

Dynamic Properties of Polymer Materials and their Measurements

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Dynamic Properties of Polymer

Materials and their Measurements

1.1 Polymers

Polymer materials in their basic form exhibit a range of characteristics and behavior from elastic solid to a viscous liquid. These behavior and properties depend on the temperature, frequency and time scale at which the material or the engineering component is analyzed. The viscous liquid polymer is defined as by having no definite shape and flow deformation under the effect of applied load is irreversible. Elastic materials such as steels and aluminium deform instantaneously under the application of load and return to the original state upon the removal of load, provided the applied load is within the yield or plastic limits of the material. An elastic solid polymer is characterized by having a definite shape that deforms under external forces, storing this deformation energy and giving it back upon the removal of applied load. Material behavior which combines both viscous liquid and solid like features is termed as Viscoelasticity. These viscoelastic materials exhibit a time-dependent behavior where the applied load does not cause an instantaneous deformation, but there is a time lag between the application of load and the resulting deformation. We also observe that in polymeric materials the resultant deformation also depends upon the speed of the applied load.

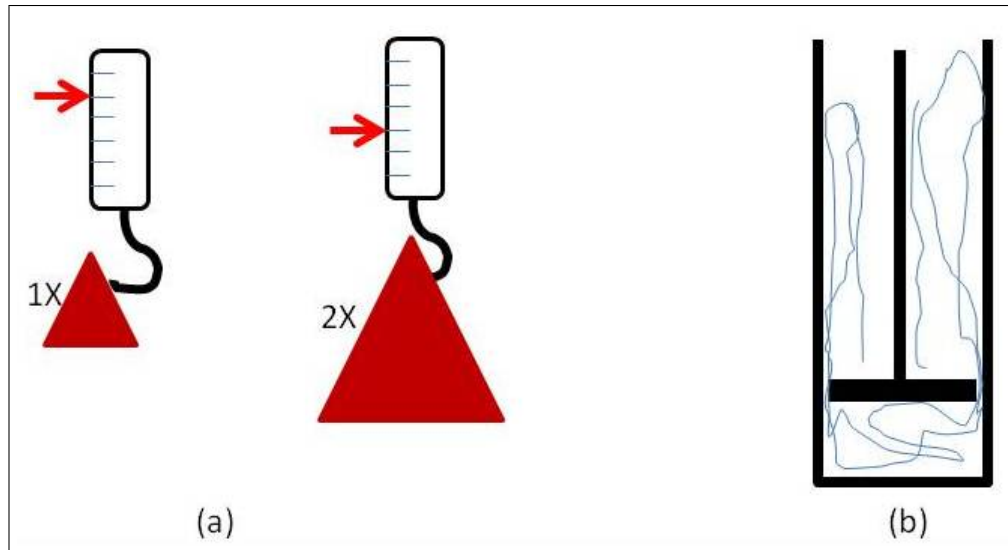


Figure 1.1: Linear Elastic and Non-linear Viscous Materials

Consider a spring based weighing scale as shown in Figure (1.1). If we put a fixed load on the scale such as a weigh bar we get a fixed amount of deflection and the needle points to point 2. Using an exactly double weight the needle moves twice as far upto point 4 and comes to rest. When we remove the weights the needle returns back to 0 position or the no-load position. The energy we put into the spring based weighing scale to cause deflection is equal to the energy the spring fully gives up when the needle moves back to 0. This concept gives the spring perfectly linear properties and 100% efficiency. If we are to consider a situation where if we were to put our weight on the scale slowly such that it takes ten minutes before the needle comes to the 2 point mark, and if we did the same action in thirty seconds, one minute, and five minutes? The needle would still come to rest at the 2 point mark. This shows that when we double the load, the needle pointer moves twice as far as originally meaning the response of the weighing scale is linear. We can also observe that the weighing scale takes the same time or the deformation rate remains the same even if we apply the weight at different times. This shows that the deformation is independent of the rate of the loading. The weighing scale thus obeys Hooke's laws and is a perfect Hookean spring. The deformation energy is always stored as elastic energy and is fully given up upon removal of the load.

Consider a tall cylindrical jar filled with 5W40 engine oil as shown in Figure (1.1b) . At the bottom of the jar is a round disc. The disc is slightly smaller than the inside of the jar so that the oil can move around this disc. Applying an X amount of force we can see that it takes 2 minute to extract the disc from the jar. To decrease the time taken by the disc to extract from the jar by 1 minute we see that we need to apply a higher force and to extract the disc in 30 seconds we need to apply an even higher force.

If the disc is moved from the bottom of the center of the jar to the center of the jar and let it rest, it remains in the same spot and after some time under the force of gravity it starts sinking to the bottom. We can feel that by moving the disc through the engine oil we are applying force or putting work into the oil system by shearing it between the disc and the wall of the jar. The faster we try to move the disc, higher the force required. Unlike the independent nature of the force in the weight scale, the amount of force required for the oil system now becomes rate dependent. e.g. It now depends upon how fast or slow we want to move the disc. The amount of force is not always proportional to the speed and now this becomes a non-linear relationship.

When we moved the disc from the bottom of the center of the jar, it stayed there and did not sink immediately to the bottom of the barrel. We put energy into the system but none of it was given back. All energy put into a viscous oil system is lost. The ideal viscous material is sometimes referred to as a Newtonian system.

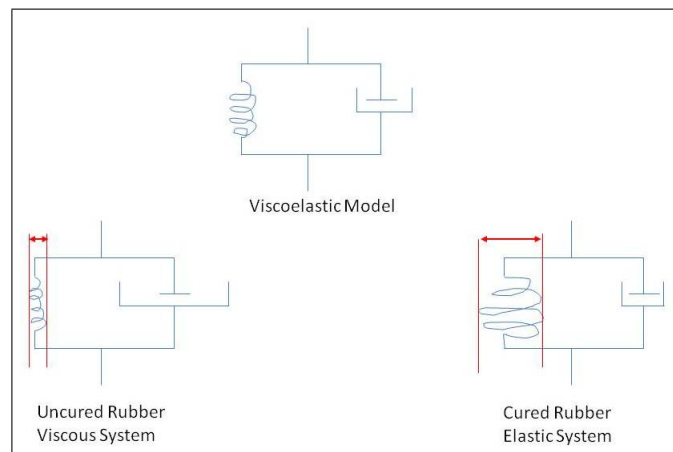


Figure 1.2: Viscous and Elastic Phases making up the Kelvin-Voigt Viscoelastic System

To summarize the response of the phases; The elastic response is linear and all the work input into the system is given up upon removal of applied load. The viscous response on the other hand is non-linear with the force and the deformation dependent upon the rate of the loading and the time. Joining the two phases; we now have a visco-elastic material that is graphically represented by a Hookean spring in parallel with a Newtonian dashpot, defined as the Kelvin-Voigt model as shown in Figure(1.2). When the viscous and elastic components are joined, we can simultaneously put energy into both of them, but the response of each phase is almost on opposites. In uncured rubber, the viscous phase dominates as evidenced by the flow of the material in the mold. As the rubber is cured during vulcanization the elastic phase slowly begins to emerge and starts dominating the deformation characteristics.

Hookes law for an elastic solid states that stress is linearly related to strain,

$$\sigma(t) = E\varepsilon(t); \quad (1.1)$$

or

$$\frac{d\sigma}{dt} = E \frac{d\varepsilon(t)}{dt} \quad (1.2)$$

Newtons law for a viscous liquid states that;

$$\sigma(t) = \eta \frac{d\varepsilon(t)}{dt}; \quad (1.3)$$

Combining equations (1.1 and 1.3), we get the Kelvin-Voigt model for a linear viscoelastic material;

$$\sigma(t) = E\varepsilon(t) + \eta \frac{d\varepsilon(t)}{dt}; \quad (1.4)$$

1.2 Viscoelastic Properties

Figure 1.3 shows the regimes of a typical polymer material from the glassy to liquid state. The material is in the glassy state below the glass transition temperature, and the modulus of the material as high as 3 GPa. The material practically behaves as a hard elastic material in this state. As the temperature increases the regime changes to glass transition state and the material modulus decreases from 3 GPa to approximately 10 MPa. Subsequently, the

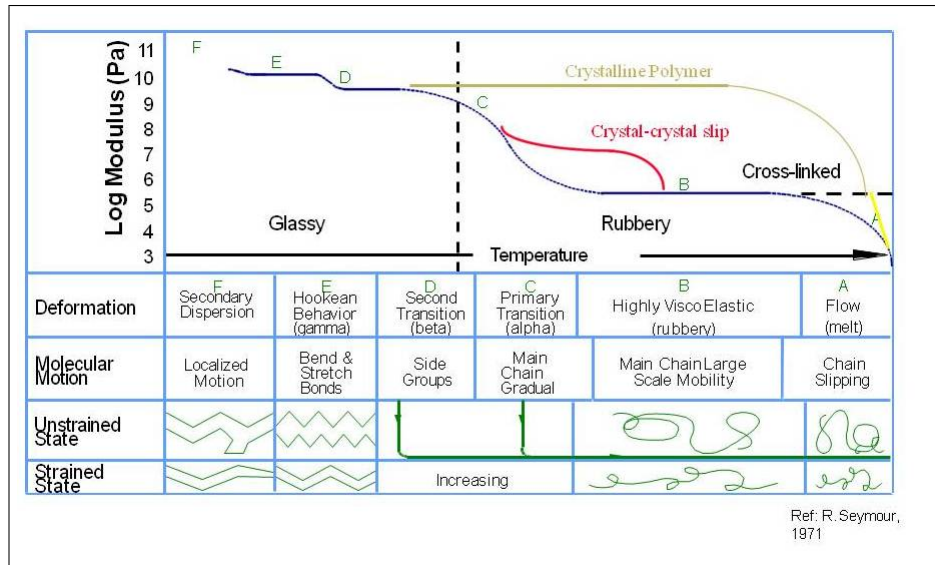


Figure 1.3: Different States and Modulus Regimes in Polymer Materials

material enters the rubber regime or rubbery plateau and is effectively at room temperature. Most of our applications of polymer materials to engineering components fall within this plateau regime. Below the rubbery plateau is the viscous regime where the modulus of the material further decreases causing the material to flow like a liquid. Processing of plastic or rubber materials in a compression-transfer mold or injection mold takes place in this regime. Below the viscous regime in the region of decomposition and complete breakdown of the polymer material and its ingredients.

Polymer materials by their very nature exhibit linear and nonlinear viscoelasticity. Linear viscoelastic behavior is exhibited by a material that is subjected to a deformation that is either very small or very slow on the application time scale. It can be said that the nature of the deformation can be predicted using a linear theoretical expression. While the application of polymers to a rapid rate of flow and deformation or sudden temperature cycling to the extremes results in deformation patterns that cannot be predicted by linear expressions, and the behavior is said to exhibit nonlinearity.

1.3 Dynamic Properties

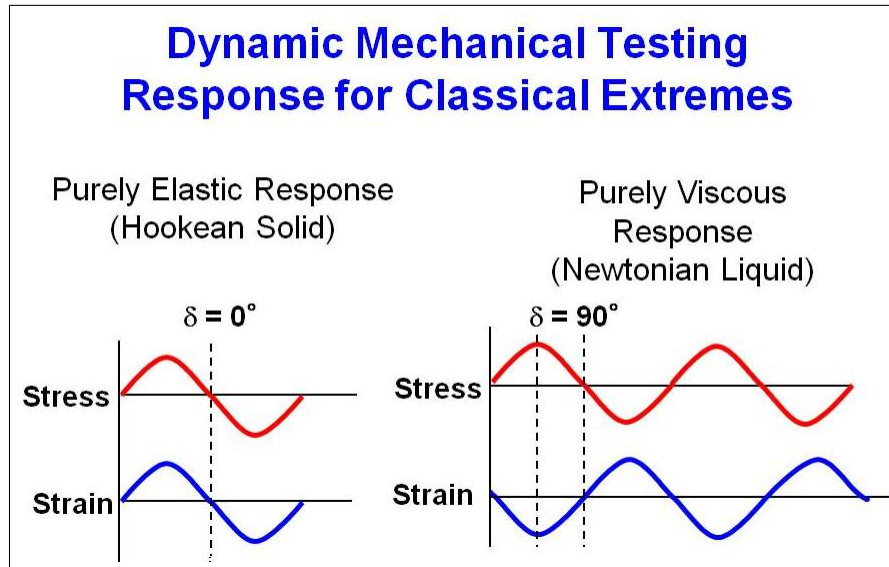


Figure 1.4: Purely Elastic and Purely Viscous Responses of Materials

Characterization of dynamic properties play an important part in comparing mechanical properties of different polymers for quality, failure analysis and new material qualification. Figures 1.4 and 1.5 show the responses of purely elastic, purely viscous and of a viscoelastic material. In the case of purely elastic, the stress and the strain (force and resultant deformation) are in perfect sync with each other, resulting in a phase angle of 0. For a purely viscous response the input and resultant deformation are out of phase by 90° . For a viscoelastic material the phase angle lies between 0 and 90° . Generally the measurements of viscoelastic materials are rerepresented as a complex modulus E^* to capture both viscous and elastic behavior of the material. The stress is the sum of an in-phase response and out-of-phase responses.

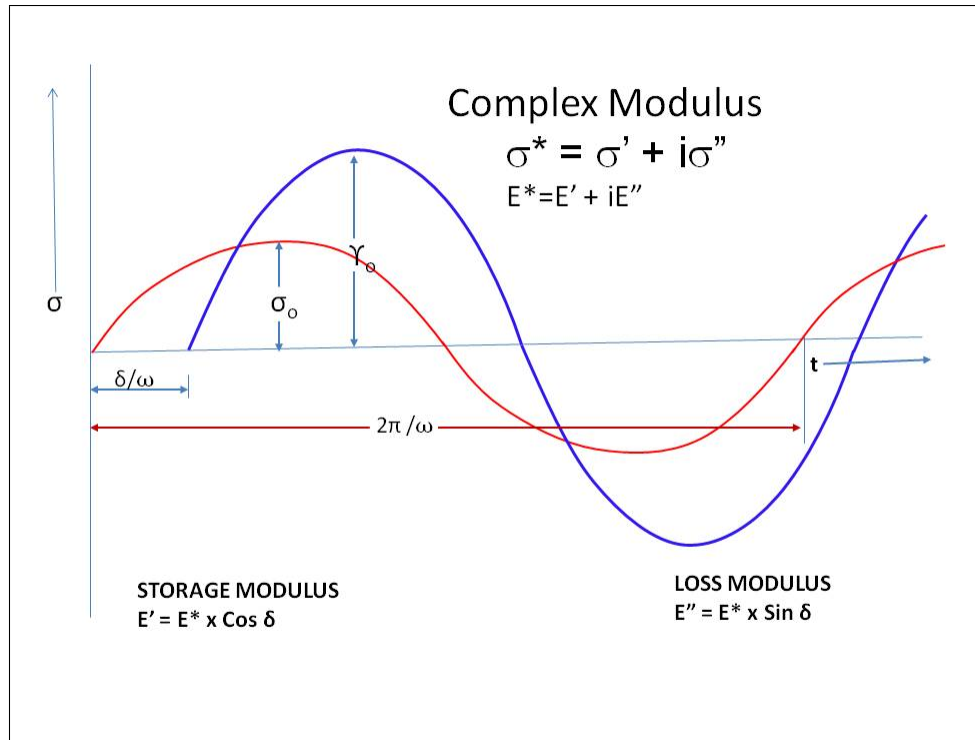


Figure 1.5: Viscoelastic Response of a Polymer Material

Figure 1.5 shows that the resultant strain lags the applied stress and can be written as,

$$\epsilon(t) = \epsilon_0 \sin \omega t \quad (1.5)$$

and the stress can be written as

$$\sigma(t) = \sigma_0 \sin(\omega t + \delta) \quad (1.6)$$

where σ_0 is the stress amplitude and ω is the angular frequency. Expanding the equation, it can be expressed as

$$\sigma(t) = \sigma_0 \cos \delta \sin \omega t + \sigma_0 \sin \delta \cos \omega t \quad (1.7)$$

The $\sigma_0 \cos \delta$ term is in phase with the strain, while the term $\sigma_0 \sin \delta$ is out of phase with the applied strain. The modulus E' is in phase with strain while, E'' is out of phase with the strain. The E' is termed as storage modulus, and E'' is termed as the loss modulus.

$$E' = \frac{\sigma_0}{\gamma_0} \cos \delta$$

$$E'' = \frac{\sigma_0}{\gamma_0} \sin \delta$$

$$E' = \frac{\text{In-phase stress}}{\text{Maximum strain}} = \text{Storage Modulus}$$

The storage modulus deals with the elastic modulus part, where the deformations are fully recoverable at the end of the displacement cycle.

$$E'' = \frac{\text{Out of phase stress}}{\text{Maximum strain}} = \text{Loss Modulus}$$

The in-phase stress and strain results in completely recoverable elastic energy while the out-of-phase stress and strain results in the dissipated energy termed as loss. Both the storage modulus and the loss modulus are functions of the applied frequency ω .

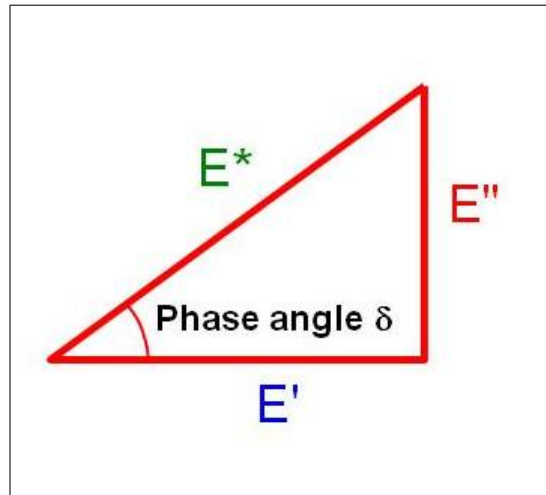


Figure 1.6: Concept of Complex, Loss and Storage Modulus

Figure 1.6 shows the graphical representation of the loss modulus, storage and complex modulus. The loss tangent or the damping coefficient is defined as

$$\tan\delta = \frac{E''}{E'} = \frac{\text{Loss.Modulus}}{\text{Storage.Modulus}} \quad (1.8)$$

Figure (1.7) shows the concept of loss and storage modulus from the example of a rubber ball. The ball when bounced off the ground from a height does not bounce to the level from where it was dropped but bounces only to a level lower. This loss of height can be defined as the energy that has been lost in energy dissipation due to deformation of the rubber.

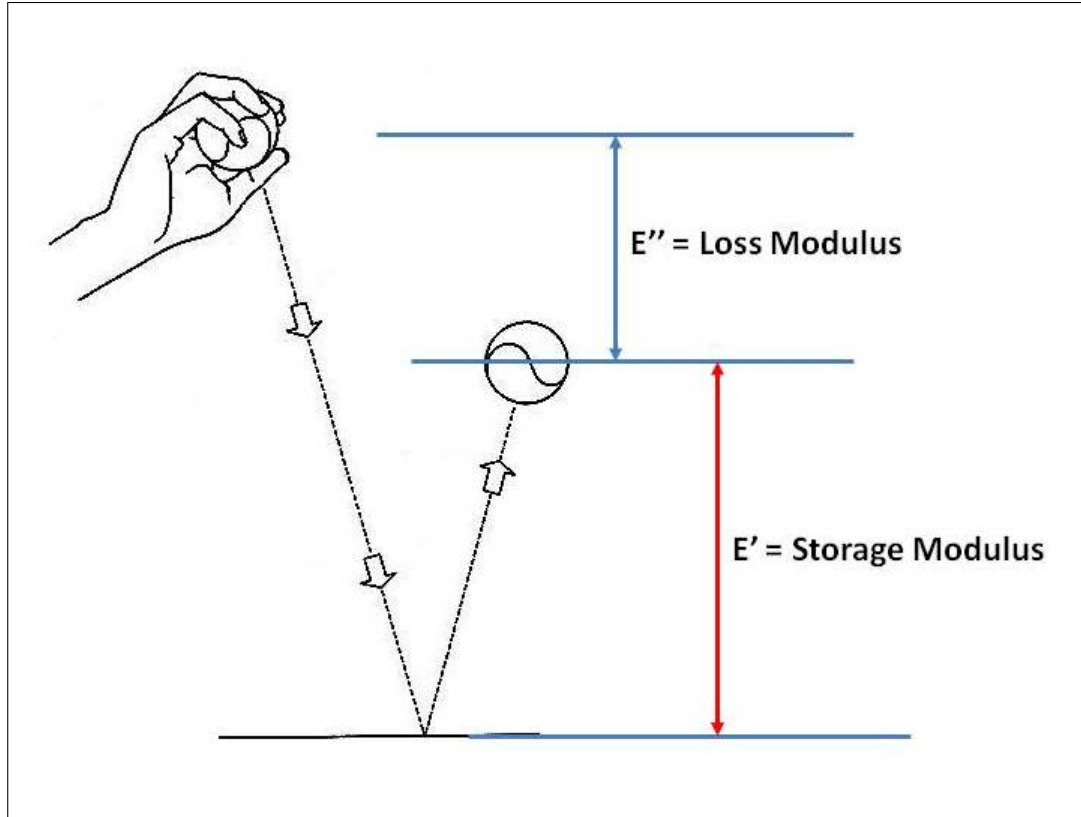


Figure 1.7: Loss and Storage Modulus in Elastomers

Polymer materials exhibit strong time and rate dependent properties. Studying these time and rate dependent properties is necessary to predict the performance of engineering components.

To accurately characterize the viscoelastic properties of polymers, material is sinusoidally deformed and the resulting stress is recorded. The deformation can be applied in tension, compression or shear mode depending on the geometric design or the application condition of the engineering component.

1.4 Stress Relaxation

Stress relaxation is a viscoelastic viscoelastic property of an elastomeric material. In a stress relaxation experiment, the sample is rapidly stretched or compressed to a predefined strain and held constant. The stress is then recorded as a function of time. Creep ex-

periments are carried out in a similar manner but instead of the application of a constant strain, a constant stress is applied and the deformations or the resultant strain is studied as a function of time. The stress relaxation modulus may be define as

$$E_{rel.}(t) = \sigma(t)/\epsilon_0 \quad (1.9)$$

If there is no viscous flow in the material, the stress decays to a finite value for polymeric materials. For amorphous linear polymers at high temperatures, the stress may eventually decay to zero. For a linear viscoelastic solid, the instantaneous stress will be proportional to applied strain and will always decrease with time.

The molecular causes of stress relaxation and creep can be classified to be based on five different processes.

1. *Chain Scission* The decrease in the measured stress over time is shown in Figure(1.8) where 3 chains initially bear the load but subsequently one of the chains degrades and breaks.

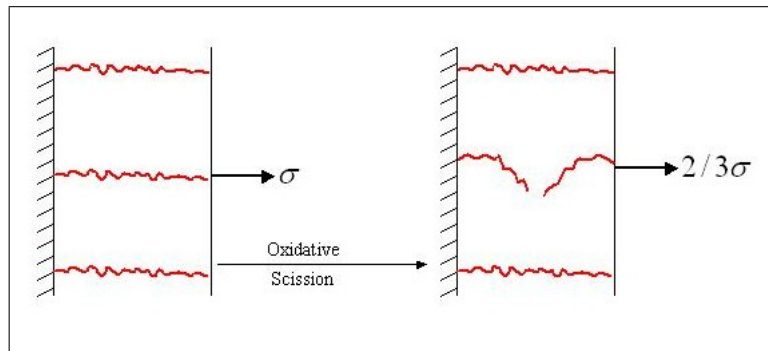


Figure 1.8: Chain Scission in an Elastomeric Material

2. *Bond Interchange* In this particular type of material degradation process, the chain portions reorient themselves with respect to their partners causing a decrease in stress.
3. *Viscous Flow* This occurs basically due to the slipping of linear chains one over the other. It is particularly responsible for viscous flow in pipes and elongation flow under stress.

4. *Thirion Relaxation* This is a reversible relaxation of the physical crosslinks or the entanglements in elastomeric networks. Generally an elastomeric network will instantaneously relax by about 5% through this mechanism.
5. *Molecular Relaxation* Molecular relaxation occurs especially near T_g (Glass Transition Temperature). The molecular chains generally tend to relax near the T_g .

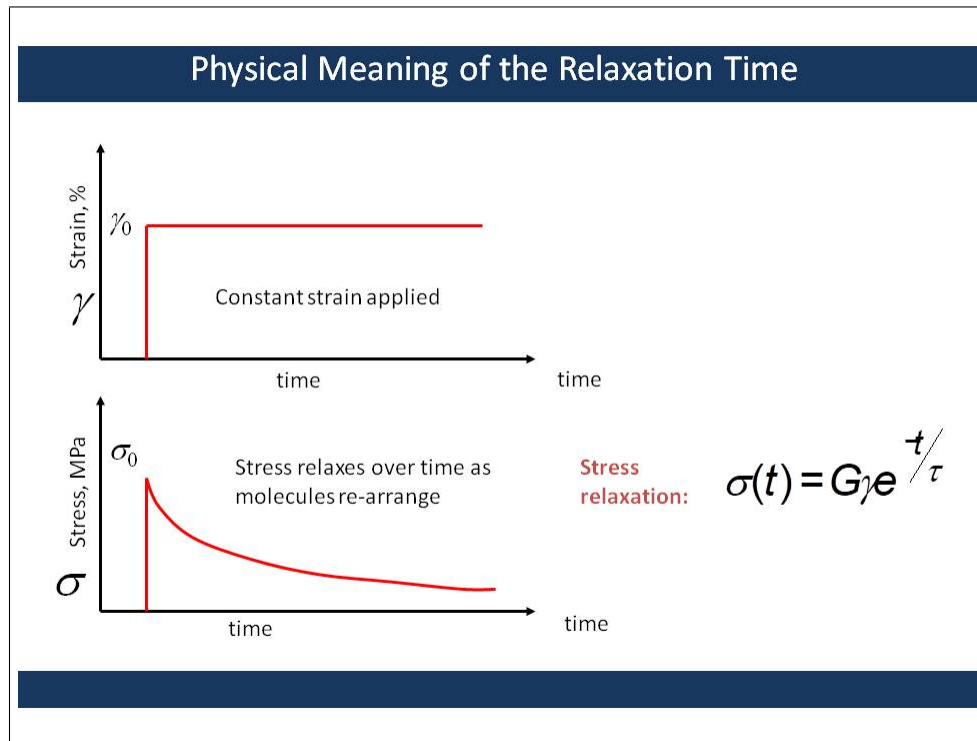


Figure 1.9: Physical Meaning of the Relaxation Time

The related effect of stress relaxation in sealing applications is the reduction in stress (i.e. sealing force) under constant strain (compression) conditions. In many applications when sealing force approaches zero, leakage is likely to occur as the seal geometry loses contact between the mating surfaces. Stress relaxation and compression set effects are undesirable and are of key importance in determining sealing performance. For amorphous linear polymers at high temperatures, the stress may eventually decay to zero. If there is no viscous flow in the material, the stress decays to a finite non-zero value.

Stress relaxation as discussed above is caused by a combination of physical relaxation, and chemical degradation. Physical relaxation is dependent on elastomer material proper-

ties. It increases with temperature, is dominant over short timescales during the initial time period of the experiment and is fully recoverable. Chemical degradation is highly dependent on temperature and on the aggressive chemical action of fluids and application environments and is applicable over longer time frames in an experiment. ASTM D6147 and ISO 3384 with methods A and B are the applicable standards for stress relaxation experiments. Method A refers to the continuous method of measuring the force over time, while method B refers to the intermittent method of measuring the force over time. Wykeham-Farrance test apparatus is the preferred method to measure the force decay over time in method B.

1.5 Creep

Creep is an increase in plastic strain under constant stress. Creep is an increased tendency of a solid material to move slowly or deform continuously under the influence of mechanical stresses. In other words it tends towards high strain and plastic deformation with no change in stress. Figure (1.10) shows a the stress and strain curves for a part undergoing creep. The material is stressed with an applied force. Creep tends to occur as a result of long-term exposure to high levels of stress that are still below the yield strength of the material. Over time, the force and stress do not change, although the shape of the part continuously deforms. When unloaded, there is additional permanent set. Old PVC pipes for electrical installations sag at the center when simply supported at the ends. This is an example of creep under the constant force of gravity. Creep in polymers at low strains (1 percent) is essentially recoverable after unloading.

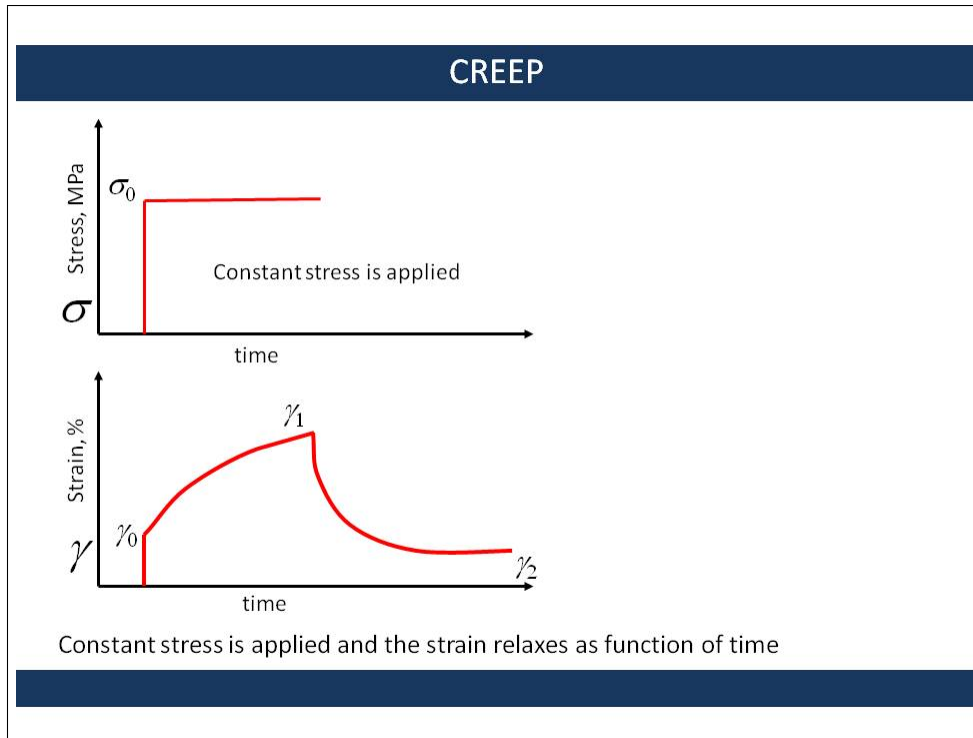


Figure 1.10: Physical Meaning of Creep

γ_1 is the immediate elastic deformation taking place under the effect of applied load. γ_2 is the elastic deformation that takes place over a period of time. γ_3 is the flow of the material or the non-recoverable creep that remains once the loading on the material is removed. The creep compliance may be define as

$$C_{comp.}(t) = \epsilon_t / \sigma(0) \quad (1.10)$$

Creep is thus a time- dependent deformation under an externally applied load. It generally occurs at high temperature (thermal creep), but can also happen at room temperature in certain materials albeit at much slower rate. As a result of Creep the material undergoes a time dependent increase in length, which could be dangerous while occurring in engineering components under service loads and boundary conditions.

ASTM F38 is the standard test method for Creep experiments on a gasket material.

1.6 Effect of Fillers on Dynamic Properties

Dynamic properties of rubbers are affected by fillers and other compound ingredients. It is found that the filler network can substantially increase the effective volume of the filler due to rubber trapped in the agglomerates, leading to a high elastic modulus. Fillers like carbon blacks increase the modulus of rubbers by forming reinforcing bonds with the polymers. The increase in modulus is due to the fact that fillers can be considered having higher rigidity as compared to the rubber. They do not participate in the deformation and increase the strain in the rubber matrix between adjacent filler particles. The strain increase because of this can be expressed by

$$X = 1 + 2.5c + 14.1c^2, \quad (1.11)$$

where x is the strain increase ratio and c is the volume fraction of the material. The equation shows that $\tan\delta$ increases linearly with x .

1.7 Application of Dynamic Material Characterization

Dynamic material characterization is a technique that measures stress as a function of strain, or force as a function of displacement and time. It also involves the application of one or more forces at various frequencies, as a means of determining how material changes in a dynamic environment where the material comes under the effect of multiple frequencies. Dynamic characterization testing normally includes components like tires, springs, dampers, biomedical implants and vibration isolation components from the automotive, aerospace and biomedical industries. These components perform under time and frequency varying conditions during their entire lifecycle making them ideal candidates for dynamic study both for product development and failure analysis.

1.7.1 Development and Failure Analysis of Rubber Rollers

Equation (1.11) can be particularly applied to materials where the carbon black filler size is larger (e.g. N990). In smaller sized filler particles the rubber is just in static form around the blacks and the effective volume fraction has to be suitably used. The strain increase or

amplification concept due to the presence of fillers also affects the energy losses per cycle of operation. Since the presence of higher rigidity fillers magnify and increase the local strain, the dynamic losses which are proportional to local strain amplitudes also increase. During cyclic strain, while the stable filler network can reduce the hysteresis of the filled rubber, the breakdown and reformation of the high structure filler network would cause an additional energy dissipation resulting in higher hysteresis. More information on this increase of losses can be obtained from *Meinecke et al.* As per studies, as compared to carbon black, silica is able to form a stronger and more developed filler network resulting in higher modulus and lower hysteresis at low and room temperature applications.

The E' , E'' , E^* or Tan Delta values are to be used as a comparative set of values from different compounds, or a single compound tested at different conditions i.e., temperature, frequency, or strain levels. When different compounds are tested, variables such as cure systems, filler types and levels and plasticizers can be evaluated and compared to provide inputs about dynamic properties.

For an example where dynamic properties testing could be helpful a filler is changed from N-762 to a N-550 black in a rubber covered pinch roller for paper applications. Some other compound adjustments were also made to maintain the same tensile, elongation and durometer values. A few weeks after the compound revision it was observed that there is a noticeable increase in failures of the roller. The operating conditions dictate that the paper roller runs at 180 rpm under 8000 Newtons resulting in the rubber warming up. A dynamic test at three Hertz and Tan Delta values is carried out to compare the compounds. The greater values of E'' and Tan delta (damping coefficient) indicate a higher hysteresis in the compound. It can be inferred from the results that higher hysteresis can cause greater heat buildup in the rollers leading to failures.

1.7.2 Viscoelastic Analysis of Tires

Tires are subjected to cyclical high deformations when vehicles are running on the road. When exposed to harsh road conditions, the service lifetime of the tires is jeopardized by many factors, such as the wear of the tread, the heat generated by friction, rubber aging, and others. As a result, tires usually have composite layer structures made of carbon-filled

rubber, nylon cords, and steel wires, etc. In particular, the composition of rubber at different layers of the tire architecture is optimized to provide different functional properties. The desired functionality of the different tire layers is achieved by the strategic design of specific viscoelastic properties in the different layers. Zones of high loss modulus material will absorb differently than zones of low loss modulus. The development of tires utilizing dynamic characterization allows one to develop tires for smoother and safer rides in different weather conditions.

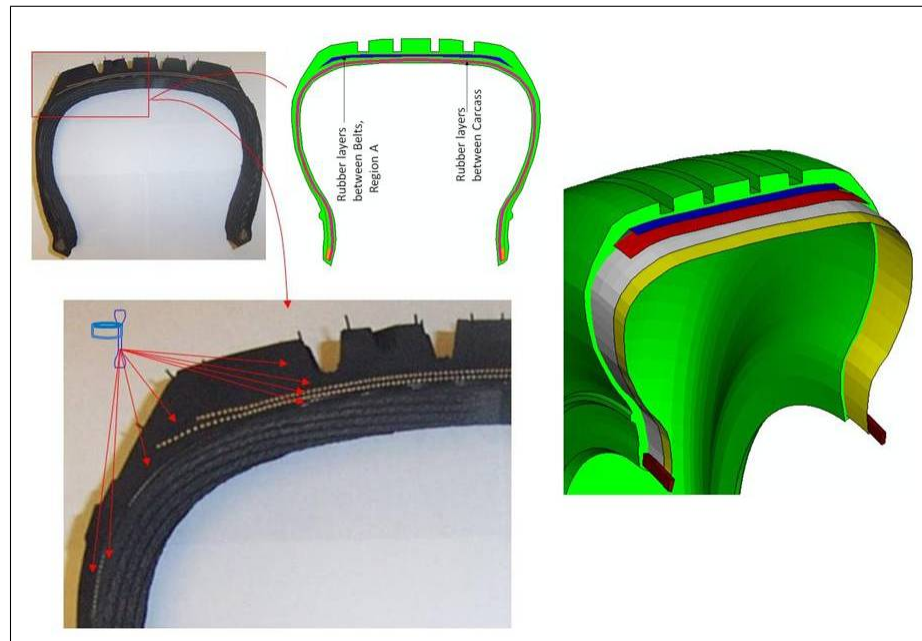


Figure 1.11: Locations of Different Materials in a Tire Design

The dynamic properties are also related to tire performance like rolling resistance, wet traction, dry traction, winter performance and wear. Evaluation of viscoelastic properties of different layers of the tire by DMA tests is necessary and essential to predict the dynamic performance. The complex modulus and mechanical behavior of the tire are mapped across the cross section of the tire comprising of the different material. A DMA frequency sweep test is performed on the tire sample to investigate the effect of the cyclic stress/strain frequency on the complex modulus and dynamic modulus of the tire, which represents the viscoelastic properties of the tire rotating at different speeds. Significant work on effects of dynamic properties on tire performance has been carried out by Ed Terrill et al. at Akron

1.7.3 Non-linear Viscoelastic Tire Simulation Using FEA

Non-linear Viscoelastic tire simulation is carried out using Abaqus to predict the hysteresis losses, temperature distribution and rolling resistance of a tire. The simulation includes several steps like (a) FE tire model generation, (b) Material parameter identification, (c) Material modeling and (d) Tire Rolling Simulation. The energy dissipation and rolling resistance are evaluated by using dynamic mechanical properties like storage and loss modulus, tan delta etc. The heat dissipation energy is calculated by taking the product of elastic strain energy and the loss tangent of materials. Computation of tire rolling is further carried out. The total energy loss per one tire revolution is calculated by;

$$\Psi^{diss} = \sum_{i=1}^{\infty} i2\pi\Psi_i Tan\delta_i, \quad (1.12)$$

where Ψ is the elastic strain energy,

Ψ^{diss} is the dissipated energy in one full rotation of the tire, and

$Tan\delta_i$, is the damping coefficient.

The temperature prediction in a rolling tire as shown in Fig (1.12) is calculated from the loss modulus and the strain in the element at that location. With the change in the deformation pattern, the strains are also modified in the algorithm to cause a change in the temperature distribution in the different tire regions.

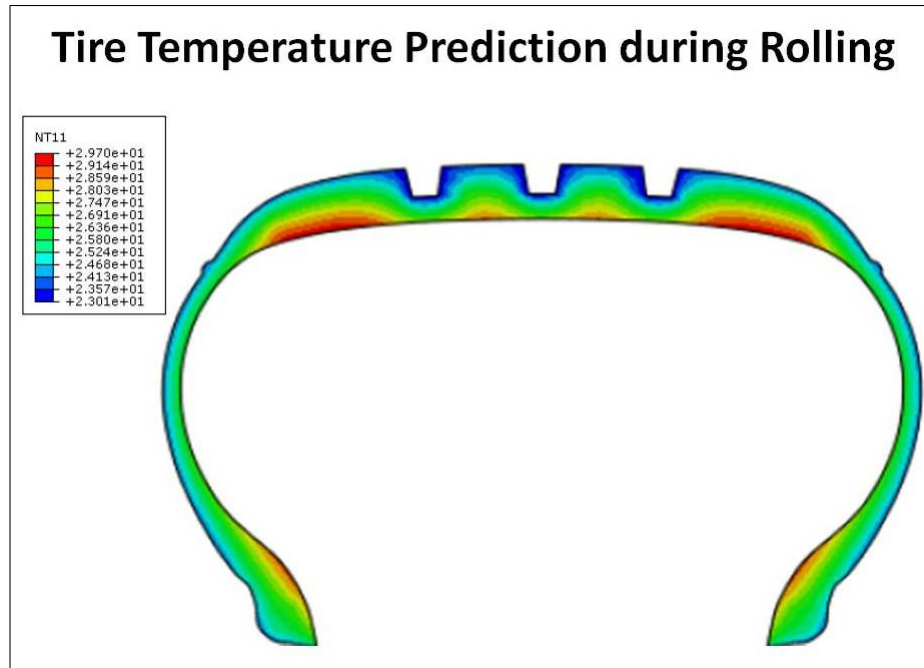


Figure 1.12: Temperature Distribution in a Tire under Rolling Conditions

Rolling resistance is now calculated from;

$$F_{RR} = \frac{-\Psi^{diss}}{2\pi R} \text{ where,} \quad (1.13)$$

F_{RR} is the Rolling Resistance

$2\pi R$ is the Circumferential length.

In summary, the absolute values from dynamic tests are meaningful, but have little values as isolated data points. They do become valuable as values when compared to each other or some other known variable. A tan delta or damping coefficient value of 0.4 is poor for a natural rubber or EPDM based compound, but very good in FKM materials where the structure of the compound makes it venerable to lower than optimum dynamic properties. Most uncured rubbery compounds start on the viscous side, and as we cure the compound, we shift towards the elastic side.

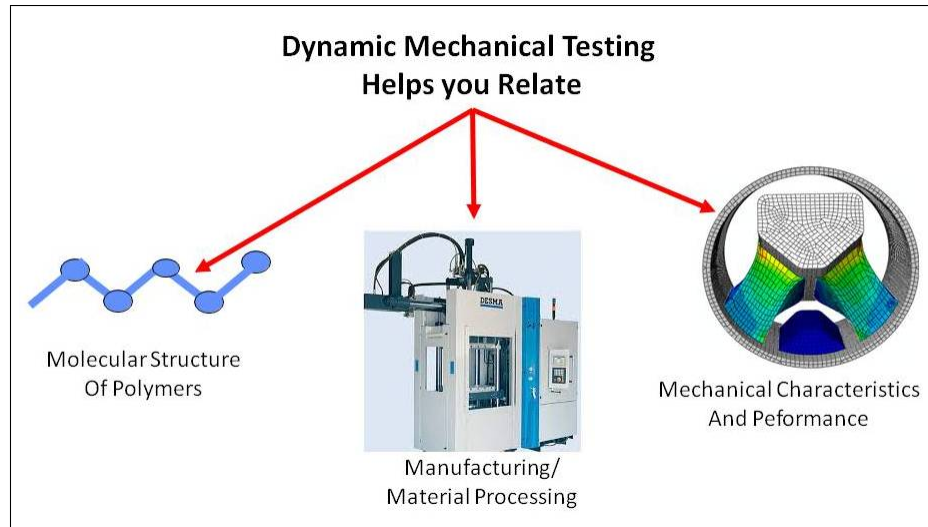


Figure 1.13: Viscoelastic Studies Correlate Molecular Structure to Manufacturing and Mechanical Properties of Engineering Components

As it stands today, the theory of dynamic properties can be applied judiciously to product development or failure analysis problems. The field of application has evolved over time with availability of highly sophisticated instruments. The problems need to be studied upfront for any time or frequency dependent loads and boundary conditions acting on the components and the theory be suitably applied. Needless to say that dynamic properties have utmost importance when rubber components show heat generation and fatigue related field failures as it relates the molecular structure of the polymer material to the manufacturing process and to the field performance of engineering products.

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This is a work in progress