
21

STRUCTURE AND MECHANICAL PROPERTIES OF POLYMERS

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21.1 STRUCTURE OF POLYMER CHAINS

A good reason for the widespread use of polymeric materials is that they present physical and chemical properties that are well tuned for different applications at a cost that is quite reasonable. Polymers, as a group of materials, present a wide range of properties, perhaps the largest of all known materials, since they can be found in the form of liquids, soft viscoelastic (rubbery) materials, or rigid solids. The wide variety of properties found in polymers are the result of their macromolecular structure since, by definition, they are molecules resulting from the covalent bonding of at least hundreds and up to thousands or millions of basic units. Properties of polymers, as in the case of any chemical compound, are highly dependent on the structure of the polymer chains and the molecular weight resulting from the number of units covalently bonded. Polymer chemical structure affects polymer properties due to the nature of the repeating units that form the macromolecule, the branching and number or crosslinks, as well as differences in the order of the macromolecular units in the case of copolymers (see also Chapter 6). The molecular weight and the molecular weight distribution determine the molecular size and give a description of the distribution of the different molecular sizes in a polymer [1, 2]. The behavior of polymers in terms of processing depends on the number-average molecular weight, M_n , and on the shape of the molecular weight distribution, measured by the molecular weight dispersity (\mathcal{D}). Mechanical properties such as tensile strength are limited by short macromolecules, while long chains control the melt flow and elasticity of the

processed polymer. Figure 21.1 shows the graph of a typical molecular weight distribution with the four main molecular weight averages commonly determined in a polymer.

For a precise definition of the molecular weight averages shown in Figure 21.1, see Section 1.5.1.

\mathcal{D} is calculated as the ratio of M_w/M_n ; a value of 1 indicates that the polymer is monodisperse. Depending on the synthetic route, \mathcal{D} can be as large as 2 in step-growth polymers and as narrow as 1 for anionic polymerization [3]. When branching is present, the value can be much larger (up to 20 or more).

Mechanical properties such as strength under tension are related to M_n , while the melt viscosity is determined by M_w . M_z is related to the viscoelastic properties or melt elasticity during processing.

It is well known that the interactions between atoms in a chemical molecule with neighboring molecules of the same or different type determine its macroscopic properties. Other physical properties are dependent on short- and long-range interactions between the atoms that constitute the molecule with other neighboring molecules. Thus, physical properties such as density, volume, and boiling or freezing points are the result of the interactive forces between molecules. On the other hand, the interactions with other chemical molecules, which have also been studied by thermodynamics, give rise to the determination of other parameters, for example, the solubility parameters, that measure the interaction energy between molecules. The interactions between different chemical molecules of low molecular weight (nonpolymers) and their properties have been estimated, and equations that relate them

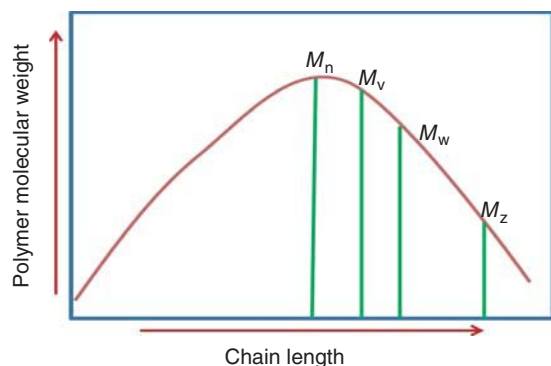


Figure 21.1 Polymer molecular weight distribution with the most common average molecular weights.

have been already developed; these properties and correlations to estimate them have been tabulated to a large extent [4].

In the specific case of polymers, the chemical structure is also quite important, since the atoms present in the polymer chain determine, as in low molecular weight structures, the interactions with other molecules; however, as polymers are synthesized from covalently bonded molecules that are repeated hundreds to thousands of times, their physical properties are different, since they do not depend on the properties of the short-range interactions of a few atoms as in simple, small molecules. Structural features, such as polymer morphology, are also affected by the configuration of the chains due to the stereoregularity in the pendant groups or in the double-bond position. Natta [5] realized the importance of tacticity and developed the nomenclature for polyolefins, for example, polypropylene, which reflects that, depending on the position of the pendant CH_3 group along the chain, polypropylene could be isotactic, syndiotactic, or atactic, as described in Figure 21.2.

Polymer stereoregularity is important since the morphology of the macromolecule depends on crystallization and the degree of crystallinity determines, in the end, several physical properties such as density, mechanical properties, as well as thermal properties. Atactic polymers have difficulties in crystallizing; they are amorphous or show a low degree of crystallinity, while the degree of crystallinity in isotactic and syndiotactic polymers is high.

The determination of the physical and chemical interaction properties of a polymer, or even better, their prediction from the simple knowledge of the polymer structure has been successfully achieved using the concept of molar additivity of the groups forming the polymer molecule by the so-called group contribution methods. These are extensively treated in the book by Van Krevelen and Nijenhuis [6], where the prediction of physical properties such as density, T_g and other physical transitions, heat

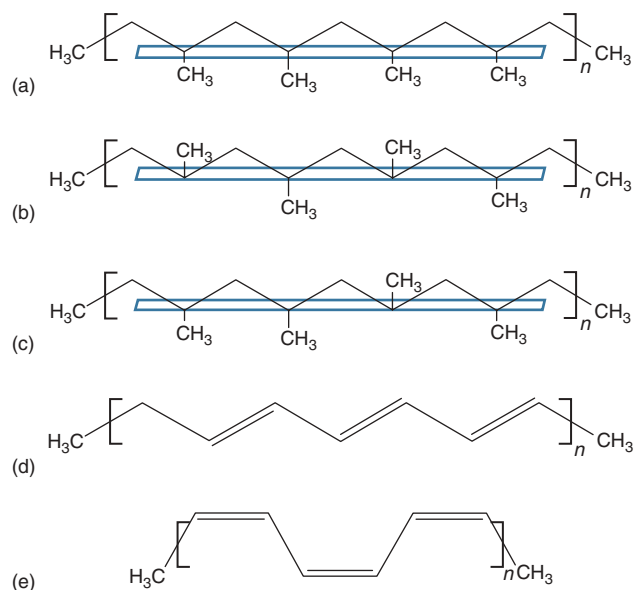


Figure 21.2 PP configurations involving pendant group position: (a) isotactic; (b) syndiotactic; (c) atactic, the dark gray line is a reference plane for symmetry distribution of atoms in the chain, and configurations of double bond in dienes; (d) 1,4-*trans*, and (e) 1,4-*cis*.

capacities, solubility parameters, optical properties, magnetic, acoustic, transport, and mechanical properties among others can be found. Another approach that has been successful for the prediction of the polymer properties starting from the knowledge of their molecular structure, is the topological index approach developed by Bicerano and coworkers, which uses a connectivity index and is the basis for commercial simulation packages that predict polymer properties [7].

21.2 MECHANICAL PROPERTIES OF POLYMERS

Depending on the final polymer application, mechanical properties are considered to be the most important in everyday use where the polymer product is subjected to all kinds of external forces such as pressure, tension, vibration, or traction. The large number of polymers available allows a wide spectrum of mechanical properties to choose from, including very soft liquid-like, elastic or rigid materials.

Mechanical properties, as in the case of other properties, can be organized in terms of their relationship to polymer structure, depending on the functional groups present in the polymer backbone and the side groups from the main chain. Other factors that affect the mechanical properties of a polymer, besides its chemical composition, are molecular weight and molecular weight distribution,

degree of branching in addition polymers, and degree of crosslinking in thermoset polymers. The mechanical properties of a polymer will also be affected by the ability of the polymer to crystallize and the size and distribution of the crystals in the bulk of the polymer (morphology), which, together with molecular orientation, has a strong influence on its mechanical properties.

It is also possible to manipulate the structure by introducing other monomers into the polymer chain, changing the mechanical properties of the final material by copolymerization. It is also common, for economic reasons or to increase mechanical properties, to add particulate solids to the polymer, such as wood flour or other additives, that will affect the final mechanical properties. Another common approach is the preparation of blends of two different polymers, which are commonly nonsoluble in each other, as a strategy to increase some mechanical properties such as impact strength, as in the well-studied case of nylon toughening by butyl rubber [8, 9].

External factors that will influence polymer mechanical properties are temperature or thermal treatment, temperature history, large differences in pressure, and environmental factors such as humidity, solar radiation, or other types of radiation. The mechanical properties of polymer are also sensitive to the methods and variables used for testing, such as strain deformation as well as the rate at which the strain is performed. Finally, the mechanical behavior of polymeric materials and the values of their mechanical properties will be sensitive to the kind of strain that is imposed by the applied force, namely, tension, compression, biaxial, or shear.

Polymers are also unique in their viscoelastic nature, a behavior that is situated between that of a pure elastic solid and that of a pure viscous liquid-like material; their mechanical properties present a strong dependence on time and temperature. Given all the factors that have to be taken into account to determine the mechanical properties of polymers, their measurement would appear to be very complex. However, there is a series of general principles that determine the different mechanical properties and that give a general idea of the expected results in different mechanical tests. These principles can be organized in a systematic manner to determine the interrelation of polymer structure and the observed mechanical properties, using equations and characteristic parameters of polymeric materials.

In the following section, the role of some of these structural and external factors on the mechanical properties of polymers is discussed. Figure 21.3 shows an example of the most common methods used to apply an external force to a polymeric material.

In general, the elastic or Young's modulus M , a characteristic property of a material, is a measure of the

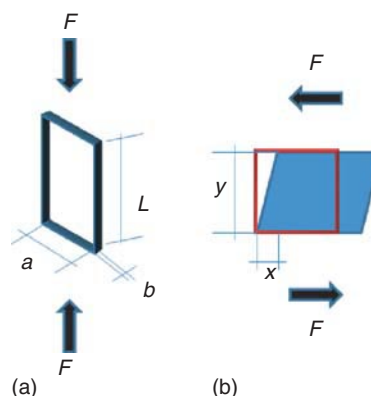


Figure 21.3 Common force fields for applied forces in a material (a) tension and (b) shear. (See insert for the color representation of the figure.)

resistance to strain (ϵ) of a material under an external force F . It is defined by the following expression:

$$\sigma = M\epsilon \quad (21.1)$$

where M stands for modulus and σ is the stress or force applied per unit area (F/A) of the material. There are three types of moduli: elastic or Young's modulus, E ; shear modulus, G ; and bulk modulus, K . If a material is isotropic, as in the case of amorphous polymers, it is only needed to know two moduli to describe the elastic behavior of the material. The moduli are related by

$$E = \frac{9GK}{3K + G} \quad (21.2)$$

The relationship between moduli can be also calculated using Poisson's ratio, $\nu = \epsilon_T/\epsilon_L$ (where ϵ_T and ϵ_L are transverse and axial strains, respectively), which measures contraction in a material subject to tension, in order to compensate for the strain:

$$E = 2G(1 + \nu) = 3K(1 - 2\nu) \quad (21.3)$$

For elastic solids $\nu = 0.5$, while for glassy polymers $0.3 < \nu < 0.44$

If the materials are anisotropic, they will present different properties in the different directions. Examples of these polymeric materials are polymer fibers, such as polyethylene terephthalate, PET, nylon fibers, injection-molded polymers, fiber-reinforced composites with a polymeric matrix, and crystalline polymers where the crystalline phase is not randomly oriented. A typical method for measuring the modulus in tension is the stress-strain test, in which the modulus corresponds to the initial slope of the stress-strain curve. Figure 21.4 shows typical stress-strain curves for different types of polymeric materials.

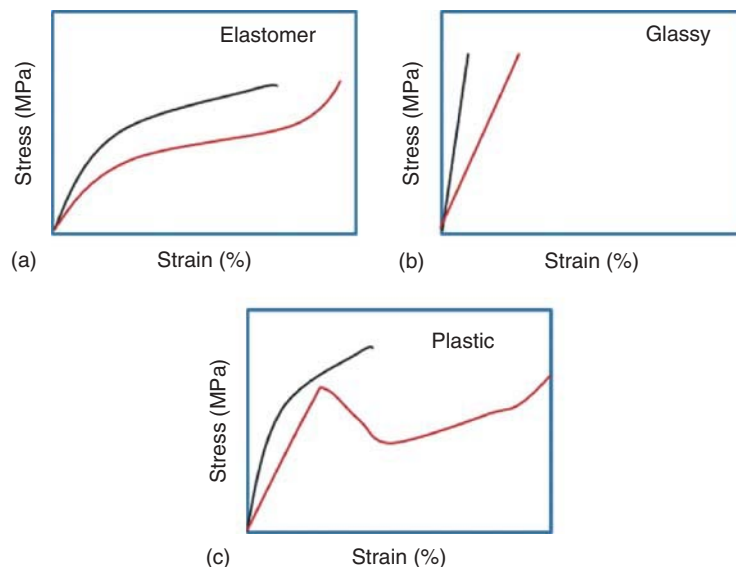


Figure 21.4 Typical stress-strain curves for different types of polymers: (a) elastomer, (b) glassy, and (c) plastic. (See insert for the color representation of the figure.)

From these experimental curves, it is possible to determine the modulus as

$$E = \left(\frac{d\sigma}{d\varepsilon} \right)_{\varepsilon \rightarrow 0} = \left(\frac{F/A}{(L - L_0)/L_0} \right)_{L \rightarrow L_0} \quad (21.4)$$

which involves the definition of stress as $\sigma = F/A$ and simple strain as $\varepsilon = (L - L_0)/L_0$ where L is the length of the specimen after the stress has been applied and L_0 is its original length. Values of modulus for shear or compression experiments can also be calculated using their stress-strain curves.

21.2.1 Molecular Structure and Mechanical Properties

There are a large number of tests to determine mechanical properties of polymers as well as instruments to perform them. A large number of these tests are already standardized by the American Society for Testing and Materials, ASTM. From the point of view of their structure, the large majority of polymers are either completely amorphous or partially crystalline. This implies that a polymer can be mechanically rigid below certain temperature, the glass-transition temperature, T_g . Above T_g , at moderate strain rates, amorphous polymers are soft and flexible and their physical appearance is that of an elastomer or a liquid-like viscous material. In the region where the glass transition occurs, polymers show a drastic change in their mechanical behavior. Their elastic modulus E or shear modulus G , at tension or shear, respectively, diminishes by a factor of 10^3 as it goes across T_g . For this reason, the T_g of polymer can

be considered the most important characteristic transition in terms of its mechanical properties. Other properties that change drastically in the glass-transition range are the thermal expansion coefficient α , refractive index n , heat capacity at constant pressure C_p , as well as some electrical properties, and, as the modulus changes, the strain ε for measurements under shear and the ultimate strength σ_u also change drastically in the glass-transition region.

In general, considering the T_g value of a polymeric material, and taking into account that most polymers are used at room temperature, it is possible to roughly classify the mechanical behavior of a polymer according to its glass-transition temperature, T_g . Thus, rubbers and elastomers have T_g values below room temperature, while for brittle and rigid polymers, T_g is above room temperature. Polymer T_g can span a large interval of temperatures, from -110°C for polyethylene to temperatures above 300°C for aromatic polyamides and thermoset resins. The value of T_g also depends on the timescale of the mechanical tests and its value can vary depending on factors such as the heating rate or frequency used for the test in dynamic mechanical analysis (DMA) measurements.

Since T_g depends on the structure of the polymer, it is possible to identify three factors that affect T_g . First, the rigidity or flexibility of the polymer chain; it is known that the presence of aliphatic $-\text{CH}_2-\text{CH}_2-$, ether, $-\text{CH}_2-\text{CH}_2-\text{O}-$, or siloxane chains with methyl substitutions, such as dimethyl siloxane, $-\text{Si}(\text{CH}_3)_2-\text{O}-$, comprises flexible polymer chains that decrease T_g . It is also known that the length of lateral aliphatic groups also diminishes T_g as in the case of the methacrylic polymers (see Table 21.1) [10].

TABLE 21.1 Glass-Transition Temperature, T_g , of Methacrylate Polymers

Acrylic Polymer	T_g ($^{\circ}\text{C}$)
$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{C}=\text{O} \\ \\ \text{CH}_3 \end{array} \text{ MMA}$	105
$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{C}=\text{O} \\ \\ \text{CH}_2-\text{CH}_3 \end{array} \text{ Ethyl MA}$	65
$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{C}=\text{O} \\ \\ \text{CH}_2-\text{CH}_2\text{CH}_3 \end{array} \text{ Propyl-MA}$	35
$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{C}=\text{O} \\ \\ \text{CH}_2-\text{CH}_2\text{CH}_2\text{CH}_3 \end{array} \text{ Butyl-MA}$	21
$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{C}=\text{O} \\ \\ \text{CH}_2-(\text{CH}_2)_4-\text{CH}_3 \end{array} \text{ Hexyl-MA}$	-5
$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{C}=\text{O} \\ \\ \text{CH}_2-(\text{CH}_2)_6-\text{CH}_3 \end{array} \text{ Octyl-MA}$	-20
$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{C}=\text{O} \\ \\ \text{CH}_2-(\text{CH}_2)_8-\text{CH}_3 \end{array} \text{ Decyl-MA}$	-65

Second, T_g is also affected by the polarity of the polymer chain moieties. As a general rule, as the polarity increases, T_g increases (Table 21.2) [10].

T_g also increases with molecular weight, M_n , until it reaches a limiting value, T_g° for $M_n \rightarrow \infty$. The change in T_g due to the increase in molecular weight can be approximated using the following equation:

$$T_g = T_g^{\circ} - \frac{K}{M_n} \quad (21.5)$$

where K is a characteristic constant for each polymer [11].

T_g can also be affected by the degree of crosslinking, an increase of which is equivalent to an increase in the polymer molecular weight toward infinity. This is due

TABLE 21.2 Effect of Polymer Polarity on T_g

Polymer Repeating Unit	T_g ($^{\circ}\text{C}$)
$-\text{CH}_2-\overset{\text{CH}_3}{\underset{ }{\text{C}}}- \text{ PP}$	-10
$-\text{CH}_2-\overset{\text{Cl}}{\underset{ }{\text{C}}}- \text{ PVC}$	85
$-\text{CH}_2-\overset{\text{C}\equiv\text{N}}{\underset{ }{\text{C}}}- \text{ PAN}$	101

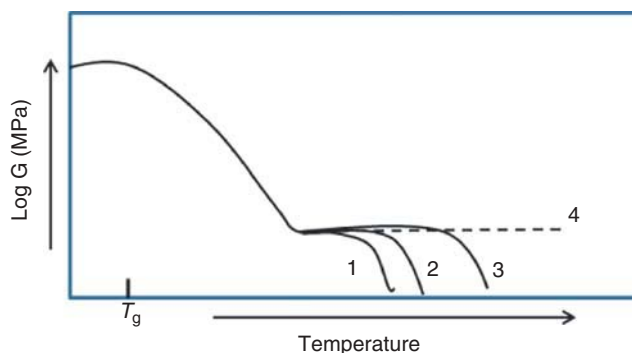


Figure 21.5 Schematic representation of shear modulus behavior as a function of temperature for a polymer with (1) low M_n , (2) medium M_n , (3) high M_n , and (4) a crosslinked polymer.

to an increased restriction in polymer chain mobility. An empirical equation derived by Nielsen from reported experimental data allows the calculation of T_g as function of the degree of crosslinking as follows:

$$T_g = T_g^{\circ} + \frac{3.9 \times 10^4}{M_c} \quad (21.6)$$

where T_g° is the T_g of the non-crosslinked polymer and M_c is the molecular weight between crosslink points. This equation allows the estimation of T_g of the polymer due to structural variations. A schematic representation of changes in the shear modulus, G , due to the effect of increasing molecular weight in the polymer or crosslinking is depicted in Figure 21.5.

21.2.2 Viscoelastic Properties and Temperature

One of the main characteristics of polymers is that polymer chains can rearrange when they are subjected to an induced stress and the strain will not be constant, but it will increase with time due to the high molecular weight and the large number of entanglements between chains. If the strain is removed, then the polymer will slowly recover its original shape if the strain was small enough. This is due to a slow

recovery of the original shape of the long entangled molecular chains that make up the polymer bulk. Furthermore, polymers show viscoelastic behavior at all temperatures, because they are not perfect elastic solids or perfect liquid-like viscous materials. A difference with respect to metals is that polymers show a dependence of mechanical properties with time at small and large strains. If a polymer sample is suddenly subjected to a given stress, σ , in tension, the strain will increase with time, $\varepsilon(t)$; if after certain time the sample is allowed to recover toward its original shape, a recovery curve can be obtained that implies a dynamic value $1/(E(t)) = D(t) = \varepsilon(t)/\sigma$, where $D(t)$ is sometimes called the *compliance of the polymer*, a quantity that measures its ability to recover its original shape.

Another test that shows the viscoelastic behavior of a polymeric material is the stress relaxation test, in which a sudden strain is imposed on the polymer sample at $t = 0$, and the stress, σ , required to maintain the strain is recorded as a function of time. As time increases, the stress, $\sigma(t)$, necessary to maintain the constant strain, ε , decreases due to relaxation of the entangled polymer chains that try to reach an equilibrium conformation. If the strain is released at short times, the sample will recover its original shape; on the other hand, long relaxation times will produce permanent deformation on the sample. If the stress, which is a function of time, is divided by the strain, a modulus value as a function of time can be defined:

$$E(t) = \frac{\sigma(t)}{\varepsilon} \quad (21.7)$$

Although these simple experiments show the viscoelastic nature of polymers due to the large number of polymer molecules with different lengths, a more quantitative expression has been suggested by Maxwell, considering the system as a combination of a spring, a pure elastic element, and a dashpot, a purely viscous element, as represented in Figure 21.6:

$$\sigma_1 = E\varepsilon_1 \quad (21.8)$$

$$\sigma_2 = \eta \frac{d\varepsilon_2}{dt} \quad (21.9)$$

In the Maxwell simple combination of mechanical elements, the stress σ and the strain ε are measured using subscript 1 for the spring element and subscript 2 for the viscous dashpot element. Given the way in which the stress is applied to the whole element, the stress on each element is the same, while the strain in each element is different:

$$\sigma = \sigma_1 = \sigma_2 \quad \text{and} \quad \varepsilon = \varepsilon_1 = \varepsilon_2$$

Using these facts,

$$\frac{d\varepsilon}{dt} = \frac{\sigma}{\eta} + \frac{1}{E} \frac{d\sigma}{dt} \quad (21.10)$$

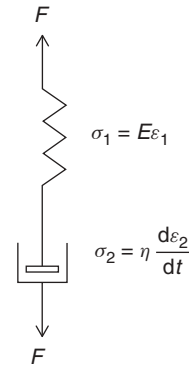


Figure 21.6 Maxwell's simple mechanical element combination of the spring and a dashpot in series as a representation of the viscoelastic behavior of a polymer.

Equation (21.10) is the general equation for the Maxwell mechanical model analogy for viscoelastic behavior.

If the creep experiment described before is performed on the basis of this model, with a constant stress applied to the Maxwell mechanical element, the strain will be function of time, as indicated in Equation (21.11).

$$\varepsilon(t) = \sigma_o \left(\frac{t}{\eta} + \frac{1}{E} \right) \quad (21.11)$$

Sometimes it is desirable to express the strain as the compliance $J(t)$:

$$J(t) = \frac{\varepsilon(t)}{\sigma_o} = \frac{t}{\eta} + \frac{1}{E} \quad (21.12)$$

The response of the model indicates that as the stress is removed, the spring immediately recovers the deformation, but the dashpot deformation is permanent or recovers very slowly. This behavior is frequently seen in polymers subjected to a sudden and permanent stress that is later removed.

In the case of a stress relaxation experiment using the Maxwell mechanical model, if an initial strain ε_o is imposed and the change in the stress is followed as a function of time, the resulting expression is as follows:

$$\sigma(t) = \sigma_o e^{-Et/\eta} \quad (21.13)$$

where η/E is the relaxation time, λ , which is a measure of the rate at which the stress decays in the polymer sample.

It is also common that polymers are subjected to forces, or stresses, such as mechanical vibration; in that case, the strain will also be sinusoidal in the same frequency but not in the same phase. In that sense, it is possible to model the responses to a periodic strain using the Maxwell mechanical model analogy. The response to an applied sinusoidal strain

as a function of time is $\varepsilon = \varepsilon_m \sin \omega t$ and, using the values of E and $\lambda = \eta/E$, is the expression for the stress, is given by:

$$\sigma = \varepsilon_m E \frac{\omega \lambda}{(1 + \omega^2 \lambda^2)^{1/2}} \sin(\omega t + \delta) \quad (21.14)$$

The stress is proportional to the modulus E , and will be ahead of the strain by an angle $\delta = \cot^{-1} \omega \lambda$.

These equations are often used in terms of complex variables such as the complex dynamic modulus, $E^* = E' + iE''$, where E' is called the *storage modulus* and is related to the amount of energy stored by the viscoelastic sample. E'' is termed the *loss modulus*, which is a measure of the energy dissipated because of the internal friction of the polymer chains, commonly as heat due to the sinusoidal stress or strain applied to the material. The ratio between E'/E'' is called $\tan \delta$ and is a measure of the damping of the material. The Maxwell mechanical model provides a useful representation of the expected behavior of a polymer; however, because of the large distribution of molecular weights in the polymer chains, it is necessary to combine several Maxwell elements in parallel to obtain a representation that better approximates the true polymer viscoelastic behavior. Thus, the combination of Maxwell elements in parallel at a fixed strain will produce a time-dependent stress that is the sum of all the elements:

$$\sigma(t) = \sum \sigma_i = \varepsilon \sum E_i e^{-t/\lambda} \quad (21.15)$$

The modulus as a function of time, $E(t)$, for the parallel arrangement of elements will be given as

$$E(t) = \frac{\sigma(t)}{\varepsilon} = \sum E_i e^{-t/\lambda_i} \quad (21.16)$$

This model indicates that the modulus of the polymer is the result of the individual moduli of each element, E_i , and the stress depends on the relaxation times, λ_i , of each element. This equation is a better approximation to the behavior of polymers. To model the viscoelastic behavior of polymers, other models have been proposed, such as the Kelvin model [12].

21.3 MECHANICAL PROPERTIES OF POLYMER COMPOSITES

Polymer composites have received widespread attention due to the large combination of materials and properties that are possible using the wide variety of different polymers and loads available. There is a large variety of composite materials that can be obtained by the combination of a polymer, usually as a matrix material, and some type of "loading." The loading can be very elaborate, such as a mat

of continuous carbon fibers with a geometry that takes into account all the possible angles to reinforce an epoxy resin matrix. This can be used in high performance applications, such as aircraft critical parts, due to its low weight and high tensile and load resistance, or in race car bodies or brakes where protection or temperature performance is critical. Other similar materials for not so critical performance are continuous glass-fiber-reinforced polyester resins, which are used in boats and more common molded products.

These long-fiber-reinforced materials present mechanical properties that can be tailored by orientation of the fibers in the desired directions. The preparation and properties of these materials has been studied by several authors [11, 13–15].

A more common and widely used process involves the preparation of short-fiber polymer composite materials and particulate composite polymeric materials, where the fibers or particles act as reinforcement of the polymer. In this particular case, when a polymer matrix is filled with fibers or particles, which in general possess higher mechanical properties than the polymer matrix, the resultant composite material presents properties that are between those of the soft polymer matrix and the rigid filler.

For polymer composites filled with small particles, either micro- or nanoparticles, mechanical properties have been extensively studied because of their versatility and importance [16–20]. The elastic modulus of polymer composite materials with particles that present an aspect ratio about 1 (spherical or near-spherical particles) improves with the use of inorganic particles that have large moduli and strength compared to the polymer matrix. To improve stress transfer between the matrix and the polymer, it is also important to increase the interfacial adhesion between the polymer and the particles. The bonding between different particles and the polymer is often obtained by the use of a coupling agent that improves the interaction within the particles and the polymer matrix. The concentration of particles in the polymer matrix is also important since they impart increased rigidity (elastic modulus) to the composite, as the concentration, usually expressed as a volume fraction, ϕ_p , increases in the polymer matrix. Several empirical and semiempirical equations have been proposed to predict the moduli of polymer composites filled with particles. The elastic modulus for particulate-filled composites can be calculated using Einstein's equation:

$$\frac{E_c}{E_m} = 1 + 2.5\phi_p \quad (21.17)$$

where E_c and E_m are the elastic moduli of the composite material and the matrix, respectively, and ϕ_p is the volume fraction of particles. This equation was obtained for a very dilute suspension of spheres and, therefore, it is only valid in the range of low particle-filled polymer. It is also

assumed that the adhesion between the polymer matrix and the solid spheres is good. A more realistic equation is the semiempirical one proposed by Halpin and Tsai:

$$\frac{E_c}{E_m} = \frac{1 + A_1 B_1 \phi_p}{1 - B_1 \phi_p} \quad (21.18)$$

where A_1 is a constant related to particle shape and matrix Poisson ratio, and B_1 is related to the moduli of the particle and the polymer matrix. An improved equation for prediction of the elastic modulus was proposed by Nielsen [11], which takes into account the particle packing fraction in the matrix:

$$\frac{E_c}{E_m} = \frac{1 + A_1 B_1 \phi_p}{1 - \Psi B_1 \phi_p} \quad (21.19)$$

where Ψ is the particle packing fraction parameter which is given by:

$$\Psi = 1 + \left[\frac{1 - \phi_{p \max}}{\phi_p^2 \max} \right] \phi_p \quad (21.20)$$

where $\phi_{p \max}$ is the maximum packing fraction of particles.

There are a number of modified equations that correlate well with different experimental data. A recent review on particulate composites lists many of them [21].

The tensile strength is usually taken as the maximum stress that a material can bear under a tensile loading. In polymer composite materials filled with particles, the stress transfer between the particles and polymer matrix affects the final tensile strength of the composite. Expressions for the prediction of tensile strength in polymer composites are difficult to find because they are associated with parameters that are difficult to measure, such as stress concentration, interfacial adhesion, and particle distribution. However, some semiempirical equations are sometimes used to model and try to predict the tensile strength of the composite material. The simplest model assumes that the stress is not transferred from the matrix to the particles; therefore, the strength of the composite is given by the amount of polymer matrix present:

$$\sigma_c = \sigma_m(1 - \phi_p) \quad (21.21)$$

where σ_c and σ_m are the composite and matrix strengths, respectively, and ϕ_p is the volume fraction of particles. An improved equation that still considers no stress transfer between particles and matrix was proposed by using geometrical considerations by Nicolais and Nicodemo [22], which improves on the above equation:

$$\sigma_c = \sigma_m(1 - 1.21\phi_p^{2/3})S_r \quad (21.22)$$

where S_r is a reduction factor that takes values between 0.2 and 1 for high and low volume fractions. If some

degree of stress transfer between the particles and the matrix exists because of a better adhesion between them, a simple general semiempirical equation, given by Equation (21.23), is proposed:

$$\sigma_c = \sigma_m(1 - a\phi_p^b + c\phi_p^d) \quad (21.23)$$

where a , b , c , and d are constants that can be obtained by experimental data fitting. In general, the strength in particulate-filled composite materials and in fiber-filled materials is that of the matrix, and only in the cases of successful surface treatment of the particles, is it possible to transfer part of the load to the filler to improve strength.

There has been an increased interest in the preparation of polymer–short natural fiber composite materials, particularly with high volume polyolefins, polypropylene, and polyethylene. The attractiveness of short-fiber natural reinforced polymers lies in the wide availability of mainly cellulosic materials from different renewable resources (Chapter 26). There are reports of hose cellulose fiber-reinforced materials [23], cellulosic fiber composites from wood pine and birch [24], or cellulosic fiber composites from henequen cellulose [25]. Some advantages of cellulosic fibers are that they do not break during processing either by milling or extrusion as rigid short fibers do, maintaining their length constant; however, their main drawback is their poor adhesion with the polyolefin matrix. Several treatments have been proposed such as *o*-hydroxybenzenediazonium salt for coir fibers in a polypropylene matrix [26], oxidation of jute fibers in PP composites post-treated with urotropine [27], and bamboo flour–HDPE composites using a maleic anhydride ethylene/propylene elastomer [28]. The use of a silane coupling agent with cellulosic fibers extracted from henequen whole fibers [25] proved to be very effective in increasing the tensile strength and increasing the surface adhesion between cellulosic fibers and the LPDE matrix (Fig. 21.7).

In general, natural fiber treatment improves the adhesion between the fiber and the polymer matrix, increasing the elastic modulus and the tensile strength under tension [29, 30]. Figure 21.8 shows micrographs of the differences in fiber treatment and the surface interaction of LDPE matrix with cellulosic fibers extracted from henequen. In the figure, the enhanced interfacial adhesion using the silane agent that increases the tensile strength of the materials is denoted by the coating of the matrix and also by the fact that the composite failed by shear yielding and tearing from the fiber.

Carbon nanotubes and carbon nanofibers have been studied lately as reinforcement materials for several different polymers because their high modulus and stiffness bear the promise of levels of reinforcement not found with micron-size particles or fibers. This performance can be achieved with concentrations

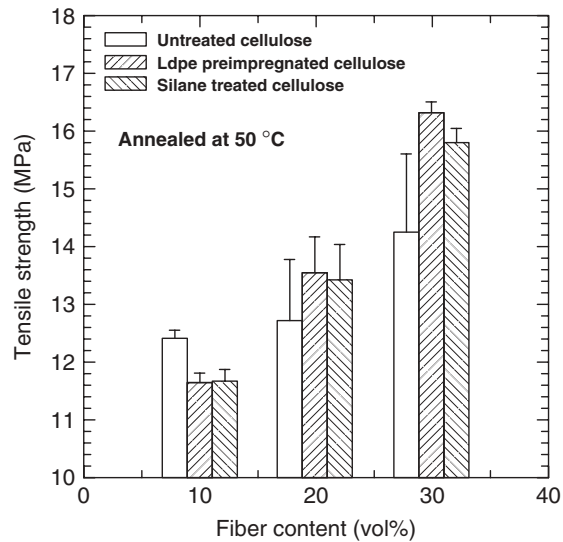


Figure 21.7 Effect of surface treatment of henequen cellulosic fibers on tensile strength of LDPE–henequen cellulosic fiber composites. *Source:* Reproduced with permission from Herrera-Franco PJ, Aguilar-Vega M. *J Appl Polym Sci* 1997;65:197 [25]. Copyright 1997 John Wiley and Sons.

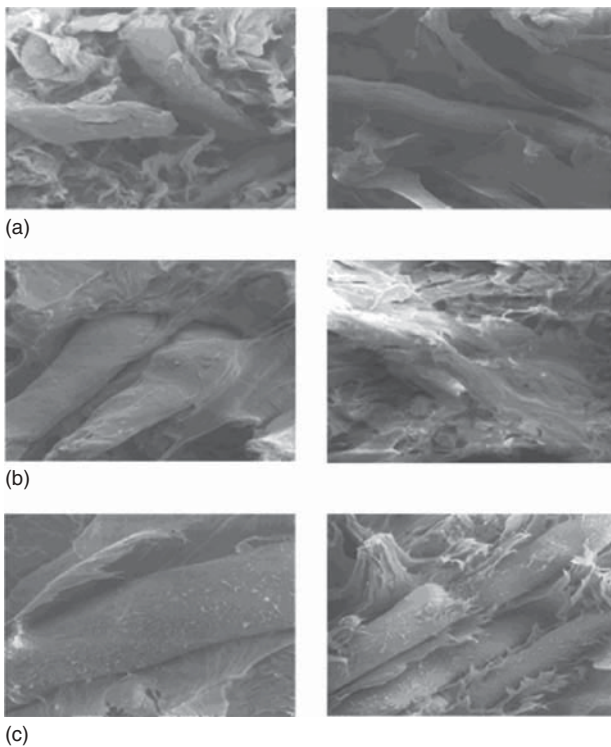


Figure 21.8 Micrographs of the failure surface by shear of LDPE–henequen cellulosic fiber composite with 20 and 30% by volume of cellulosic fiber: (a) untreated cellulose; (b) LDPE preimpregnated cellulose; and (c) silane-treated cellulose. *Source:* Reproduced with permission from Herrera-Franco PJ, Aguilar-Vega M. *J Appl Polym Sci* 1997;65:197 [25]. Copyright 1997 John Wiley and Sons.

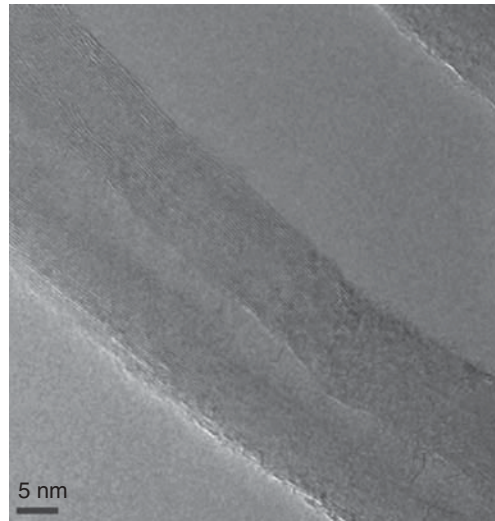


Figure 21.9 TEM micrograph of multiwalled carbon nanotube, Baytubes C150P. (Courtesy of Dr. Francis Aviles.)

below 10% of fibers [31, 32]. Single-walled carbon nanotubes are reported to have tensile strengths between 50 and 500 GPa and tensile moduli about 1500 GPa, while multiwalled nanotubes present tensile strengths between 15 and 60 GPa and tensile moduli about 1000 GPa. Figure 21.9 is a micrograph of a multiwalled carbon nanotube.

It is also known that polymers containing nanofillers present better surface finishing and reinforcement than those prepared using microfillers owing to the small size of the filler [33]. One of the drawbacks in the preparation of nanotubes and nanofibers filled polymer composites is the difficulty found to disperse them in the polymer matrix without breaking them, which in the end may affect the L/d aspect ratio of the nanotube (where L is the length and d the diameter of the fiber or nanotube). At the nanoscopic level, the forces between nanotubes and nanofibers tend to agglomerate them into bundles. If the filler is not properly dispersed in the matrix, the polymer composite will have poor mechanical properties because the agglomerates will act as stress concentration centers. Nanotubes and nanofibers can be dispersed by *in situ* polymerization, solution and evaporation of the solvent [34], melt spinning, spin casting, or melt mixing. From these techniques, melt mixing seems to be the easiest one to use; the dispersion can be facilitated by using grafted maleic anhydride, PP or PE [32]. Maleic anhydride can also improve the interfacial adhesion between the nanotubes or nanofibers with the matrix.

As in the case of microfillers, stress transfer between the matrix and the nanotubes increases with an increase in nanofiber or nanotube aspect ratio (L/d). Nanotubes can be considered as hollow cylinders, and their critical length

for reinforcement, l_c , can be calculated from the following equation:

$$l_c = \frac{\sigma_f D}{2\tau} \left[1 - \frac{D_i^2}{D^2} \right] \quad (21.24)$$

Here, σ_f is the fiber tensile strength, τ is the interfacial shear stress, and D and D_i are the external and internal diameters of the cylinder, respectively. Out of these parameters, τ is the critical factor that measures the stress transfer from the matrix to the polymer.

Elastic moduli of polymer composite materials filled with nanotubes and nanofibers can be estimated from Cox's equation [32]:

$$E_c = (1 - \phi_f)E_m + n\phi_f(\eta_f E_f) \quad (21.25)$$

where E_c is the composite elastic modulus, ϕ_f is the filler volume fraction, E_m is the elastic modulus of the polymer matrix, η_f is the filler efficiency factor, E_f is the filler elastic modulus, and n is a constant that takes into account the orientation of the nanotubes or nanofibers. This equation takes into account the filler aspect ratio and has been used successfully for the prediction of short-fiber composite materials. Halpin-Tsai's equation (Eq. 21.18) has also been used [32].

Particulate polymer composites with fibers are a very active area of development, particularly carbon nanotubes and nanofiber composites, and the new graphite and polymer composites [35]. This fact, combined with the continued interest in nanocomposites based in nanometric clays [36], suggests that improvements in mechanical properties of particulate and short-fiber polymer composite materials will continue to be reported.

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