

Introduction to the Viscoelastic Response in Polymers

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A polymer is made up of many (“poly” = many) repeated units (= “mer”) of a monomer (mono = one). Consequently, polymer molecules are composed of a large number of identical building blocks, labeled as macromolecules. The length of the polymeric chain is specified by the number of repeat units in the chain. This is called the 'degree of polymerization' (DP). Therefore, the molecular weight (MW) of a polymer is defined by:

$$\text{MW} = \text{Degree of polymerization} \times \text{molecular weight of repeat unit}$$

All processes used in polymer production lead to chains of varying lengths and hence with different molecular weights. Accordingly, there is not a single molecular weight in a given polymer but a distribution of molecular weights that is more or less broad depending upon uniformity in length of chains that composed its macromolecules. Consequently, molecular weights of polymers are represented as average molecular weights. Optimum molecular weight for a polymer depends on the structure and its end use. It has to be said that polymers with very high molecular weights are difficult to process. Typically, molecular weights in industrial polymers are in the interval of 50.000-300.000.

On the other hand, flexible macromolecules may adopt a large number of conformations that are determined by the position taken in the space by their atoms since this location changes by simple rotation about single bonds, as represented in *Figure 1* for three carbon atoms. However, a limited number of conformations is accessible in polymers with rigid chains. Additionally, flexible polymer in the crystalline state adopt fixed conformations whereas in solution or in the molten state they exhibit a wide range of conformations.

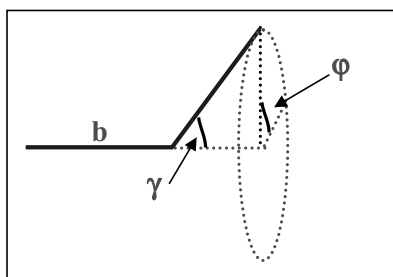


Figure 1. Flexible macromolecules

The different macromolecules composed of a large number of identical building blocks interact each to the others. These inter and intramolecular interactions provide strength that will be smaller or larger depending on the sort of interaction. There are four different types in polymeric materials, as shown in *Figure 2*.

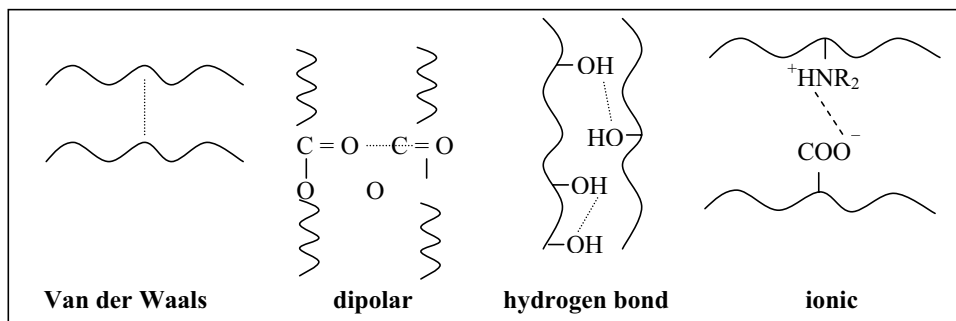


Figure 2. Inter and intramolecular interactions

These three mentioned characteristics: a large and heterogeneous molecular weight, the possibility of adopting a great number of conformations and the existence of intra e intermolecular interactions are variables in polymers that promote their peculiar and versatile mechanical behavior which is very important from a practical point of view.

Classical theories of elasticity and viscosity of a body assume steady state stress, strain and strain rate. Therefore, the time it takes to reach equilibrium conditions is not considered. Observers over one hundred of years ago found that most materials failed to reach equilibrium in an observable time period. Moreover, the constant coefficients of viscosity and elasticity were dependent on pre-treatments and loading history. Such effects, which were not accounted for the classical theories were called “elastic after-effects”. These were more pronounced in some materials such a food dough, wet clays, pitch and unvulcanized rubbers. With the development of synthetic polymers along XX century, these effects became even more prevalent and dominated equilibrium properties.

Another observation made a long time ago was that the properties of such materials are dependent upon the rate of loading or deformation rate. This feature is analogous to that of a fluid, where the stress is proportional to the strain rate. In particular, slow deformation rates made the material act like a liquid and high deformation rates made the same material act like a elastic solid. Eventually, researchers accepted the idea that all materials behave in a viscous or elastic manner that depends on how quickly or slowly they were deformed. This behavior led to a new term: viscoelasticity. In other words, the mechanical properties of materials, primarily polymers, are time-dependent and perfectly elastic deformation and perfectly viscous flow are idealizations that are approximately reached in some limited conditions.

Viscoelasticity is, then, the study of the response of polymers (or other materials) which exhibit some of the features of both elastic and viscous behavior. Elastic materials deform instantaneously when a load is applied, and “remember” their original configuration, returning there instantaneously when the load is removed. In solids, the relaxation of the structure at the molecular level is extremely low and, therefore, their response is essentially elastic. On the other hand, viscous materials do not show such characteristics, but instead exhibit a time-dependent behavior. While under a constant stress, a viscous body strains at a constant rate, and when this load is removed, the material has “forgotten” its original configuration, remaining in the

deformed state. In ordinary liquids, molecular reorganization occurs very rapidly and structural memory at the molecular level is very short. The response is essentially viscous unless the frequency of the testing experiment is very high. Viscoelastic materials exhibit certain characteristics of these two behaviors as manifested in time-dependent behavior, a “fading memory”, partial recovery, energy dissipation, etc. Such behavior may be linear (stress and strain are proportional) or nonlinear.

Polymers are the most important viscoelastic systems. Above glass transition temperature, the response of these materials to a mechanical perturbation field involves several types of molecular motions. For instance, the rearrangement of flexible chains may be very fast on the length scale of a repeated unit. These movements imply some type of cooperativity in the conformational transitions that produce them. Cooperativity occurs even as the relaxation propagates along the chains, involving a growing number of segments of the backbone as time passes. At very long times, disentanglements of the chains takes place, and the longest relaxation time associated with this process shows a strong dependence on both the molecular weight and the molecular architecture of the system. The disentanglement process governs the flow of the system. In consequence of the complexity of the molecular responses, polymer chains exhibit a wide distribution of relaxation time that extend over several decades in the time or frequency domain. At short time or at long frequency the response is mainly elastic, whereas at long time or short frequency it is mainly viscous, as depicted in *Figure 3*. Obviously, the elastic component of the deformation is recoverable but the viscous component. The elastic component of the deformation is of an entropic nature and, consequently, is time-dependent, as will be discussed below.

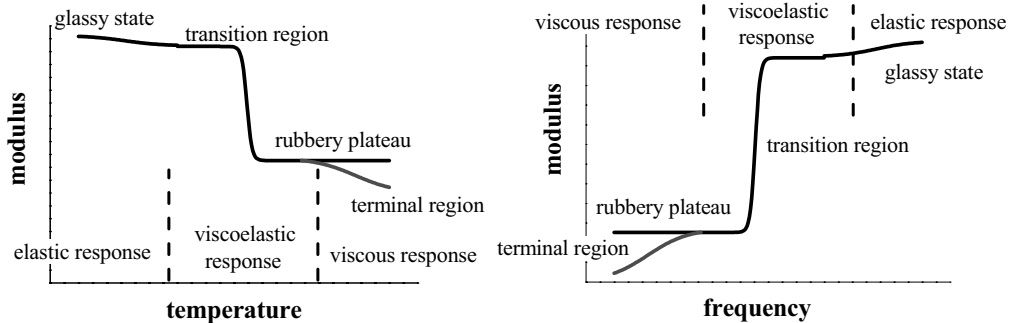


Figure 3.

1. Superposition principles

There are two superposition principles that are important in the theory of viscoelasticity. The first of these is the *Boltzmann superposition principle*, which describes the response of a material to different loading histories. This principle suggests that small changes in stress are equal to small changes in modulus multiplied by the strain. This means that the modulus is independent of the amount of material that deforms. Therefore, each loading step makes independent contribution to total loading history and the total final deformation is the sum of each contribution. Another

consequence of this principle is that the deformation of a specimen is directly proportional to the applied stress when all deformations are compared at equivalent times. Embodied in this principle is the linearity of viscoelasticity.

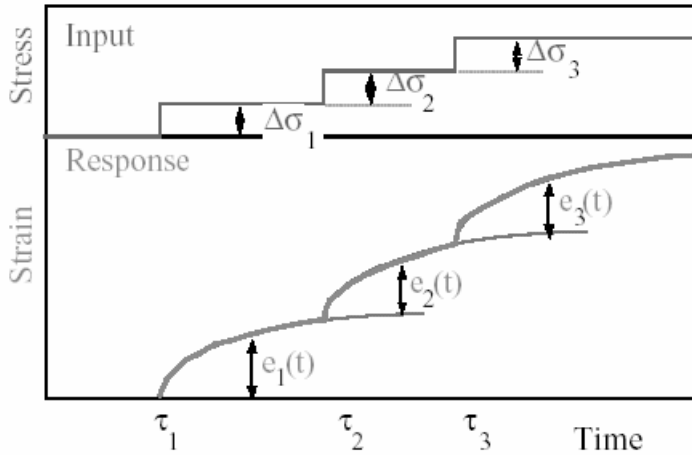


Figure 4.

The second one is the *time-temperature superposition principle* that establishes the correspondence between time and temperature. It has been used for a long time. Viscoelastic curves made at different temperatures are found to be superposable by horizontal shifts along a logarithmic time scale to give a unique curve covering a very large range of times or frequencies. Such curves made by superposition, using some temperature as a reference temperature, cover time outside the range easily accessible by practical experiments. Consequently, if the principle is held, from short-term experiments is feasible to predict the long-term behavior of a polymeric material. The curve made by superposition is called as *master curve* (see *Figure 5*).

The accomplishment of this time-temperature correspondence requires that there be no change in the relaxation/retardation mechanism with temperature and that the relaxation time, τ , values for all the mechanisms must change identically with temperature. A term that moves the time scale of the response function, labeled as horizontal shift factor (a_T), is defined as the ratio of any relaxation time τ at some temperature T to that at reference temperature T_0 :

$$a_T = \frac{\tau_i}{\tau_{i0}}$$

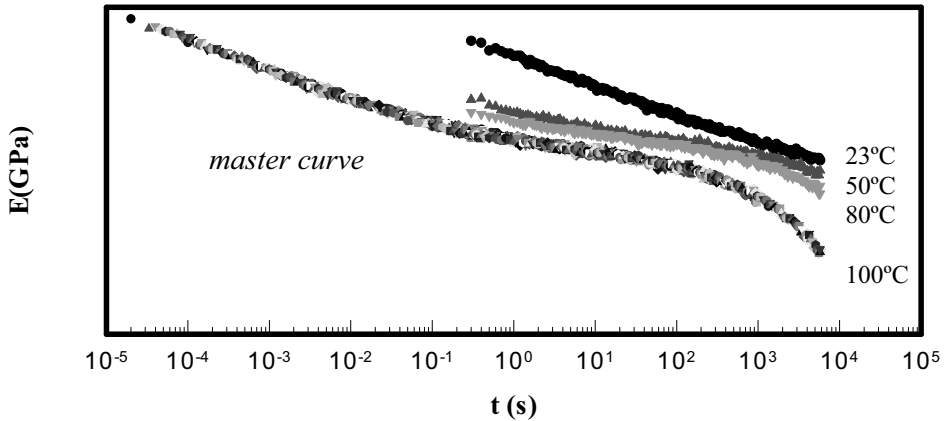


Figure 5. Master curve

The method of relating the horizontal shifts along the log time scale to temperature changes as developed by William, Landel and Ferry is known as the WLF method. The amount of horizontal shift of the log time scale is given by $\log a_T$. If the glass transition temperature is chosen as reference temperature, the temperature dependence of the shift factor for most amorphous polymers is:

$$\log a_T = \frac{-C_1^g (T - T_g)}{C_2^g + T - T_g}$$

2. Non-linear viscoelastic response

If the Boltzmann superposition principle holds, the strain is directly proportional to the stress at any given time and, similarly, the stress at any particular time is directly proportional to the strain depending upon which of these two magnitudes are the stimulus and the corresponding response. These assumptions are generally true for small stresses or strains, but the principle is not exact. If large loads are applied in creep measurements or large strains in stress relaxation ones, as can occur in practical structural applications, non-linear effects come into play. One result is that the response $\epsilon(t)$ or $\sigma(t)$, respectively, is not longer directly proportional to the excitation (σ or ϵ). The distribution of retardation or relaxation times can also change, and so can a_T .

The problem is very complex even in cases when complications such as microcracking or phase changes (*e.g.* appearing of crystallinity, as in the stretching natural rubber or variation in percent of crystallinity in polyethylene) are absent. It involves unsolved problems in non-equilibrium thermodynamics, mathematical approximation and the physics of any underlying process. As a results, there is no general solution and each specific case has to be treated in a particular manner.

3. Structural parameters affecting the viscoelastic response

There are several accountable inherent parameters that condition the viscoelastic behavior of polymeric materials. The primary ones are the following:

- chemical structure

- molecular architecture
- molecular weight and crosslinking
- copolymers and blends
- effect of plasticizers
- molecular orientation
- fillers and fibers

4. Types of experiments

The analysis of the viscoelastic response is basically carried out by four different types of tests:

- creep
- stress relaxation
- stress-strain experiments
- dynamic mechanical measurements

5. Creep

Creep and stress relaxation tests measure the dimensional stability of a polymer, and because the tests can be of long duration, such tests are of great practical importance. Creep measurements, especially, are of interest to engineers in any application where the polymer must sustain loads for long periods. Creep and stress relaxation measurements are also of major importance to anyone interested in the theory of or molecular origins of viscoelasticity.

Creep measurements consist of loading with a constant stress and analyzing the increase of strain in time. For an ideal elastic solid, Hookean solid since its behavior is described by the Hooke equation,

$$E = \frac{\sigma}{\varepsilon}$$

being E the elasticity modulus, σ the stress and ε the strain, the amount it deforms is controlled completely by its modulus. The time it takes for the process to occur is instantaneous, so time is not a variable. This strain-time dependence is shown in *Figure 6*. However, in an ideal liquid, Newtonian liquid since its response is described by Newton law,

$$\sigma = \eta \cdot \frac{d\varepsilon}{dt}$$

being τ the shear stress, η the viscosity and $d\varepsilon/dt$ the rate of shear, when a constant stress is applied it will flow as the stress is maintained. Therefore, the strain in the liquid is a function of two variables: stress and time, as seen in *Figure 6*.

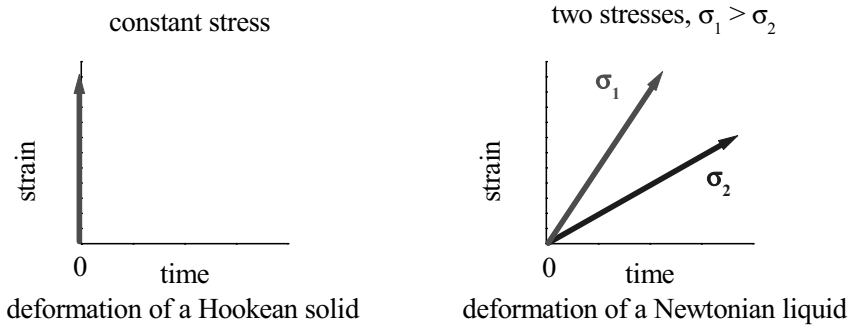


Figure 6.

For a viscoelastic polymeric material subjected to a constant stress, the strain observed is constituted by different components: initially, there is an instantaneous elastic deformation (ϵ_1 in Figure 7), like in a Hookean solid, followed by other time-dependent strain (ϵ_2 in Figure 7) that is curved at the beginning and eventually reach a limiting slope. After removing the load, a recovery process is observed. This mechanism also consists of various contributions: an immediate elastic deformation recovery (ϵ_1), other time-dependent one (ϵ_2), and a permanent deformation (ϵ_3) due to the viscous character.

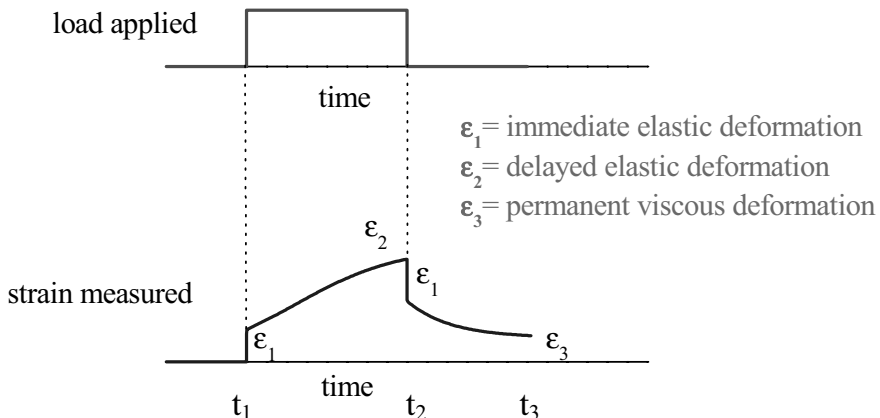


Figure 7.

An equation that describes the viscoelastic behavior from t_1 to t_2 is

$$\epsilon(t) = \epsilon_{\infty} [1 - e^{-t/\tau}]$$

where τ is the retardation time and ϵ_4 is the limit of strain when $t \neq 4$. On the contrary, when stress is removed, the strain that is recovered follows this other equation

The viscoelastic function $\epsilon(t) = \epsilon_\infty \cdot e^{-t/\tau}$ evaluated from creep experiments is the compliance, $J(t)$, that it is defined as the ratio of the variation of strain in time, $\epsilon(t)$, with the constant stress applied, σ ,

$$J(t) = \frac{\epsilon(t)}{\sigma}$$

6. Stress relaxation

In stress relaxation tests, the specimen is quickly deformed a given amount and the stress required to hold the deformation constant is measured as a function of time. Stress relaxation experiments are very important for a theoretical understanding of viscoelastic materials. However, such tests have not been as popular as creep measurements with experimentalists. There are probably at least two reasons for this:

- stress relaxation experiments, specially on rigid materials, are more difficult to make than creep tests
- creep tests are generally more useful to engineers and designers.

For an ideally elastic material, the stress necessary to keep ϵ constant will remain constant for a $t > 0$. However, for a model viscous liquid, the stress will be instantaneously infinite at $t = 0$ and then zero for $t > 0$, as represented in *Figure 8*.

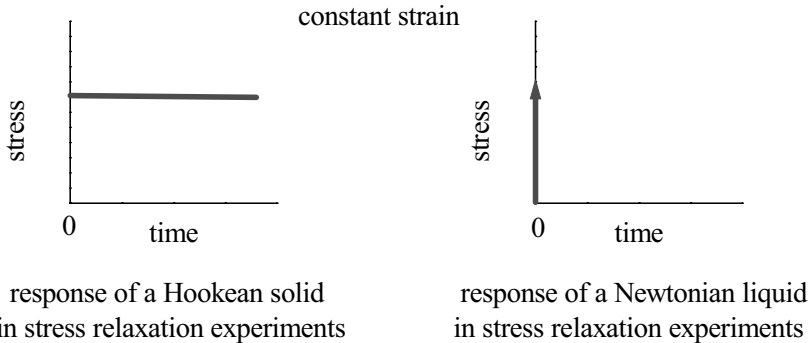


Figure 8.

However, for a viscoelastic material the stress will decrease slowly with time. A typical stress relaxation curve is shown in *Figure 9*.

The mathematical representation of the stress relaxation curve is

$$\sigma(t) = \sigma_0 \cdot e^{-t/\tau}$$

where σ_0 is the initial stress. The viscoelastic function obtained is the stress relaxation modulus, $E(t)$, that is defined as

$$E(t) = \frac{\sigma(t)}{\varepsilon} = E_0 \cdot e^{-t/\tau}$$

In the linear viscoelastic regime, creep compliance function is a time-dependent reciprocal modulus.

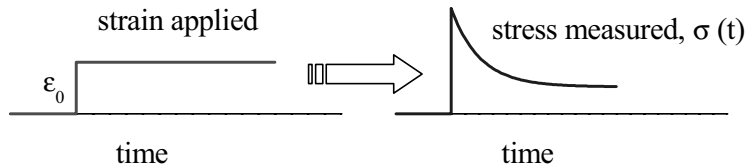


Figure 9.

7. Stress-strain experiments

This type of test measures the response (strain) of a sample subjected to a force that varies with time at constant rate. It is widely used, resulting a very important practical measurement. However, the relationship of this test to use applications is not as clear as is generally assumed. Because of the viscoelastic nature of polymers with their sensitivity to many factors, the stress-strain test is, at best, only a rough guide to how a polymer will behave in a finished object. To give the engineer or designer a complete and realistic information, tests at many temperatures, rates of testing and other conditions are required. Consequently, it needs much time and material.

The shape of stress-strain curves is used to define brittle and ductile behavior. Since the mechanical properties of polymers depend on both temperature and observation time, the shape of the stress-strain curves deeply changes with the strain rate and temperature for a given polymer, as seen in *Figure 10*. The curves represented in *Figure 10a* for hard and brittle polymers show that the stress increases more or less linearly with the strain. This behavior is characteristic of amorphous and semicrystalline polymers well below the glass transition temperature, T_g . These materials fails at low strains (usually lower than 10 %) leading to a brittle fracture. The curve in *Figure 10b* describes polymers showing a ductile behavior that yields before failure. The most ductile polymers undergo necking and cold drawing failing at higher strains (around 250-400 %). Semicrystalline polymers are typical examples that display this behavior at temperatures intermediate between glass transition and melting. The curves depicted in *Figure 10c* are characteristic of elastomers or amorphous polymers above their T_g , showing an elastomeric behavior reaching very high deformations before breaking. The deformation takes places homogeneously in these materials or at these temperatures.

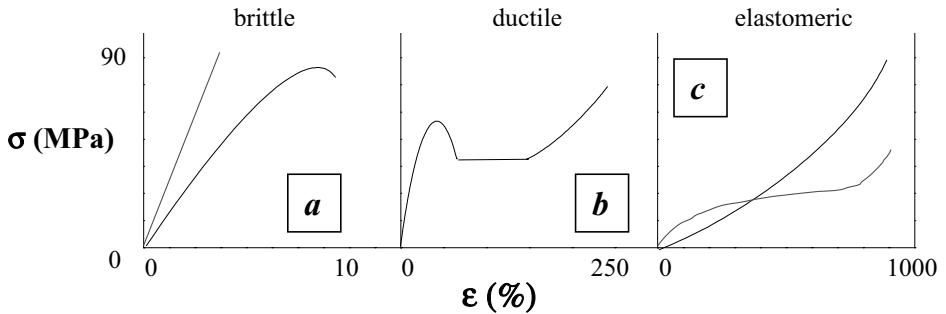


Figure 10.

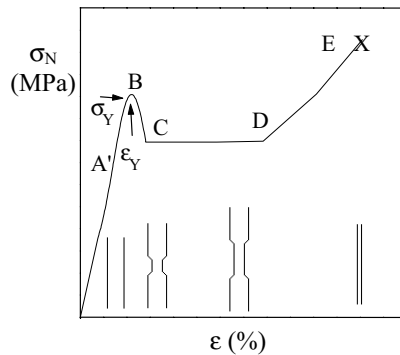


Figure 11.

Figure 11 shows a stress-strain curve corresponding to a tensile test for ductile polymers. Nominal stress (load divided by initial cross-sectional area of the strip) is plotted against strain. In the bottom part of the Figure 11, the change in the cross section of a specimen is seen. It has been observed for many years that some thermoplastics can be deformed at room temperature as a result of cold drawing. This is a remarkable phenomenon, in which the plastic deformation is concentrated in a small region of the specimen. The behavior at low strains (from A to A') is homogeneous and the stress rises steadily with increasing strain. Therefore, the relationship between these two magnitudes is linear since this region is that where Hooke's law is obeyed and the polymer might recover the original shape if the stress is removed (linear elastic or viscoelastic behavior, *i.e.*, instantaneously or temporally delayed). At B the sample thins to a smaller cross-section at some point with the formation of the neck. A maximum point is reached, that is called yield point, and characterized by its two coordinates:

yield strain and yield stress (ϵ_Y , σ_Y). In general, the yield point indicates the beginning of the plastic deformation. Further extension occurs by the movement of this neck through the specimen as it progressively thins from its initial state to the final drawn state. A decrease of the nominal stress is observed at strains higher than ϵ_Y until the value corresponding to point C. In the region CD, the material is deformed without any apparent change of the nominal stress, giving rise to the phenomenon called cold drawing. Starting from point D, stress begins again to considerably go up indicating that the material becomes rigid. This process is labeled as strain hardening. After that, fracture of the material occurs at point X.

Information about three important mechanical parameters can be obtained from this type of test: stiffness, strength and toughness. The stiffness is evaluated by the elasticity modulus, E , that is the slope in the initial linear region (AA'). The mechanical strength is related to the highest stress that material can bear before its breaking. Its value is usually given by the breaking stress. The concept of toughness might be defined in several ways, one of which is in terms of the area under the stress-strain curve. It is, therefore, an indication of the energy that a material can store before its rupture.

Dynamic mechanical measurements

The transient experiments referred above provide information on the viscoelastic behavior of materials in the time-domain for values of t larger than 0.1 seconds. However, it is often necessary to obtain the responses of viscoelastic materials to perturbation force fields at very short times. For instance, it is important to know how the storage and loss viscoelastic functions change with the frequency of the perturbation when materials are used as acoustic isolators in buildings, or to eliminate noise in vibrating metallic sheets by depositing layer of viscoelastic materials on them, etc. Information of this kind can be obtained by studying the responses of materials to dynamic perturbation fields. Moreover, taking into consideration that an experiment carried out at a frequency ω is qualitatively equivalent to others performed in the time domain $t = \omega^{-1}$, the combination of transient and dynamic experiments provides information on the viscoelastic behavior of materials in a wide range of time scale covering several decades. The information thus achieved is important not only on practical grounds but also from a basic point of view. Actually, the knowledge of viscoelastic responses over a wide time scale is important to the analysis of the molecular motions responsible for the viscoelastic behavior of materials. In the Dynamic Mechanical Thermal Analysis, DMTA, when a polymer reaches the temperature or frequency range at which a chain movement occurs, the energy dissipated increases up to a maximum. Thus, dynamic mechanical analysis allows to study these maxima, not only the main one, related to the glass transition, but also local movements not detected by other techniques.

When a perfectly elastic solid undergoes a sinusoidal deformation, the corresponding stress is in phase with the strain. On the contrary, in a completely viscous fluid the phase angle will be ninety degrees. In a viscoelastic solid, as polymers are, the phase lag is in between these two extreme archetypes, usually up to 20 degrees, depending on the temperature range studied. Therefore, the stress wave is delayed with respect to the strain one and its decomposition leads to a component in phase and another one out of phase (see *Figure 12*).

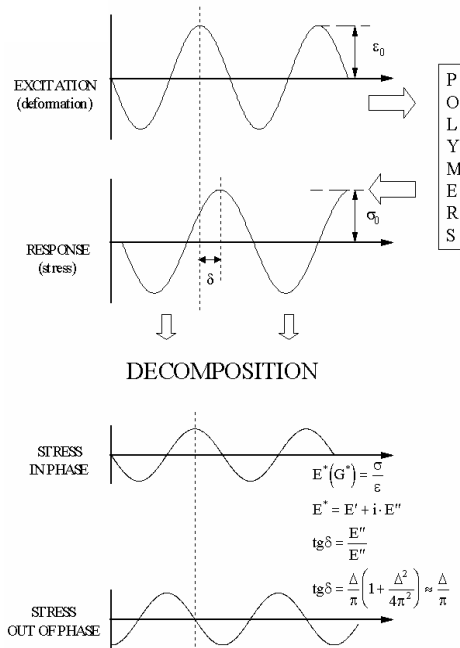


Figure 12.

These two components allow obtaining the two parts of the complex modulus (shear, bending, compression or tensile modulus, depending on the geometry of the sample clamping). These two contributions are named storage and loss modulus, E' and E'' respectively, related to the part of energy absorbed for the next cycle of the wave and that one dissipated, respectively. The ratio of loss modulus to storage modulus is the loss tangent, connected with the mechanical damping, δ , by the formula:

$$\tan \delta = \frac{E''}{E'} \cong \frac{\Delta}{\pi}$$

which is almost exact for low values of loss tangent, as occurs for polymers. Thus, the close relation between mechanical damping and loss tangent is seen.

When a polymer presents any movement the corresponding relaxation is depicted as a maximum in the loss tangent and loss modulus while the storage modulus displays an abrupt change. Depending on the variable considered, frequency or temperature, the characteristics related with a single relaxation are shown in this *Figure 13*, which has mirror symmetry.

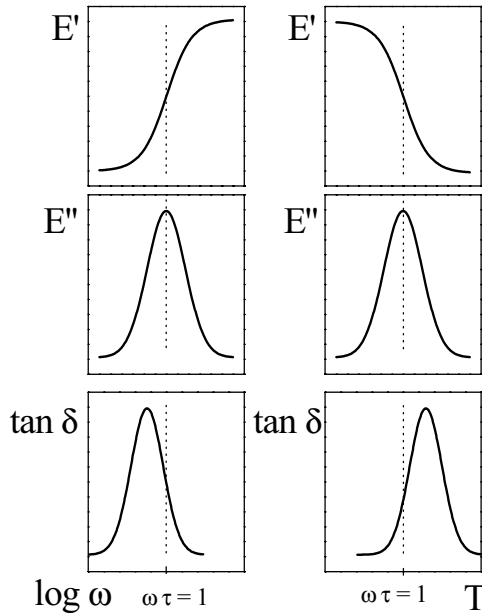


Figure 13.

Therefore, the variation of these viscoelastic parameters can be studied as a function of either frequency or temperature. In the first case, the real part (storage modulus) exhibits a strong increase in the relaxation zone, where the imaginary component (loss modulus) will show a maximum, observable equally in the values of $\tan \delta$ to slightly smaller frequencies. In a similar fashion, the variation of moduli and of $\tan \delta$ as a function of the temperature is proved at a given working frequency by a storage modulus diminution upon increasing temperatures, this decrease being the most accused in the relaxation zones at which the loss modulus presents maxima of variable intensity. These maxima also appear upon plotting the variation of $\tan \delta$ as a function of temperature, though at temperatures higher than in the case of the loss modulus maxima.

The location of a relaxation is dependent on frequency, as shown in Figure 14 on the magnitude plotted, E'' , for the two glass transitions found in graft copolymers of poly(*tert*-butyl acrylate-*g*-styrene). Therefore, it is needed to choose standard conditions for expressing results. It is mostly used the loss modulus vs temperature plot at 1 Hz of frequency. This representation for the relaxation associated to the glass transition leads to a value some degrees higher than the glass transition temperature measured by differential scanning calorimetry, DSC. Even though the T_g location can be easier measured by DSC, in some cases it is more easily found by means of DMTA. Moreover, dynamic mechanical analysis shows other chain movements and it can be also used for studying local motions.

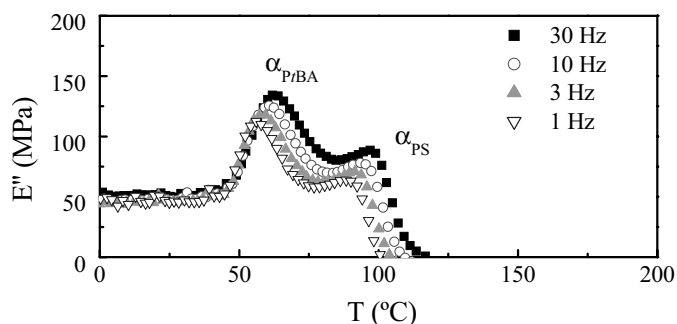


Figure 14.

The temperature dependence of molecular mobility is characterized by various relaxation processes in which a certain mode of chain motion sets in (or freezes in with decreasing temperatures). The most important mechanism in amorphous polymers or amorphous regions in semicrystalline polymers is the glass transition at the temperature of which, T_g , the micro-Brownian motion of segments of the main chain becomes active. The length of these segments is inversely proportional to the flexibility of the main chain; in common polymers it is estimated to be several tens of C-C bonds. The glass transition has received much attention in polymer physics because it is accompanied by significant changes in the mechanical (modulus of elasticity decreases by three or four orders of magnitude) and other physical properties of the sample. All of them are important also with respect to its applications. The rest of relaxation processes that appear in glassy polymers are called secondary relaxations. Since they are associated with the motions of short segments of main chains or with the motions of parts or the whole of the side chains, they are accompanied by much smaller changes in the physical quantities than those exhibited at around the glass transition. Until now, secondary processes have received relatively little attention, probably also because of their less practical importance so that the understanding of the molecular mechanism involved is still incomplete and the description of the observed phenomena is semiquantitative at best.

Secondary relaxations are closely associated with limited molecular mobility, *i.e.*, with the rotational and vibrational motions of relatively short chain sections. The motional units may be identified with sequences of the main chains consisting of four to six groups or with side chains and their parts. Generally, it is believed that such a motional unit may assume several stable conformations separated from each other by potential barriers. The frequency of the jumps over a potential barrier is inversely proportional to its height and proportional to the absolute temperature. Therefore, these types of relaxations are well-described by an Arrhenius expression

$$f = f_0 \cdot e^{\frac{-\Delta H}{RT}}$$

where f is the working frequency T is the absolute temperature at which the maximum of a relaxation occurs and H is the activation energy of the relaxation process. However, this expression is not fulfilled in the case of the relaxation associated to glass transition, but the process is adjusted to the equation of Williams, Landel and Ferry. Consequently, the plots $\ln f$ vs T^{-1} are straight lines only for the secondary relaxations. Relaxation associated to the glass transition do not follow this dependence excepting for measurements performed in small intervals of low frequencies, in whose case straight lines (with high slope) are also obtained for the glass transition. The activation energy, usually named with the adjective "apparent", obtained from the slope of those plots (called relaxation maps), measures the easiness in the cooperativity of the movement. Therefore, the glass transition usually has the highest apparent activation energy (around 400 kJmol^{-1}) and other local movements (parts of the chain, lateral chains, bulky groups) have activation energies as low as 30 kJmol^{-1} . This fact can be seen in *Figure 15*, which also shows the merging of alpha and beta relaxations at frequencies around 10^{13} Hz .

The Arrhenius plot for the relaxation related to the glass transition is not a straight line in the whole temperature range but a curve, as aforementioned. However, at low frequencies (those of dynamic mechanical analysis, circles in *Figure 15*) the line is almost straight and has a high slope. The squares in the plot are results from dielectric measurements. The dielectric analysis has different physical basis but gives a similar information on macromolecular movements, referred obviously to polymers with dipoles in the chain, and allows working at frequencies much higher than the mechanical ones. However, dielectric analysis hardly detects movements in chains with weak dipoles, as polyolefins. Therefore, even though dynamic mechanical analysis cannot be accomplished in a frequency interval so wide as the dielectric one, DMTA results obtained at several frequencies in an interval of only two or three decades and at a heating rate sufficiently low, provide a very complete information of the molecular dynamics in the polymer, including the activation energy of the different relaxations.

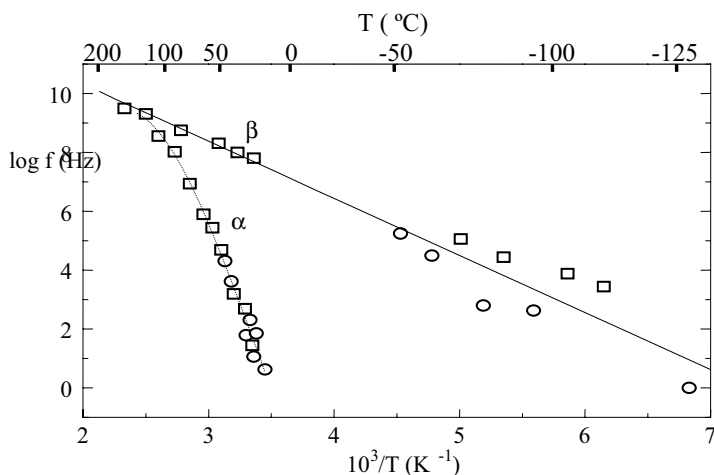


Figure 15.

Molecular motions underlying secondary relaxation process are a function of the constitution and structure of the polymer, but it is possible to find groups of polymers, usually of a similar composition, which exhibit an analogous relaxation (or relaxations) characterized by similar values of temperature location, activation energy, relaxation strength, etc. Molecular motions which give rise to secondary relaxation processes above the liquid nitrogen temperature have been tentatively divided into:

- Local main chain, A in the *Figure 16*
- Side chain rotations about the bonds linking side chains to the main chain, B in the *Figure 16*
- Internal motions within the side chain, C in the *Figure 16*
- Motions occurring within the crystalline regions
- Diluent-induced secondary relaxations, D in the *Figure 16*

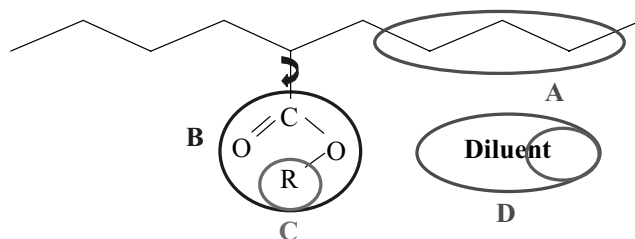


Figure 16.

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