AN004

Viscoelasticity and dynamic mechanical testing

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VISCOELASTICITY

Most materials are not purely viscous and often show significant elastic behavior. Such materials are referred to as viscoelastic materials and the key parameter, the time determines whether viscous or elastic behavior prevails.

Therefore in a slow deformation or flow process the viscous behavior dominates, whereas in a short time process the material behaves predominately elastic. Whether a process is fast or slow depends on a characteristic internal material time.

A material will be perceived as a viscous liquid if the material time is very short in comparison to the time of the deformation process. For example, the material time of water is about 10-10 s and any deformation process must seem very long compared to that value. If on the other hand the material time is long, it will be seen as an elastic solid, e.g. glass which has a material time in the range of hundreds of years.

The relationship between experiment or process time and material time is given by a dimensionless number, the Deborah number De (or Weissenberg number) and is defined as the ratio of material to process time. If a rheological experiment is faster than the relaxation process, the material will appear elastic (high De number), otherwise the viscous part will dominate (low De number). Measurements in the elastic region provide information about the materials internal structure, e.g. molecular or physical (morphology) structure; in the viscous region information about the flow behavior, important for processing e.g. extrusion, mixing, pumping, leveling, etc. is obtained.

MECHANICAL MODELS TO DESCRIBE VISCOELASTICITY

Viscoelastic materials can exhibit both viscous and elastic behavior. They can therefore be seen as a combination of both ideal types of materials: purely viscous fluids and ideally elastic solids.

The flow properties of a purely viscous material can be determined in a simple flow experiment. If the material deforms at a constant rate the applied constant stress is constant and described by a simple relationship known as Newton's law. Such liquids are known as Newtonian fluids, and the material constant is referred to as *Newtonian viscosity.* The deformation for Newtonian fluids is irreversible. **Liquids** of this type are characterized by a **dashpot** model (Figure 1a).

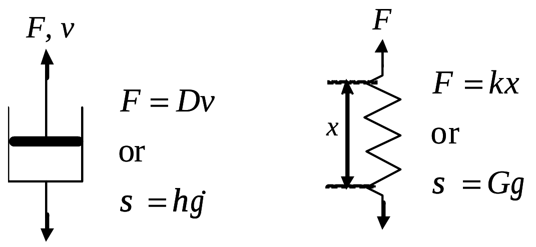


Figure 1a: The Dashpot model describes purely viscous fluid
Figure 1b: The Spring model describes an ideally elastic body

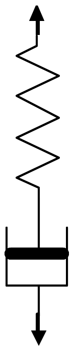
$$s = h \cdot \frac{dg}{dt} \quad \text{with the viscosity } \eta \qquad (1)$$

For an elastic **solid** material (e.g., a steel spring or crosslinked rubber) a simple linear relationship exists between the stress and the strain. The material deforms instantaneously when subjected to a sudden stress and the strain will remain constant until the stress is removed. There is no loss of energy and the solid will return to its original shape (the deformation is fully reversible).The material constant is the *modulus* of the material. The equation relating the stress and the strain is known as Hooke's law. Materials of this type are repre-sented by a **spring** (Figure 1b).

$$s = G \cdot g \quad \text{with the sear modulus G} \qquad (2)$$

The Newtonian and Hookean laws represent two extremes. Most materials however show some characteristics of both elastic and viscous behavior and can be described by combining spring(s) and dashpot(s) parallel or in series. These mechanical models do not represent the actual structure of a material but provide a physical framework to describe the general behavior of viscoelastic fluids. The simplest models are the Maxwell and the Kelvin model.

The **Maxwell model** is a spring and dashpot assembled in series (figure 2). In this model, the applied stress is the same for each element, the strain is additive. If a constant strain (relaxation experiment) is applied to this model, the stress increases instantly to a maximum value determined by the elastic modulus of the spring and then relaxes exponentially to zero. How fast the stress relaxes is given by the relaxation time t=G/h.



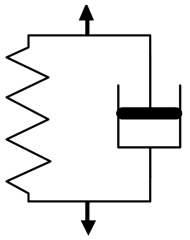
strain $g = g_s + g_d = \frac{s}{G} + \int \frac{s}{h} dt$

stress $\sigma = \sigma_S = \sigma_d$

shear rate $\dot{g} = \frac{\dot{s}}{G} + \frac{s}{h}$

Figure 2: The Maxwell model combines the spring and dashpot in series

The **Kelvin Model** consists of a spring and dashpot in parallel (figure 3). The strain for this model is the same for both elements whereas the stress is additive. If a constant stress is applied (retardation or creep experiment), the dashpot will initially take the entire load and the model deforms at maximum rate. As the deformation increases, the spring contribution to the total stress increases and the deformation rate exponentially slows down to zero (deformation reaches its maximum value). At this point the spring supports the total stress applied to the model. How fast the deformation reaches the maximum is given by the retardation time τ=G/η.



stress

$s = s_s + s_d = G \cdot g + h \cdot \frac{dg}{dt}\dot{g}$

strain $\gamma = \gamma_S = \gamma_d$

Figure 3: The Kelvin model combines a spring and dashpot in parellel

DYNAMIC MECHANICAL TESTING

In an oscillatory measurement the material is subjected to a sinusoidal stress or strain and the strain or stress response is measured (figure 4). The dynamic mechanical analysis (DMA) analyzes both elastic and viscous material response simultaneously. In this type of experiment, a motor is used to either apply a sinusoidal strain or stress to a material (in tension, bending, or shear) and the resulting stress is measured with a force transducer or the resulting strain is measured with a position sensor.

The rheological material behavior can be measured as a function of time, temperature, strain or stress amplitude and frequency. The results

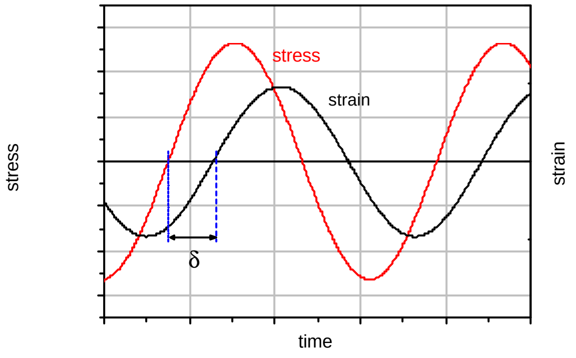


Figure 4: Stress and Strain signals during an oscillation experiment

obtained provide information about the sample structural properties such as MW, MWD, concentration, crosslinking density for polymers or particle/domain size, shape, interface properties, etc. for multiphase fluids. This information is important in product development (formulation) to predict product performance and processing behavior of new or modified materials.

The general rheological behavior in an oscillation experiment can be described with the Maxwell model. At the application of a sinusoidal stress, the spring will expand instantaneously. The dashpot however retards the deformation of the overall system. Therefore, a phase shift d between strain and stress is found as shown in the figure 4

The phase shift would be zero for an elastic material, as the spring follows the stress directly. If the material consisted of a dashpot only, the stress follows the strain rate directly and the phase shift becomes 90o for the strain. For a viscoelastic material the phase shift for the strain is between 0o and 90o.

The phase shift d is a measure of the amount of elasticity present in a sample. A material is equally elastic and viscous if the phase shift is 45° or $\tan\delta=1$. The frequency of this event is characteristic for a material and therefore an ideal description of the material time ($\tau_{mat}=1/(\omega(\tan\delta=1))$).

A series of material parameters can be calculated from the measured strain and stress. If the experiment has been performed in shear (plate-plate or cone-plate geometry) then the shear modulus *(G)* is obtained. Tensile and bending tests measure the tensile modulus *(E)*. In an oscillatory experiment, the phase shift is used to separate the measured stress into a component in phase and to determine the *elastic or storage modulus (G'* or *E')* of a material, defined as the ratio of the elastic (in-phase) stress to strain. The storage modulus relates to the material's ability to store energy elastically. Similarly, the *loss modulus (G"* or *E")* of a material is the ratio of the viscous (out of phase) component to the stress, and is related to the material's ability to dissipate stress through heat.

The figure 5 shows the frequency dependence of G' and G'' as the result of an oscillatory shear measurement for a high viscosity viscoelastic silicone oil. This material bounces back like a rubber ball when it hits a hard surface, but if left at rest, starts to flow after a few minutes under the effect of gravity. Please note the change of the phase in figure 5. It is quite low at high frequencies (which correspond to short times) and approaches 90° at very low frequencies, indicating mainly viscous behavior.

Following additional information can be obtained from this experiment:

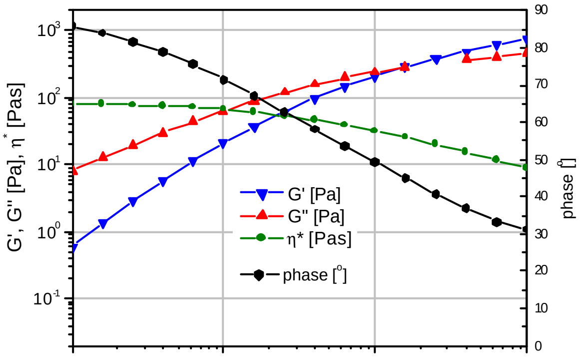


Figure 5: Frequency dependence of a high viscosity silicone oil (silicone putty).

Relaxation time

The relaxation time is calculated by t= 1/(2pf) where f is the frequency at which the phase shift reaches 45°.

The Storage or elastic modulus G' and the Loss or viscous modulus G"

The storage modulus gives information about the amount of structure present in a material. It represents the energy stored in the elastic structure of the sample. If it is higher than the loss modulus the material can be regarded as mainly elastic, i.e. the phase shift is below 45°. The loss modulus represents the viscous part or the amount of energy dissipated in the sample. The 'sum' of loss and storage modulus is the so-called complex modulus G*.

Viscosity h*

The complex viscosity *h** is a most usual parameter and can be calculated directly from the complex modulus. This viscosity can be related to the viscosity measured in a steady shear test by a relation known as the Cox-Merz rule. Note, that the application of the Cox-Merz rule is limited to neat polymer resins. The complex viscosity approaches a finite value at low frequencies. This value is the zero shear viscosity of the material.

Damping or Loss

The ratio of the moduli *(G"/G' or E"/E')* is defined as *tand*, and indicates the relative degree of energy dissipation or damping of the material..

All oscillatory experiments have to be carried out at small strain or stress amplitude in order to remain within the so-called linear viscoelastic region. Inside this region, which is limited by the critical stress (or strain), the material's structure is in equilibrium and the relation between the applied stress and the measured quantities is linear; this means they are only a function of time or frequency at constant temperature.

The linear viscoelastic region of a material is determined in an oscillatory measurement at a constant frequency with increasing stress or strain amplitude. The measured Moduli remain constant as long as the critical strain has not been reached. The end of the linear region is given by a decrease in viscosity or elastic modulus and an increase of the phase shift, shown in figure 6. The critical strain for this material, a polypropylene melt is approximately 50.

An oscillation strain sweep measurement is usually the first test carried out on an unknown material. All subsequent tests have to be carried out at strains below the critical strain value.

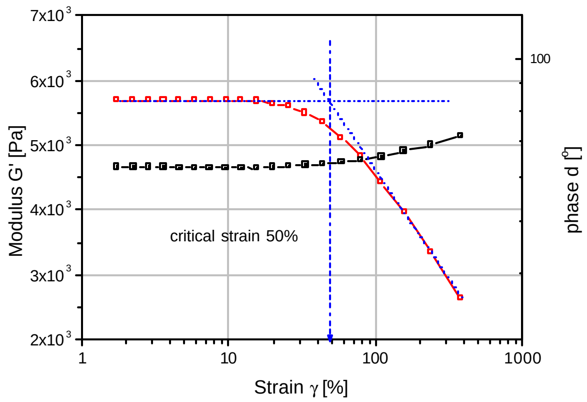


Figure 6: Strain sweep of a polypropylene melt

TEST GEOMETRIES

A variety of test geometries are used in rheological testing. Solids are tested in shear, tension, and bending using rectangular or cylindrical samples. The properties of fluids are measured using parallel plate, cone and plate, or concentric cylinder fixtures. The fixture used to test a material depends on several factors including the material's stiffness, viscosity, instrument sensitivity, and type of measurement. Testing is generally non-destructive and sample sizes are usually small.

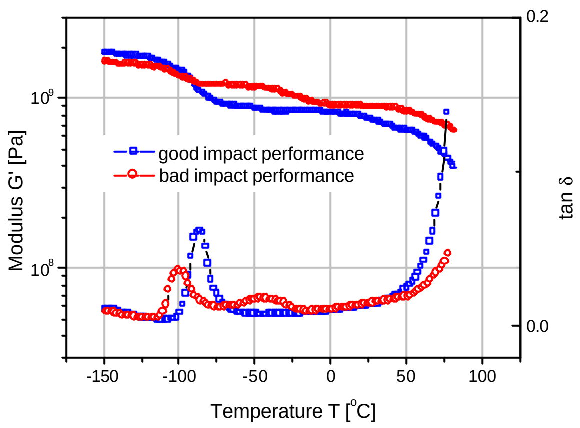


Figure 7: Modulus and tan d as a function of temperature for a rubber modified PS (HIPS)

TEST MODES AND RESULTS

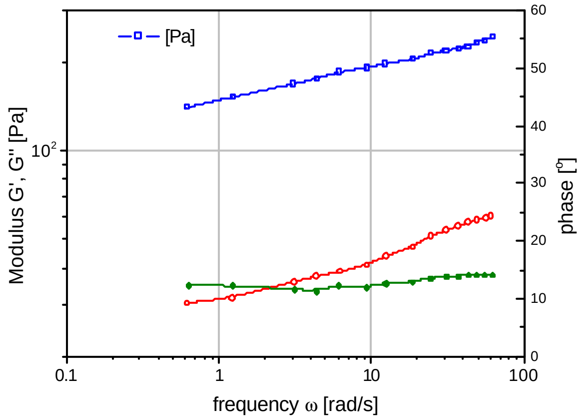
Three parameters are controlled in any given single test: frequency of oscillation, amplitude of oscillation, and test temperature. A typical test sweep (a sweep is a continuous variation of a parameter) holds two of these parameters constant while varying the third. In a frequency sweep the test frequency is varied to establish the frequency dependence of a material (figure 5). Typical applications are the determination of material's viscosity, elasticity or shear thinning. Strain sweeps are used to measure the range of linear viscoelastic behavior of materials. The shear moduli of a material are independent of strain amplitude up to a given applied strain. Within this range a material is said to be linear viscoelastic. Beyond that point the structure of the material begins to break down and the elastic modulus drops (figure 6).

Temperature sweeps are useful for measuring the temperature dependence of the viscosity or the thermal transitions in polymers. Phase transitions (such as the β- transition manifested by the peak in *tand* in Figure 7) can be detected and analyzed to locate components in polymer blends. Impact properties, crystallinity, and other morphological properties can be derived from these experiments.

Following some application examples of oscillatory measurements

1) The silicone oil (figure 5) shows a rheological behavior typical for polymer liquids with a high molecular weight.

Frequency dependent oscillation measurement on a yoghurt gel are presented in figure 8. In this case the phase shift is nearly constant with frequency and the material remains elastic over the complete range. Typical for gels is, that the storage and loss modulus are approximately parallel. Gels show this behavior as long as the structure is undisturbed.



Frequency 8: Frequency response of a yoghurt in the linear range

2) Oscillatory measurements are quite useful for studying processes that involves a change of structure in the sample. The strain has to remain small enough, not to disturbed the ongoing physical or chemical process.

Figure 9 shows the melting of two different chocolate samples as a function of temperature. The chocolate with the lower melting point contains cocoa butter only, the other sample includes higher melting fats also.

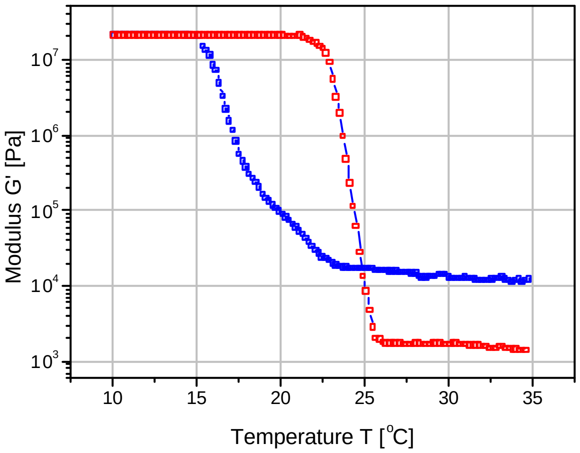


Figure 9: Melting behavior of chocolate with different types of fat

3) The frequency response of two polymer melts used for injection molding is shown in figure 10. One of them has been described as good, the other exhibits abnormal behavior, which shows in the quality of the dimensional stability of the final product. The two samples show significant differences in the viscosity at low frequency (low shear rates). The abnormal sample has a higher viscosity, which results in a reduced flow in the mold. Consequently less filling occurs under identical processing conditions, which is the reason for the quality of the final product.

CONCLUSION

Dynamic mechanical analysis is a sensitive method for exploring the structure, the processability and the end use performance of many materials. It enables characterization of the

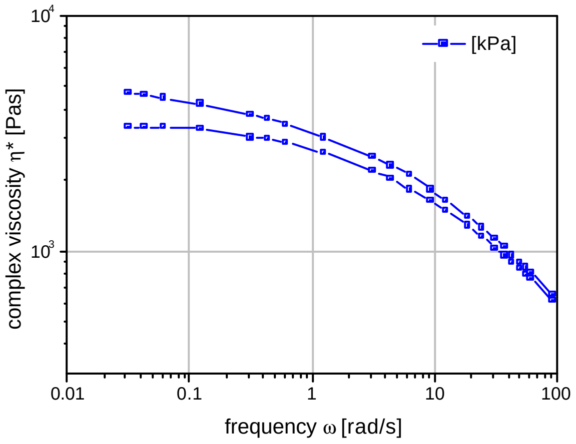


Figure 10: Viscosity curve of two injection molding compounds

structural differences between materials and provides information about how the materials will process. Such information is important both for product development as well as process design and optimization. Most materials are viscoelastic and full characterization of a material's rheology requires elasticity information in addition to viscosity information. Dynamic mechanical analysis is a uniquely powerful method because it measures both properties simultaneously.

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