecules possess the ability to form polymers. In order to understand the type of molecules that can form a polymer, let us introduce the term *functionality*. The functionality of a molecule is simply its interlinking capacity, or the number of sites it has available for bonding with other molecules under the specific polymerization conditions. A molecule may be classified as monofunctional, bifunctional, or polyfunctional depending on whether it has one, two, or greater than two sites available for linking with other molecules. For example, the extra pair of electrons in the double bond in the styrene molecules endows it with the ability to enter into the formation of two bonds. Styrene is therefore bifunctional. The presence of two condensable groups in both hexamethylenediamine ($-NH_2$) and adipic acid ($-COOH$) makes each of these monomers bifunctional. However, functionality as defined here differs from the conventional terminology of organic chemistry where, for example, the double bond in styrene represents a single functional group. Besides, even though the interlinking capacity of a monomer is ordinarily apparent from its structure, functionality as used in polymerization reactions is specific for a given reaction. A few examples will illustrate this.

A diamine like hexamethylenediamine has a functionality of 2 in amide-forming reactions such as that shown in Equation 1.2. However, in esterification reactions a diamine has a functionality of zero. Butadiene has the following structure:



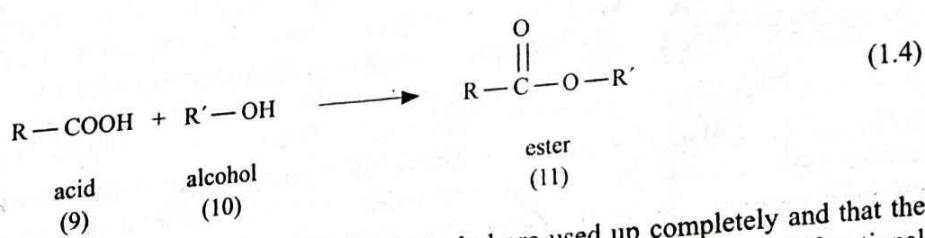
1 2 3 4

From our discussion about the polymerization of styrene, the presence of two double bonds on the structure of butadiene would be expected to prescribe a functionality of 4 for this molecule. Butadiene may indeed be tetrafunctional, but it can also have a functionality of 2 depending on the reaction conditions (Equation 1.3).

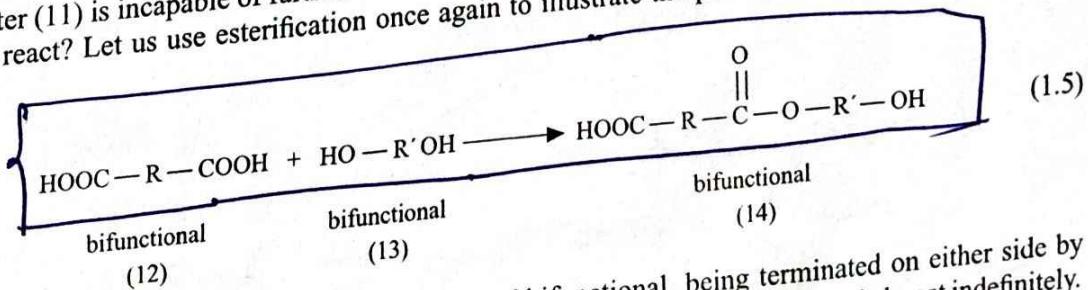


Since there is no way of making a distinction between the 1,2 and 3,4 double bonds, the reaction of either double bond is the same. If either of these double bonds is involved in the polymerization reaction, the residual or unreacted double bond is on the structure attached to the main chain [i.e., part of the pendant group (7)]. In 1,4 polymerization, the residual double bond shifts to the 2,3 position along the main chain. In either case, the residual double bond is inert and is generally incapable of additional polymerization under the conditions leading to the formation of the polymer. In this case, butadiene has a functionality of 2. However, under appropriate reaction conditions such as high temperature or cross-linking reactions, the residual unsaturation either on the pendant group or on the backbone can undergo additional reaction. In that case, butadiene has a total functionality of 4 even though all the reactive sites may not be activated under the same conditions. Monomers containing functional groups that react under different conditions are said to possess *latent functionality*.

Now let us consider the reaction between two monofunctional monomers such as in an esterification reaction (Equation 1.4).



You will observe that the reactive groups on the acid and alcohol are used up completely and that the product ester (11) is incapable of further esterification reaction. But what happens when two bifunctional molecules react? Let us use esterification once again to illustrate the principle (Equation 1.5).



The ester (14) resulting from this reaction is itself bifunctional, being terminated on either side by groups that are capable of further reaction. In other words, this process can be repeated almost indefinitely. The same argument holds for polyfunctional molecules. It is thus obvious that the generation of a polymer through the repetition of one or a few elementary units requires that the molecule(s) must be at least bifunctional.

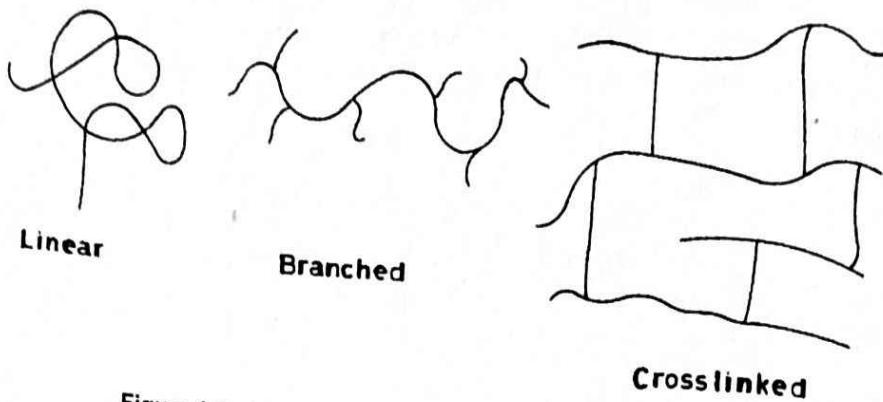
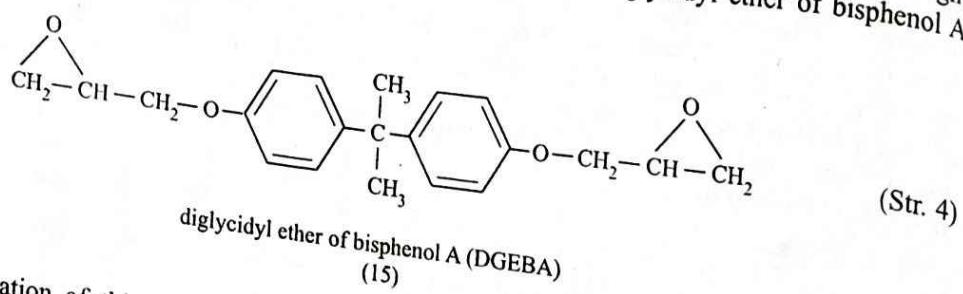


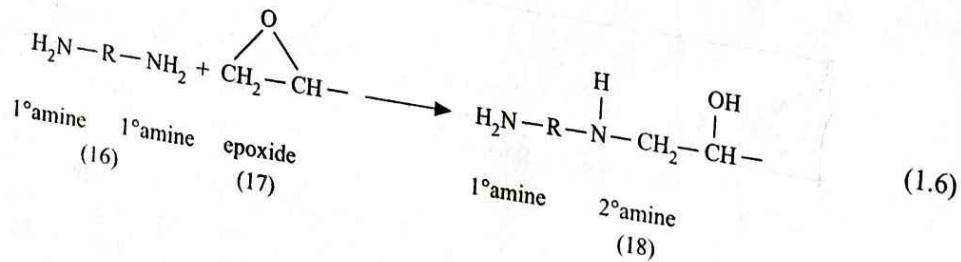
Figure 1.2 Linear, branched, and cross-linked polymers.

The structural units resulting from the reaction of monomers may in principle be linked together in any conceivable pattern. Bifunctional structural units can enter into two and only two linkages with other structural units. This means that the sequence of linkages between bifunctional units is necessarily linear. The resulting polymer is said to be linear. However, the reaction between polyfunctional molecules results in structural units that may be linked so as to form nonlinear structures. In some cases the side growth of each polymer chain may be terminated before the chain has a chance to link up with another chain. The resulting polymer molecules are said to be branched. In other cases, growing polymer chains become chemically linked to each other, resulting in a cross-linked system (Figure 1.2). The formation of a cross-linked polymer is exemplified by the reaction of epoxy polymers, which have been used traditionally as adhesives and coatings and, more recently, as the most common matrix in aerospace composite materials. Epoxies exist at ordinary temperatures as low-molecular-weight viscous liquids or prepolymers. The most widely used prepolymer is diglycidyl ether of bisphenol A (DGEBA), as shown below (15):

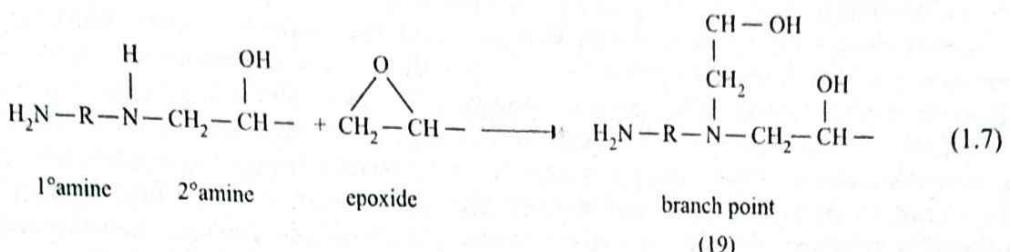


The transformation of this viscous liquid into a hard, cross-linked three-dimensional molecular network involves the reaction of the prepolymer with reagents such as amines or Lewis acids. This reaction is referred to as *curing*. The curing of epoxies with a primary amine such as hexamethylene-diamine involves the reaction of the amine with the epoxide. It proceeds essentially in two steps:

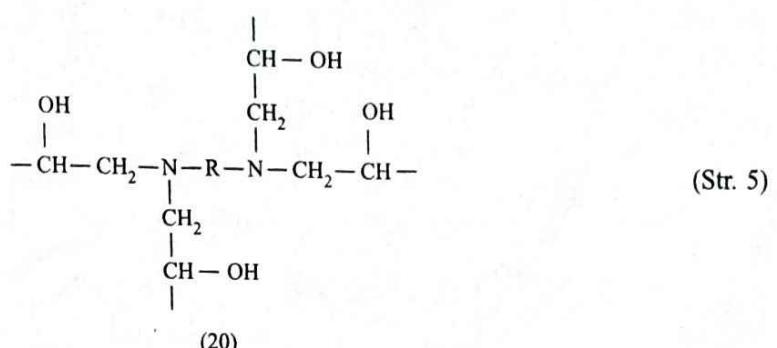
1. The attack of an epoxide group by the primary amine



2. The combination of the resulting secondary amine with a second epoxy group to form a branch point (19).

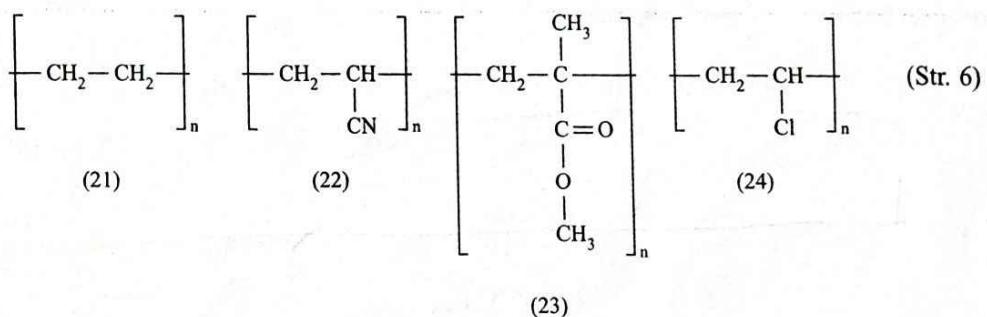


The presence of these branch points ultimately leads to a cross-linked infusible and insoluble polymer with structures such as (20).



In this reaction, the stoichiometric ratio requires one epoxy group per amine hydrogen. Consequently, an amine such as hexamethylenediamine has a functionality of 4. Recall, however, that in the reaction of hexamethylenediamine with adipic acid, the amine has a functionality of 2. In this reaction DGEBA is bifunctional since the hydroxyl groups generated in the reaction do not participate in the reaction. But when the curing of epoxies involves the use of a Lewis acid such as BF_3 , the functionality of each epoxy group is 2; that is, the functionality of DGEBA is 4. Thus the curing reactions of epoxies further illustrate the point made earlier that the functionality of a given molecule is defined for a specific reaction. By employing different reactants or varying the stoichiometry of reactants, different structures can be produced and, consequently, the properties of the final polymer can also be varied.

Polystyrene (2), polyethylene (21), polyacrylonitrile (22), poly(methyl methacrylate) (23), and poly(vinyl chloride) (24) are typical examples of linear polymers.



Substituent groups such as $-\text{CH}_3$, $-\text{O}-\overset{\text{O}}{\underset{\text{C}}{\text{C}}}-\text{CH}_3$, $-\text{Cl}$, and $-\text{CN}$ that are attached to the main chain of skeletal atoms are known as *pendant groups*. Their structure and chemical nature can confer unique properties on a polymer. For example, linear and branched polymers are usually soluble in some solvent at normal temperatures. But the presence of polar pendant groups can considerably reduce room temperature solubility. Since cross-linked polymers are chemically tied together and solubility essentially

Chapter 2

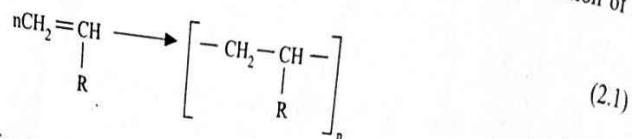
Polymerization Mechanisms

I. INTRODUCTION

As discussed in Chapter 1, under a scheme proposed by Carothers, polymers are classified as addition or condensation polymers depending on the type of polymerization reaction involved in their synthesis. This classification scheme, however, does not permit a complete differentiation between the two classes of polymers. A more complete but still oversimplified scheme that is still based on the different polymerization processes places polymers into three classes: condensation, addition, and ring-opening polymers. This scheme reflects the structures of the starting monomers. Probably the most general classification scheme is based on the polymerization mechanism involved in polymer synthesis. Under this scheme, polymerization processes are classified as step-reaction (condensation) or chain-reaction (addition) polymerization. In this chapter, we will discuss the different types of polymers based on the different polymerization mechanisms.

M. CHAIN-REACTION POLYMERIZATION

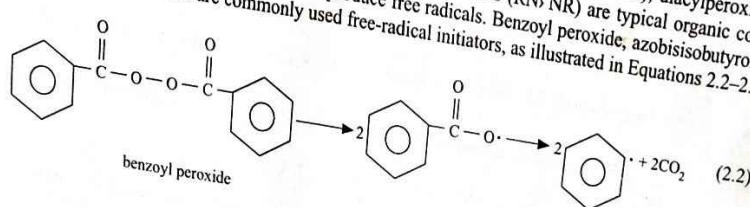
Chain-reaction polymerization, an important industrial method of polymer preparation, involves the addition of unsaturated molecules to a rapidly growing chain. The most common unsaturated compounds that undergo chain-reaction polymerization are olefins, as exemplified by the following reaction of a generalized vinyl monomer.



The growing polymer in chain-reaction polymerization is a free radical, and polymerization proceeds via chain mechanism. Chain-reaction polymerization is induced by the addition of free-radical-forming reagents or by ionic initiators. Like all chain reactions, it involves three fundamental steps: initiation, propagation, and termination. In addition, a fourth step called chain transfer may be involved.

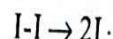
A. INITIATION

Initiation involves the acquisition of an active site by the monomer. This may occur spontaneously by the absorption of heat, light (ultraviolet), or high-energy irradiation. But most frequently, initiation of free-radical polymerization is brought about by the addition of small quantities of compounds called initiators. Typical initiators include peroxides, azo compounds, Lewis acids, and organometallic reagents. However, while initiators trigger initiation of the chain and exert an accelerating influence on polymerization rate, they are not exactly catalysts since they are changed chemically in the course of polymerization. An initiator is usually a weak organic compound that can be decomposed thermally or by irradiation to produce free radicals, which are molecules containing atoms with unpaired electrons. A variety of compounds decompose when heated to form free radicals. Dialkyl peroxides (ROOR), diacylperoxides (RCO-O-O-CO-R), hydroperoxides (ROOH), and azo compounds (RN_2NR) are typical organic compounds that can be decomposed thermally to produce free radicals. Benzoyl peroxide, azobisisobutyronitrile, and di-*t*-butylperoxide are commonly used free-radical initiators, as illustrated in Equations 2.2-2.4.

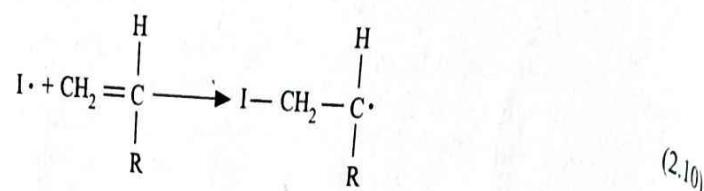


processes do not require stringent exclusion of atmospheric moisture, but can be inhibited by substances such as oxygen. Free radicals are inactivated by reaction with oxygen to form peroxides or hydroperoxides. For monomers such as styrene and methylmethacrylate that are susceptible to such initiation reactions are carried out in an oxygen-free atmosphere such as nitrogen. It must be emphasized also that organic peroxides, when subjected to shock or high temperature, can detonate. Therefore, C₁ in t rad pc ai compounds must be handled with caution.

The initiation of polymerization occurs in two successive steps. The first step involves the formation of radicals according to the processes discussed above. This may be represented broadly as:



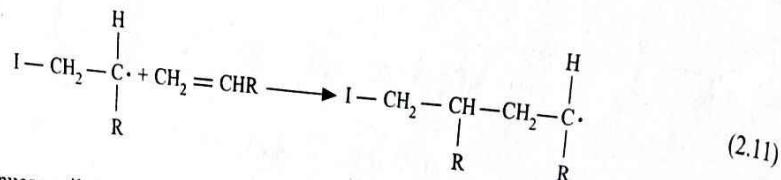
The second step is the addition of the initiator radical to a vinyl monomer molecule:



Initiator fragments have been shown by end-group analysis to become part of the growing chain. In commercial practice, 60 to 100% of all the free radicals generated do initiate polymerization.

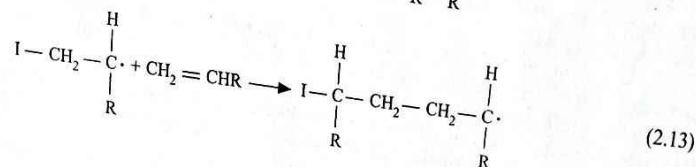
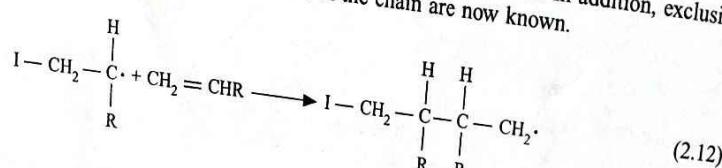
B. PROPAGATION

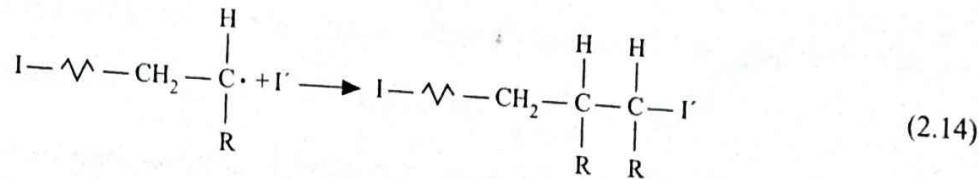
During propagation, the initiated monomer described above adds other monomers — usually thousands of monomer molecules — in rapid succession. This involves the addition of a free radical to the double bond of a monomer, with regeneration of another radical. The active center is thus continuously relocated at the end of the growing polymer chain (Equation 2.11).



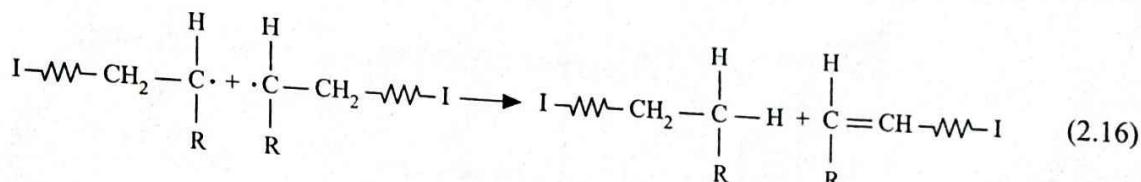
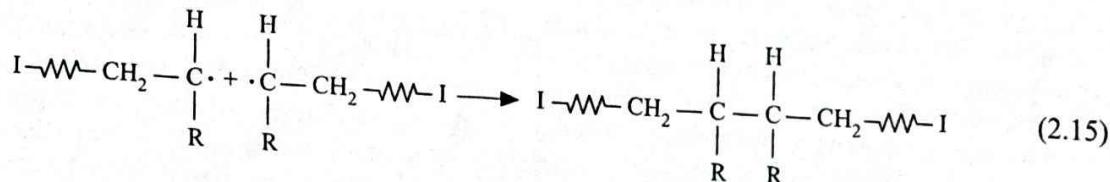
Propagation continues until the growing chain radical is deactivated by chain termination or transfer as discussed below.

The substituted carbon atom is regarded as the head and the unsubstituted carbon atom the tail of the vinyl monomer. There are, therefore, three possible ways for the propagation step to occur: head-to-tail (Equation 2.11), head-to-head (Equation 2.12), and tail-to-tail (Equation 2.13). A random distribution of these species along the molecular chain might be expected. It is found, however, that head-to-tail linkages in which the substituents occur on alternate carbon atoms predominate; only occasional interruptions of this arrangement by head-to-head and tail-to-tail linkages occur. In addition, exclusive head-to-head or tail-to-tail arrangements of monomers in the chain are now known.





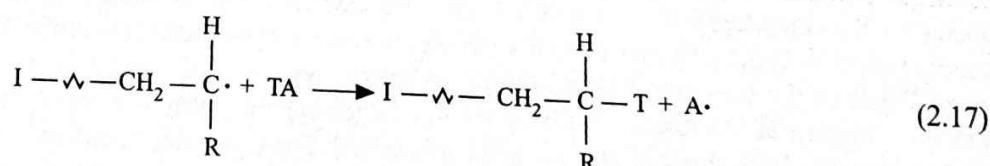
The termination reactions that are more important in polymer production are combination (or coupling) and disproportionation. In termination by combination, two growing polymer chains react with the mutual destruction of growth activity (Equation 2.15), while in disproportionation a labile atom (usually hydrogen) is transferred from one polymer radical to another (Equation 2.16).



Coupling reactions produce a single polymer, while disproportionation results in two polymers from the two reacting polymer chain radicals. The predominant termination reaction depends on the nature of the reacting monomer and the temperature. Since disproportionation requires energy for breaking of chemical bonds, it should become more pronounced at high reaction temperatures; combination of growing polymer radicals predominates at low temperatures.

D. CHAIN TRANSFER

Ideally, free-radical polymerization involves three basic steps: initiation, propagation, and termination, as discussed above. However, a fourth step, called chain transfer, is usually involved. In chain-transfer reactions, a growing polymer chain is deactivated or terminated by transferring its growth activity to a previously inactive species, as illustrated in Equation 2.17.



The species, TA, could be a monomer, polymer, solvent molecule, or other molecules deliberately or inadvertently introduced into the reaction mixture. Depending on its reactivity, the new radical, A·, may or may not initiate the growth of another polymer chain. If the reactivity of A· is comparable to that of the propagating chain radical, then a new chain may be initiated. If its reactivity toward a monomer is less than that of the propagating radical, then the overall reaction rate is retarded. If A· is unreactive toward the monomer, the entire reaction could be inhibited. Transfer reactions do not result in the creation or destruction of radicals; at any instant, the overall number of growing radicals remains unchanged. However, the occurrence of transfer reactions results in the reduction of the average polymer chain length, and in the case of transfer to a polymer it may result in branching.

Chapter 10

Polymer Reaction Engineering

I. INTRODUCTION

Several important differences exist between the industrial production of polymers and low-molecular-weight compounds:^{6,7}

- Generally, polymers of industrial interest have high molecular weights, usually in the range of 10^4 to 10^7 . Also, in contrast to simple compounds, the molecular weight of a polymer does not have a unique value but, rather, shows a definite distribution. The high molecular weight of polymers results in high solution or melt viscosities. For example, in solution polymerization of styrene, the viscosity can increase by over six orders of magnitude as the degree of conversion increases from zero to 60%.
- The formation of a large polymer molecule from small monomer results in a decrease in entropy. It follows therefore from elementary thermodynamic considerations that the driving force in the conversion process is the negative enthalpy gradient. This means, of course, that most polymerization reactions are exothermic. Consequently, heat removal is imperative in polymerization reactions — a problem that is accentuated by the high medium viscosity that leads to low heat transfer coefficients in stirred reactors.
- In industrial formulations, the steady-state concentration of chain carriers in chain and ionic polymerization is usually low. These polymerization reactions are therefore highly sensitive to impurities that could interfere with the chain carriers. Similarly, in step-growth polymerization, a high degree of conversion is required in order to obtain a product of high molecular weight (Chapters 6 and 7). It is therefore necessary to prevent extraneous reactions of reactants and also exclude interference of impurities like monofunctional compounds.
- The quality of a product from a low-molecular-weight compound can be usually improved by such processes as distillation, crystallization, etc. However, if the performance of a product from a polymerization process is inadequate, it is virtually impossible to upgrade its quality by subsequent processing.

Given these possible differences in the production processes between polymers and low-molecular-weight compounds, it is vitally important to choose the most suitable reactor and operating conditions to obtain the required polymer properties from a polymerization reaction. This demands a detailed knowledge of the phenomena that occur in the reactor. This, in turn, requires an accurate model of the polymerization kinetics, the mass and heat transfer characteristics of the polymerization process. Our approach in this chapter is largely qualitative, and our treatment involves a discussion of the various polymerization processes, followed by a brief review of polymerization reactors. It is hoped that this approach will enable the reader to gain insight into the complex problem of selecting a reactor for a specific polymerization reaction.

II. POLYMERIZATION PROCESSES

Polymerization processes may be conveniently classified as homogeneous or heterogeneous. In homogeneous polymerization, as the name suggests, all the reactants, including monomers, initiators, and solvents, are mutually soluble and compatible with the resulting polymer. On the other hand, in heterogeneous systems, the catalyst, the monomer, and the polymer product are mutually insoluble. Homogeneous polymerization comprises bulk (mass) or solution systems while heterogeneous polymerization reactions may be categorized as bulk, solution, suspension precipitation, emulsion, gas phase, and interfacial polymerization.

A. HOMOGENEOUS SYSTEMS

1. Bulk (Mass) Polymerization

In bulk polymerization the reaction mixture consists essentially of the monomer, a soluble initiator and possibly modifiers. In the case of

*and in case of chain
homogeneous bulk*

much higher exothermic nature of chain-growth polymerization, coupled with the difficulty of mixing the reaction mixture due to high viscosities, leads to much lower heat transfer efficiencies in chain growth polymerization than in step-growth polymerization.

Example 10.2: Purified styrene monomer is charged along with initiators into an aluminum prepolymerization vessel. Polymerization is carried out at about 90°C to 30% conversion. The resulting syrup is then poured into molds where the reaction is completed. Comment on the probable molecular weight distribution of the product polymer.

Solution: This process is essentially batch polymerization of styrene. Most of the conversion takes place in the finishing trays. Because of the relatively poor heat transfer in these trays, the polymerizing mass may reach high temperatures at some spots. Consequently, the resulting polystyrene will have a broad molecular weight distribution, with very high molecular weights being produced at low temperatures and lower molecular weights produced at high temperature.

B. Solution Polymerization

In solution polymerization, the monomer, initiator, and resulting polymer are all soluble in the solvent. Solution polymerization may involve a simple process in which a monomer, catalyst, and solvent are stirred together to form a solution that reacts without the need for heating or cooling or any special handling. On the other hand, elaborate equipment may be required. For example, a synthetic rubber process using a coordination catalyst requires rigorous exclusion of air (to less than 10 ppm); moisture, carbon dioxide; and other catalyst deactivators from the monomer, solvent, and any other ingredient with which the catalyst will come in contact before the reaction. In addition, exclusion of air prevents the tendency to form dangerous peroxides. To avoid product contamination and discoloration, materials of construction also need to be selected with the greatest care.

Polymerization is performed in solution either batchwise or continuously. Batch reaction takes place in a variety of ways. The batch may be mixed and held at a constant temperature while running for a given time, or for a time dictated by tests made during the progress of the run. Alternatively, termination is dictated by a predetermined decrease in pressures following monomer consumption. A continuous reaction train, on the other hand, consists of a number of reactors, usually up to about ten, with the earlier ones overflowing into the next and the later ones on level control, with transfer from one to the next by pump.

As the reaction progresses, solution polymerization generally involves a pronounced increase in viscosity and evolution of heat. The viscosity increase demands higher power and stronger design for pumps and agitators. The reactor design depends largely on how the heat evolved is dissipated. Reactors in solution polymerization service use jackets; internal or external coils; evaporative cooling with or without compression of the vapor or simple reflux-cooling facilities, a pumped recirculation loop through external heat exchanger; and combinations of these. A typical reactor has agitation, cooling, and heating facilities; relief, temperature level, and pressure connections; and, frequently, cleanout connections in addition to inlet and outlet fittings.

Solution polymerization has certain advantages over bulk, emulsion, and suspension polymerization techniques. The catalyst is not coated by polymer so that its efficiency is sustained and removal of catalyst residues from the polymer, when required, is simplified. Solution polymerization is one way of reducing the heat transfer problems encountered in bulk polymerization. The solvent acts as an inert diluent, increasing overall heat capacity without contributing to heat generation. By conducting the polymerization at the reflux temperature of the reaction mass, the heat of polymerization can be conveniently and efficiently removed. Furthermore, relative to bulk polymerization, mixing is facilitated because the presence of the solvent reduces the rate of increase of reaction medium viscosity as the reaction progresses.

Solution polymerization, however, has a number of drawbacks. The solubility of polymers is generally limited, particularly at higher molecular weights. Lower solubility requires that vessels be larger for a given production capacity. The use of an inert solvent not only lowers the yield per reactor volume but also limits the reaction rate and average chain length since these quantities are proportional to monomer concentration. Another disadvantage of solution polymerization is the necessity of selecting an inert solvent to eliminate the possibility of chain transfer to the solvent. The solvent frequently presents

hazards of toxicity, fire, explosion, corrosion, and odor problems not associated with the product itself. Also, solvent handling and recovery and separation of the polymer involve additional costs, and removal of unreacted monomer can be difficult. Complete removal of the solvent is difficult in some cases. With certain monomers (e.g., acrylates) solution polymerization leads to a relatively low reaction rate and low-molecular-weight polymers as compared with aqueous emulsion or suspension polymerization. The problem of cleaning equipment and disposal of dirty solvent constitutes another disadvantage of solution polymerization.

Solution polymerization is of limited commercial utility in free-radical polymerization but finds ready applications when the end use of the polymer requires a solution, as in certain adhesives and coating processes [i.e., poly(vinyl acetate) to be converted to poly(vinyl alcohol) and some acrylic ester finishes]. Solution polymerization is used widely in ionic and coordination polymerization. High-density polyethylene, polybutadiene, and butyl rubber are produced this way. Table 10.2 shows the diversity of polymers produced by solution polymerization, while Figure 10.2 is the flow diagram for the solution polymerization of vinyl acetate.

C. HETEROGENEOUS POLYMERIZATION

1. Suspension Polymerization

Suspension polymerization generally involves the dispersion of the monomer, mainly as a liquid in small droplets, into an agitated stabilizing medium usually consisting of water containing small amounts of suspension and dispersion agents. The catalyst or initiator is dissolved in the monomer if the monomer is a liquid or included in the reaction medium if a gaseous monomer is used. The ratio of monomer to dispersing medium ranges from 10 to 40% suspension of monomer or total solids content of polymer at the finish of polymerization. When polymerization is completed, the polymer suspension is sent to a blowdown tank or stripper where any remaining monomer is removed, using a vacuum or antifoaming agent if necessary. Several stripped batches are transferred and blended in a hold tank. The slurry mixture is finally pumped to a continuous basket-type centrifuge or vibrating screen where the polymer is filtered, washed, and dewatered. The wet product, which may still contain as much as 30% water or solvent, is dried in a current of warm air (66 to 149°C) in a dryer. It is then placed in bulk storage or transferred to a hopper for bagging as powdered resin or put through an extruder for forming into a granular pellet product. Figure 10.3, which shows a flow sheet of the suspension polymerization of methyl methacrylate, is typical of many suspension polymerization processes for the production of thermoplastic resins.

For the monomer to be dispersible in the suspension system, it must be immiscible or fairly insoluble in the reaction medium. In some instances, partially polymerized monomers or prepolymers are used to decrease the solubility and also increase the particle size of the monomer. The initiators employed in the polymerization reaction are mainly of the peroxide type and, in some cases, are azo and ionic compounds. Examples include benzoyl, diacetyl, lauroyl, and *t*-butyl-peroxides. Azo-bis-isobutyronitrile (AIBN) is one of the most frequently used azo initiators, while aluminum and antimony alkyls, titanium chloride, and chromium oxides are typical ionic initiators. The amount of catalyst used depends on the reactivity of the monomer and the degree of polymerization, varying from 0.1 to 0.5% of the weight of the monomer.

Apart from the monomer itself, the most important ingredient in suspension polymerization is the suspension agent. Even though it is used in relatively small amounts (0.01 to 0.50% weight of monomer), it is vital to the successful control of the polymerization process and the uniformity of the product obtained. The major problem in suspension polymerization is in the formation and the maintenance of the stability of the thermodynamically unstable droplets as they are slowly transformed from a highly mobile immiscible liquid, through the viscous, sticky stage to the final solid beads (rigid granules) without their coalescence or agglomeration into a conglomerate mass. During the transformation of the liquid monomer droplet to the solid resin, the viscous or sticky phase first appears when 10 to 20% conversion has occurred. This phase persists for up to 75 to 80% conversion before the particles take on a nonsticky solid appearance. The tendency for agglomeration of the particles, which is particularly critical at the stage when the particles become sticky, is prevented by proper agitation and the use of suspending agents. The stabilizing agents are employed in two ways. (1) Surface-acting agents (surfactants) such as fatty acids and some inorganic salt such as magnesium and calcium carbonates, calcium phosphate, titanium and aluminum oxides reduce the surface tension between water and the monomer droplets, thus providing greater stability for this interface. They also reduce the surface viscosity of the

The use of an external circulating loop and exchanger requires that a portion of the reaction mass is pumped through an external heat exchanger and cooled and returned to the reactor. In suspension polymerization, a controlled degree of agitation is imperative to prevent agglomeration and maintain the desired polymer particle size. It is difficult to design the equipment and the recirculating loop to avoid zones of too little agitation, where the coalescence of monomer droplets occurs. When the reaction slurry is pumped through an external loop, the pump may impose an order-of-magnitude increase in the shear rate, thereby forcing an agglomerating polymer particles as they pass through a sticky phase of polymerization. Also, some polymer buildup is inevitable and an external circulating cooling loop will present cleaning problems.

2. Emulsion Polymerization

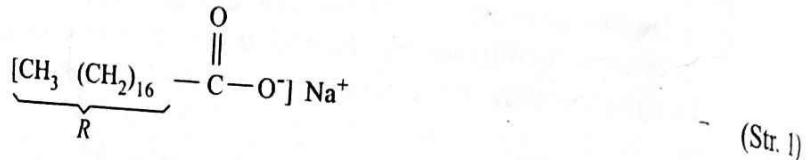
Emulsion polymerization was developed in the U.S. during World War II for the manufacture of GR rubber (Government-Rubber-Styrene) or SBR (styrene-butadiene rubber) when the Japanese cut off the supply of rubber from the East. Emulsion polymerization is now widely used commercially for the production of a large variety of polymers. All polymers made by this process are addition polymers rather than condensation polymers and require free-radical initiators. In general, an emulsion polymerization system would consist of the following ingredients: monomer(s), dispersing medium, emulsifying agent, water-soluble initiator, and, possibly, a transfer agent. Water serves as the dispersing medium in which the various components are suspended by the emulsifying agent. The water also acts as a heat transfer medium. Monomers such as styrene, acrylates, methacrylates, vinyl chloride, butadiene, and chloroprene used in emulsion polymerization show only a slight solubility in water.

Reactors for the emulsion polymerization process vary in size from 1000 to 4000 gal depending upon production requirements. Reactors may be glass lined or made of stainless steel. Glass-lined reactors are preferred for the production of acrylic polymer emulsions, while stainless steel is usually preferred for the manufacture of poly(vinyl acetate) because it can be cleaned easily with a boiling solution of dilute caustic. Both types of reactors have been employed in the production of butadiene-styrene copolymers and poly(vinyl chloride). Reactors are necessarily jacketed for heat control purposes. In processes [e.g., poly(vinyl acetate) manufacture] where monomer, catalyst, and surfactant are added to the reactor incrementally and the available jacket heat-transfer area is not initially available for cooling, supplemental cooling is both necessary and attractive. This involves the use of reflux cooling. Here, the heat of polymerization vaporizes unreacted monomer, and the monomer vapor is condensed in a reflux condenser and returned to the reactor. In this case, however, the foaming characteristics of the latex must be determined first since a stable foam carried into the reflux condenser will foul the exchanger surface. Reactors must also be rated to withstand a minimum internal pressure ranging from 50 psi for acrylic, methacrylic and acrylic-styrene vinyl acetate and its copolymers to at least 300 psi for vinyl chloride homopolymers and copolymers. Figure 10.4 shows a flow sheet for a typical emulsion polymerization plant.

In order to understand the quantitative relations governing emulsion polymerization kinetics, it is necessary to give a qualitative description of the process.

a. Distribution of Components

A typical recipe for emulsion polymerization in parts by weight consists of 180 parts of water, 100 parts of monomer, 5 parts of fatty acid soap (emulsifying agent), and 0.5 parts of potassium persulfate (water-soluble initiator). The question, of course, is how these components are distributed within the system. By definition, soaps are sodium or potassium salts of organic acids, for example, sodium stearate:



When a small amount of soap is added to water, the soap ionizes and the ions move around freely. The soap anion consists of a long oil-soluble portion (R) terminated at one end by the water-soluble portion.



c. Kinetics of Emulsion Polymerization

A number of questions need to be resolved from the qualitative description of emulsion polymerization given in the previous section. For example, it is necessary to consider whether the diffusion of monomers to the polymer particles is high enough to sustain polymerization given the low solubility of monomer in the aqueous phase. It is also important to know the average radical concentration in a polymer particle. Also, the validity of the assumption that only the monomer-polymer particles capture the radicals generated by the initiator needs to be established convincingly. The answers to these questions were provided by Smith and Ewart³ and this forms the basis for the quantitative treatment of the steady-state portion of emulsion polymerization.

(1) Rate of Emulsion Polymerization

In emulsion polymerization, the rate of generation of free radicals is about $10^{13}/\text{m-s}$ while the number of monomer-polymer particles for typical recipes, N , is in the range 10^{13} to 10^{15} particles/ml of the aqueous phase. Consequently, if all the initiator radicals are captured by the monomer-polymer particles, each particle will acquire, at the most, a radical every 1 to 100 s. It can be shown that if a particle contains two radicals, mutual annihilation of radical activity will occur within a time span of the order

Average lifetime of a radical from generation to its capture by a polymer particle is

$$\frac{\text{concentration of radicals}}{\text{rate of radical generation}} = \frac{10^8 \text{ radicals cm}^{-3}}{10^{13} \text{ radicals cm}^{-3} \text{ s}^{-1}} = 10^{-5} \text{ s}$$

d. Degree of Polymerization

Whenever a primary radical enters an inactive polymer particle, polymerization occurs as it would in normal homogeneous polymerization. In this case the rate of polymerization is given by

$$r_p = k_p [M] \quad (10.2)$$

where k_p is the propagation rate constant. The rate of capture of primary radicals is given by

$$r_c = \frac{r_i}{N} \quad (10.3)$$

where r_i is the rate of generation of primary radicals (in radicals per milliliter per second). From our discussion in the previous section, the growth of a polymer is terminated immediately following the entry of another radical. Therefore the rate of termination should be essentially equal to the rate of capture of primary radicals. The degree of polymerization, in the absence of transfer, should then be the ratio of the rate of polymer growth to the rate of capture of primary radicals.

$$\overline{X}_n = \frac{r_p}{r_c} = \frac{k_p[M]}{r_i/N} = \frac{k_p N[M]}{r_i} \quad (10.4)$$

Both the degree of polymerization and the rate of polymerization show a direct variation with the number of polymer particles N . However, unlike the rate of polymerization, the degree of polymerization varies indirectly with the rate of generation of primary radicals. This is as should be expected intuitively since the greater the rate of radical generation, the greater the frequency of alternation between polymer particle growth and dormancy and therefore the lower the chain length.

e. The Number of Particles

Equations 10.1 and 10.4 show that the number of polymer particles is crucial in determining both the rate and degree of polymerization. The mechanism of polymer particle formation indicates clearly that the number of polymer particles will depend on the emulsifier, its initial concentration (which determines the number of micelles), and the rate of generation of primary radicals. Smith and Ewart³ have shown that

$$N = k \left(\frac{r_i}{\mu_s} \right)^{0.4} (a_s [E])^{0.6} \quad (10.5)$$

where k is a constant with a value between 0.4 and 0.53; μ_s is the rate of increase in volume of a polymer particle; a_s is the interfacial area occupied by an emulsifier molecule; and $[E]$ is the soap or emulsifier concentration. Note that all the units are in cgs. Equations 10.1, 10.4, and 10.5 establish the quantitative

Unit Operations in Polymer Processing

I. INTRODUCTION

Polymer processing may be divided into two broad areas. The first is the processing of the polymer into some form such as pellets or powder. The second type describes the process of converting polymeric materials into useful articles of desired shapes. Our discussion here is restricted to the second method of polymer processing. The choice of a polymer material for a particular application is often difficult given the large number of polymer families and even larger number of individual polymers within each family. However, with a more accurate and complete specification of end-use requirements and material properties the choice becomes relatively easier. The problem is then generally reduced to the selection of a material with all the essential properties in addition to desirable properties and low unit cost. But then there is usually more than one processing technique for producing a desired item from polymeric materials or, indeed, a given polymer. For example, hollow plastic articles like bottles or toys can be fabricated from a number of materials by blow molding, thermoforming, and rotational molding. The choice of a particular processing technique is determined by part design, choice of material, production requirements, and, ultimately, cost-performance considerations.

The number of polymer processing techniques increases with each passing year as newer methods are invented and older ones modified. This chapter is limited to the most common polymer processing unit operations, but only extrusion and injection molding, the two predominant polymer processing methods, are treated in fairly great detail. Our discussion is restricted to general process descriptions only, with emphasis on the relation between process operating conditions and final product quality. Table 11.1 summarizes some polymer processing operations, their characteristics, and typical applications.

II. EXTRUSION¹

Extrusion is a processing technique for converting thermoplastic materials in powdered or granular form into a continuous uniform melt, which is shaped into items of uniform cross-sectional area by forcing it through a die. As shown in Table 11.1, extrusion end products include pipes for water, gas, drains, and vents; tubing for garden hose, automobiles, control cable housings, soda straws; profiles for construction, automobile, and appliance industries; film for packaging; insulated wire for homes, automobiles, appliances, telephones and electric power distribution; filaments for brush bristles, rope and twine, fishing line, tennis rackets; parisons for blow molding. Extrusion is perhaps the most important plastics processing method today.

A simplified sketch of the extrusion line is shown in Figure 11.1. It consists of an extruder into which is poured the polymer as granules or pellets and where it is melted and pumped through the die of desired shape. The molten polymer then enters a sizing and cooling trough or rolls where the correct size and shape are developed. From the trough, the product enters the motor-driven, rubber-covered rolls (puller), which essentially pull the molten resin from the die through the sizer into the cutter or coiler where final product handling takes place.

A. THE EXTRUDER

Figure 11.2 is a schematic representation of the various parts of an extruder. It consists essentially of the barrel, which runs from the hopper (through which the polymer is fed into the barrel at the rear) to the die at the front end of the extruder. The screw, which is the moving part of the extruder is designed to pick up, mix, compress, and move the polymer as it changes from solid granules to a viscous melt. The screw turns in the barrel with power supplied by a motor operating through a gear reducer.

The heart of the extruder is the rotating screw (Figure 11.3). The thread of an extruder screw is called a flight, and the axial distance from the edge of one flight to the corresponding edge on the next flight is called the pitch. The pitch is a measure of the coarseness of the thread and is related to the helix

B. EXTRUSION PROCESSES

The die shapes the polymer extrudate into the desired article. There are a large number of extrusion processes, the simplest of which is compounding. In one variation of extrusion, the die has a series of holes and as the polymer exudes from these holes it is cooled and cut into pellets. In pipe extrusion, the extrudate exiting the die is vacuum-sized and quenched in a water trough. Polymer melts, being viscoelastic, recover the stored elastic energy as they emerge from the die — a process known as die swell. In pipe extrusion, die swell must be controlled to ensure that the pipe dimensions meet standard codes. Profile extrusion is similar to pipe extrusion. However, unlike pipes whose shape is round, hollow, and uniform, the shapes of profiles depend on the end product, which usually is the raw material for downstream processing.

Fibers of various gauges and lengths are obtained in fiber extrusion. These can range from monofilament such as fishing lines to hundreds of continuous filaments extruded from the same die and drawn to hair-sized thickness. The continuous filaments may be crimped for added bulk or made into staple. Almost all electrical wire and cable insulation is currently done by covering the wires or cables with one or more layers of thermoplastic insulation. These take different forms: wire strands may be covered with several layers by successive insulation; multiple preinsulated wires may be covered to form a single cable; or several bare wires may be drawn through the die simultaneously and covered with insulation forming a ribbon cable. In coextrusion, two or more different materials or the same material with two different colors are extruded through the same die so that one material flows over and coats the other. Coextrusion is used to achieve different objectives: a solid cap may be extruded over a foamed core for overall weight reduction or to obtain insulation in addition to a serviceable outer surface; for materials with surfaces sensitive to color, a virgin cap may be extruded over reground, or several different materials may be coextruded so that each material contributes a derived property to the end product.

III. INJECTION MOLDING²⁻⁴

Injection molding is one of the processing techniques for converting thermoplastics, and recently, thermosetting materials, from the pellet or powder form into a variety of useful products. Forks, spoons, computer, television, and radio cabinets, to mention just a few, are some of these products. Simply, injection molding consists of heating the pellet or powder until it melts. The melt is then injected into and held in a cooled mold under pressure until the material solidifies. The mold opens and the product is ejected. The injection molding machine must, therefore, perform essentially three functions:

1. Melt the plastic so that it can flow under pressure.
2. Inject the molten material into the mold.
3. Hold the melt in the cold mold while it solidifies and then eject the solid plastic.

These functions must be performed automatically under conditions that ideally should result in a high quality and cost-effective part. Injection molding machines have two principal components to perform the cyclical steps in the injection molding process. These are the injection unit and the clamp unit (Figure 11.4). We now describe the operation of the various units of the injection molding machine that perform these functions.

A. THE INJECTION UNIT

The injection unit essentially has two functions: melt the pellet or powder and then inject the melt into the mold. It consists of the hopper, a device for feeding process material; a heated cylinder or chamber where the material is melted; and a device for injecting the molten material into the mold. In the early days when the amount of processed material was relatively small, the two functions of melting and injecting the polymer were accomplished by using a simple plunger machine (Figure 11.5). In this system, a measured volume of the plastic material is delivered into the heated cylinder from the hopper while the ram is retracted. At the beginning of the injection cycle, the plunger pushes forward and forces the material through the heated cylinder compacting it tightly behind and over the centrally located spreader or torpedo. The material is melted by heat convection and conduction. The sustained forward motion of the plunger forces the melt through the nozzle of the cylinder into the mold.

In the plunger-type machine, material flow in the cylinder is essentially laminar. Consequently there is hardly any mixing in this system and, as such, large temperature gradients exist in the melt, and cold

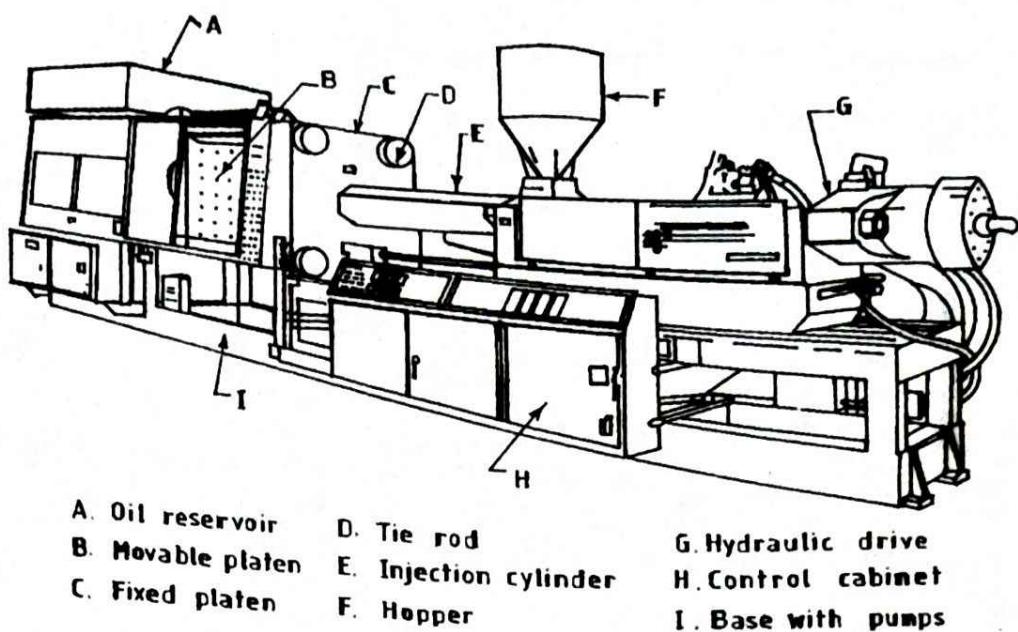
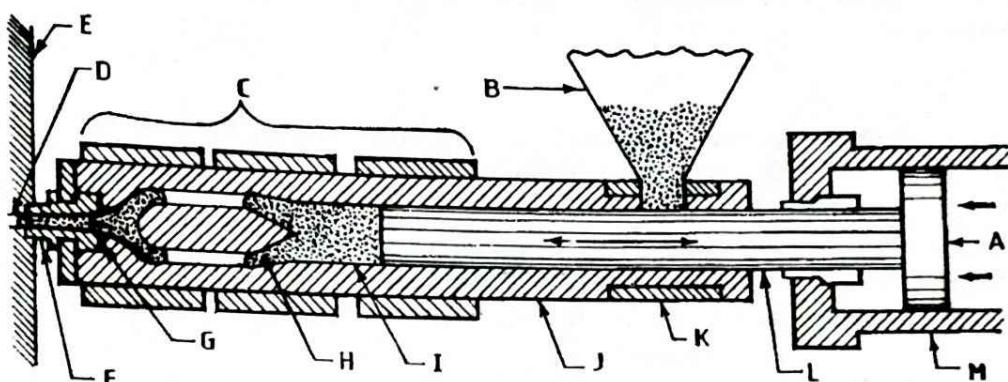


Figure 11.4 Major parts of a typical injection-molding machine. (From Weir, C.L., *Introduction to Molding*, Society of Plastics Engineers, CT, 1975. With permission.)



A. Ram pressure F. Nozzle I. Injection chamber
 B. Hopper G. Back-pressure plate J. Heating cylinder
 C. Heater bands H. Torpedo K. Cooling zone
 D. Sprue L. Plunger M. Hydraulic cylinder
 E. Mold

Figure 11.5 Schematic diagram of a plunger-type injection molding machine. (From Weir, C.L., *Introduction to Molding*, Society of Plastics Engineers, CT, 1975. With permission.)

blending is thus problematic. Also, as a result of the friction between the cold resin pellets in the neighborhood of the hopper and the barrel walls, a considerable loss of pressure, up to 80% of the total ram pressure, occurs. This necessitates long injection time. As indicated above, the resin is melted by heat conduction from the walls of the cylinder and the resin itself. Since plastics are poor heat conductors, high cylinder temperatures are required to achieve fast resin plasticization. This can result in the degradation of the material. To avoid such possible material deterioration, the heating of the cylinder is limited, and this also limits the plasticizing capacity of plunger-type injection machines.

Today, the plunger has been replaced almost totally by the plasticating screw. As described in Section II, the screw consists basically of three sections: the feed, the transition zone, and the metering section. Melting normally starts halfway down the length of the screw at which point the depth of the screw flights decreases initiating the compression of the melt. This marks the beginning of the transition zone, which terminates at that metering section — the point where the depth of the flights is minimum. A

$$Q = \frac{50 \times 0.6}{0.0004 \times 0.8 (500 - 72)}$$

= 219 lb/h

$$Q = \frac{50 \times 0.6}{0.0004 \times 0.4 (500 - 72)}$$

= 438 lb/h

Example 11.4: Explain the following observations:

- a. It is generally necessary to mold plastics at the lowest possible melt temperature.
- b. If two screws with different diameters but with the same L/D ratio are operated under identical conditions, the polymer material has a longer residence time in the larger diameter screw machine even though the machine output is the same. However, it is preferable sometimes to operate machines with the larger diameter screws.

Solution:

- a. From Problem 11.3 it is obvious that raising the material processing temperature lowers output. Also, it increases the cycle time because the mold cooling time is longer. Therefore, to maximize output and increase overall productivity, it is best to mold at the lowest possible melt temperature.
- b. Productivity or machine output is the primary concern of injection molders. However, high screw speeds and hence high productivity can result in material degradation and poor product quality. Consequently, it is generally prudent to operate machines at reasonably slower speeds. But because of the inverse relation between torque and screw speed (Equation 11.1) for the same power input drive, the magnitude of the torque developed by the smaller diameter screw will be higher than that of the larger diameter screw and may be high enough to shear the screw. Therefore, even when machine output is the same, larger diameter screws may be preferable to smaller ones to prevent possible screw damage.

C. THE HEATING CYLINDER

The heating or plasticizing cylinder of the injection molding machine is the primary element of the machine. It is here that the polymer material is softened or conditioned for injection into the mold cavity where it is shaped. The temperature and pressure of the melt as it leaves the cylinder nozzle into the mold cavity are two important variables that determine product quality. Cylinders are generally rated on the basis of their plasticizing capacity which is the rate at which the given cylinder can condition a given polymer material into a state suitable for injection. As may be expected, for a given cylinder, this varies with the particular plastic material being processed because the molding (softening or melting) — temperature, specific heat, thermal conductivity, and specific gravity — all of which contribute to the complex heat generation and transfer processes which occur during processing — differ for various materials. Consequently, the plasticizing capacity of a machine is rated conventionally on the basis of one material — general purpose polystyrene, which is taken as the standard. The machine capacity with respect to other materials is then related to this standard material using the relative specific gravities of the two materials.

Table 11.2 gives the specific gravities of some plastic materials, while Table 11.3 shows the appropriate cylinder heater inputs and power requirements of typical machine sizes.

Solution: The machine output or plasticizing capacity, Q , is the ratio of the shot weight W to the cycle time t_c .

$$Q = \frac{W(\text{oz})}{t_c(\text{s})}$$

$$\frac{W(\text{oz})}{t_c(\text{s})} \frac{1 \text{ lb}}{16 \text{ oz}} \frac{3600 \text{ s}}{1 \text{ h}}$$

$$= 225 \frac{W}{t_c} \frac{\text{lb}}{\text{h}}$$

$$Q = \frac{225 \times 100 \text{ oz}}{30} = 750 \text{ lb/h}$$

Residence or contact time in the heating cylinder, t_c , is given by the inventory weight, I_w , divided by the machine output Q .

$$t_c = \frac{I_w}{Q}$$

$$t_c(\text{s}) = 225 \left(\frac{I_w \text{ oz}}{Q \text{ lb/h}} \right) = \frac{225 \times 50}{750} = 15 \text{ s}$$

$$\begin{aligned} \text{Plasticizing capacity for LDPE} &= \frac{0.93}{1.05} \times 750 \\ &= 657 \text{ lb/h} \end{aligned}$$

D. THE CLAMP UNIT

The clamp unit or press end of the injection molding machine performs three functions: opens and closes the mold at appropriate times during the molding cycle; ejects the molded part; and provides enough pressure to prevent the mold from opening due to the pressure developed in the mold cavity as it is filled with the melt by the injection unit. Injection pressures in the plasticating cylinder can range from 15,000 to 20,000 psi in a given system. As a result of possible pressure drops in the cylinder and the nozzle, the effective pressure within the mold cavity may be reduced to 25 to 50% of this value. Consequently, the force needed to resist the premature opening of the mold and obtain an acceptable part can be quite large. For example, assuming a 50% pressure drop and using the upper possible pressure in the cylinder stated above, the melt pressure in the mold cavity becomes 10,000 psi. This translates into a clamp force of 5 tons/in² of the projected area of the part. However, as a result of greater degree of homogenization achievable in screw-type machines, the clamp tonnage required in these machines is generally less than in plunger-type machines.

The halves of the mold are attached to the platens, one of which is stationary and one of which moves as the clamp mechanism is opened or closed. Molds are generally designed so that the ejection side of the mold (mold core) is on the movable platen and the injection side of the mold (mold cavity) is on the stationary platen, which must provide an entry for the nozzle of the plasticizing chambers. When the mold opens, the movable platen must be moved sufficiently for the part to be ejected. Shrinkage usually accompanies part solidification and this results in the part sticking to the core as the mold opens. Consequently, the movable platen is provided with an ejector or knockout system to eject the part. The ejector usually consists of a hydraulically actuated ejector plate mounted off the back face of the movable platen. The ejector system causes the knockout plate to change its location relative to the rest of the mold. The ejector pins attached to this plate push against the molded part and eject it from the mold. The force required to eject the part is usually less than 1% of the nominal clamp force; its magnitude depends on the part geometry, material, and packing pressure.

E. AUXILIARY SYSTEMS

The operation of the injection and clamp units and other components of the injection molding machine (opening and closing of the mold and melting and injection of the polymer material) requires power, which is supplied by an electric motor. The orderly delivery of this power depends on auxiliary systems: the hydraulic and control systems. The hydraulic system, the muscle for most machines, transmits and controls the power from the electric motor to the various parts of the machine. Machine functions are regulated by a careful control of the flow, direction, and pressure of the hydraulic fluid. The elements of the hydraulic system for most injection molding machines are essentially the same: fluid reservoir, pumps, valves, cylinders, hydraulic motors, and lines (Figure 11.8).

The pump driven by the electric motor draws oil from the reservoir and delivers it to the cylinder through the suction filter. The restriction of oil flow by the control valve and/or the resistance of the cylinder compress the oil and lead to pressure buildup. A pressure buildup of appropriate amount drives the hydraulic cylinder, and if this pressure reaches that set for the relief valve, the valve opens and excess fluid is bypassed to the reservoir. The opening of the relief valve decompresses the oil, converting the excess pressure energy into heat, which raises the oil temperature. The oil is cooled by passing it through a heat exchanger.

The injection molding operation involves a sequence of carefully ordered events, e.g., precise heating and cooling of the mold, appropriate timing of injection pressures and cycles. The control system is the nerve center responsible for the orderly execution of the various machine functions. Over the years, the control system has developed from a collection of relays that perform logic, plug-in timers for timing functions, and plug-in temperature controllers for cylinder temperature regulation to solid-state circuitry for the control of these functions to the current microcomputer control, which has greatly enhanced process control.

F. THE INJECTION MOLD

The injection mold is a series of steel plates, which when assembled produces the cavity that defines the shape of the molded part. Conventional molds consist of the mold frame, components, runners, cooling channels, and ejector system. The mold frame is a collection of steel plates that contain mold components and runners, cooling and ejection systems. Components are parts inserted into either bored holes or cutout pockets in the mold frame. The polymer melt enters into the mold cavity or cavities through the runners, which are passages cut into the mold frame. The hot polymer material in the mold

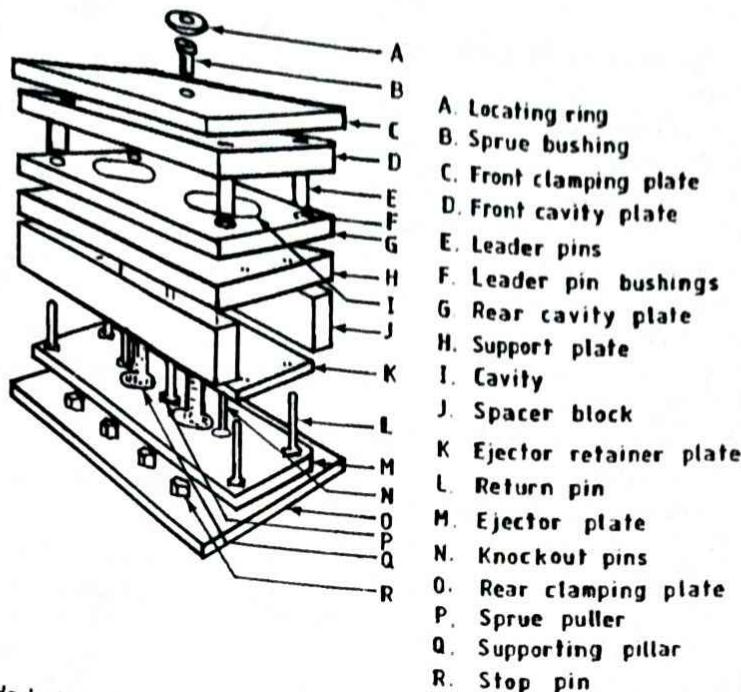


Figure 11.9 Exploded view of a six-plate mold base. (From Weir, C.L., *Introduction to Molding*, Society of Plastics Engineers, CT, 1975. With permission.)

is cooled by a coolant, usually water, which circulates through the cooling channels drilled at strategic locations into the mold frame and components for proper mold temperature control. When the material has cooled (hardened) sufficiently, the mold opens and the hardened part is removed from the mold by the ejector system.

Since the quality of the molded part depends to a large extent on the mold, it is essential to expand on the functions of the various parts of the mold. Details of mold components are shown in Figure 11.9. The register or retainer ring, which is fitted into the stationary platen, aligns the mold with the cylinder nozzle. Sometimes, the retainer ring, as the name suggests, also acts as the retainer of the sprue bushing within the mold. The sprue is the pathway through which the molten polymer material is introduced as small as practical since large diameter sprues have been known to require longer cooling time and consequently prolong cycle time beyond what is usually necessary for part thickness. In some newer mold designs, the sprue is completely eliminated.

The front clamp plate, which houses the retaining ring and sprue bushings, is used to support the stationary half of the mold, including the front cavity plate. The cavity (cavities) of the part to be molded is contained in the cavity plate in either of two ways. In one case the cavity is drilled directly into the steel plate, and in the other the cavity plate provides sockets for the insertion of cavities that have been constructed separately. The rear cavity plate, mounted on the rear support plate, contains the core section of the molded part or second half of the mold cavity. The leader (guide) pins and guide pin bushings are housed in the front cavity and rear cavity plates, respectively. The passage of the guide pins through the bushings ensures that the plates are properly aligned during closing of the mold. The knockout and reset pins are mounted on a series of plates that compose the ejector plate. At appropriate times during the molding cycle, these pins pass through holes in the cavity and cavity retainer plates and make contact with either the molded part to effect its ejection or the stationary cavity plate to initiate the movement of the pin plate back in readiness for the next injection shot. The movable half of the mold is anchored to the movable platen by the rear clamp plate.

As the mold cavity is filled with polymer melt, the pressure increase within the cavity can produce stresses of up to 10,000 to 180,000 psi in the mold cavity material. The resulting deformation is substantial but can be accommodated provided the elastic limit of the material is not exceeded. However, where the dimensional tolerance of the molded part is critical, it is imperative that the mold material modulus is sufficiently stiff to ensure part dimensional accuracy. Maintenance of proper temperature of the mold cavity and core is also necessary in this respect as well as for the production of a molded part with good physical and mechanical properties. Dimensional accuracy of the part also demands that the dimensions

C. INJECTION BLOW MOLDING

The injection blow molding process is a noncontinuous cyclic process consisting essentially of two phases. In the first phase, a preform is molded by injecting melted plastic into a steel mold cavity where it is kept hot and conditioned. In the second or subsequent phase, the preform is metered into the blow mold where the blowing operation takes place to form the final part. The major advantages of injection blow molding are the quality of the molded part and productivity. There is no flash production. Therefore, the molded part neither has a pinch-off scar from flash nor requires additional trimming or other finishing steps for waste retrieval. Also, the molded parts show hardly any variation in weight, wall thickness, and volume from the accurately molded preform. However, only blow-molded parts with limited size and shape and without handles are feasible with the injection blow molding process.

~~V. ROTATIONAL MOLDING^{4,5}~~

A. PROCESS DESCRIPTION

Rotational molding is a process used for producing hollow, seamless products having heavy and/or complex shapes. In rotational molding a premeasured amount of powder or liquid polymer is placed in the bottom half of the mold, and the two halves of the mold are locked together mechanically. The mold is then rotated continuously about its vertical and horizontal axes to distribute the material uniformly over the inner surface of the mold (Figure 11.11). The rotating mold then passes through a heated oven. As the mold is heated, the powdered polymer particles fuse forming a porous skin that subsequently melts and forms a homogeneous layer of uniform thickness. In the case of a liquid polymer, it flows over and coats the mold surface and then gels at the appropriate temperature. While still rotating axially, the mold passes into a cooling chamber where it is cooled by forced air and/or water spray. The mold is then moved to the work station and opened, and the finished solid part whose outside surfaces and contour faithfully duplicate those of the inner mold surface is removed. The mold is recharged for the next cycle.

B. PROCESS VARIABLES

Different types of heating systems, including hot air, molten salts, or circulation of oil through a jacketed mold have been used. The essential requirement of any heating system is to ensure that the mold is heated uniformly and at a properly controlled rate so that the desired part thickness is obtained without causing resin degradation. Given the potential hazards and maintenance problems associated with the use of molten salts, the use of hot oil has gained wide commercial acceptance because of the relatively cleaner, cheaper, and safer operation involved.

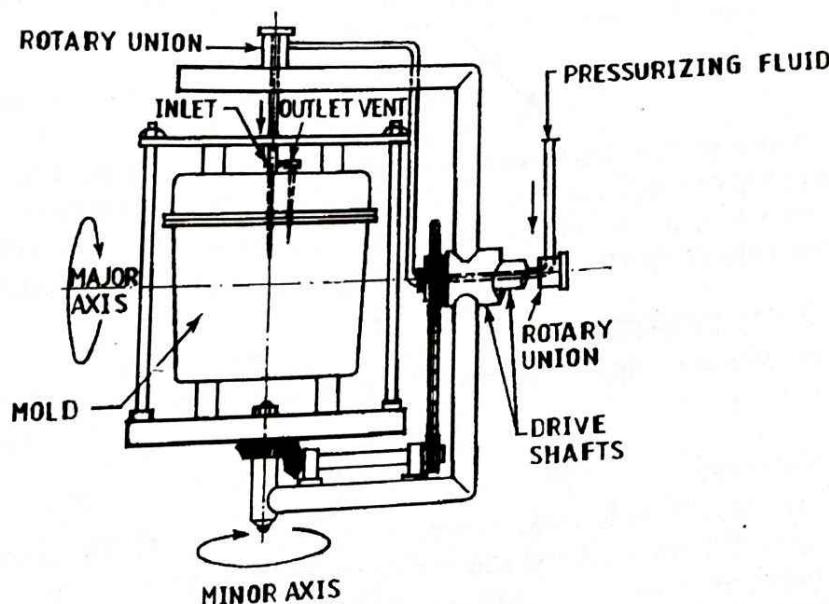


Figure 11.11 Schematic diagram of rotation molding showing major and minor axes of rotation.

IV. BLOW MOLDING^{4,5,6}

Blow molding is a process used extensively for the production of bottles and other hollow plastic items with thin walls. Blow-molded objects may range in size from less than 1 oz to a few hundred gallons.

A. PROCESS DESCRIPTION

The blow molding process consists of a sequence of steps leading to the production of a hollow tube or parison from a molten thermoplastic resin. This is then entrapped between the two halves of a mold of the desired shape. Air, usually at about 100 psi, is blown into the soft parison, expanding it against the contours of the cold mold cavity. The part is cooled and removed from the mold, and where necessary the excess plastic material or flash accompanying the molded part is trimmed and reclaimed for reuse.

The blow molding process therefore involves essentially two properly synchronized operations: parison formation from the plastic material and blowing the parison into the shape of the desired part. There are two techniques for plasticizing the resin for parison formation. These are extrusion blow molding (which is the most common method and which is characterized by scrap production) and injection blow molding. The latter process is versatile and scrap free and is beginning to be more understood and accepted by processors.

B. EXTRUSION BLOW MOLDING

In extrusion blow molding, an extruder, as described in Section II, is used to plasticize the resin and form the parison. The process may be continuous or intermittent. In the continuous process, a continuous parison is formed at a rate synchronized with the rates of part blowing, cooling, and removal. Two general mold clamp mechanisms are used for part formation from the extruded parison. In the first arrangement or shuttle system, the blowing station is situated on one or both sides of the extruder. As soon as an appropriate length of parison is extruded, the clamp mechanism moves from the blowing station to a position under the die head, captures and cuts the parison, and then returns to the blowing station for part blowing, cooling, and removal. This ensures that there is no interference with parison formation. In the second or rotary system, a number of clamping stations are mounted on a vertical or horizontal wheel. As the wheel rotates at a predetermined rate, blowing stations successively pass the parison head(s) where it is entrapped for subsequent part formation. In this case, parison entrapment and blowing, part cooling, and removal occur simultaneously in a number of adjacent blowing stations.

In the intermittent extrusion process, molding, cooling, and part removal take place under the extrusion head. An extruder system, which may be of the reciprocating screw, ram accumulator, or accumulator head type, extrudes the parison in a downward direction where it is captured at the proper time between the two halves of the mold. The part is then formed and ejected and a new cycle begins (Figure 11.10). As the name suggests, in the intermittent extrusion blow molding process, parison formation is not continuous. For example, with the reciprocating screw machine, after the parison is extruded, melt is accumulated in front of the screw causing a retraction of the screw. After the molded part has cooled and the mold opens and ejects the part, the screw is immediately pushed forward by hydraulic pressure, forcing the melt into the die to initiate the formation of the next parison.

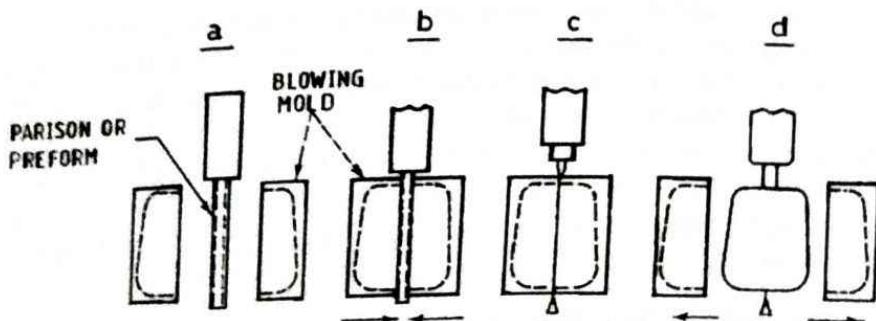


Figure 11.10 Schematic of the blowing stage. (a) The molten, hollow tube — the parison or preform — is placed between the halves of the mold; (b) the mold closes around the parison; (c) the parison, still molten, is pinched off and inflated by an air blast that forces its wall against the inside contours of the cooled mold; (d) when the piece has cooled enough to have become solid, the mold is opened and the finished piece is ejected. (From Kaufman, H.S. and Falsetta, J.J., Eds., *Introduction to Polymer Science and Technologies*, John Wiley & Sons, New York, 1977. With permission.)

While the heating cycle has virtually no effect on the properties of the finished part, the cooling rate determines part shrinkage, final density, brittleness, and other physical properties. Mold cooling is accomplished by the use of forced air and/or application of water spray.

Rotational molding machines vary from the simple one-arm rotocast system with capability to producing parts of up to 20 gal size to the industrially predominant three-arm machines that are capable of producing up to 5000 gal capacity tanks. In the latter case, each arm is always in one of the stations: load-unload, oven, or cooling. More recently, shuttle-type machines with molds mounted on large self-driven shuttle carts have been developed. The carts move on tracks from the oven to the cooling chamber. These machines can make products of much larger capacities. Rotational molding machines with microprocessor controls and other solid-state devices for regulating operating variables such as cycle time, oven temperature, rotational speed ratio (ratio of the speed of major to minor axis), and fan and water on-off times are now available.

The rotational molding operation involves neither high pressure nor shear rates. In addition, precise metering of materials is not crucial. Therefore, rotational molding machinery is relatively cheap and has a more extended lifetime. Other advantages of rotational molding include favorable cost-performance (productivity) ratio, absence of additional finishing operations even of complex parts, minimal scrap generation, and capability for simultaneous production of multiple parts and colors.

Example 11.8: Explain the variation in the physical properties of rotational molded parts from polypropylene and polystyrene shown in Table E11.8 with changes in the cooling cycle

Table E11.8 Physical Properties of Rotational Molded Parts

Property	Polypropylene Cooling Time		Polystyrene Cooling Time	
	10 min	2 min	10 min	2 min
Specific gravity	0.96	0.90	1.20	1.19
Shrinkage	0.040	0.015	0.003	0.004
Elongation at break (%)	300	100	1.5	1.3

Solution: A reduction in cooling time means faster cooling rates of the rotational molded parts. This is accompanied by marked changes in the physical properties of the part from polypropylene (crystalline polymer). On the other hand, the cooling rate has little effect on the part from polystyrene (amorphous polymer). A longer cooling time permits a greater ordered molecular arrangement in the crystalline polymer. The resultant enhanced crystallinity leads to higher specific gravity and shrinkage and reduced brittleness. Cooling rates do not seriously affect molecular arrangement in the amorphous polymer.

VI. THERMOFORMING^{4,5}

Thermoforming is a process for forming moderately complex shaped parts that cannot be injection molded because the part is either very large and too expensive or has very thin walls. It consists essentially of two stages: elevation of the temperature of a thermoplastic sheet material until it is soft and pliable and forming the material into the desired shape using one of several techniques.

A. PROCESS DESCRIPTION

Thermoforming techniques may be grouped into three broad categories: vacuum, mechanical, and air blowing processes.

1. Vacuum Forming

The vacuum forming process is shown schematically in Figure 11.12. The plastic sheet is clamped in place mechanically and heated. A vacuum is then placed beneath the hot elastic sheet, and this makes atmospheric pressure push the sheet down onto the contours of the cold mold. The plastic material cools down, and after an appropriate time the cooled part is removed.

Polymer Viscoelasticity

I. INTRODUCTION

Traditional engineering practice deals with the elastic solid and the viscous liquid as separate classes of concrete, or steel in various applications based on design equations arising from this type of material classification. However, it has become increasingly obvious that elastic and viscous material responses of polymeric materials falls between these two extremes of a broad spectrum of material behavior. The behavior compared with traditional materials like metals and ceramics. Several examples illustrate this point. (1) The stress-strain properties of polymers are extremely rate dependent. For traditional materials, the of polymeric material increases with time (creep). (2) Under a constant load, the deformation deformation, the stress required to maintain this deformation decreases with increasing time (stress relaxation). (4) The strain resulting from a polymer subjected to a sinusoidal stress has an in-phase component and an out-of-phase component. The phase lag (angle) between the stress and strain is a measure of the internal friction, which in principle is the mechanical strain energy that is convertible to heat. Traditional materials, for example, metals close to their melting points, exhibit similar behavior. However, at normal temperatures, creep and stress relaxation phenomena in metals are insignificant and are usually neglected in design calculations. In choosing a polymer for a particular end-use situation, particularly structural applications, its time-dependent behavior must be taken into consideration if the polymer is to perform successfully.

Our discussion of the viscoelastic properties of polymers is restricted to the linear viscoelastic behavior of solid polymers. The term *linear* refers to the mechanical response in which the ratio of the overall stress to strain is a function of time only and is independent of the magnitudes of the stress or strain (i.e., independent of stress or strain history). At the onset we concede that linear viscoelastic behavior is observed with polymers only under limited conditions involving homogeneous, isotropic, amorphous samples under small strains and at temperatures close to or above the T_g . In addition, test conditions must preclude those that can result in specimen rupture. Nevertheless, the theory of linear viscoelasticity, in spite of its limited use in predicting service performance of polymeric articles, provides a useful reference point for many applications.

To aid our visualization of viscoelastic response we introduce models that represent extremes of the material response spectrum. This is followed by the treatment of mechanical models that simulate viscoelastic response. These concepts are developed further by discussion of the superposition principles.

II. SIMPLE RHEOLOGICAL RESPONSES

A. THE IDEAL ELASTIC RESPONSE

The ideally elastic material exhibits no time effects and negligible inertial effects. The material responds instantaneously to applied stress. When this stress is removed, the sample recovers its original dimensions completely and instantaneously. In addition, the induced strain, ϵ , is always proportional to the applied stress and is independent of the rate at which the body is deformed (Hookean behavior). Figure 14.1 shows the response of an ideally elastic material.

The ideal elastic response is typified by the stress-strain behavior of a spring. A spring has a constant modulus that is independent of the strain rate or the speed of testing: stress is a function of strain only. For the pure Hookean spring the inertial effects are neglected. For the ideal elastic material, the mechanical response is described by Hooke's law:

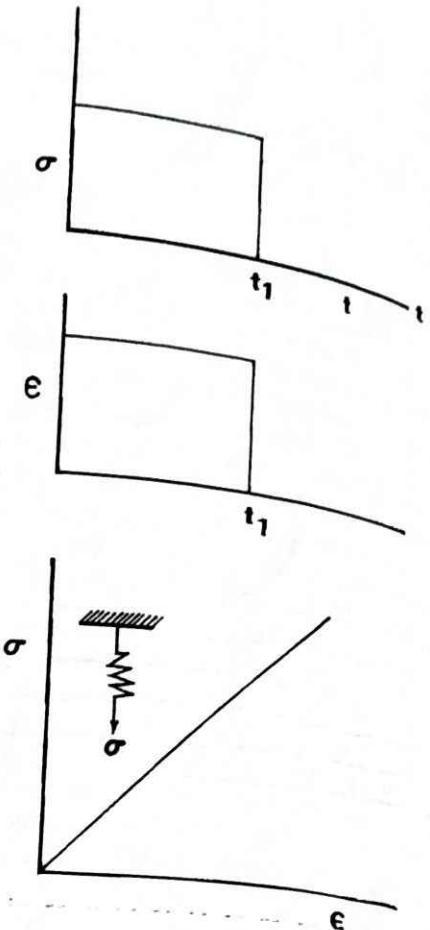


Figure 14.1 *Ideal elastic response.*

$$\sigma = E\epsilon$$

where σ is the applied stress, ϵ is the strain, and E is Young's modulus.

(14.1)

B. PURE VISCOUS FLOW

Fluids have no elastic character; they cannot support a strain. The dominant characteristic of fluids is their viscosity, which is equivalent to elasticity in solids. According to Newton's law, the response of a fluid to a shearing stress τ is viscous flow, given by

$$\left\{ \frac{dy}{dt} \right\} = f(t)_{\text{linear}} \quad \tau = \eta \frac{dy}{dt} \quad (14.2)$$

where η is viscosity and dy/dt is strain rate. Thus in contrast to the ideal elastic response, strain is a linear function of time at an applied external stress. On the release of the applied stress, a permanent set results. Pure viscous flow is exemplified by the behavior of a dashpot, which is essentially a piston moving in a cylinder of Newtonian fluid (Figure 14.2). A dashpot has no modulus, but the resistance to motion is proportional to the speed of testing (strain rate).

However, no real material shows either ideal elastic behavior or pure viscous flow. Some materials, for example, steel, obey Hooke's law over a wide range of stress and strain, but no material responds without inertial effects. Similarly, the behavior of some fluids, like water, approximate Newtonian response. Typical deviations from linear elastic response are shown by rubber elasticity and viscoelasticity.

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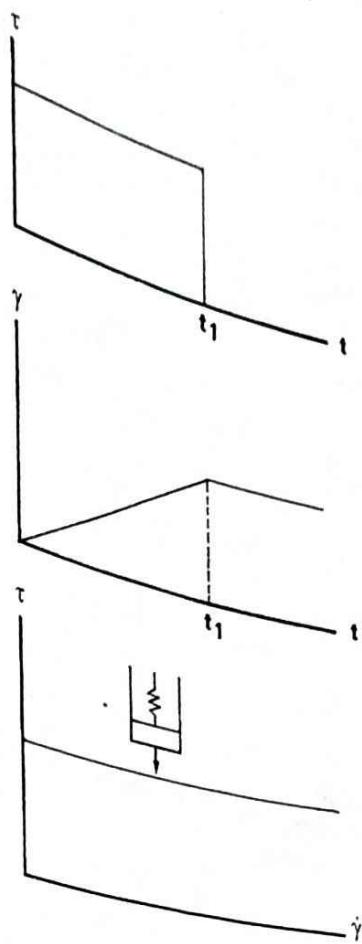


Figure 14.2 Pure viscous behavior.

C. RUBBERLIKE ELASTICITY

The response of rubbery materials to mechanical stress is a slight deviation from ideal elastic behavior. They show non-Hookean elastic behavior. This means that although rubbers are elastic, their elasticity is such that stress and strain are not necessarily proportional (Figure 14.3).

III. VISCOELASTICITY

Viscoelastic material such as polymers combine the characteristics of both elastic and viscous materials. They often exhibit elements of both Hookean elastic solid and pure viscous flow depending on the experimental time scale. Application of stresses of relatively long duration may cause some flow and irrecoverable (permanent) deformation, while a rapid shearing will induce elastic response in some polymeric fluids. Other examples of viscoelastic response include creep and stress relaxation, as described previously.

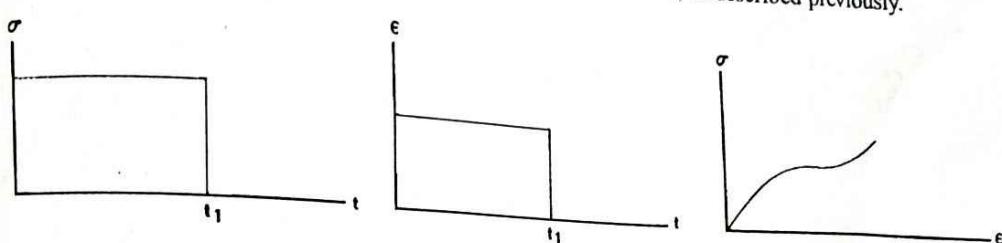


Figure 14.3 Rubber elasticity.

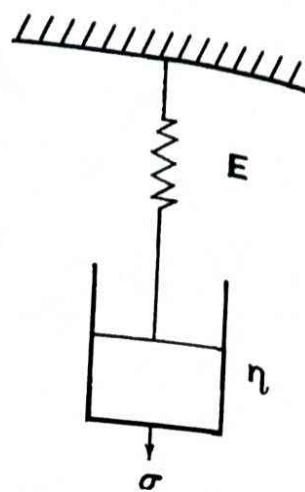


Figure 14.4 The Maxwell element.

It is helpful to introduce mechanical elements as models of viscoelastic response, but neither the spring nor the dashpot alone accurately describes viscoelastic behavior. Some combination of both elements is more appropriate and even then validity is restricted to qualitative descriptions; they provide valuable visual aids. In most polymers, mechanical elements do not provide responses beyond strains greater than about 1% and strain rates greater than 0.1 s^{-1} .

IV. MECHANICAL MODELS FOR LINEAR VISCOELASTIC RESPONSE

A. MAXWELL MODEL

To overcome the poor description of real polymeric materials by either the spring or the dashpot, Maxwell suggested a simple series combination of both elements. This model, referred to as the Maxwell element, is shown in Figure 14.4. In the Maxwell model, E , the instantaneous tensile modulus, characterizes the response of the spring while the viscosity, η , defines viscous response. In the following description we make no distinction between the types of stress. Thus, we use the symbol E even in cases where we are actually referring to shearing stress for which we have previously used the symbol G . This, of course, does not detract from the validity of the arguments.

In the Maxwell element, both the spring and the dashpot support the same stress. Therefore,

$$\sigma = \sigma_s = \sigma_d \quad (14.3)$$

where σ_s and σ_d are stresses on the spring and dashpot, respectively. However, the overall strain and strain rates are the sum of the elemental strain and strain rates, respectively. That is,

$$\varepsilon_T = \varepsilon_s + \varepsilon_d \quad (14.4)$$

or

$$\dot{\varepsilon}_T = \dot{\varepsilon}_s + \dot{\varepsilon}_d \quad (14.5)$$

But

$$\dot{\varepsilon}_s = \frac{\sigma}{E} \text{ and } \dot{\varepsilon}_d = \sigma/\eta \quad (14.6)$$

where $\dot{\varepsilon}_T$ is the total strain rate, while $\dot{\varepsilon}_s$ and $\dot{\varepsilon}_d$ are the strain rates of the spring and dashpot, respectively. The rheological equation of the Maxwell element on substitution of Equation 14.6 in 14.5 becomes

$$\dot{\varepsilon}_T = \frac{1}{E} \dot{\sigma} + \frac{1}{\eta} \sigma \quad (14.7)$$

Example 14.1: A polystyrene sample of $0.02/\text{m}^2$ cross-sectional area is subjected to a creep load of 10^5 N . The load is removed after 30 s. Assuming that the Maxwell element accurately describes the behavior of polystyrene and that viscosity is $5 \times 10^{10} \text{ P}$, while Young's modulus is $5 \times 10^5 \text{ psi}$, calculate:

- The compliance
- The deformation recovered on the removal of the dead load
- The permanent

Solution: a. The creep equation for the Maxwell element is

$$\epsilon(t) = \sigma_0 \left[\frac{1}{E} + \frac{t}{\eta} \right] \quad \text{or}$$

$$\frac{\epsilon(t)}{\sigma_0} = \left[\frac{1}{E} + \frac{t}{\eta} \right] \text{ or compliance.}$$

$$\begin{aligned} E &= 5 \times 10^5 \text{ psi} = 5 \times 10^5 \text{ psi} \times 6.894 \times 10^3 (\text{N/m}^2/\text{psi}) \\ &= 3.45 \times 10^9 \text{ N/m}^2 \end{aligned}$$

$$\eta = 5 \times 10^{10} \text{ P} = 5 \times 10^9 \frac{\text{N} \cdot \text{s}}{\text{m}^2}$$

$$J = \frac{1}{3.45 \times 10^9} + \frac{30}{5 \times 10^9} \text{ m}^2/\text{N} = 6.29 \times 10^{-9} \text{ m}^2/\text{N}.$$

b. The deformation recovered on the removal of load is due to the spring ϵ_s .

$$\epsilon_s = \frac{\sigma_0}{E}$$

$$\sigma_0 = \frac{P_0}{A} = \frac{10^5}{0.02} \text{ N/m}^2 = 5 \times 10^6 \text{ N/m}^2$$

$$\epsilon_s = \frac{5 \times 10^6}{3.45 \times 10^9} = 1.45 \times 10^{-3}$$

c. The permanent set is due to the viscous flow ϵ_d .

$$\begin{aligned} \epsilon_d &= \frac{\sigma_0}{\eta} t \\ &= \frac{5 \times 10^6 (\text{N/m}^2)}{5 \times 10^9 (\text{Ns/m}^2)} \times 30 (\text{s}) \\ &= 0.03 \end{aligned}$$

3. Dynamic Experiment

Let us consider the response of a Maxwell element subjected to a sinusoidal stress. The corresponding strain will be sinusoidal but out of phase with the stress by an angle δ , as discussed in Chapter 13. Thus,

$$\sigma = \sigma_0 \sin \omega t \quad (14.15)$$

Now the rheological equation for the Maxwell element is

$$\dot{\epsilon}(t) = \frac{1}{E} \sigma + \frac{1}{\eta} \sigma$$

$$\frac{d\epsilon}{dt} = \frac{\sigma_0 \omega}{E} \cos \omega t + \frac{\sigma_0}{\eta} \sin \omega t$$

Integration of Equation 14.16 between two time limits and noting that $\epsilon(0)$ is not necessarily zero yields

$$\tan \delta = \frac{1}{\tau \omega}$$

$$E^I = \frac{E\tau^2 \omega^2}{1 + \omega^2 \tau^2}$$

$$E^{II} = \frac{E\tau \omega}{1 + \omega^2 \tau^2}$$

where $\tau = \eta/E$.

B. THE VOIGT ELEMENT

Since, as we saw above, the Maxwell element is not perfect, it seems logical to consider a parallel arrangement of the spring and the dashpot. This is the so-called Voigt or Voigt-Kelvin element (Figure 14.7).

The Voigt element has the following characteristics:

- The spring and the dashpot always remain parallel. This means that the strain in each element is the same.
- The total stress supported by the Voigt element is the sum of the stresses in the spring and the dashpot.

$$\sigma_T = \sigma_s + \sigma_d$$

Thus, the rheological equation for the Voigt element is given by

$$\sigma_T = E\epsilon + \eta \frac{d\epsilon}{dt}$$

(14.19)

(14.20)

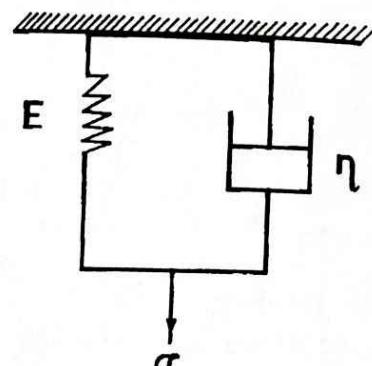


Figure 14.7 The Voigt element.

- a. Car tire
b. Engine mount

Explain the basis of your selection.

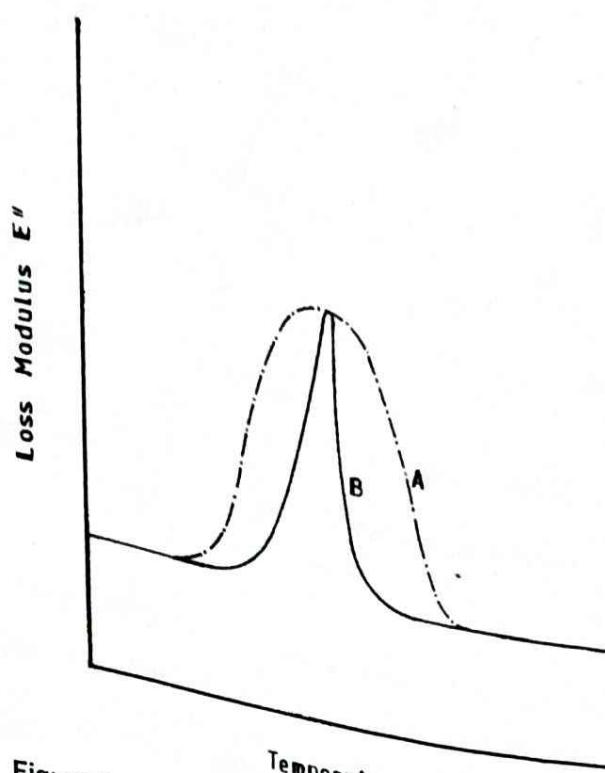


Figure E.14.4 Energy absorption profiles for two materials.

- Solution:** The area under the loss modulus-temperature curve is a measure of the damping capacity or ability to absorb energy of the material. Obviously, A has a higher damping capacity than B.
- In car tires, temperature buildup contributes to rapid deterioration and wear of tire and loss of traction. Consequently, material B will be more suitable for use as a car tire since it will absorb less energy and hence result in less temperature buildup.
 - A critical requirement for an engine mount is the ability to absorb the vibrational loads from the engine. In this case, a material with the ability to dissipate the vibrational energy as heat would be preferable; that is, material A.

C. THE FOUR-PARAMETER MODEL

Neither the simple Maxwell nor Voigt model accurately predicts the behavior of real polymeric materials. Various combinations of these two models may more appropriately simulate real material behavior. We start with a discussion of the four-parameter model, which is a series combination of the Maxwell and Voigt models (Figure 14.9). We consider the creep response of this model.

Under creep, the total strain will be due to the instantaneous elastic deformation of the spring of modulus E_1 , and irrecoverable viscous flow due to the dashpot of viscosity η_2 , and the recoverable retarded elastic deformation due to the Voigt element with a spring of modulus E_3 and dashpot of viscosity η_3 . Thus, the total strain is the sum of these three elements. That is,

$$\epsilon(t) = \epsilon_1 + \epsilon_2 + \epsilon_3 \quad (14.27)$$

$$\epsilon(t) = \frac{\sigma_0}{E_1} + \frac{\sigma_0 t}{\eta_2} + \frac{\sigma_0}{E_3} \left[1 - \exp^{-t/\tau_3} \right] \quad (14.28)$$

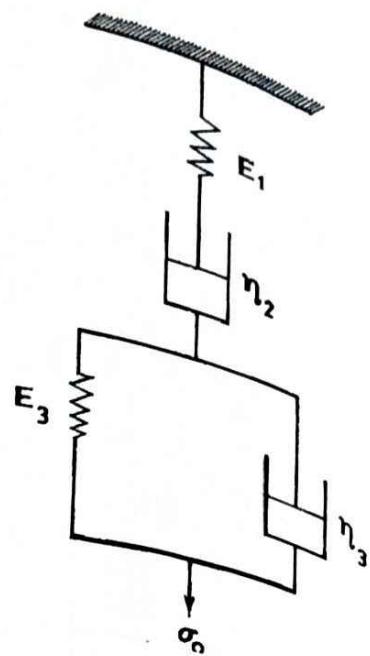


Figure 14.9 Schematic of the four-parameter model.

where σ_0 is the imposed constant stress and τ_3 equals η_3/E_3 and is referred to as the retardation time. In creep recovery, say, the load is removed at time t_i ; the deformation, σ_0/E_1 , due to the spring, modulus E_1 is recovered instantaneously. This will be followed by the retarded elastic creep recovery due to the Voigt element given by ε_3 or

$$\varepsilon_3 = \frac{\sigma_0}{E_3} \left[1 - \exp - t_i / \tau_3 \right] \quad (14.29)$$

Only the deformation due to the dashpot of viscosity η_2 is retained as a permanent set. The creep and creep recovery curve of this model is shown in Figure 14.10.

The four-parameter model provides a crude qualitative representation of the phenomena generally observed with viscoelastic materials: instantaneous elastic strain, retarded elastic strain, viscous flow, instantaneous elastic recovery, retarded elastic recovery, and plastic deformation (permanent set). Also, coelastic behavior of linear amorphous polymers under creep conditions. The analogies to the molecular mechanism can be made as follows.

1. The instantaneous elastic deformation is due to the Maxwell element spring, E_1 . The primary valence bonds in polymer chains have equilibrium bond angles and lengths. Deformation from these equilibrium values is resisted, and this resistance is accompanied by an instantaneous elastic deformation.
2. Recoverable retarded elastic deformation is associated with the Voigt element. This arises from the resistance of polymer chains to coiling and uncoiling caused by the transformation of a given equilibrium conformation into a biased conformation with elongated and oriented structures. The process of coiling and uncoiling requires the cooperative motion of many chain segments, and this can only occur in a retarded manner.
3. Irrecoverable viscous flow is due to the Maxwell element dashpot η_3 . This is associated with slippage of polymer chains or chain segments past one another.

c. Permanent set

$$\epsilon_2 = \frac{\sigma_0 t}{\eta_2}$$

$$= \frac{(10^8 \text{ N/m}^2)(200 \text{ s})}{5 \times 10^{10} \text{ N.s/m}^2} = 0.4$$

V. MATERIAL RESPONSE TIME — THE DEBORAH NUMBER

A physical insight into the viscoelastic character of a material can be obtained by examining the material response time. This can be illustrated by defining a characteristic time for the material — for example, the relaxation time for a Maxwell element, which is the time required for the stress in a stress relaxation experiment to decay to e^{-1} (0.368) of its initial value. Materials that have low relaxation times flow easily and as such show relatively rapid stress decay. This, of course, is indicative of liquidlike behavior. On the other hand, those materials with long relaxation times can sustain relatively higher stress values. This indicates solidlike behavior. Thus, whether a viscoelastic material behaves as an elastic solid or a viscous liquid depends on the material response time and its relation to the time scale of the experiment or observation. This was first proposed by Marcus Reiner, who defined the ratio of the material response time to the experimental time scale as the Deborah number, D_n . That is,

$$D_n = \frac{\text{material response time}}{\text{experimental time scale (observation time)}}$$

(14.30)

A high Deborah number that is a long response time relative to the observation time implies viscoelastic solid behavior, whereas a low value of Deborah number (short response time relative to the time scale of experiment) is indicative of viscoelastic fluid behavior. From a conceptual standpoint, the Deborah number is related to the time one must wait to observe the onset of flow or creep. For example, the Deborah number of a wooden beam at 30% moisture is much smaller than that at 10% moisture content. For these materials the onset of creep occurs within a reasonably finite time. At the other extreme, the Deborah number of a mountain is unimaginably high. Millions of years must elapse before geologists find evidence of flow. This apparently is the genesis of Marcus Reiner's analogy ("The mountains flowed before the Lord" from the Song of Deborah, Book of Judges V).

It must be emphasized, however, that while the concept of the Deborah number provides a reasonable qualitative description of material behavior consistent with observation, no real material is characterized by a simple response time. Therefore, a more realistic description of materials involves the use of a distribution or continuous spectrum of relaxation or retardation times. We address this point in the following section.

VI. RELAXATION AND RETARDATION SPECTRA

Real polymers are not characterized by a simple response time. Instead, a distribution or continuous spectrum of relaxation or retardation times is required for a more accurate description of real polymers. Many complex models have been proposed to simulate the viscoelastic behavior of polymeric materials. We discuss two of these models.

A. MAXWELL-WEICHERT MODEL (RELAXATION)

The generalized model consists of an arbitrary number of Maxwell elements in a parallel arrangement (Figure 14.11).

Consider the generalized Maxwell model in a stress relaxation experiment. The strain in all the individual elements is the same, and the total stress is the sum of the stress experienced by each element. Thus,

$$\sigma = \sigma_1 + \sigma_2 + \sigma_3 + \dots + \sigma_{n-1} + \sigma_n \quad (14.31)$$

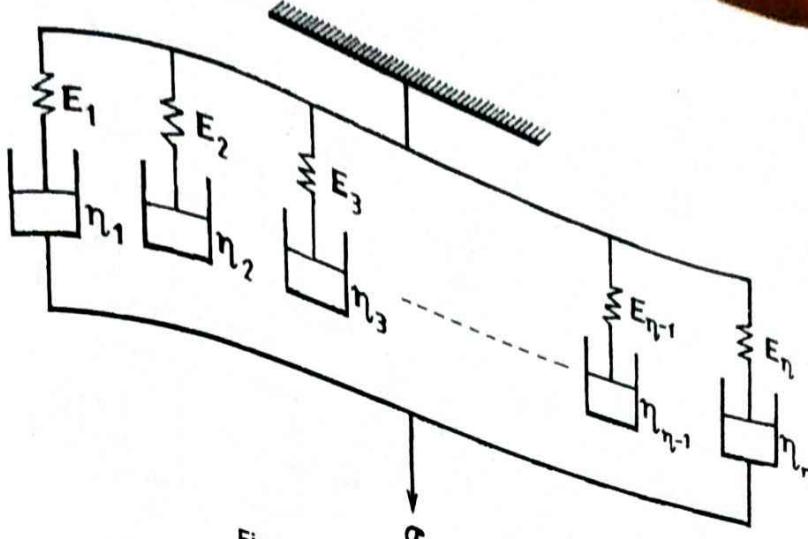


Figure 14.11 The Maxwell-Weichert model.
The individual stress in each element is given by

This gives the stress relaxation of an individual element under a constant strain ε_0 as

$$\sigma_i = \sigma_0 e^{-\gamma \tau_i} \quad (14.32)$$

where $\tau_i = \eta_i/E_i$. For the Maxwell-Reichert model under a constant strain, ε_0 ,

$$\sigma_i(t) = \varepsilon_0 E_i e^{-\gamma \tau_i} \quad (14.33)$$

or

$$\sigma(t) = \varepsilon_0 \sum_{i=1}^n E_i e^{-\gamma \tau_i} \quad (14.34)$$

$$E(t) = \sum_{i=1}^n E_i e^{-\gamma \tau_i} \quad (14.35)$$

If n is large, the summation in the equation may be approximated by the integral of a continuous distribution of relaxation times $E(r)$.

$$E(t) = \int_0^\infty E(\tau) e^{-\gamma \tau} d\tau \quad (14.36)$$

If one of the Maxwell elements in the Maxwell-Weichert model is replaced with a spring or a dashpot of infinite viscosity, then the stress in such a model would decay to a finite value rather than zero. This would approximate the behavior of a cross-linked polymer.

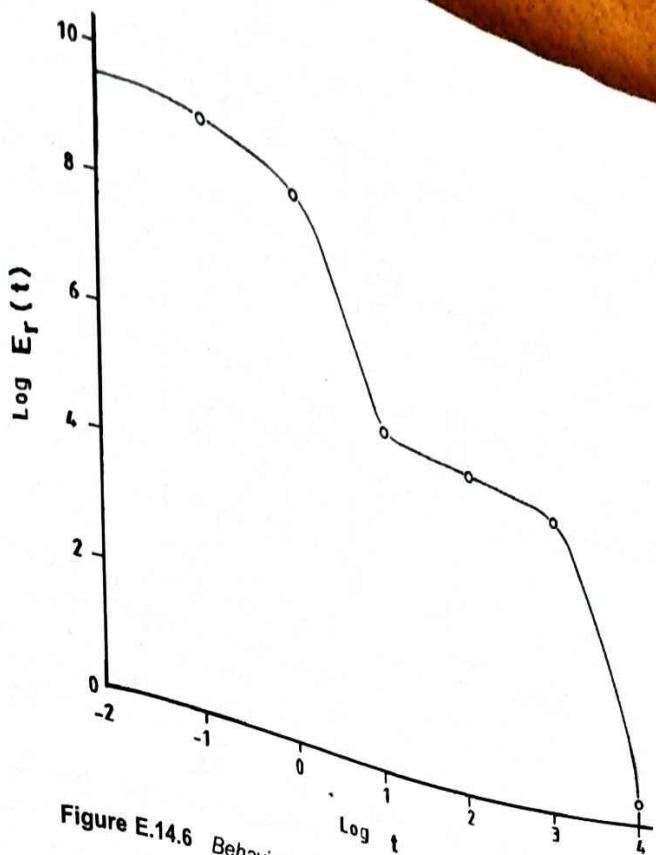
B. VOIGT-KELVIN (CREEP) MODEL

The generalized Voigt element or the Voigt-Kelvin model is a series arrangement of an arbitrary number of Voigt elements (Figure 14.12). Under creep, the creep response of each individual element is given by

$$\varepsilon_i(t) = \sigma_0 J_i (1 - e^{-\gamma \tau_i}) \quad (14.37)$$

or

$$J_i(t) = \frac{\varepsilon_i(t)}{\sigma_0} = J_i (1 - e^{-\gamma \tau_i}) \quad (14.38)$$



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Figure E.14.6 Behavior of a 2-component Maxwell-Reichert model.

VII. SUPERPOSITION PRINCIPLES

In the following sections we discuss the two superposition principles that are important in the theory of viscoelasticity. The first is the Boltzmann superposition principle, which is concerned with linear viscoelasticity, and the second is time-temperature superposition, which deals with the time-temperature equivalence.

A. BOLTZMANN SUPERPOSITION PRINCIPLE

As discussed earlier for a Hookean solid, stress is a linear function of strain, while for a Newtonian fluid, stress is a linear function of strain rate. The constants of proportionality in these cases are modulus and viscosity, respectively. However, for a viscoelastic material the modulus is not constant; it varies with time and strain history at a given temperature. But for a linear viscoelastic material, modulus is a function of time only. This concept is embodied in the Boltzmann principle, which states that the effects of mechanical history of a sample are additive. In other words, the response of a linear viscoelastic material to a given load is independent of the response of the material to any load previously on the material. Thus the Boltzmann principle has essentially two implications — stress is a linear function of strain, and the effects of different stresses are additive.

Let us illustrate the Boltzmann principle by considering creep. Suppose the initial creep stress, σ_0 , on a linear, viscoelastic body is increased sequentially to $\sigma_1, \sigma_2, \dots, \sigma_n$ at times t_1, t_2, \dots, t_n , then according to the Boltzmann principle, the creep at time t due to such a loading history is given by

$$\epsilon(t) = J(t)\sigma_0 + J(t-t_1)[\sigma_1 - \sigma_0] + \dots + J(t-t_{n-1})[\sigma_n - \sigma_{n-1}] \quad (14.41)$$

Here J is compliance, whose functional dependence on time is denoted by the parentheses. The square brackets denote multiplication. For a continuous loading history, then, the creep is expressed by the integral: