

Fundamentals of DMA

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1. Definitions

1.1. Rheology

The term Rheology was coined by Professor Bingham of Lafayette College, Indiana. Professor Bingham described it as the science of flow and deformation of materials [1], a definition accepted by the American Society of Rheology in 1929. Howard Barnes said that the flow was a deformation, at least part of which was non-recoverable [2]. William W. Graessley considered deformation a change in shape [3]. For Russell R. Ulbrich, Rheology was the study of stress-deformation relationships [4], allowing one to analyze the constitutive equations linking the stresses and deformations in materials [5-7]. According to N. W. Tschoegl, a constitutive equation or rheological equation of state finds a relationship between a dynamic quantity, stress, and a kinematic quantity, strain, through one or more parameters or functions representing the characteristic response of the material per unit volume, regardless of size or shape [8].

1.2. DMA

Dynamic Mechanical Analysis (DMA) studies the behavior of materials which are subjected to a dynamic or steady deformation. It looks at how they respond to an imposed stress. Stress deforms the materials and DMA measures the strain, calculating how much energy is stored or dissipated during the process. Although gels and some viscous samples can be tested, a DMA instrument is specially adapted to the rheological study of solid-like materials. DMA is also considered a thermal analysis technique. Because temperature can be controlled during a test, thermal properties, such as glass transition, can be studied by means of DMA.

1.3. Flow and deformation parameters

Since any rheological study deals with deformation and stress, the following terms will be used consistently:

Stress: the force deforming the sample per unit area. Its units in SI are Pa.

$$\tau \text{ (or) } \sigma = F/A$$

Strain: the distance a sample moves in response relative to the sample length. It has no units.

$$\text{In shear: } \gamma = \Delta X / \Delta Y$$

$$\text{In tensile: } \epsilon = \Delta L / L_0$$

Strain rate: change of shear strain per unit time. It is represented by $\dot{\gamma}$ in shear, and by $\dot{\epsilon}$ in tensile. Its units are s^{-1} .

2. Ideal and Real Behaviors

The range of a material's rheological behavior falls between the two classical extremes: ideal solid and ideal fluid. They are described by Hooke and Newton's laws, respectively.

2.1. Hooke's Law

Describes the behavior of an ideal elastic solid, relating the applied strain to the resultant stress (or vice versa).

The proportionality factor is called the material's modulus and is denoted as E or G.

Young's Modulus is the ratio of dynamic stress to strain, E^* (measured in tensile or bending mode)

$$E = \sigma / \epsilon$$

Shear Modulus is the ratio of dynamic shear stress to strain, G^*

$$G = \tau / \gamma$$

for most rubbery polymers: $E=3G$, assuming a Poisson ratio of 1/2 (Poisson's ratio is the linear contraction relative to the extension in tensile).

2.2. Newton's Law

Describes the behavior of ideal fluids according to stress and shear. The proportionality factor is viscosity, η . Ideal viscous fluids are linear in terms of shear rate, not shear thinning.

$$\tau = \eta \, d\gamma / dt = \eta \dot{\gamma}$$

In order to distinguish Newtonian and non-Newtonian behaviors, it is important to bear in mind that the shear viscosity of Newtonian fluids does not vary with shear rate and is constant with time of shearing.

2.3. Actual Materials: linear and non-linear regions

Most materials obey these laws over a limited range of stresses. Beyond this range, they show non-linear behavior. This unit will provide examples of how materials actually behave. Figure 1 shows the strain stress plot obtained from a wire made from a nickel-titanium alloy subjected to DMA. The behavior is similar to that of an ideal solid until breaking point. One finds in Figure 2 the typical strain-stress plot obtained from a thermoplastic. In this case, after the linear region, there is a wide range of non linear behavior, where creep is involved. Most polymer melts reveal a viscosity dependence with shear rate as shown in Figure 3, with a linear region for a low shear rate and shear thinning for higher shear rates.

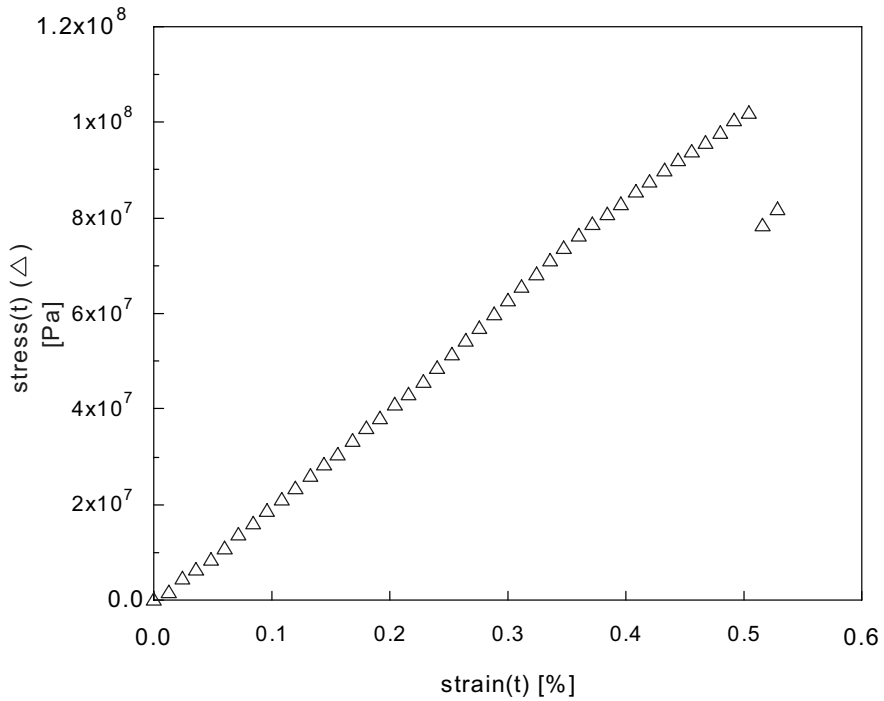


Figure 1. Strain rate test of a nickel-titanium alloy

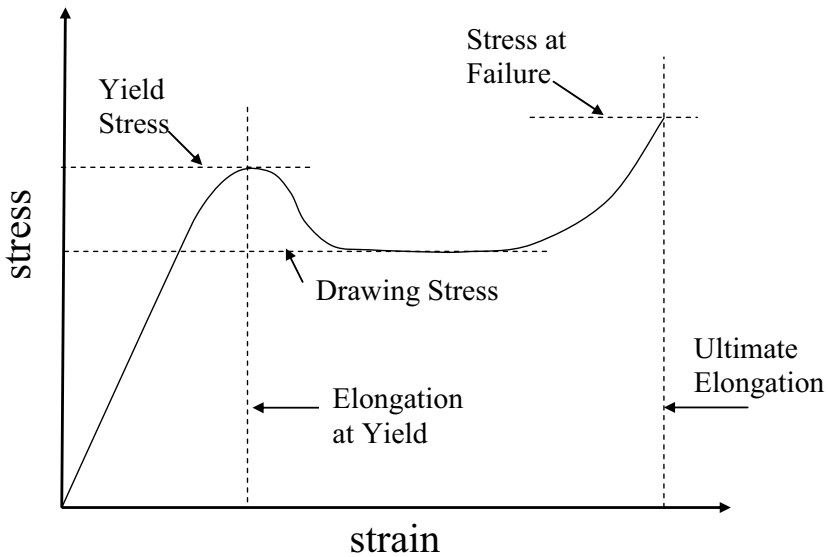


Figure 2. Typical plot of a strain rate test for a thermoplastic polymer.

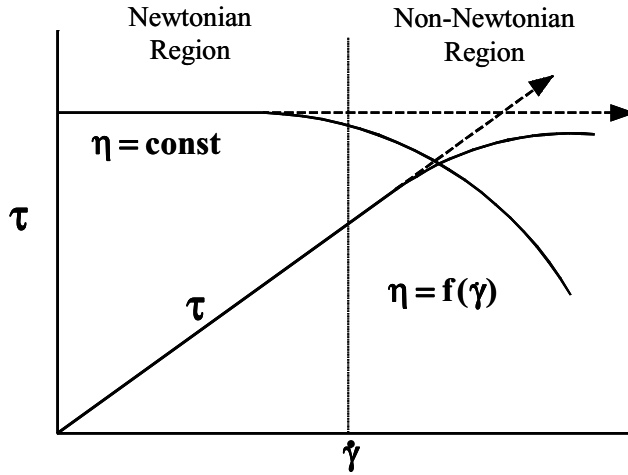


Figure 3. Typical stress-shear stress plot of a fluid showing linear and non-linear regions.

2.4. Non-Newtonian time independent liquids

Liquid viscosity is dependent on the shear rate, but independent of the time of shearing. The following cases are possible:

- Pseudoplasticity: viscosity decreases while the shear rate increases; this is also known as shear thinning.
- Dilatancy or shear thickening: both viscosity and shear rate increase.
- Bingham Fluids: there is no deformation below a yield stress. Above the yield stress the behavior may be Newtonian or non-Newtonian.

Figure 4 summarizes Newtonian and non-Newtonian time independent flow types.

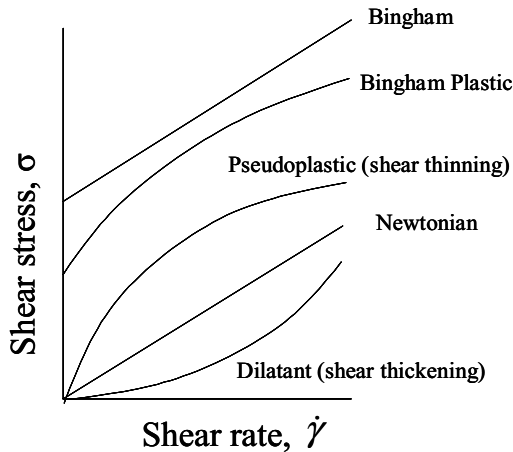


Figure 4. Newtonian and non-Newtonian time independent flow types.

2.5. Non-Newtonian time dependent fluids.

The viscosity of a fluid is dependent on the shear rate and the time during which the shear rate is applied. There are two typical cases:

- Tixotropy: apparent viscosity decreases time under constant shear rate or shear stress. This is followed by a gradual recovery when the stress or shear rate is removed.
- Reopexy: an increase in apparent viscosity appears with time under constant shear rate or shear stress. There is a gradual recovery when the stress or shear rate is removed.

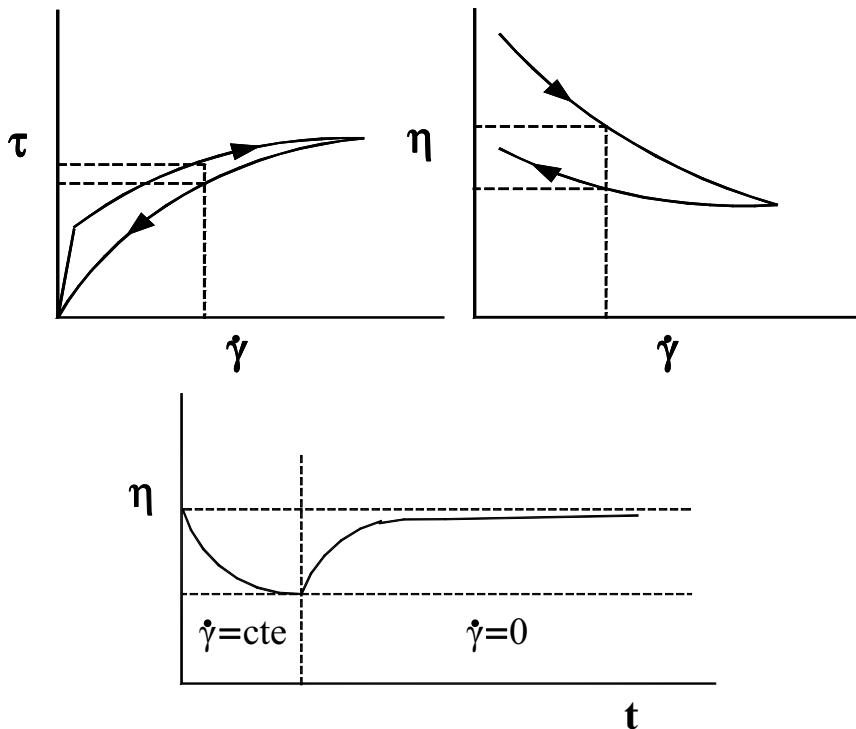


Figure 5. Idealized plot showing viscosity and a dependence on shear rate and time in a tixotropic fluid.

3. Viscoelasticity

3.1. Phenomena where viscoelasticity is involved

Viscoelasticity is the word used to describe material behaviors found among ideal solids and liquids. Examples in which viscosity effects are very evident include:

- Rate dependent behavior in solids. Solids in general behave with greater stiffness at high deformation rates. “Silly putty” is a silicone in which a dramatic change of stiffness occurs at deformation rates that fall under normal use.
- Rod climbing in liquids. Newtonian and viscoelastic behaviors of a liquid subjected to stirring action are depicted in Figure 6. Viscoelastic liquids tend to climb the stirring rod.
- Die swell in the extrusion of thermoplastics (Figure 7).
- Plastic “memory” in the injection molding of thermoplastics. It is well known that if the mold is open when the temperature of a part is still high, the part tends to twist remembering the movement imposed by the screw in the extruder.
- Melt fracture. One of the most frequent problems in extrusion, it is related to the deformation rate when a material passes through a nozzle. It is represented in Figure 8.

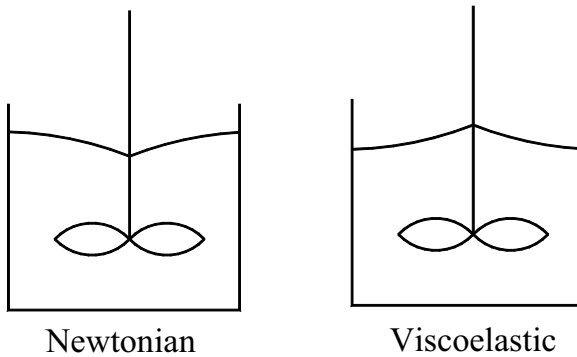


Figure 6. Newtonian and viscoelastic liquids under stirring action

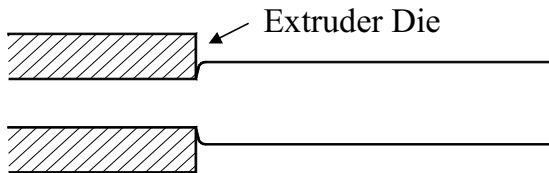


Figure 7. Die swell in extrusion

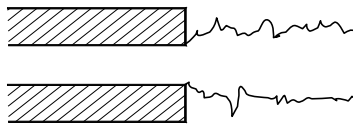


Figure 8. Melt fracture

3.2. Viscoelasticity and Time Dependence

Nothing behaves like an ideal solid or an ideal liquid. This fact seems to be reinforced by sayings like “everything flows if you wait long enough”. Actually, apart from the case of silly putty, mentioned above, there are many examples in nature and real life. Ice is considered a solid, but it is well known that glaciers have flowed over millennia. Another case in point is how old stained glass windows in European cathedrals is reported to be thicker at the bottom. This phenomenon is attributed to the slow flow of the glass while in place. Although water is a liquid, an impact at high speed against water may cause damage because, with high speed deformation, water behaves more like a solid. The time scale is critical, with solid-like behavior being favored by short time scales, and liquid-like behavior by longer time scales.

3.3. Viscoelastic Characterization

Although another section offers a more detailed description of test types, three methods of viscoelastic characterization may be mentioned here:

- Creep: stress remains constant while the strain is recorded as a function of time. The most accurate instrument for this kind of test in solids is a TMA (thermo mechanical analyzer). DMA also works in TMA mode.
- Stress relaxation: the strain is held constant while the stress is recorded as a function of time.
- Dynamic mechanical analysis: the sample is subjected to sinusoidal stress and the stress is recorded as a function of time. These kinds of tests are normally performed with DMA instruments, although they may be done with other rheometers.

3.4. Time-Temperature Superposition

Williams, Landell and Ferry [9] observed relationships between time and temperature in the mechanical properties of many polymers. They empirically obtained an equation that made it possible to shift the data away from the experimental range. Later on, a theoretical basis and other models were developed.

- Relationship between time and temperature

A short time is equivalent to a low temperature. Figure 9 shows how the modulus changes with time and temperature in a typical polymer.

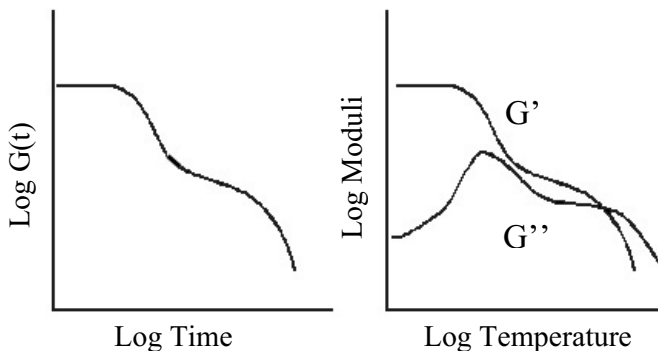


Figure 9. Modulus plotted against time and temperature in polymers.

- Relationship between frequency and temperature

The effect of a high temperature is similar to a low frequency or deformation rate. Figure 10 shows the modulus variation along with temperature and frequency.

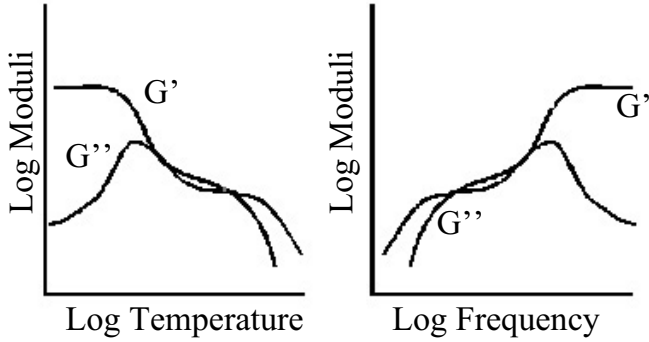


Figure 10. Modulus variation with temperature and frequency in polymers.

- Time and temperature superpositioning

Since data taken at higher temperatures represent data taken at lower frequencies (long times), and data taken at lower temperatures represent the behavior at high frequencies (short times), the data can be shifted horizontally to create a master curve that describes the behavior beyond the experimental range. Figures 11 and 12 show, respectively, the storage modulus variation with frequency at different temperatures and the master curve constructed over a wider range of frequencies.

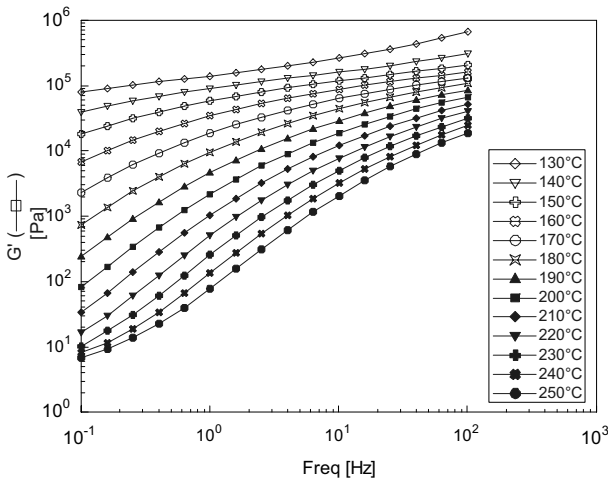


Figure 11. Overlay of storage modulus-frequency plots obtained at different temperatures.

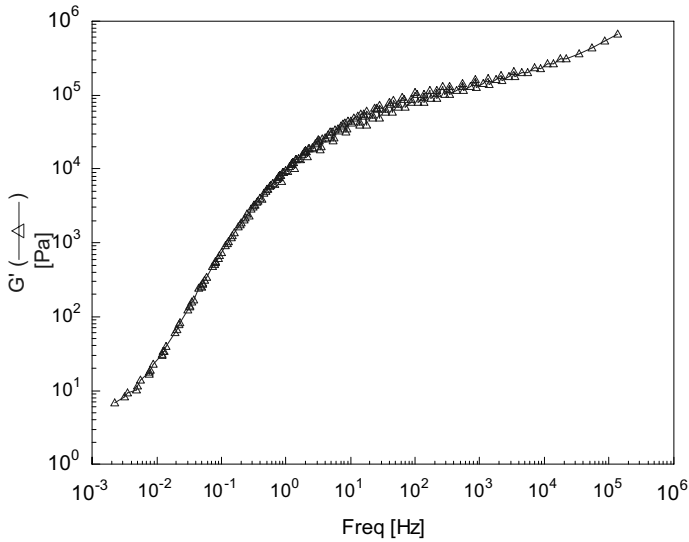


Figure 12. Master curve obtained by shifting the data obtained at different temperatures.

4. Principle of DMA

As seen below, a DMA apparatus may be used for working in several modes. However, a stress controlled instrument has been devised for working in dynamic mode. The stress controlled dynamic mode consists of measuring the strain in the sample, while applying a controlled sinusoidal or waveform stress. It is also possible to work with strain control. In this case, a controlled sinusoidal strain is applied while the stress response is measured.

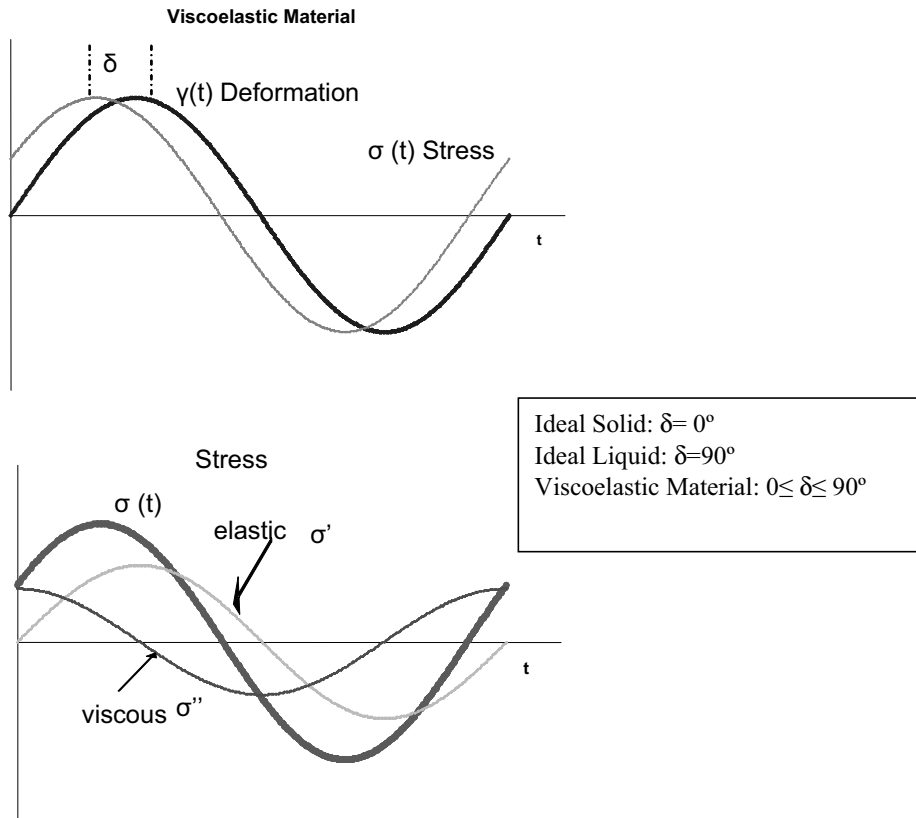


Figure 13. Above: stress and strain variations with time in a dynamic experiment. Below: separation of the elastic and viscous components of stress.

$$\varepsilon = \varepsilon_0 \sin(\omega t)$$

$$\sigma = \sigma_0 \sin(\omega t + \delta)$$

$$\sin(a + b) = \sin(a)\cos(b) + \cos(a)\sin(b)$$

$$\sigma = \sigma_0 \sin(\omega t)\cos(\delta) + \sigma_0 \cos(\omega t)\sin(\delta)$$

Define:

$$\sigma' = \sigma_0 \cos(\delta) \quad \text{In phase component}$$

$$\sigma'' = \sigma_0 \sin(\delta) \quad \text{Out of phase component}$$

Complex Stress:

$$\sigma^* = \sigma' + i\sigma'' = \sigma_0 \cos(\delta) + i\sigma_0 \sin(\delta)$$

What is Complex Strain?

$$\varepsilon = \varepsilon_0 \sin(\omega t)$$

$$\varepsilon' = \varepsilon_0$$

$$\varepsilon'' = 0$$

because the time is defined as zero based on ε .

Thus, the Complex Strain is:

$$\varepsilon^* = \varepsilon' + i\varepsilon'' = \varepsilon_0$$

What is the Complex Modulus?

Starting from Hooke's Law:

$$\sigma = E\varepsilon$$

that, in its complex form, it is:

$$\sigma^* = E^* \varepsilon^*$$

Then,

$$E^* = \sigma^* / \varepsilon^* = (\sigma' + i\sigma'') / (\varepsilon' + i\varepsilon'')$$

$$E^* = (\sigma_0 \cos(\delta) + i\sigma_0 \sin(\delta)) / \varepsilon_0$$

$$E^* = (\sigma_0 / \varepsilon_0) \cos(\delta) + i(\sigma_0 / \varepsilon_0) \sin(\delta)$$

$$E^* = E' + iE''$$

$$E' = (\sigma_0 / \varepsilon_0) \cos(\delta) \quad E'' = (\sigma_0 / \varepsilon_0) \sin(\delta)$$

where E' is the storage modulus that represents recoverable energy, that is, solid like behavior. E'' , the loss modulus, represents dissipated energy or liquid like behavior.

For an ideal solid, $\delta=0$, then

$$E' = (\sigma_0 / \varepsilon_0) \text{ and}$$

$$E'' = 0$$

For an ideal liquid,

$$E' = 0 \text{ and}$$

$$E'' = (\sigma_0 / \varepsilon_0)$$

The magnitude of the Complex Modulus

$$|E^*| = \left((E')^2 + (E'')^2 \right)^{1/2} = (\sigma_0 / \varepsilon_0) (\cos^2(\delta) + \sin^2(\delta))$$

$$|E^*| = \sigma_0 / \varepsilon_0$$

The $\tan \delta$

The $\tan \delta$, also called the loss factor and the loss tangent, is related to the storage and loss modulus as follows

$$E^* = E' + iE''$$

$$E' = (\sigma_0 / \varepsilon_0) \cos(\delta) \quad E'' = (\sigma_0 / \varepsilon_0) \sin(\delta)$$

$$E'' / E' = \sin(\delta) / \cos(\delta) = \tan(\delta)$$

For an Ideal Solid: $\tan(\delta) = 0$

For an Ideal Liquid: $\tan(\delta) = \infty$

5. Geometries

The actuator in DMTA is a drive shaft that moves in a linear way, forward and backwards. Some fixtures were designed to permit testing different samples in different ways.

With single and double cantilever bending, this geometry was devised to test solid bars. For instance, laminates can be directly tested in this manner. Thin layers can also be tested on a solid bar support. Figure 14 shows a single cantilever assembly.

The three point flexural test, considered the most suitable for very stiff materials, can be found in Figure 15. The boundary effect of the clamps, often the case with cantilever geometries, is avoided. This test also works well with materials that expand significantly with temperature.

Cylindrical and rectangular tensile geometry is ideal for samples that require a small force for deformation, such as films, fibers and elastomers. Figure 16 shows a rectangular sample assembled to the fixtures.

Compression fixtures, seen in Figure 17, are appropriate for resilience evaluation in foams and gels.

The next type is the shear sandwich. Although DMA was developed to test more or less solid like materials, this geometry can be used to test pastes, gels, melts and viscous fluids. Care must be taken to prevent the sample from leaking on the drive shaft. Normally, a horizontal position is preferred for this kind of test, as shown in **Figure 18**. Elastomers can also be tested with this geometry.

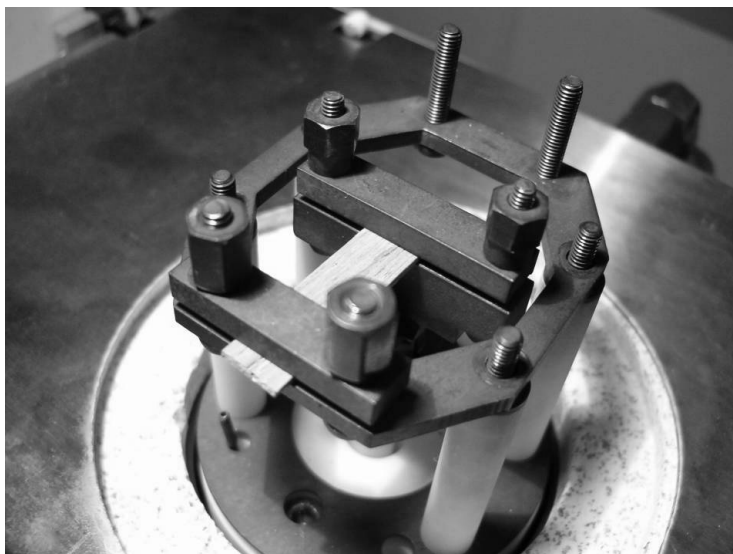


Figure 14. Single cantilever geometry



Figure 15. Three point flexion geometry

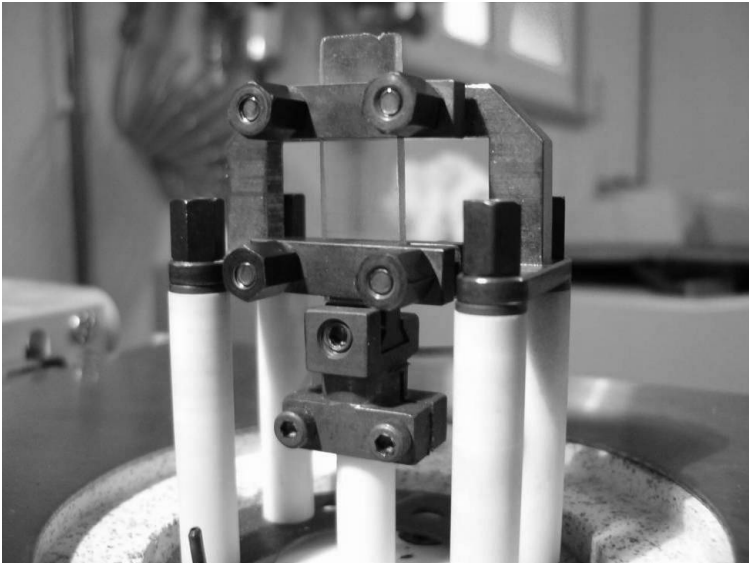


Figure 16. Rectangular tensile geometry

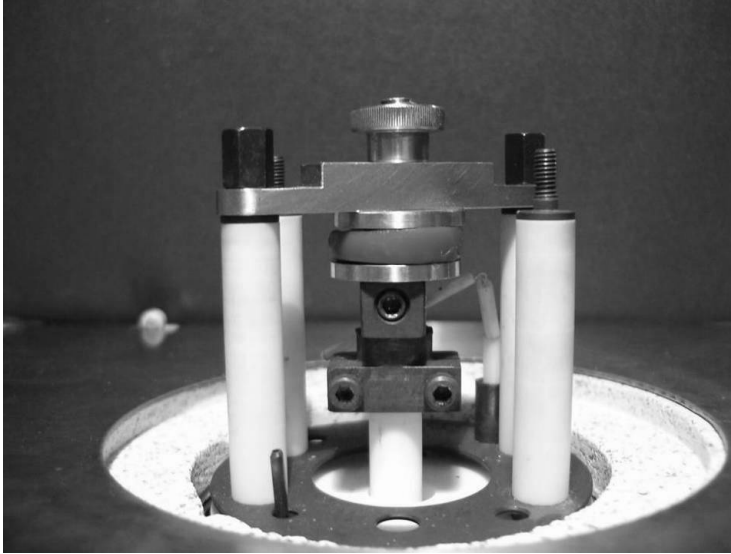


Figure 17. Compression geometry



Figure 18. Shear geometry

6. Modes of operation and variables

Although in DMA, instruments are built with internal stress control, in practice they can work under both stress and strain control. In either case, the instrument can be operated in dynamic and stationary-transient modes.

The tests are usually classified according to the type of control and mode of operation. These can be summarized as follows:

- Transient
 - Static load: creep and TMA mode
 - Constant strain: stress relaxation
 - Strain rate testing: stress- strain curves
- Dynamic
 - Single point: to set parameters
 - Time sweep at constant frequency and strain (or stress)
 - Dynamic strain sweep
 - Frequency sweep
 - Temperature sweep
 - Combinations of frequency and temperature sweep

The main variables involved in a strain controlled DMA test are

- Deformation or strain
- Rate or frequency of deformation
- Temperature ramp or step isothermal
- Time
- Stress, which is the response, since it is a strain controlled experiment

In a stress controlled experiment, strain is the measured response.

Figures 19 to 25 illustrate the evolution of the controlled variables and responses in typical operational modes. Figure 19 shows how the strain amplitude varies in a dynamic strain sweep test. It is normal to find a region of strain amplitude where the storage modulus is constant or varies linearly, followed by a non-linear region where the storage modulus decreases. The normal evolution of moduli with frequency is plotted in Figure 20: the higher the frequency, the higher the modulus. Viscosity decreases, an outcome consistent with the pseudoplastic behavior of most polymers. On the left-hand side of Figure 21 there are two possible temperature profiles in a temperature controlled experiment. The evolution of moduli and $\tan \delta$ is plotted on the right, showing a peak in $\tan \delta$ that corresponds with the glass transition. Many amorphous polymers decrease by three decades in the storage modulus of the glass transition region.

Figures 22 to 24 represent the responses of ideal solids (elastic), ideal liquids (viscous) and polymers (viscoelastic) to step changes in: stress deformation, strain deformation and rate deformation, respectively. Earlier, a strain-stress curve obtained from a nickel-titanium wire in a strain rate test was presented in Figure 1. Its behavior, almost linear until breaking, is very different from the one obtained with thermoplastics. Figure 25 shows the temperature profile and response of a memory shape alloy under constant stresses of different magnitude.

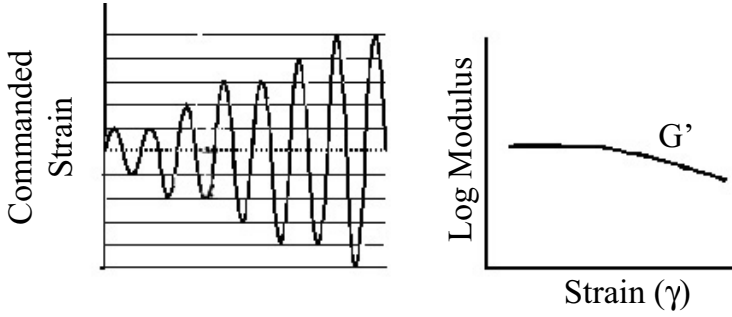


Figure 19. Commanded strain and typical storage modulus evolution of a polymer under dynamic strain sweep testing.

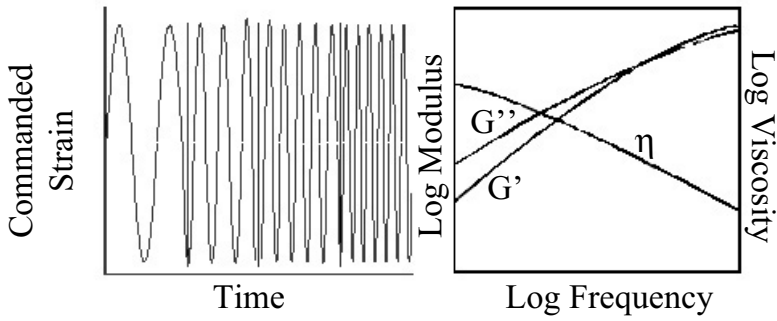


Figure 20. Frequency dependence of moduli and viscosity in a frequency sweep test.

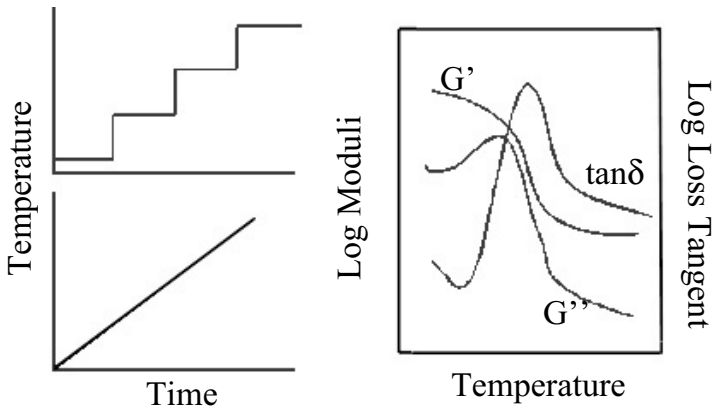


Figure 21. Step and ramp profiles of temperature on the left. Temperature dependence of the moduli on the right.

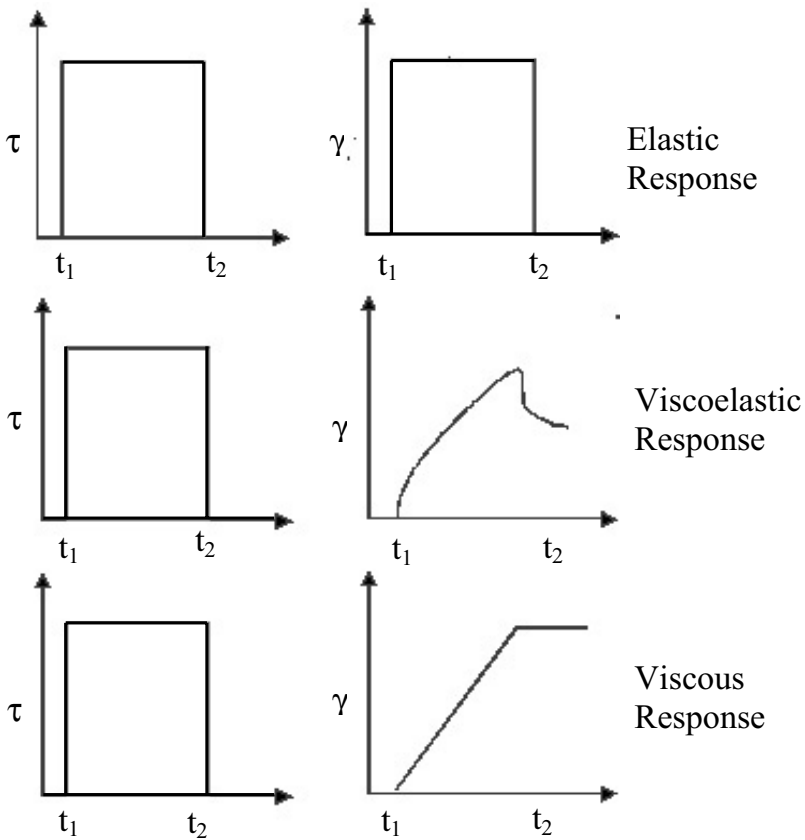


Figure 22. Material response to a step change in stress deformation (Creep Testing)

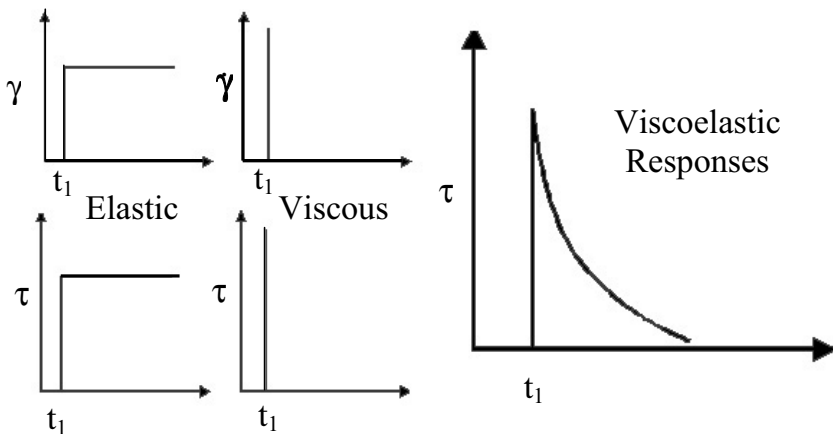


Figure 23. Material response to a step change in strain deformation (Stress relaxation testing)

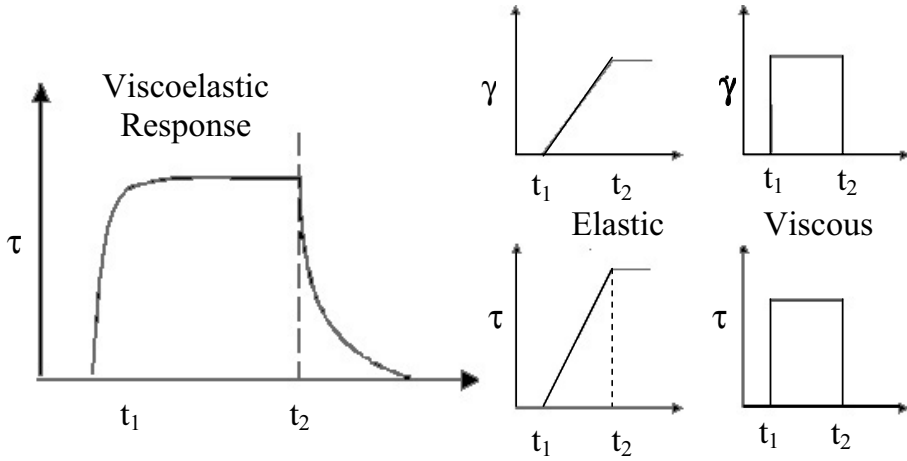


Figure 24. Material response to a step change in strain rate deformation (steady testing)

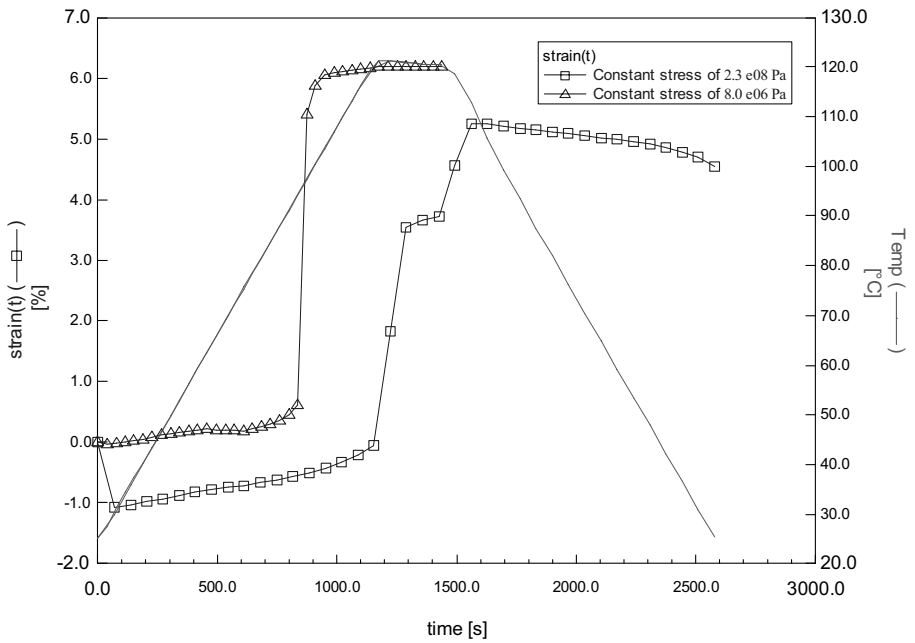


Figure 25. Strain plots at two different constant stresses, with a ramp-iso-ramp temperature profile, for a nickel-titanium alloy.

7. Choosing the magnitude for the controlled parameters

Sometimes, previously gathered information may help one choose the experimental conditions for analyzing a new material. In any case, the experimental setup should take into account what parameters have to be known about the material and what the physical form of that material is.

When considering the test of a new sample in DMA, many questions may arise, such as which geometry or mode of operation is most suitable. In general, these questions can be answered by following the criteria indicated in the previous paragraphs and remembering the limitations of the instrument. For example, for testing a gel, shear sandwich is possible in principle. An uncured thermosetting resin can be supported on a wire mesh and tested in double cantilever mode. A very stiff metal bar is not appropriate for testing in tensile mode because the force needed to deform it is higher than the maximum force allowed by the instrument. On the other hand, a very thin wire made of the same metal can be tested in tensile mode.

Once the geometry and operational mode have been chosen, assuming that it is clear which parameters are of interest, it is necessary to set up the magnitude of the controlled parameters. This is especially true with dynamic experiments where one parameter is kept constant. To illustrate the problem, consider the case of a dynamic strain controlled temperature ramp test. The range of temperature is of interest to the study and is constrained by the instrument's highest limit, as well as the sample's features, such as melting point. The other two magnitudes to set up are the frequency and strain amplitude. It is a good idea to perform two quick tests at room temperature to choose these magnitudes: a dynamic strain and frequency sweep.

- Dynamic strain sweep test

This test is designed to find the regions of the material's linear behavior. The range of strain amplitude for this test can be as wide as the instrument allows. Logarithmic variation is less time consuming. A provisional value for the frequency has to be chosen. In general, one Hertz is recommended.

- Frequency sweep test

Looking at the dynamic strain sweep test result, a strain amplitude value has to be chosen from the linear region. Again, the range for the frequency variation is limited by the instrument and logarithmic variation is possible. In general, frequencies lower than 0.1 Hertz are not recommended since they are more time consuming and do not hold any practical advantage.

Considering the results obtained in both preliminary tests, a combination of frequency and strain should be selected, making sure that this combination falls within the linear regions of both tests. Otherwise, additional preliminary tests should be performed until this requirement is fulfilled. One Hertz is recommended, whenever possible, because a lot of work has been accomplished using this frequency and, therefore, comparison is possible.

8. Interpreting Phenomena

Polymers may show several relaxation transitions along the temperature ranges that can be detected by DMA. These relaxation phenomena are characterized by a decreasing step in the storage modulus and a peak within the $\tan \delta$. All of these are frequency dependent. Figure 26 provides an idealized plot of the storage modulus and loss tangent for an amorphous polymer. Figure 27 reveals the effect of an increase in the frequency, shifting the transitions to higher temperatures. The transitions are normally denoted by Greek symbols, starting from α , for the transition closest to the apparent melting process. The α transition corresponds with glass transition in amorphous polymers. In the case of some crystalline polymers, it is not clear which transition corresponds with glass transition, since certain relaxation phenomena involving chain segments or slippage between crystallites may happen inside the crystalline superstructures, at temperatures between T_g and T_m . They strongly affect the properties within this temperature range.

It is generally accepted that glass transition is due to large scale main chain molecular movement.

Other relaxations may happen at temperatures below glass transition. They are caused by the motions of smaller segments within the main chain or pendant groups and may correlate to important properties, such as toughness.

Cold crystallization may also happen in crystalline polymers at temperatures above the T_g . It appears as an increase in the storage modulus.

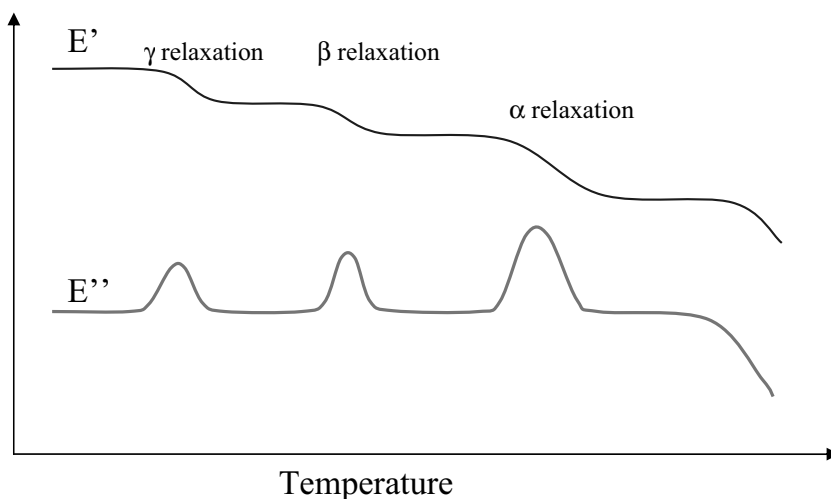


Figure 26. Idealized plot of the moduli evolution with the temperature showing typical relaxations in a thermoplastic polymer.

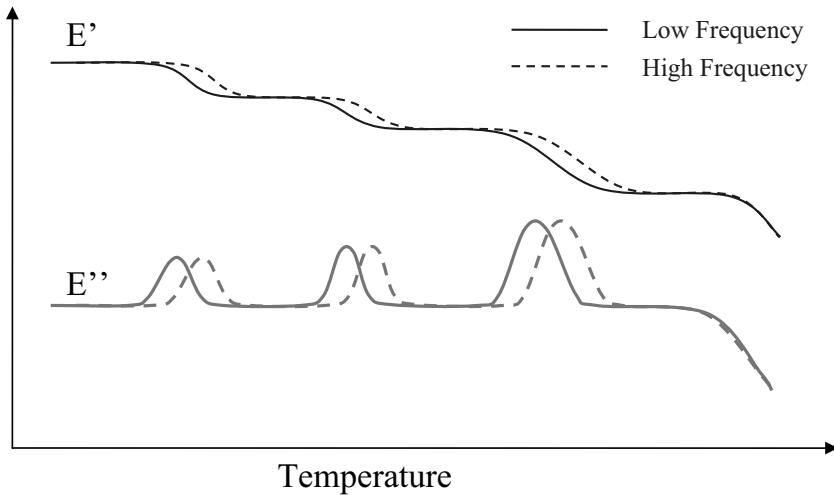


Figure 27. Idealized plot showing how the frequency shifts the relaxation peaks along the temperature axis.

9. Applications

- Determining mechanical properties, such as the storage modulus, loss modulus and loss tangent of materials over a spectrum of time or frequency and temperature. Although there are many quantities which can be determined by DMA, knowing any two allows one to calculate the remainder.
- Determining mechanical T_g. DMA is a very sensitive method for measuring glass transition. It is especially indicated for some polymers that show a slight change of heat flow at glass transition so that it cannot be seen by DSC. The reason is that their content in the amorphous phase is small. Nevertheless, even in those cases, the stiffness changes sharply at glass transition.
- Determining low temperature relaxations, common to impact resistance behavior.
- Predicting long term mechanical behavior.
- Analyzing thin samples, fibers and supported systems. The high sensitivity of DMA for measuring stress and strain means that one can analyze samples where very small forces are involved. This is the case of fibers and films. For non self standing samples, it is possible to use a support material. The support should show a constant storage modulus throughout the experiment and a very low loss modulus. Some classical forms of support include a wire mesh or a thin glass plate.
- Analyzing cure reactions. The gel point can be accurately measured by means of DMA. The value that is reported for the gel point is the time at which the storage modulus equals the loss modulus (see Figure 28). It is relatively independent of the frequency. Vitrification appears in isothermal experiments through DMA as an increasing step in the storage modulus (see Figure 29). The vitrification time

is calculated as the extrapolated end point of the process. Cure kinetics can be calculated from gel times obtained at different temperatures.

- Developing property- structure relationships.

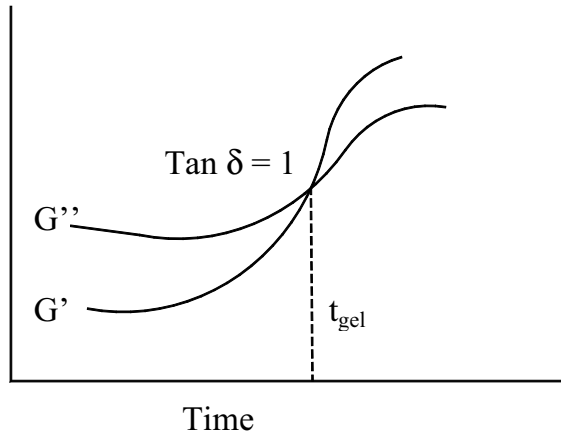


Figure 28. Idealized plot of G' and G'' illustrating the gel point location.

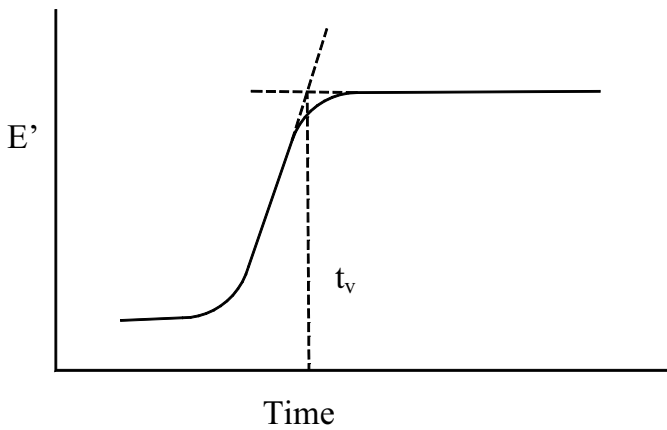


Figure 29. Idealized plot of E' along the vitrification process.

10. Choosing an instrument

Features that should be taken into account for choosing an instrument:

- Frequency range. Although one can compare instruments according to their specifications, it is important to take into account that very low frequencies are not commonly used on the whole since they are time consuming and do not report practical information.
- Range of strain amplitude.
- Sensitivity in displacement
- Sensitivity in force.

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