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Rotational Rheology: Interpretation of Data by Application





Everything Flows: *Panta Rhei*...

Has been adopted as the motto of the American Society of Rheology. Although rheology only came to the scene after the end of the World War II, in one sense it can be considered a very old science, with roots in antiquity and this motto originates from a quotation from the Greek Philosopher Heraclitus. He, in turn, was citing from the Book of Judges Chapter 5 and the Jewish prophetess Deborah who said, 'even the mountains flow before the Lord'. Interestingly, we now know if you change your observational timescale, that with the movement of tectonic plates, the earth's crust does appear to flow!

Rheometry refers to the experimental technique used to determine the rheological properties of materials; rheology being defined as the study of the flow and deformation of matter which describes the interrelation between force, deformation and time.

The term rheology originates from the Greek words 'rheo' translating as 'flow' and 'logia' meaning 'the study of'. From this definition, rheology is as much about the deformation of solid-like materials as it is about the flow of liquid ones, and in particular deals with the behavior of complex viscoelastic materials that show both solid and liquid-like properties in response to force, temperature, deformation and time.

We hope you find this booklet helpful and even if your application isn't specifically mentioned, that you'll be inspired as to how a similar test method can be adapted to give an indication of your material's properties in a specific process.

Enjoy reading!

Philip Rolfe and Dr. Levente Szántó

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Introduction to Rotational Rheology

Introduction to Rotational Rheology

Method

The rheological analysis of samples is a fundamental part of developing many types of products. Unlike a viscometer, a rheometer can actually measure sample properties at extremely low shear rates, as in sedimentation, or the high shear rates seen in pumping, mixing and application. Making measurements in the correct shear range, we can adequately simulate a flow process and so differentiate good products from poor ones. The rheometer can also determine the effect of adding different quantities of an additive, or process changes and so be used to optimize the formulation and production of a product.

The rheometer not only measures the viscosity of the product at room temperature, but can also be used to evaluate the viscosity during a programmed temperature profile. This can also be used with polymers to evaluate processability and glass transition temperatures. Results are accurate with minimal time spent testing, as a pre-programmed analysis may be started and left to run unattended, or even overnight.



Fig. 1. The Kinexus Rotational Rheometer

Overview

Rotational rheometers can accommodate many different measuring systems, although the most common are cone and plate, parallel plates, coaxial cylinders and torsional fixtures. When using cone and plate or parallel plates, the sample is loaded onto a temperature controlled flat lower plate and an upper cone or flat plate is lowered onto the sample, squeezing it into a defined space. After trimming away excess sample, the upper measuring system is then either sheared continuously in one direction (viscometry) or oscillated rotationally (oscillation, as shown in Figure 2).

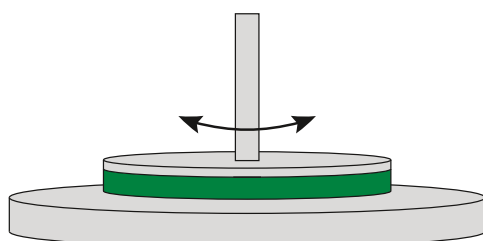


Fig. 2. Rotational oscillation of a sample loaded between a cone and a plate

Viscometry can be used to investigate the yield stress, i.e., the stress required to initiate sample flow, simulate a shearing process, measure shear stability or analyze how viscosity changes with temperature. Oscillation tests usually investigate the viscoelastic structure of a sample without breaking it down. Initially, an amplitude sweep is run to determine how large an oscillation the sample can withstand before the structure breaks down, this is known as the linear viscoelastic region. Once the linear viscoelastic region has been determined, a frequency sweep, time sweep or temperature sweep may be performed to investigate how the viscoelastic structure and viscosity changes under dynamic conditions.

Typical Setup for a Rotational Rheology Test

- Geometry: Cone 2°/40 mm or C25 Cup&Bob
- Temperature: 25°C
- Working gap: 70 μm and 9.15 mm, respectively
- Viscosity experiments: Table of shear from 0.01 to 500 s^{-1} , log, 5 points per decade

Typical Viscometry Results

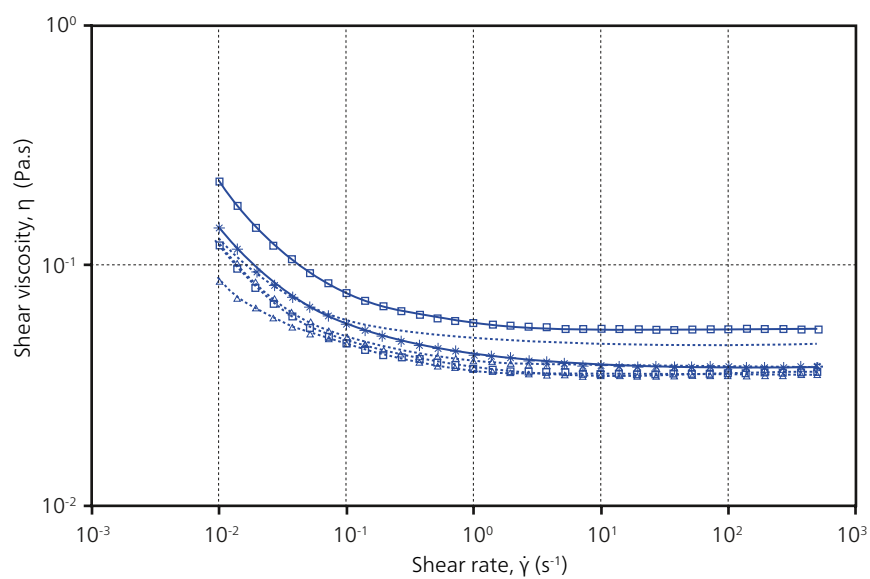


Fig. 3. Viscosity flow curves of six oil and water emulsions at 25°C

Introduction to Rotational Rheology

Terminology: A Basic Introduction to Rheology

Viscosity

There are two basic types of flow: shear flow and extensional flow. In shear flow, components shear past one another while in extensional flow, components flow away or towards each other. The most common flow behavior and one that is most easily measured on a rotational rheometer or viscometer is shear flow, and this viscosity introduction will focus on that behavior and how to measure it.

Shear Flow

Shear flow can be depicted as layers of fluid sliding over one another with each layer moving faster than the one beneath it. The uppermost layer has maximum velocity while the bottom layer is stationary. For shear flow to take place, a shear force must act on the fluid. This external force takes the form of a shear stress (σ) which is defined as the force (F) acting over a unit area (A), as shown in Figure 1. In response to this force, the upper layer will move a given distance x , while the bottom layer remains stationary. Hence, we have a displacement gradient across the sample (x/h) termed shear strain (γ). For a solid, which behaves like a single block of material, the strain will be finite for an applied stress – no flow is possible. However, for a fluid, where the constituent components can move relative to one another, the shear strain will continue to increase for the period of applied stress. This creates a velocity gradient termed shear rate or strain rate ($\dot{\gamma}$) which is the rate of change of strain with time ($d\gamma/dt$).

When we apply a shear stress to a fluid, we are transferring momentum, indeed the shear stress is equivalent to the momentum flux or rate of momentum transfer to the upper layer of fluid. That momentum is transferred through the layers of fluid by collisions and interactions with other fluid components, giving a reduction in fluid velocity and kinetic

energy. The coefficient of proportionality between the shear stress and shear rate is defined as the shear viscosity or dynamic viscosity (η), which is a quantitative measure of the internal fluid friction, and is associated with damping or loss of kinetic energy in the system.

$$\eta = \sigma / \dot{\gamma} \text{ (Pa.s)}$$

Newtonian and Non-Newtonian Fluids

Newtonian fluids are fluids in which the shear stress is linearly related to the shear rate, and hence, the viscosity is invariable with shear rate or shear stress. Typical Newtonian fluids include water, simple hydrocarbons and dilute colloidal dispersions. Non-Newtonian fluids are those in which the viscosity varies as a function of the applied shear rate or shear stress.

It should be noted that fluid viscosity is both pressure and temperature dependent, with viscosity generally increasing with increased pressure and decreasing temperature. Temperature is more critical than pressure in this regard, with higher viscosity fluids such as asphalt or bitumen, much more temperature dependent than low-viscosity fluids such as water.

Rotational Rheometer

To measure shear viscosity using a single head rotational rheometer with parallel plate measuring systems, the sample is loaded between the plates at a known gap (h) as shown in Figure 2. Single head rheometers are capable of working in controlled stress or controlled rate mode, which means it is possible to apply a torque and measure the rotational speed or alternatively, apply a rotational speed and measure the torque required to

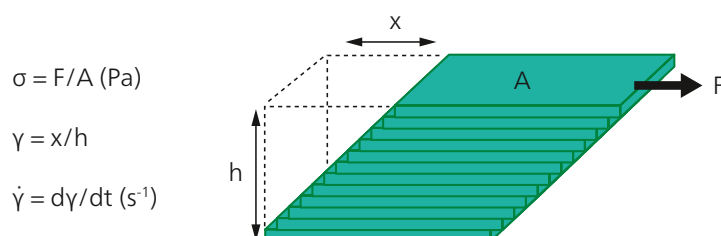


Fig. 1. Quantification of shear rate and shear stress for layers of fluid sliding over one another

maintain it. In controlled stress mode, a torque is requested from the motor, which translates to a force (F) acting over the surface area of the plate (A) to give a shear stress (F/A). In response to an applied shear stress, a liquid-like sample will flow with a shear rate dependent on its viscosity. If the measurement gap (h) is accurately known, the shear rate (V/h) can be determined from the measured angular velocity (ω) of the upper plate, which is determined by high precision position sensors, and the plate radius (r), since $V = r \omega$.

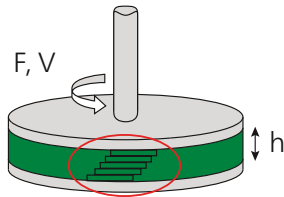


Fig. 2. Illustration showing a sample loaded between parallel plates and shear profile generated across the gap

Other measuring systems including cone-plate and concentric cylinders are commonly used for measuring viscosity, with cone-plate often preferred since the shear rate is constant across the sample. The type of measuring system used and its dimensions depend on the sample type and its viscosity. For example, when working with large particle suspensions, a cone-plate system is often not suitable, while a measuring system with a larger surface area such as a double gap concentric cylinder can be preferable for measuring low viscosity and volatile fluids.

Shear Thinning

The most common type of non-Newtonian behavior is shear thinning or pseudoplastic flow, where the fluid viscosity decreases with increasing shear. At low enough shear rates, shear thinning fluids will show a constant viscosity value, η_0 , termed the zero-shear viscosity or zero-shear viscosity plateau. At a critical shear rate or shear stress, a large drop in viscosity is observed which signifies the beginning of the shear thinning region. This shear thinning region can be mathematically described by a power-law relationship, which appears as a linear section when viewed on a double logarithmic scale (Figure 3) – this is how rheological flow curves are often presented. At very high shear rates, a second constant viscosity plateau is observed, called the infinite shear viscosity plateau. This is given the symbol η_∞ and can be several orders of magnitude lower than η_0 depending on the degree of shear thinning.

Some highly shear-thinning fluids also appear to have what is termed a yield stress, where below a critical stress, the viscosity becomes infinite and hence characteristic of a solid. This type of flow response is known as plastic flow and is characterized by an ever increasing viscosity as the shear rate approaches zero (no visible plateau). Many prefer the description 'apparent yield stress' since some materials which appear to demonstrate yield stress behavior, over a limited shear rate range, may show a viscosity plateau at very low shear rates.

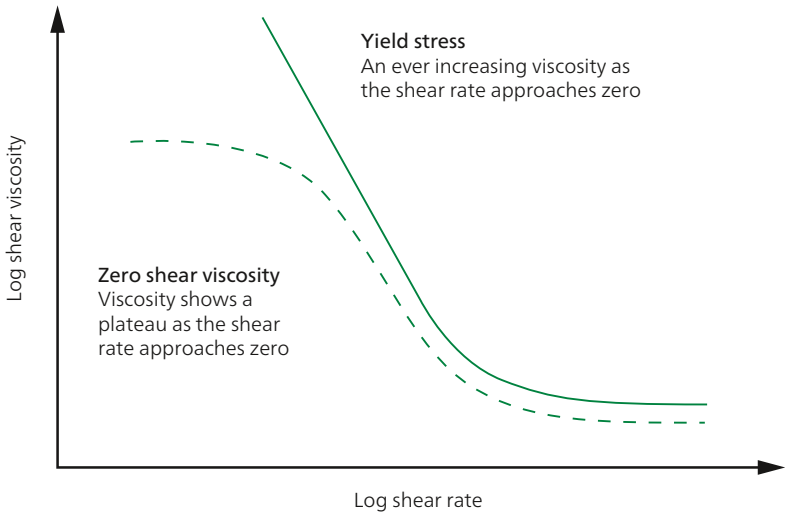


Fig. 3. Typical flow for shear thinning fluids with a zero shear viscosity and an apparent yield stress

Introduction to Rotational Rheology

Why does shear thinning occur? Shear thinning is the result of micro-structural rearrangements occurring in the plane of applied shear and is commonly observed for dispersions, including emulsions and suspensions, as well as polymer solutions and melts. An illustration of the types of shear induced orientation which can occur for various shear thinning materials is shown in Figure 4.

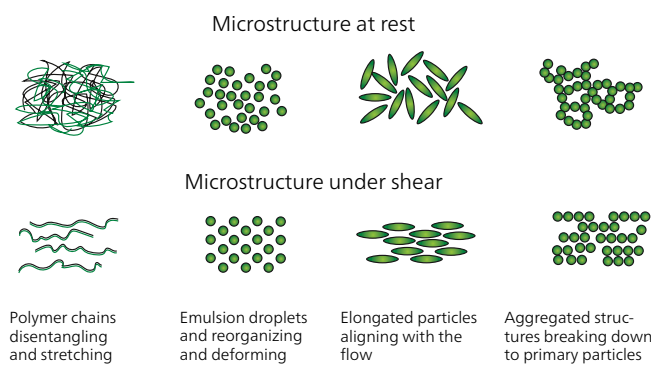


Fig. 4. Illustration showing how different micro-structures might respond to the application of shear

At low shear rates, materials tend to maintain an irregular order with a high zero shear viscosity (η_0) resulting from particle/molecular interactions and the restorative effects of Brownian motion. In the case of yield stress materials, such interactions result in network formation or jamming of dispersed elements, which must be broken or unjammed for the material to flow. At shear rates or stresses high enough to overcome these effects, particles can rearrange or reorganize in to string-like layers, polymers can stretch out and align with the flow, aggregated structures can be broken down and droplets deformed from their spherical shape. A consequence of these re-arrangements is a decrease in molecular/particle interaction and an increase in free space between dispersed components, which both contribute to the large drop in viscosity. η_∞ is associated with the maximum degree of orientation achievable and hence the minimum attainable viscosity – this is influenced largely by the solvent viscosity and related hydrodynamic forces.

Model Fitting

The features of the flow curves shown in Figure 3 can be adequately modeled using some relatively straight forward equations. The benefits of such an approach are that it is possible to describe and compare the shape and curvature

of a flow curve through a relatively small number of fitting parameters and to predict behavior at unmeasured shear rates (although caution is needed when using extrapolated data).

Three of the most common models for fitting flow curves are the Cross, Power-law and Sisko models. The most applicable model largely depends on the range of the measured data or the region of the curve you would like to model (Figure 5). There are a number of alternative models available such as the Carreau-Yasuda model and Ellis models for example. Other models accommodate the presence of a yield stress; these include Casson, Bingham, and Herschel-Bulkley models.

Cross model
$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + (K\dot{\gamma})^m}$$

Power law model
$$\sigma = k\dot{\gamma}^n$$

Sisko Model
$$\sigma = k\dot{\gamma}^n + \eta_\infty \dot{\gamma}$$

η_0 is the zero shear viscosity; η_∞ is the infinite shear viscosity; K is the cross constant, which is indicative of the onset of shear thinning; m is the shear thinning index which ranges from 0 (Newtonian) to 1 (Infinitely shear thinning); n is the power law index which is equal to $(1 - m)$, and similarly related to the extent of shear thinning but with $n \rightarrow 1$ indicating a more Newtonian response; k is the consistency index which is numerically equal to the viscosity at 1 s^{-1} .

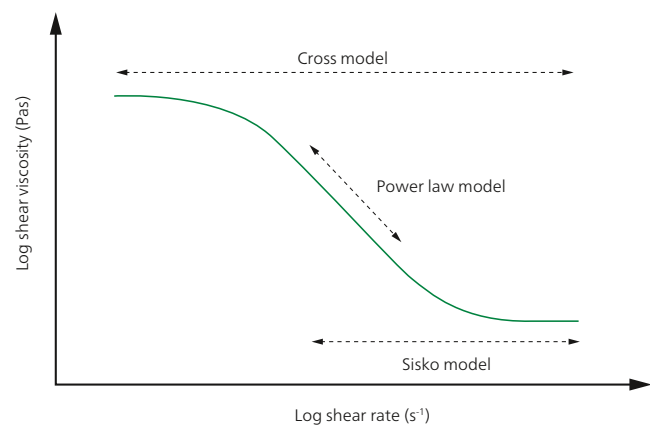


Fig. 5. Illustration of flow curve and the relevant models for describing its shape

Shear Thickening

While most suspensions and polymer structured materials are shear thinning, some materials can also show shear thickening behavior where viscosity increases with increasing shear rate or shear stress. This phenomenon is often called dilatancy, and although this refers to a specific mechanism for shear thickening associated with a volume increase, the terms are often used interchangeably.

In most cases, shear thickening occurs over a decade of shear rates and there can be a region of shear thinning at lower and higher shear rates. Usually, dispersions or particulate suspensions with a high concentration of solid particles exhibit shear thickening. Materials exhibiting shear thickening are much less common in industrial applications than shear thinning materials. They do have some useful applications such as in shock absorbers and high impact protective equipment but for the most part, shear thickening is an unwanted effect which can lead to major processing issues.

For suspensions, shear thickening generally occurs in materials that show shear thinning at lower shear rates and stresses. At a critical shear stress or shear rate, the organized flow regime responsible for shear thinning is disrupted and so called 'hydro-cluster' formation or 'jamming' can occur. This gives a transient solid-like response and an increase in the observed viscosity. Shear thickening can also occur in polymers, in particular amphiphilic polymers, which at high shear rates may open-up and stretch, exposing parts of the chain capable of forming transient intermolecular associations.

Thixotropy

For most liquids, shear thinning is reversible and the liquids will eventually gain their original viscosity when the shearing force is removed. When this recovery process is sufficiently time dependent, the fluid is considered to be thixotropic. Thixotropy is related to the time dependent microstructural rearrangements occurring in a shear thinning fluid following a step change in applied shear (Figure 6). A shear thinning material may be thixotropic but a thixotropic material will always be shear thinning. A good practical example of a thixotropic material is paint. A paint should be thick in the can when stored for long periods to prevent separation but should thin down easily when stirred for a period time – hence it is shear thinning. Most often, its structure does not rebuild instantaneously on ceasing stirring – it takes time for the structure and hence viscosity to rebuild to give sufficient working time.

Thixotropy is also critical for leveling of paint once it is applied to a substrate. Here, the paint should have a low enough viscosity at application shear rates to be evenly distributed with a roller or brush, but once applied should recover its viscosity in a controlled manner. The recovery time should be short enough to prevent sagging but long enough for brush marks to dissipate and a level film to be formed. Thixotropy also affects how thick a material will appear after it has been processed at a given shear rate, which may influence customer perception of quality, or whether a dispersion is prone to separation and/or sedimentation after high shear mixing, for example.

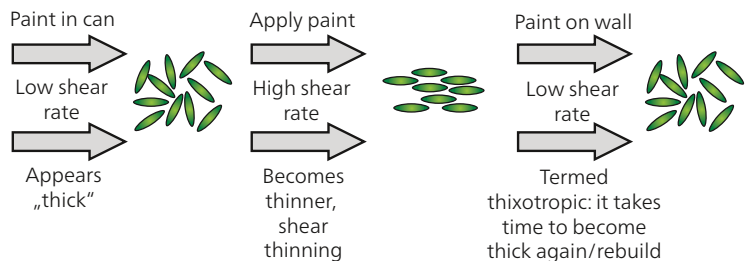


Fig. 6. Illustration of thixotropy due to particle orientation before during and after shear flow for a paint sample

Introduction to Rotational Rheology

The best way to evaluate and quantify thixotropy is using a three-step shear test as shown in Figure 7. A low shear rate is employed in stage one, which is meant to replicate the samples at near-rest behavior. In stage two, a high shear rate is applied for a given time to replicate the breakdown of the sample's structure and can be matched to the process of interest. In the third stage, the shear rate is again dropped to a value generally equivalent to that employed in stage one and viscosity recovery followed as a function of time. To compare thixotropic behavior between samples, the time required to recover 90% (or a defined amount) of the initial viscosity can be used. This time can therefore be viewed as a relative measure of thixotropy— a small rebuild time indicates that the sample is less thixotropic than a sample with a long rebuild time.

Yield Stress

Many shear-thinning fluids can be considered to possess both liquid and solid like properties. At rest, these fluids are able to form intermolecular or interparticle networks as a result of polymer entanglements, particle association, or some other interaction. The presence of a network structure gives the material predominantly solid-like characteristics associated with elasticity, the strength of which is directly related to the intermolecular or interparticle forces (binding force) holding the network together, and hence its yield stress.

If an external stress is applied which is less than the yield stress, the material will deform elastically. However, when the external stress exceeds the yield stress, the network structure begins to collapse and the material will start flowing as if it is a liquid. Despite yield stress clearly being apparent in a range of daily activities such as squeezing toothpaste from a tube or dispensing ketchup from a bottle, the concept of a true yield stress is still a topic of much debate.

While a glassy liquid and an entangled polymer system will behave like a solid when deformed rapidly, at longer deformation times, these materials show properties of a liquid and hence do not possess a true yield stress. For this reason, the term 'apparent yield stress' is widely used. Figure 8 shows a plot of shear stress against shear rate for various fluid types. Materials which behave like fluids at rest will have curves that meet at the origin, since any applied stress will induce a shear rate flow. For yield stress fluids, the curves will intercept the stress axis at a non-zero value indicating that a shear rate can only be induced when the yield

stress has been exceeded. A Bingham plastic is one that has a yield stress but shows Newtonian behavior after yielding. This idealized behavior is rarely seen and most materials with an apparent yield stress show non-Newtonian behavior after yielding, which is generalized as plastic behavior.

There are a number of experimental tests for determining yield stress, including multiple creep testing, oscillation amplitude sweep testing and also steady shear testing; the latter usually with the application of appropriate models such as the Bingham, Casson and Herschel-Bulkley models.

Bingham
$$\sigma = \sigma_y + \eta_B \dot{\gamma}$$

Herschel-Bulkley
$$\sigma = \sigma_y + K \dot{\gamma}^n$$

where σ_y is the yield stress and η_B the Bingham viscosity, represented by the slope of shear stress versus shear rate in the Newtonian region, post yield. The Herschel-Bulkley model is just a power-law model with a yield stress term and hence represents shear thinning post yield, with K the cross constant and n the power law index. All of the various tests for measuring yield stress are discussed in [5].

One of the quickest and easiest methods for measuring the yield stress is to perform a shear stress ramp and determine the stress at which a viscosity peak is observed (Figure 9). Prior to this viscosity peak, the material is undergoing elastic deformation where the sample is simply stretching. The peak in viscosity represents the point at which this elastic structure breaks down (yields) and the material starts to flow. If there is no peak, this indicates that the material does not have a yield stress under the conditions of the test.

Yield stress can be related to the stand-up properties (slump) of a material, the stability of a suspension, or sagging of a film on a vertical surface, as well as many other applications.

Viscoelasticity

As the name suggests, visco-elastic behavior describes materials which show behavior somewhere between that of an ideal liquid (viscous) and ideal solid (elastic). There are a number of rheological techniques for probing the visco-elastic behavior of materials, including creep testing, stress relaxation and oscillatory testing. Since oscillatory shear rheometry is the primary technique that is used to measure viscoelasticity on a rotational rheometer, this will be discussed in greatest detail, although creep testing will also be introduced.

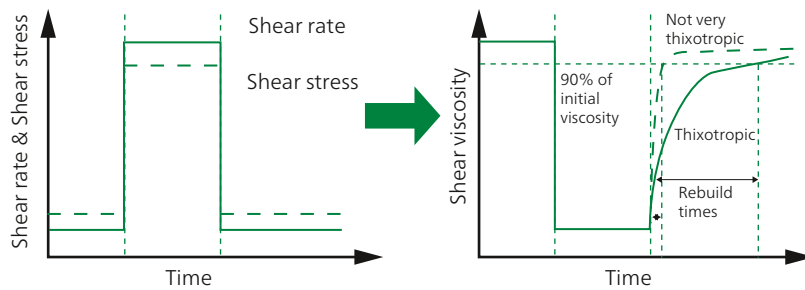


Fig 7. Illustration showing a step shear rate for evaluating thixotropy and expected response for non-thixotropic and thixotropic fluids

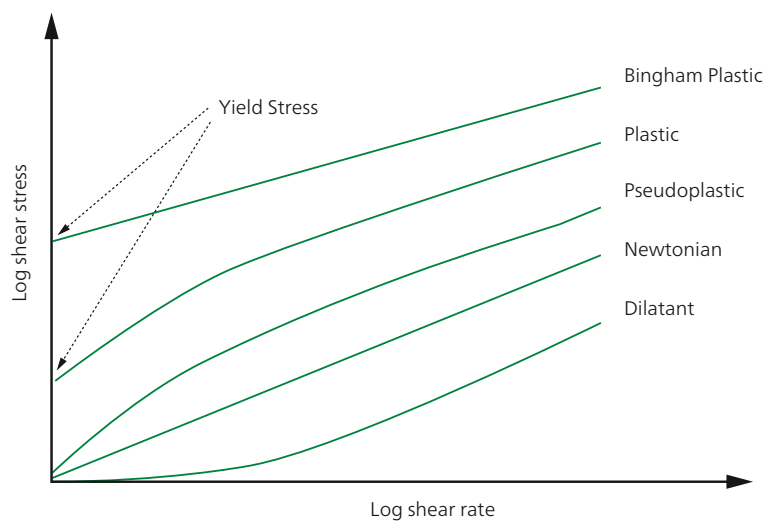


Fig. 8. Shear stress/shear rate plot depicting various types of flow behavior

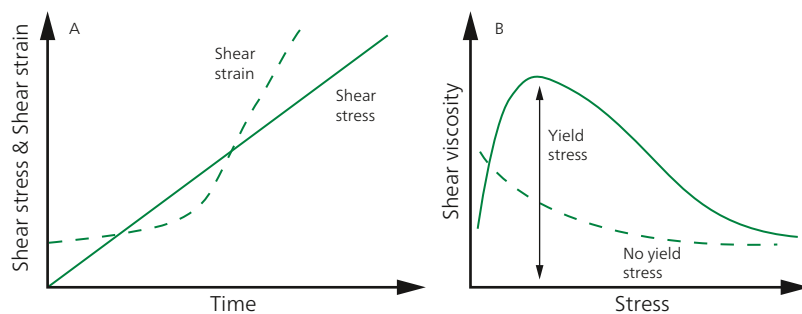


Fig. 9. Linear shear stress ramp and shear strain response (left) and corresponding viscosity plotted against shear stress for materials with and without a yield stress

Introduction to Rotational Rheology

Elastic Behavior

Structured fluids have a minimum (equilibrium) energy state associated with their 'at rest' micro-structure. This state may relate to inter-entangled chains in a polymer solution, randomly ordered particles in a suspension, or jammed droplets in an emulsion. Applying a force or deformation to a structured fluid will shift the equilibrium away from this minimum energy state, creating an elastic force that tries to restore the micro-structure to its initial state.

This is analogous to a stretched spring trying to return to its undeformed state. A spring is representative of a linear elastic solid that obeys Hooke's law, in that the applied stress is proportional to the resultant strain as long as the elastic limit is not exceeded, and will return to its initial shape when the stress is removed, as shown in Figure 10. If the elastic limit is surpassed, the relationship will become non-linear and the spring may be permanently distorted. These same principles can also be applied to simple shear deformation, as illustrated in Figure 11.

For simple shear elastic deformation, the constant of proportionality is the elastic modulus (G). The elastic modulus is a measure of stiffness or resistance to deformation just as viscosity is a measure of the resistance to flow. For a purely elastic material, there is no time dependence so when a stress is applied an immediate strain is observed, and when the stress is removed the strain immediately disappears.

This can be expressed as: $\gamma = \frac{\sigma}{G}$

Viscous Behavior

Just as a spring is considered representative of a linear elastic solid that obeys Hooke's law, a viscous material can be modeled using a dashpot which obeys Newton's law. A

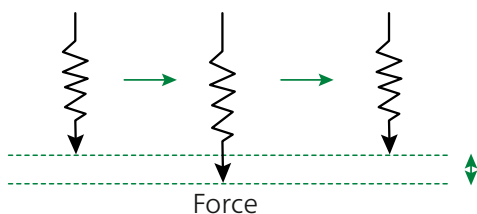


Fig 10. The response of an ideal (spring) to the application and subsequent removal of a strain including force

dashpot is a mechanical device consisting of a plunger moving through a viscous Newtonian fluid the wall to support the applied stress [18, 21, and 22].

When a stress (or force) is applied to a dashpot, the dashpot immediately starts to deform and goes on deforming at a constant rate (strain rate) until the stress is removed (Figure 12). The energy required for the deformation or displacement is dissipated within the fluid (usually as heat) and the strain is permanent. The strain evolution in an ideal liquid is given by the following expression:

$$\gamma = \frac{\sigma t}{\eta}$$

Visco-Elastic Behavior

A vast majority of materials show rheological behavior that classifies them in a region somewhere between that of liquids and solids and are therefore classed as viscoelastic materials. Consequently, it is possible to combine springs and dashpots in such a way as to model or describe real viscoelastic behavior. The simplest representation of a visco-elastic liquid is a spring and dashpot connected in series, which is called the Maxwell model. A visco-elastic solid can be similarly represented by the Kelvin-Voigt model which utilizes the same combination of elements but connected in parallel (Figure 13).

If a stress is applied to a Maxwell model then at very short times the response is predominantly elastic and governed by G , while at much longer times viscous behavior prevails and response is governed largely by η . The strain evolution in a Maxwell model can be described by the following expression:

$$\gamma = \sigma \left(\frac{1}{G} + \frac{t}{\eta} \right)$$

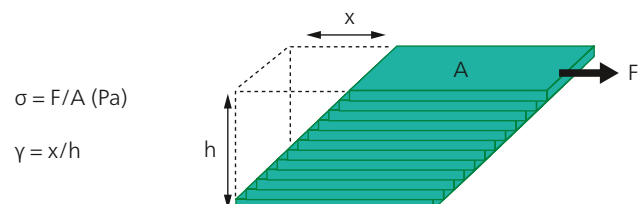


Fig. 11. Quantification of stress, and strain for an ideal solid deforming elastically in shear

If a stress is applied to a Kelvin-Voigt model the strain takes time to develop since the presence of the dashpot retards the response of the spring and the system behaves like a viscous liquid initially and then elastically over longer time scales as the spring becomes more stretched. The timescale or rate at which this transition occurs depends on the retardation time λ , which is given by η/G . This can be defined as the time required for the strain to reach approximately 63% of its final asymptotic value. The strain evolution in a Kelvin-Voigt model can be described by the following expression.

$$\gamma = \frac{\sigma}{G} \left[1 - e^{-t/\lambda} \right]$$

The model which best describes the viscoelastic behavior of real systems in response to an applied stress is the Burgers model (Figure 14) which is essentially a Maxwell and Kelvin-Voigt model connected in series.

The strain dependence of a Burgers model can be determined by combining both mathematical expressions to give the following equation.

$$\gamma = \sigma \left(\frac{1}{G_1} + \frac{1}{G_2} \left(1 - e^{-t/\lambda} \right) + \frac{t}{\eta_2} \right)$$

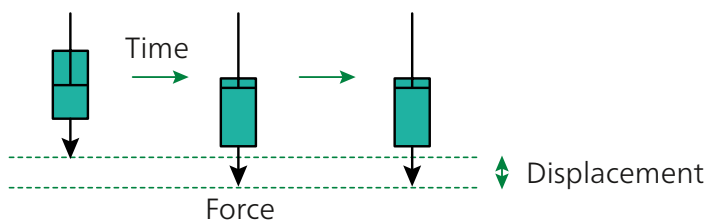


Fig. 12. Response of an ideal liquid (dashpot) to the application and subsequent removal of a strain including a force

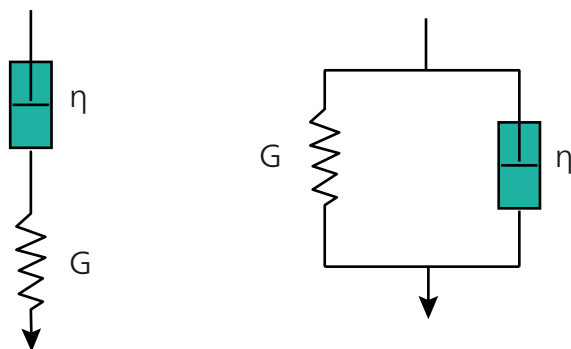


Fig. 13. (Left) Maxwell model representative of a simple visco-elastic liquid; (Right) Kelvin-Voigt model representative of a simple visco-elastic solid

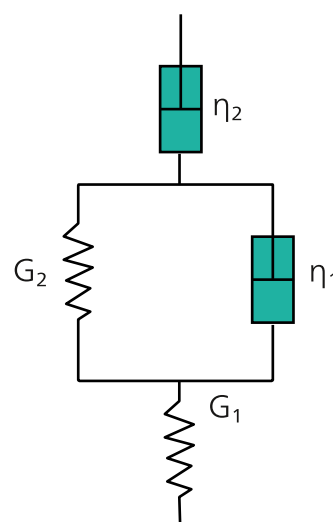


Fig. 14. Representation of a Burgers model which combines Kelvin-Voigt and Maxwell elements in series

Introduction to Rotational Rheology

Creep Testing

The test protocol described in the previous section whereby a constant stress is applied to a visco-elastic material and the strain response measured is what is called a creep test. This kind of measurement is usually applied to solid-like materials like metals which creep on long timescales rather than flow, although the test is applicable to all kinds of visco-elastic material. The test involves applying a constant shear stress over a period of time and measuring the resultant shear strain. The test must be performed in the linear visco-elastic region (see next section) where the microstructure remains intact. The measured response in a creep test is usually presented in terms of the creep compliance $J(t)$ which is the ratio of the measured strain to the applied stress, or inverse modulus.

A typical creep and recovery profile for a material showing Burgers type behavior is shown in Figure 15. An initial elastic response is first observed, followed by a delayed elastic response and finally a steady-state (linear) viscous response at longer times. The gradient of this line at steady state is equal to the strain rate and can therefore be used to calculate the zero shear viscosity of the fluid. If the steady-state linear response is extrapolated back to zero time, then the intercept is equal to the equilibrium compliance (J_E). This is the compliance or strain response associated with just the elastic components of the material, i.e., springs in the Burgers model. The recovery step begins once steady state has been attained and involves removing the applied stress and monitoring the strain as the stored elastic stresses relax. Only the elastic deformation of the sample is able to recover fully because the viscous deformation is permanent, and J_R , the recovery compliance, should eventually equal J_E . To accurately model the response of real systems in creep testing, it is often necessary to use multiple Kelvin-Voigt elements.

If a material has a true yield stress, then no steady state response is observed; η_2 will then be infinite and the creep compliance will plateau to the equilibrium compliance (J_E), as shown in Figure 16.

Small Amplitude Oscillatory Testing

The most common method for measuring visco-elastic properties using a rotational rheometer is small amplitude oscillatory shear (SAOS) testing where the sample is oscillated about its equilibrium position (rest state) in a continuous cycle. Since oscillatory motion is closely related to circular

motion, a full oscillation cycle can be considered equivalent to a 360° or 2π radian revolution. The amplitude of oscillation is equal to the maximum applied stress or strain, and frequency (or angular frequency) represents the number of oscillations per second.

To perform oscillation testing with a parallel plate measuring system, the sample is loaded between the plates at a known gap (h) and the upper plate oscillated back and forth at a given stress or strain amplitude and frequency (Figure 17). This motion can be represented as a sinusoidal wave with the stress or strain amplitude plotted on the y-axis and time on the x-axis. In a controlled stress measurement, an oscillating torque is applied to the upper plate and the resultant angular displacement measured from which the strain is calculated. In a controlled strain experiment, the angular displacement is controlled and the torque required to give that displacement is measured, from which the shear stress can be calculated.

The ratio of the applied stress (or strain) to the measured strain (or stress) gives the complex modulus (G^*) which is a quantitative measure of material stiffness or resistance to deformation, where

$$|G^*| = \sigma_{max} / \gamma_{max}$$

Phase Angle

For a purely elastic material (stress is proportional to strain), the maximum stress occurs at maximum strain (when deformation is greatest) and both stress and strain are said to be in phase. For a purely viscous material (stress is proportional to strain rate), the maximum stress occurs when the strain rate is maximum (when flow rate is greatest) and stress and strain are out of phase by 90° or $\pi/2$ radians (quarter of a cycle). For a visco-elastic material, the phase difference between stress and strain will fall somewhere between the two extremes. This is illustrated in Figure 18.

It is this phase difference which allows the viscous and elastic components contributing to the total material stiffness (G^*) to be determined; the phase angle δ being a relative measure of the materials viscous and elastic characteristics. For a purely elastic material, δ will have a value equal to 0°, while a purely viscous material will have a δ value equal to 90°. Visco-elastic materials demonstrating both characteristics will have a δ value between 0 and 90°, with 45° representing the boundary between solid-like and liquid-like behavior.

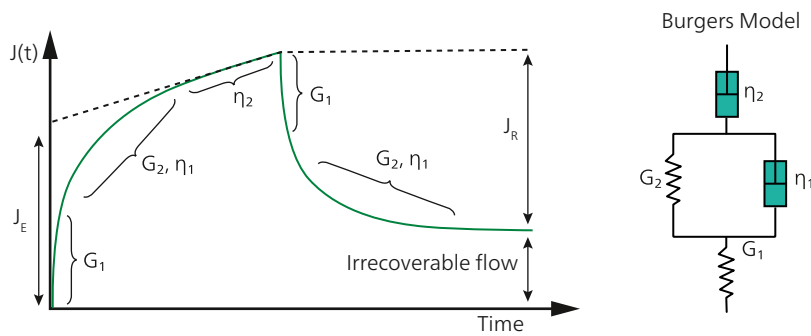


Fig 15. (right) representation of a Burger model and (left) expected profile of a Burger model undergoing creep and recovery testing with equilibrium compliance (J_E) and recovery compliance (J_R)

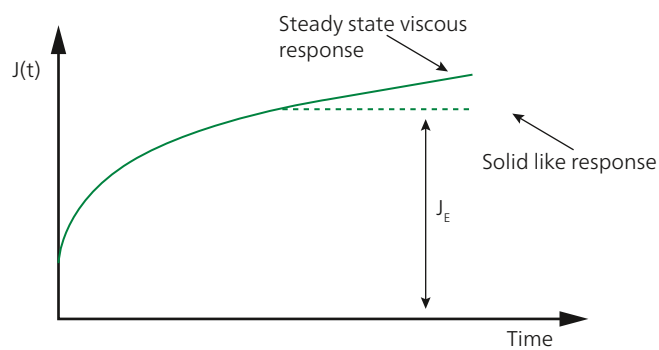


Fig. 16. Expected creep response for a viscoelastic liquid and viscoelastic solid

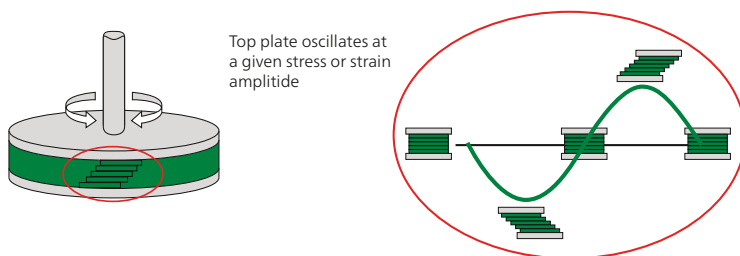


Fig. 17. Illustration showing a sample loaded between parallel plates with an oscillatory (sinusoidal) shear profile applied

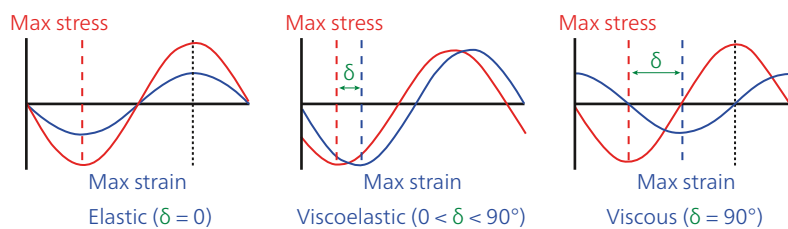


Fig. 18. Stress and strain wave relationships for a purely elastic (ideal solid), purely viscous (ideal liquid) and a viscoelastic material

Introduction to Rotational Rheology

This value may be considered indicative of a gel (or sol) point which signifies the onset of network formation (or breakdown). The phase angle is often expressed in terms of the loss tangent ($\tan \delta$), particularly when working with polymer systems.

Using trigonometry, it is possible to determine the viscous and elastic contributions to G^* as shown by the vector diagram in Figure 19.

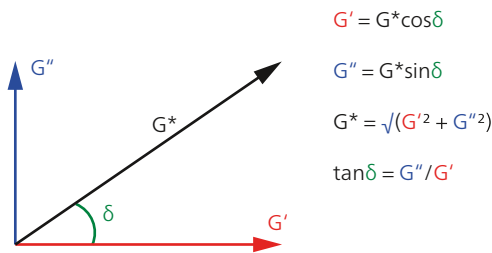


Fig. 19. Geometric relationship between G^* and its components G' and G''

The elastic contribution to G^* is termed the storage modulus (G') since it represents the storage of energy. The viscous contribution is termed the loss modulus (G'') since it represents energy loss. An alternative mathematical representation makes use of complex number notation since G^* is a complex number (hence complex modulus) and i is the imaginary number equal to $\sqrt{-1}$. G' can be considered to represent the real part and G'' the imaginary part of G^* . These are orthogonal on an Argand diagram, which graphically represents the complex plane, with the x-axis the real axis and y-axis the imaginary axis. An Argand diagram is shown in Figure 20.

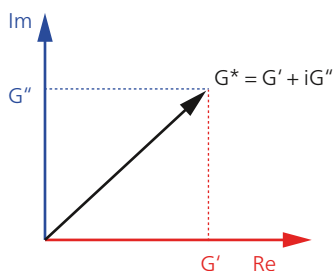


Fig 20. Argand diagram showing the relationship between G' , G'' and G^* in the complex plane

The relationship can be expressed in the following form.

$$G^* = G' + iG''$$

It is also possible to define a complex viscosity η^* which is a measure of the total resistance to flow as a function of angular frequency (ω) and is given by the quotient of the maximum stress amplitude and maximum strain rate amplitude.

$$\eta^* = G^* / \omega$$

As with G^* , η^* can be broken down into its component parts which include the dynamic viscosity (η') and the storage viscosity (η''). These represent the real and imaginary parts of η^* , respectively.

$$\eta^* = \eta' + i\eta''$$

Linear Visco-Elastic Region (LVER)

It is important when measuring the visco-elastic characteristics previously defined that measurements are made in the materials linear visco-elastic region, where stress and strain are proportional. In the LVER, applied stresses are insufficient to cause structural breakdown (yielding) of the structure and hence microstructural properties are being measured. When applied stresses exceed the yield stress, non-linearities appear and measurements can no longer be easily correlated with micro-structural properties. The linear visco-elastic region can be determined from experiment by performing a stress or strain sweep test and observing the point at which the structure begins to yield (Figure 21). This corresponds to the point at which G' becomes stress or strain dependent.

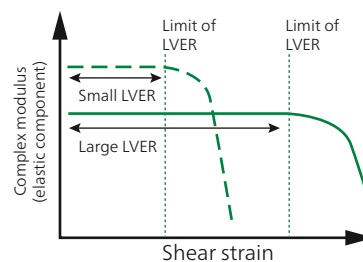


Fig. 21. Illustration showing the LVER for different materials as a function of applied strain

Oscillatory Frequency Sweep

Visco-elastic materials show time dependence hence G' and G'' are not material constants. In a creep test, this time dependence is measured directly by monitoring the creep compliance with time of applied stress. In an oscillatory test, time dependence can be evaluated by varying the frequency of the applied stress or strain, with high frequencies corresponding to short time scales and low frequencies to longer time scales, since $\omega \approx 1/t$. A frequency sweep performed on a visco-elastic liquid (representative of Maxwell type behavior) yields a plot of the type shown in Figure 22, since for a Maxwell model (Figure 13) G' and G'' vary with angular frequency according to the following expressions:

$$G' = \frac{G (\omega\tau)^2}{1 + (\omega\tau)^2}$$

$$G'' = \frac{G(\omega\tau)}{1 + (\omega\tau)^2}$$

At high frequencies, G' is larger than G'' and therefore, solid-like behavior predominates ($\delta < 45^\circ$), while at lower frequencies, the situation is reversed with G'' and therefore, liquid like behavior dominant ($\delta > 45^\circ$). The frequency at which G' and G'' cross ($\delta = 45^\circ$) is equal to $1/\tau$, with τ the relaxation time or time for the elastic stress to decay by approximately 63% of its initial value. This process is called stress

relaxation which is why such plots are often called relaxation spectrums – stored elastic stresses are relaxed through rearrangement of the microstructure and converted to viscous stresses. Knowing the longest relaxation time of a material (real materials can have a spectrum of relaxation times) can be useful for predicting the visco-elastic response of a material stressed for a given time. This can be assessed by means of the Deborah number (De) which is the ratio of the relaxation time (τ) to the test time, or time period over which stress is applied (t). Consequently, ($De > 1$) indicates solid-like behavior while ($De < 1$) indicates liquid-like behavior.

A frequency sweep performed on a visco-elastic solid representative of a Kelvin-Voigt model is more straightforward since G' is equal to the modulus of the spring, G , and frequency independent, while G'' is equal to $\eta\omega$ and linearly dependent on frequency. Hence, G' is constant and dominates at low frequencies while G'' decays with decreasing frequency but dominates at high frequencies. This kind of behavior tends to be seen in glass-like materials.

For a gel-like material, G' and G'' are parallel and δ is constant with a value between 0 and 45° . A suitable mechanical model for describing gel-like behavior is a spring in parallel with a Maxwell element. Both visco-elastic solid and gel-like systems show yield stress behavior since they require any associated structure (represented by single springs in their respective models) to be broken for macroscopic flow to occur.

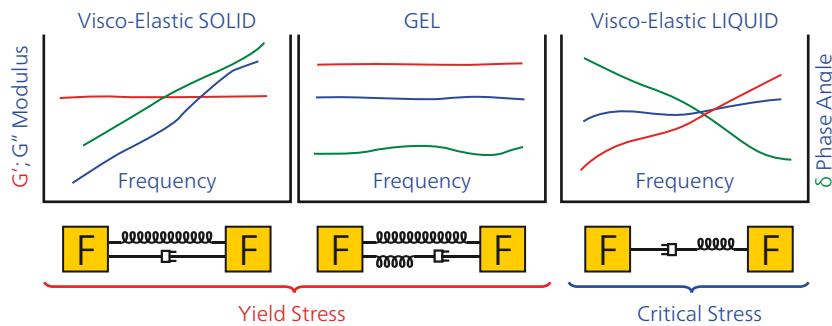


Fig. 22. Typical frequency response for a visco-elastic solid, visco-elastic liquid and a gel in oscillatory testing

Introduction to Rotational Rheology

The Visco-Elastic Spectrum

The visco-elastic response of real materials can be considered as a combination of Voigt and Maxwell elements, such as the Burgers model (Figure 14) with the former representing behavior at very high frequencies and the latter at lower frequencies. A typical viscoelastic spectrum for an entangled polymer system spanning a range of frequencies is shown in Figure 23. It is often only possible to observe a portion of this spectrum using standard rheometric techniques depending on the sensitivity of the rheometer and the relaxation time(s) of the material under test.

A principle, which is widely used to extend the relaxation spectrum to include long time relaxation processes is the time-temperature superposition principle, which makes use of the concept that time and temperature are equivalent for visco-elastic materials throughout certain regions of behavior. As a result, higher frequencies can be used at higher temperatures to predict low frequency behavior at lower temperatures. The resultant curves can then be shifted by a pre-determined factor to give a master curve.

Another technique which can be used for reducing the time required for collection of frequency data is creep testing. Although not mathematically straightforward, there are algorithms for transforming $J(t)$ to $G'(\omega)$ and $G''(\omega)$ and their associated parameters. Microrheological techniques can also be used for extending visco-elastic measurements to high frequencies, especially for weakly structured materials.

Finally, another important rule which allows steady shear viscosity data to be predicted from oscillatory data is the Cox-Merz rule, which states that the complex viscosity as a function of frequency is equivalent to the steady shear viscosity as a function of shear rate. This rule seems to hold for simple solutions including polymer melts, however, more complex dispersions may show variations.

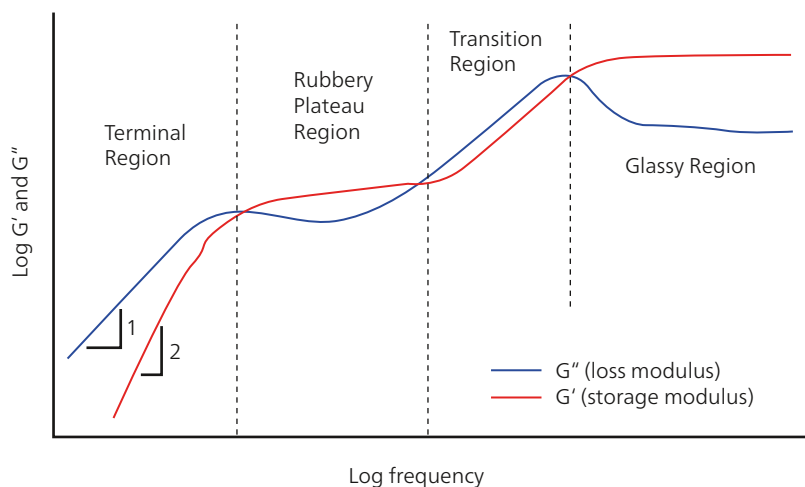


Fig 23. A typical visco-elastic spectrum for an entangled polymer system

References

- [1] Barnes HA; Handbook of Elementary Rheology, Institute of Non-Newtonian Fluid Mechanics, University of Wales (2000)
- [2] Shaw MT, Macknight WJ; Introduction to Polymer Viscoelasticity, Wiley (2005)
- [3] Larson RG; The Structure and Rheology of Complex Fluids, Oxford University Press, New York (1999)
- [4] Rohn CL; Analytical Polymer Rheology – Structure-Processing-Property Relationships Hanser-Gardner Publishers (1995)
- [5] NETZSCH White Paper – Understanding Yield Stress Measurements
- [6] Larsson M, Duffy J; An Overview of Measurement Techniques for Determination of Yield Stress, Annual Transactions of the Nordic Rheology Society Vol 21 (2013)
- [7] Malvern Instruments Application Note – Suspension stability; Why particle size, zeta potential and rheology are important
- [8] Malvern Instruments White Paper – An Introduction to DLS Microrheology
- [9] Duffy JJ, Rega CA, Jack R, Amin S; An algebraic approach for determining viscoelastic moduli from creep compliance through application of the Generalised Stokes-Einstein relation and Burgers model, Appl. Rheol. 26:1 (2016)

Paints, Coatings and Inks





Paints, Coatings and Inks

Characterizing 'Snap-back' Properties Using Dynamic Measurements

Introduction

Many coating systems are canned before retailing. A common problem for the manufacturer during this process is that when the can is filled, the dispenser stops pouring paint, but if the paint is viscously natured, it will continue to flow for a few seconds. As the conveyor belt continues to move, the paint 'tail' falls over the side of the can. This rheological problem with the paint can slow down the filling process considerably if not resolved. If the sample is found to be more elastic than viscously natured, the material will cleanly stop flowing and snap, like a yogurt or mayonnaise, rather than continue to flow like honey or viscous oil.

The ability of the coating to 'snap back', hence not causing a tail, can be measured very quickly with a dynamic frequency sweep, as this can characterize its elastic properties.

Interpretation

The profiles of G' (the elastic or 'storage' modulus) and G'' (the viscous or 'loss' modulus) against frequency (shown in Figure 1) indicate how the paint will respond under different shearing conditions. If the viscous modulus is greater than

| Test Conditions | |
|--|--|
| Samples | Water-based paints |
| Geometry | Cone and plate system 4°/40 mm with a solvent trap |
| Temperature | 25°C |
| Toolkit_0002 Frequency Table (strain controlled) | 10 - 0.1 Hz |
| Strain | 0.010 (or in the LVER) |

the elastic modulus, the paint is viscously dominated and is likely to continue 'running' slightly when the main flow is stopped. If the elastic modulus is dominant, the paint is more likely to snap back up to the feeder and into the vessel being filled.

Conclusion

The paint can be re-formulated and evaluated in the laboratory by addition of suitable modifiers to provide an elastically dominated end product that will not cause filling problems.

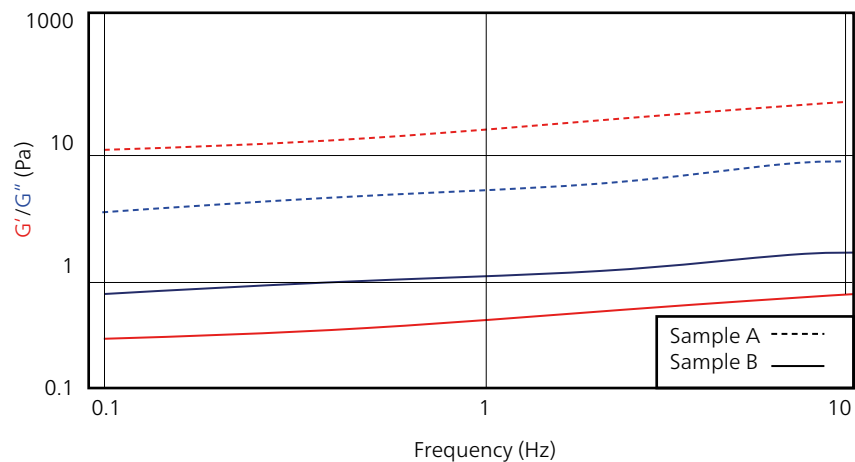


Figure 1. Elastic and viscous moduli vs. frequency. Oscillation frequency sweep results show whether a sample is elastically dominated (as sample A) or viscously (as sample B)

Determining and Measuring Thixotropy on Paints

Introduction

Thixotropy is a decrease in the apparent viscosity under shearing, followed by a gradual recovery when the shear is removed. **The effect is time dependent.** If the viscosity reduces and **immediately** returns after shearing, the material is not thixotropic but just 'shear thinning'. It is important to recognize thixotropy in materials, otherwise the shear history of the sample may adversely affect the accuracy and reproducibility of the test.

Interpretation

In this 'hysteresis loop test', the sample is subjected to increasing shear and then reducing shear. The results shown in Figure 2 give an indication whether the sample is thixotropic. Sample A has a high degree of thixotropy, so a loop is seen between the UP and DOWN curves, i.e., the samples behave differently before and after shearing. Sample B appears to have only a shear thinning nature, as the UP and DOWN curves almost overlay each other. Traditionally, users have related the degree of thixotropy to the magnitude of the integrated loop area, although there are now other techniques as indicated below which give more meaningful results.

| Test Conditions | |
|--------------------------------------|---|
| Samples | Paints |
| Geometry | Cone and Plate system 4°/40 mm with a solvent trap |
| Temperature | 25°C |
| Shear rate ramp Up and Down (linear) | 0 - 500 s ⁻¹ (Measure_0027 – Shear rate ramp up and down linear) |

Conclusion

If the coating is found to be thixotropic, this should be taken into account when carrying out subsequent tests. Sample application will need to be carried out in a reproducible way, or the samples should be pre-sheared so that they all have the same shear history. To quantify thixotropy in a more meaningful way, it is usual to perform a dynamic test as shown in the next section.

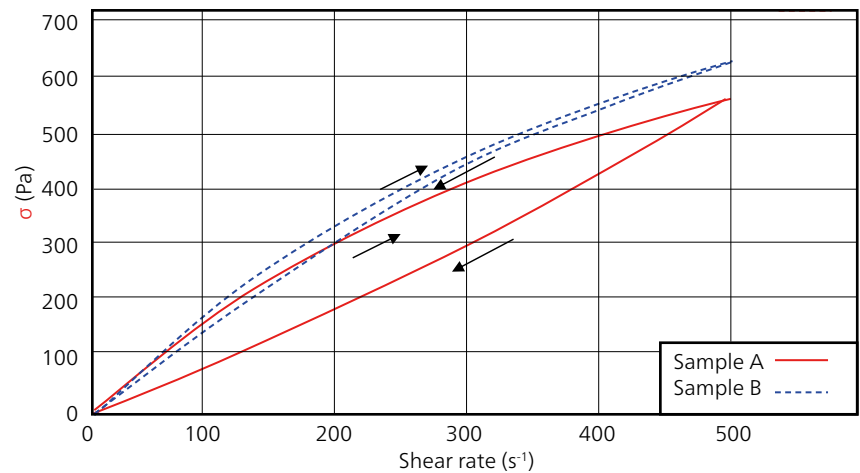


Figure 2. Shear stress vs. shear rate. Viscosity ramp up and down to show thixotropy. Sample A is thixotropic whereas sample B is only shear thinning.

Paints, Coatings and Inks

Quantifying Thixotropy with a Presheared Oscillation Test

Introduction

A single frequency oscillation test at constant stress is used to measure structure rebuild after a period of shearing at the beginning of the test known as pre-shear. The pre-shear is normally a constant shear rate, the value is determined directly from the simulated process or the limiting high shear region of the flow curve. The required time for the pre-shear could either simulate the application, or be until the sample reaches an equilibrium viscosity, as shown in Figure 3. If the latter is needed, a constant shear rate test can be run and viscosity plotted against time. When the viscosity reaches a plateau, this time can be used in the pre-shear. The viscometry results show that the time taken for the structure to be fully broken down is approximately 40 seconds.

An amplitude sweep is performed as a precursor experiment to the single frequency rebuild test, enabling the 'linear value' of the modulus to be determined. This modulus is representative of the fully structured sample. Comparison of the linear modulus with the rebuilding modulus provides a convenient method of determining the extent of structure recovery.

| Test Conditions | |
|--|--|
| Samples | Coatings in general |
| Geometry | Cone and plate system 4°/40 mm with a solvent trap |
| Temperature | 25°C |
| rSolution_0001 - monitoring structure rebuild following extrusion from a bottle, tube or spray head | Shear rate: 500 s ⁻¹ Shear time: 30 seconds Equilibrium time: 2 seconds |
| Single Frequency Oscillation | Strain: 0.1% Frequency: 1 Hz |

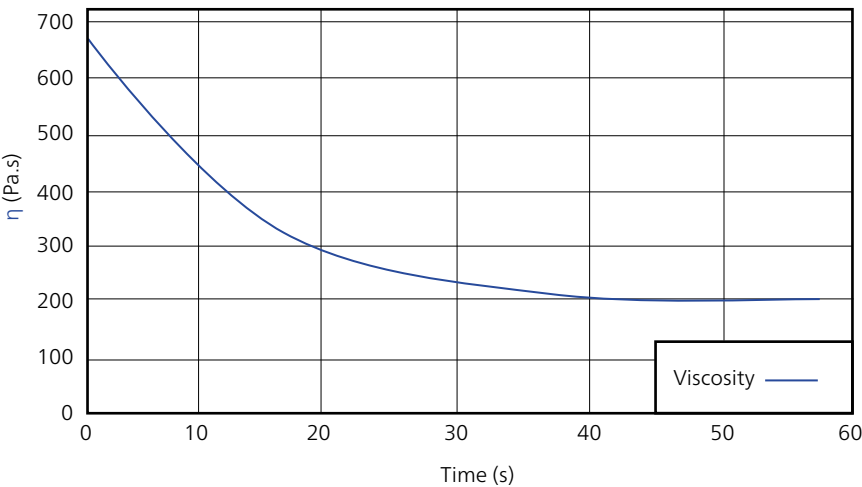


Figure 3. Shear viscosity vs. time to determine the time of shear needed until an equilibrium is reached

Interpretation

In this test, the sample is initially oscillated to determine the original viscoelastic structure of the sample, then subjected to the pre-shear and then oscillated again to monitor the rebuild. In the oscillation rebuild experiment, the structure rebuilds during the test before reaching a plateau where it has fully recovered as in Figure 4. The crossover point of the elastic and viscous moduli indicates when the structure becomes predominantly elastic and this can be used as an indication of a weak gel structure forming. Formulations with an earlier crossover may therefore show reduced sagging, whereas a later crossover would give better levelling characteristics.

Conclusion

The thixotropic nature of a coating can be accurately quantified, so a suitable pre-shear and equilibrium time can be used in subsequent tests; the equilibrium time can be taken from the total rebuild time which in this case is 600 seconds. This will then allow all samples to be assessed either after they have fully recovered, or at least with the same 'shear history', allowing comparable and reproducible results. Also, the microstructure of the material can be probed with oscillation measurements and so the mechanism of thixotropic rebuild can be clearly seen.

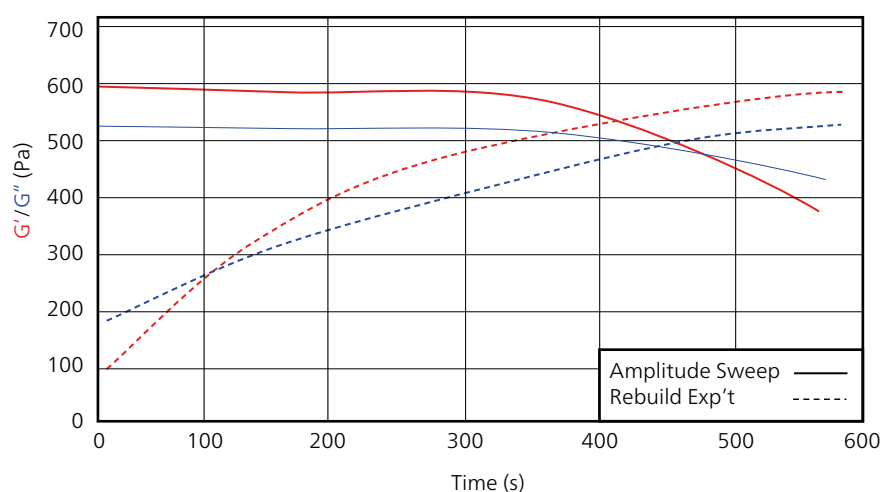


Figure 4. Amplitude sweep and pre-sheared oscillation rebuild time data overlaid can show the initial full structure of the sample, the degree of breakdown and the recovery time.

Paints, Coatings and Inks

Improving the Sag Resistance or Easing Pumping of Coatings

Introduction

Some materials have a very high viscosity at low stresses, such that they will not flow during normal experimental time scales, however when more stress is applied, the viscosity falls rapidly and the sample starts to flow noticeably. The minimum stress required to make the material flow is called the '**yield stress**'. On application of low stresses, these materials initially act like an elastic solid and as more stress is applied to the sample, the instantaneous viscosity appears to increase. When the yield stress is reached, the sample starts to flow and the measured viscosity falls rapidly. This is because the viscosity is not being measured under equilibrium conditions – in reality it isn't increasing, but when measured over a short timescale, we see an increase of shear stress without flow and so this calculates as an apparent viscosity increase. The peak of the viscosity curve is one way of defining the yield stress of the sample. The yield stress of a material will directly relate to its sag resistance and its ability to be pumped.

| Test Conditions | |
|--|--|
| Samples | Coatings in general |
| Geometry | Cone and Plate system 4°/40 mm with a solvent trap |
| Shear Stress Ramp, Measure_0022 – Shear stress ramp linear | 1 - 100 Pa Up Linear |
| Ramp time | 60 seconds |

Interpretation

The results in Figure 5 indicate that sample A exhibits a yield stress of 35 Pa and will therefore resist sagging much more effectively than sample B possessing a yield stress of 10 Pa. There is, however, a more mathematical approach to finding the critical stress needed to cause sagging, given below.

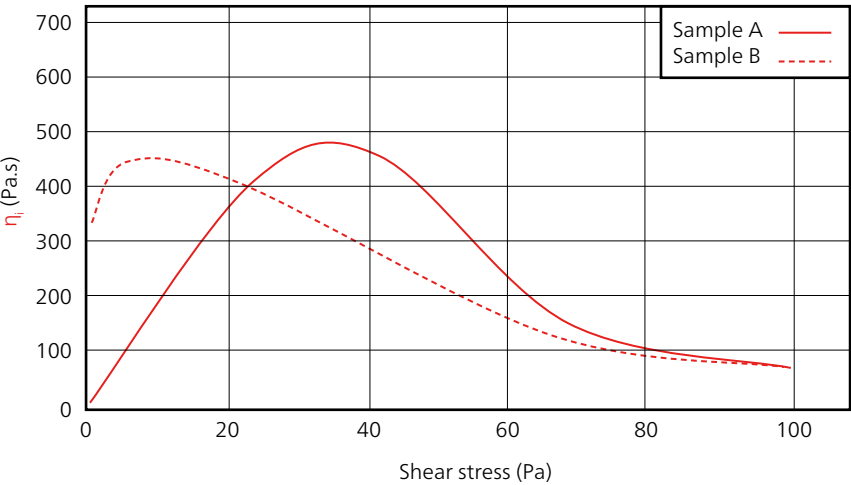


Figure 5. Viscosity vs. shear stress showing yield stress of the sample sfrom the peak of the viscosity curve

Sag Resistance

Sagging is usually due to the action of gravitational forces on a coating applied to an inclined surface as shown below. Since the flow does not involve acceleration, a balance exists between the gravitational forces and the stresses in the fluid (see Figure 6):

$$\frac{\delta \sigma}{\delta y} + \rho \cdot g \cdot \sin \beta = 0$$

This gives the maximum shear stress σ_{\max} as $\rho \cdot g \cdot h \cdot \sin \beta$, i.e., sagging will not occur for coatings with yield stresses greater than σ_{\max} .

For viscous materials, the maximum shear rate will be:

$$\dot{\gamma}_{\max} = \rho \cdot g \cdot h \cdot \sin \beta / \eta$$

The distribution of velocity across the film is given by:

$$(h - 1/2y) \cdot \rho \cdot g \cdot \sin \beta / \eta$$

The maximum velocity occurs at the surface; therefore, thicker areas of coating will sag with a higher speed thus promoting runs.

If the drying time of the film is T_d , then sagging will not occur if:

$$\rho \cdot g \cdot h \cdot \sin \beta \cdot T_d / 2\eta \ll 1$$

Notation Key:

| | |
|--|---|
| ρ = density ($\text{kg} \cdot \text{m}^{-3}$) | g = gravitational acceleration ($9.81 \text{ m} \cdot \text{s}^{-2}$) |
| h = film thickness (m) | β = tilt angle (degrees) |
| η = film viscosity (Pa.s) | T_d = drying time of the film (s) |
| γ = shear rate (s^{-1}) | x & y = Cartesian coordinates |

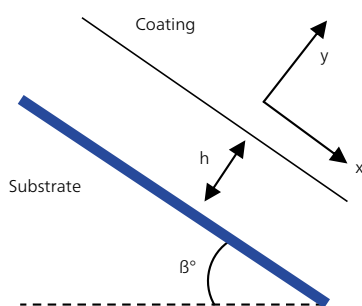


Figure 6. Sketch of a coating on an inclined substrate

Pumping

A coating's resistance to start pumping will also be proportional to its yield stress. It can be seen that the shear stress (at the wall) of a fluid running through a pipe (ignoring entrance and exit effects) is:

$$\sigma_w = \frac{DP}{4L}$$

where D = Diameter of the pipe
 P = Min pressure through the pipe
 L = Length of the pipe

So if the pipe pressure exceeds $4L\sigma_o/D$, then the sample will start to flow in the pipe, where σ_o is the yield stress. At very high shear rates, the flow may become turbulent and this equation does not hold true. The flow rate will then depend on the viscosity profile of the product and the pipe end effects.

Conclusion

The yield stress can be used to calculate whether a sample is likely to sag on application, as well as whether it will be difficult to start pumping or stirring. Good rheological product design will dramatically enhance processing and end-use performance.



Sag Resistance

Sag resistance is defined as the ability of a paint or coating to resist sagging failure, which is bending or dropping of the wet coating. Sagging is a factor of the coating's composition and viscosity. A coating with a high viscosity has a greater sag resistance than one with a low viscosity.

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Paints, Coatings and Inks

Predicting Sedimentation / Stability Problems

Background

Suspensions may be acceptably stable to sedimentation for three reasons. Either the bulk material has a yield stress high enough to hold the particles in suspension, or the material has a 'zero shear viscosity' high enough that sedimentation occurs in an acceptably slow manner. Lastly, if the particles are sub-micron and stabilized to not agglomerate, their Brownian motion will usually keep them suspended indefinitely. The first two reasons will be addressed separately in A and B below.

If a material has a yield stress but a very weak structure, the sample may still give sedimentation during transportation and handling. The stability of the suspension therefore needs to be measured, shown in C.

A. Materials with a Yield Stress

The yield stress of the sample may be measured using the experiment described on page 28. Sufficient yield stress may prevent sedimentation, as the downward stress exerted by a spherical particle in dilute suspension is given by:

$$\sigma_s = \frac{r \cdot g \cdot (d - \rho)}{3}$$

Notation Key:

r = particle radius g = acceleration due to gravity
 ρ = density of suspending fluid d = particle density
 η_0 = zero shear viscosity σ_s = sedimentation stress on particle

Test Conditions

Samples Filled materials in general. The yield stress test is described on page 28 and similar conditions may be used.

Thus, if the material has a yield stress greater than σ_s , the sample should resist sedimentation, providing the structure is stable to vibrations that may arise during transportation and handling.

B. Materials with Zero Shear Viscosity

Introduction

Stokes Law gives the sedimentation velocity in a suspension:

$$V_s = \frac{2 \cdot r^2 \cdot g \cdot (d - \rho)}{\eta_0}$$

The sedimentation velocity can then be used to calculate the time that a particle will take to reach the bottom of the container. If this time is very long, the formulation can be considered to be stable. Also, the shear rate of a falling particle can be calculated from the following formula:

$$\text{Shear rate}_{\max} = \frac{3 V_s \cdot \eta_0}{2r}$$

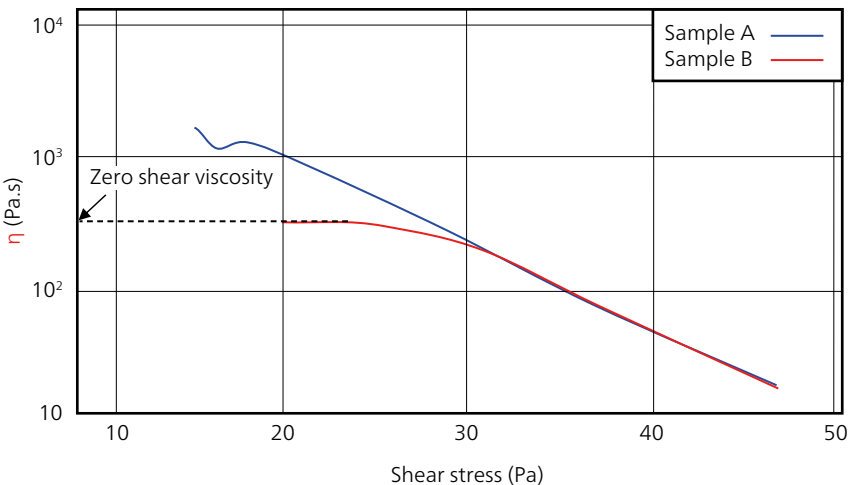


Figure 7. Viscosity flow curve test from higher shear stresses down to low to determine whether a sample has a yield stress (as sample A) or zero shear viscosity plateau (as sample B)

| Test Conditions | |
|-------------------------------|---|
| Geometry | Cone and Plate system 1° / 60 |
| Toolkit_V001 Shear Rate Table | 50 - 0.01 s ⁻¹ / down / log (plot viscosity versus stress) |
| Gap | 30 μm |
| Delay time | 15 seconds |
| Integration time | 30 seconds |

These formulas describe ideal systems and the assumptions made are that the particles are spherical, uncharged and in a dilute suspension. However, the results obtained from a zero-shear viscosity test can give an indication of sedimentation time.

Interpretation

The results in Figure 7 show that sample B's viscosity reached a plateau and the value at zero shear can be extrapolated easily. Sample A, however, did not reach a plateau in this experiment, and the viscometry data became slightly less accurate at extremely low shear rates. This low shear area can be further investigated by running creep tests as shown.

| Test Conditions Creep | |
|--|---|
| Creep_0004 – Multiple creep end by time with increasing stress | where the curve needs extending from Figure 7 |
| Geometry | As used in the previous experiment |
| Creep time | 600 seconds |

C. Creep Testing to Find Zero Shear Viscosity

Interpretation

Successively lower stress creep experiments are conducted until the creep compliance curves start to overlay each other as shown in Figure 8. When this occurs and the test is run until the sample is at steady state, the viscosity value given is the zero-shear viscosity. It may be necessary to renew a polymer sample if it starts to degrade during the testing, however, the sample life may be extended by gently passing nitrogen gas around the measuring system.



Viscosity Plateau

The viscosity plateau as the shear rate approaches zero, i.e., remains liquid-like when stationary.

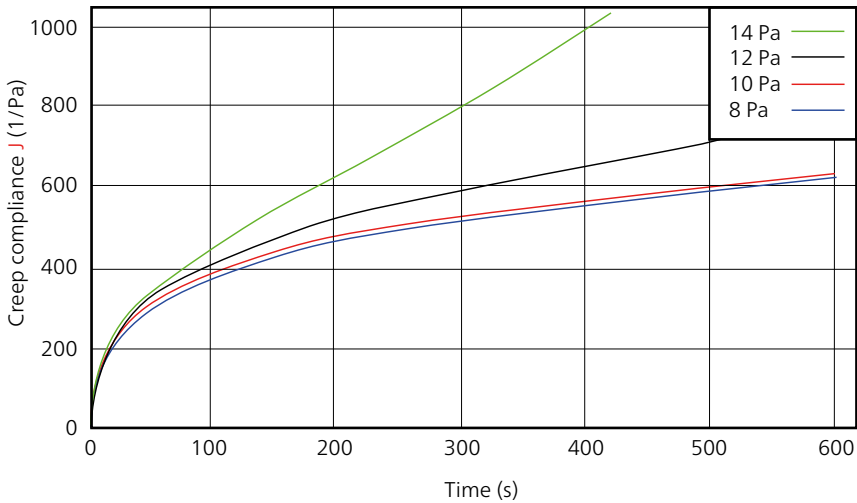


Figure 8. Creep tests at lower and lower stresses until the results all start to overlay one another, as at 8 and 10 Pa, showing a viscosity plateau below 10 Pa.

Paints, Coatings and Inks

D. Measurement of Suspension Stability

Introduction

In this amplitude sweep experiment, the sample is oscillated with an increasing stress and the determined storage and loss moduli are plotted against shear stress. The moduli initially are independent of stress, giving a plateau known as the linear viscoelastic region (LVR). The length of the linear viscoelastic region shows how far the material can be deformed before the onset of structure breakdown.

Interpretation

Figure 9 shows that sample A has a much shorter linear viscoelastic region than sample B and may, therefore, be expected to break down much more easily with vibrations and small movements.

Conclusion

Sample stability and sedimentation can be determined by several methods. Firstly, if a material has a sufficient yield stress, particles present will be unable to sediment. If the material doesn't possess a large enough yield stress to prevent sedimentation, the time of sedimentation may also be sufficiently long enough for an acceptable product

| Test Conditions | |
|------------------------|--|
| Geometry | Cone and Plate system 4° / 40 mm with a solvent trap |
| Temperature | 25°C |
| Stress amplitude sweep | 0.1 - 100 Pa up logarithmic |

performance. Stokes Law may be used in these situations to calculate the sedimentation velocity and thus, the time for the product to be unacceptably separated. Where the zero shear viscosity is difficult to measure by a viscometry test, it could be accessed through multiple creep tests at lower and lower shear stresses. Lastly, there has also been a strong correlation between the length of the linear viscoelastic region and the stability of a product.

A relatively quick amplitude sweep experiment can probe the microstructure of the sample indicating the dispersion stability of a suspension (solid in liquid). The length of the linear viscoelastic region can also show energy absorption by interfacial interactions, and is therefore also a good indication of the stability of an emulsion to resist syneresis (where a layer of the one component forms on the surface of the mixture, e.g., oil in water). The amplitude sweep results can be used to eliminate many unstable formulations without the need for storage testing.

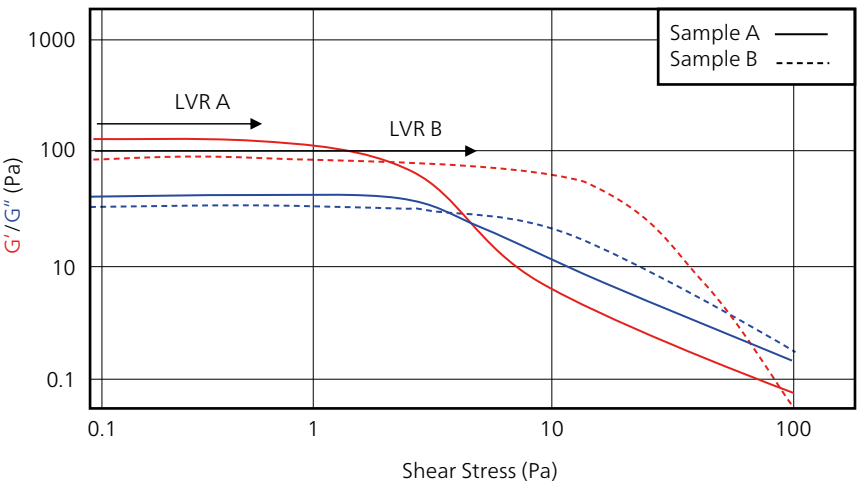


Figure 9. Amplitude sweep results showing elastic and viscous moduli (G' and G'' , respectively) vs. shear stress.

Determining Pumping and Spraying Characteristics

Introduction

The pumping and spraying characteristics of materials will be directly related to the viscosity at a high shear rate. The shear rates experienced during pumping are approximately 1 - 1000 s⁻¹ and during spraying are approximately 10,000 – 100,000 s⁻¹. In this test, we can evaluate the viscosity in the same shear rate region. Higher shear rates may be reached by further reduction of the gap, to as little as 20 microns for a well-aligned system. In general terms, a lower viscosity or a more shear thinning response will enhance spraying and pumping.

Interpretation

From the viscosity curves shown in Figure 10, it is clear that sample A is less shear thinning than sample B, and therefore, may be more difficult to spray. Sample A would also probably support less film thickness before runs appear on the surface, as the low shear viscosity is also lower than that of sample B.

| Test Conditions | |
|--|--|
| Samples | Paint or spray applied adhesives |
| Geometry | Parallel plate system 40 mm |
| Gap | 50 µm |
| Toolkit_V001 Shear Rate Table – with a reduced maximum sampling interval of 5-10 seconds per point | 10 - 50,000 s ⁻¹ Up Logarithmic |

Conclusion

The flow profile of coatings indicate their suitability for end use, with respect to whether they will flow easily through pipes and the spray nozzle. The low shear viscosity can also indicate the maximum film thickness that can be achieved before sagging occurs on the substrate.

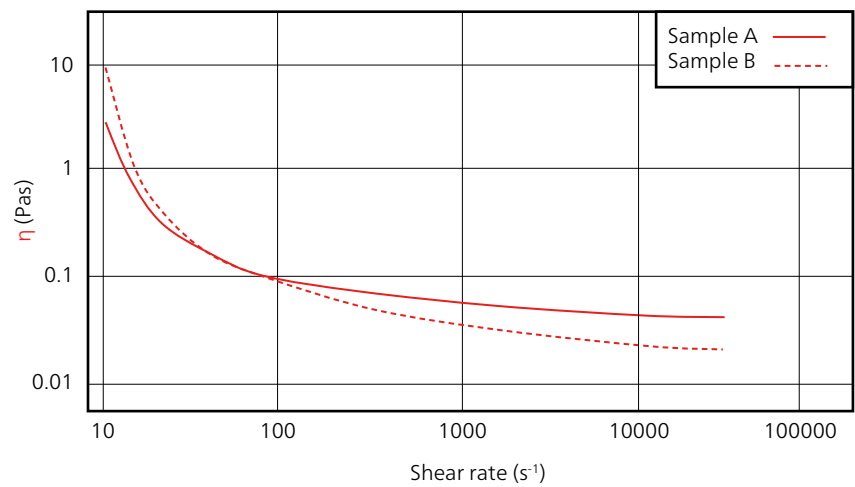


Figure 10. Viscosity vs. shear rate. The viscosity at high shear rates shows how the material will spray, where lower viscosity materials usually spray and atomize more easily than viscous materials.



Paints, Coatings and Inks

Thixotropy – Rheological Design of Paints to Remove Brush Marks and Enhance Resistance to Sag Sedimentation / Stability Problems

Introduction

In this experiment, the sample is subjected to high shear initially, simulating brushing or spraying of paint. The pre-shear can be optimized from running a viscometry shear ramp as described on page 26. After this, microscopic oscillations are used to investigate structure rebuild, without retarding the process.

Interpretation

The results in Figure 11 show the rebuild profiles of two samples. During its rebuild, sample A will initially flow and have the ability to level-out because the viscous modulus is dominant over the elastic component. When the elastic modulus becomes dominant, the sample starts to show gel-like properties and the sample is unlikely to continue flowing. Sample A is a typical example of a thixotropic system.

Levelling characteristics are not solely dictated by the rheology, but also by the paint's dynamic surface tension and the film thickness.

The levelling is fastest when a sample has a low viscosity, a thicker coating layer and a higher surface tension. Therefore, a sample that thins dramatically on shearing and rebuilds slowly enough to level will eradicate surface striations. The rebuild time must be sufficiently fast to prevent sag and so the coating is usually formulated to give a balance between these two properties.

| Test Conditions | |
|--|--|
| Samples | Oil-based paints |
| Geometry | Parallel plate system 40 mm with a 200 μm gap with a solvent trap |
| Temperature | 20°C |
| Pre-shear | Shear rate: 1,000 s^{-1} Shear time: 30 seconds Equilibrium time: 2 seconds |
| Single Frequency Oscillation rSolution_0001 | |
| Monitoring structure rebuild (thixotropy) following extrusion from a bottle, tube or spray head.rseq | Stress: 0.1 Pa Frequency: 1 Hz |

Sample B appears not to be at all thixotropic since there is no significant change in modulus with time. The viscous modulus is much higher than the elastic modulus and both values are higher than those of sample A. The sample will continue to flow continuously until it dries.

As shown on page 27 (Figure 4), we can also merge on the results from the Amplitude Sweep. The difference between the curves shows how much the sample's structure was destroyed and how long the recovery will take to return completely to the original modulus.

Conclusion

The leveling characteristics of coatings can be accurately quantified, so that a formulation may be optimized to give good levelling characteristics, with sufficient sag resistance.

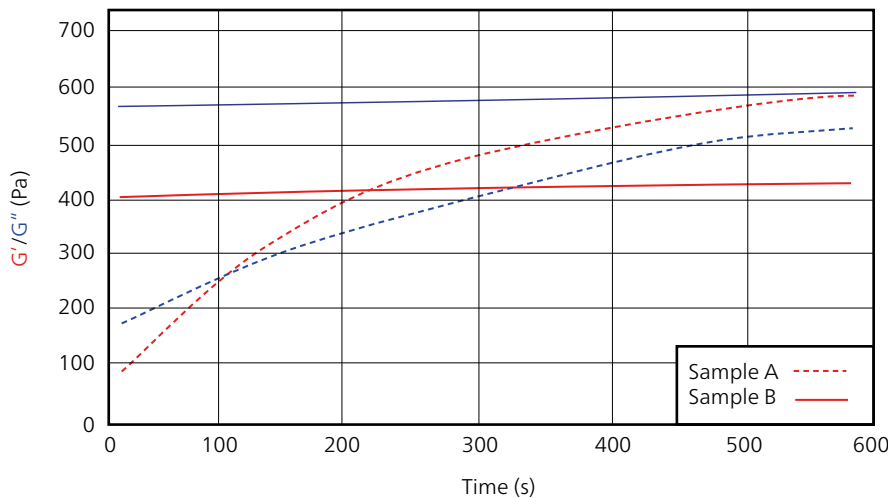


Figure 11. Elastic (G') and viscous (G'') moduli vs. time. Presheared Oscillation Rebuild Test Results showing how quickly the sample rebuilds after a period of shearing. If the Solve level sequence cited was run, this graph would be the data from the third step of the test, oscillation after shear.

Using Normal Force to Determine Coating Performance

Introduction

Normal force is a phenomenon where under shearing the sample exerts a vertical force upwards on the cone and downwards on the plate. In simple terms, the sample is exhibiting stringy behavior and being coiled around the center of the cone. Normal force plays an important part in blade and roller coating processes, as under shear the coating can push the blade away from the substrate and cause migration under the roller. This gives an increased coat weight and an increased drying time, which in itself can cause more serious problems.

Interpretation

The normal force data in Figure 12 clearly shows that at high shear rates, sample A produces significantly higher normal stresses than sample B. The former may be problematic especially in terms of 'metering' a precise coat weight or layer.

| Test Conditions | |
|--|--|
| Samples | Paper coatings or pressure-sensitive adhesives |
| Geometry | Cone and plate system CP 0.5° / 40 mm and a solvent trap cover |
| Gap | 15 µm |
| Toolkit_V001 Shear Rate Table – with a reduced maximum sampling interval of 5-10 seconds per point | 10 - 20000 s ⁻¹ , UP Linear |

Conclusion

The normal force of coatings can have a dramatically detrimental effect on their processing characteristics if it is not within manageable limits. This test could be used to quickly identify a sample's first normal stress difference (N1) and therefore eliminate poor formulations.

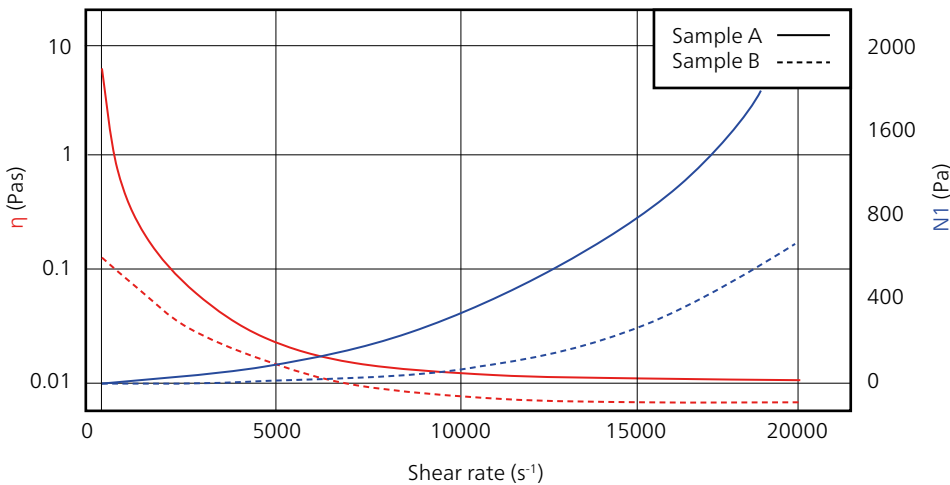


Figure 12. Viscosity (red) and first normal stress difference (N1) vs. shear rate. A sample that has a high normal force when sheared is likely to show stringy behavior and not coat so well as one with a lower normal force.

Paints, Coatings and Inks

Rheological Analysis of Dispersions by Frequency Sweep Testing

Introduction

A paint or pigmented coating is typically a dispersion of pigment particles in a fluid matrix. Most dispersion manufacturers realize that success or failure of a product is dependent on properties such as storage stability, sag resistance, good leveling, brushing and spraying. These factors are often in conflict with one another and so to produce a successful product, a 'balance' must be obtained. Measurement of the rheological properties can provide microstructural information enabling better understanding of the application and end-use characteristics. One of the best techniques for determination of a sample's microstructure is oscillation (dynamic) testing.

Before making detailed dynamic measurements to probe a sample's microstructure, the linear viscoelastic region (LVER) must first be defined. This is determined by performing an amplitude sweep as described on page 32. As discussed previously, the LVER can also be used to determine the stability of a suspension. The length of the LVER of the elastic modulus (G') can be used as a measurement of the stability of a sample's structure, since structural properties are best related to elasticity. A sample that has a long LVER is indicative of a well-dispersed and stable system. From the amplitude sweep test, a stress or strain must be selected from the LVER and incorporated into subsequent oscillation measurements.

| Test Conditions | |
|---|---|
| Samples | Any dispersion system use for coating |
| Geometry | Cone and parallel plate system 4° / 40 mm with a solvent trap |
| Temperature | 25°C |
| Toolkit_O002 Frequency Table (Strain Control) | 10 - 0.1 Hz |
| Strain | 0.010 |

Interpretation

A frequency sweep is a particularly useful test as it enables the viscoelastic properties of a sample to be determined as a function of timescale. Several parameters can be obtained, such as the Storage (Elastic) Modulus (G'), the Viscous (Loss) Modulus (G''), and the Complex Viscosity (η^*). The storage modulus can be used as a measure of the elastic component of the sample and similarly the loss modulus, the viscous component of the sample. Whichever modulus is dominant at a particular frequency will indicate whether the fully structured material appears to be elastic or viscous in a process of similar time scale. The mechanical response of most dispersion coatings is viscoelastic, since the presence of suspended solids, high additive concentrations, colloidal thickeners, etc., will induce some sort of structure upon the bulk phase. Some examples are considered in the frequency sweep data sets plotted in Figures 13, 14 and 15.

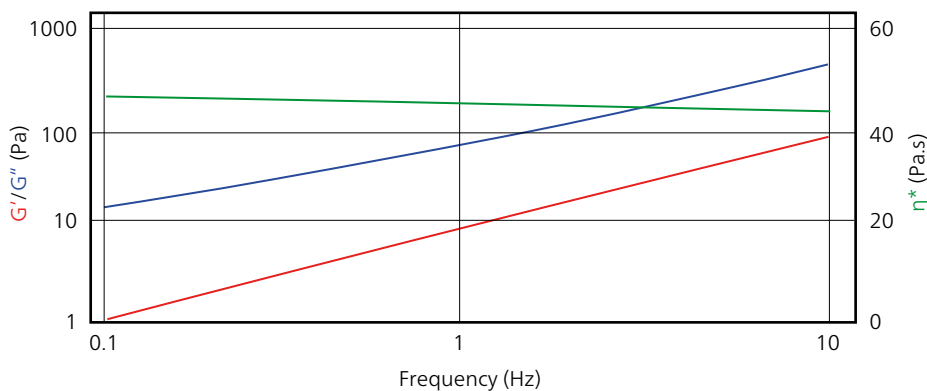


Figure 13. Elastic (G'), viscous (G'') modulus and shear viscosity (complex component) η^* vs. frequency. In a non-associated dispersion of particles, the material is viscously natured, and there is little or no elasticity.

Figure 13 is typical of a **non-associated particulate dispersion** and the viscosity is almost independent of frequency. The viscous modulus is dominant over the elastic modulus and both of these are highly dependent on frequency. In this situation, sedimentation is likely to occur.

Figure 14 shows a **weakly structured system**. The viscous modulus will still dominate over the elastic modulus, however the difference between these is less great than in the non-associated system. The complex viscosity is also now dependent on the frequency. In this system, sedimentation may occur.

Figure 15 could be classified as a **well-structured** (gelled) system. In this case, particles are strongly associated, the storage modulus (G') is greater than the loss modulus (G''), and both are almost independent of frequency. Sedimentation is unlikely to occur.

Conclusion

The degree of dispersion and interparticle association can be clearly seen from the profile of the frequency sweep data. Where a pigment or thixotrope needs to be well dispersed into a fluid matrix, the process can be optimized by sampling and running repeated frequency sweep tests. The fully dispersed sample will give the most gelled system. Similarly, the effectiveness of surfactants and other colloidal thickeners can be quantified in situ.

The frequency sweep curve gives a good rheological description of how the product will behave during storage and application.

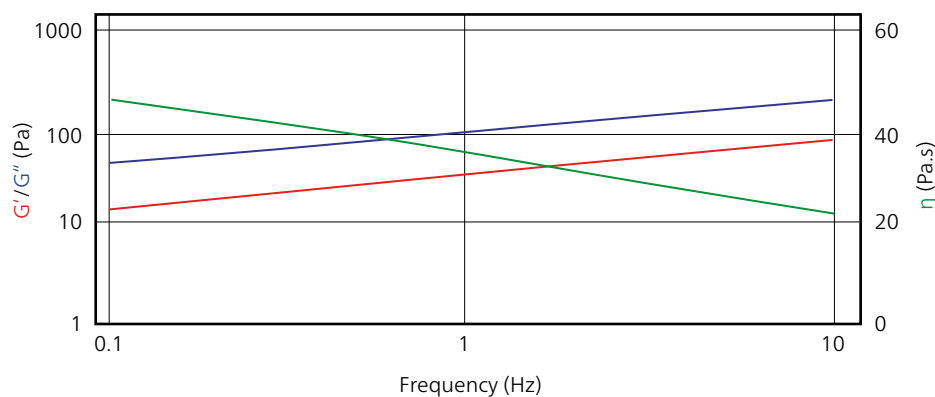


Figure 14. Elastic (G'), viscous (G'') modulus and shear viscosity (complex component) η^* vs. frequency. In a weakly-associated dispersion of particles, the material is viscously natured, however some elasticity is also seen.

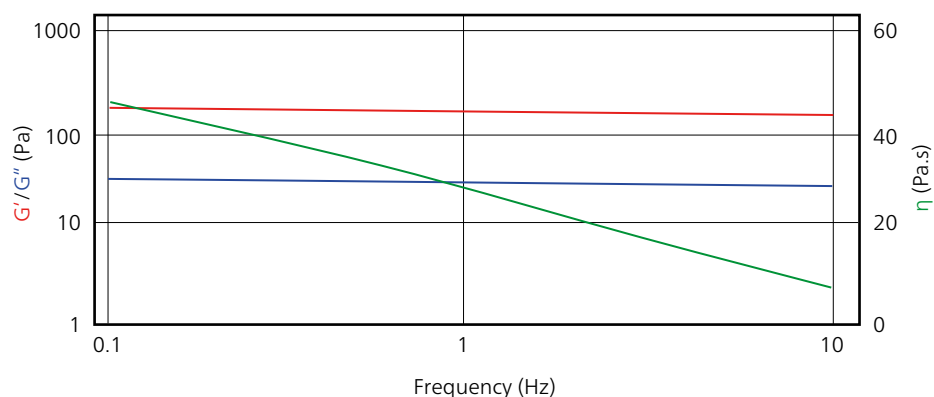


Figure 15. Elastic (G'), viscous (G'') modulus and shear viscosity (complex component) η^* vs. frequency. In a strongly-associated dispersion of particles, eg a gel, the material is elastically natured and the moduli are independent of frequency.

Paints, Coatings and Inks

Rheological Properties of High-Speed Roller Coating

Introduction

High-speed roller coatings need to fulfill several demanding rheological requirements. Their low shear viscosity will affect the storage, roller pick-up and levelling characteristics of the coating. A higher **low shear viscosity** will resist sedimentation and pick up a heavier mass of the adhesive, but possibly not level so effectively or absorb as quickly into the substrate. The **high shear rates** provide information about the adhesive's transfer properties and its mechanical stability. A lower high shear viscosity will give better transfer properties between rollers. Viscosity-time characteristics will invariably determine the sample's mechanical stability.

Very high shear rate measurements can be made with a rotational rheometer up to approximately $1 \times 10^5 \text{ s}^{-1}$, which is approaching conditions taking place in the coating head of a high-speed coater. This enables the sample's mechanical response and transfer properties during coating to be investigated. The ability to measure performance across a spectrum of shear rates (see Figure 16) that more closely mirrors those observed through the whole coating process gives valuable information to the adhesive formulators enabling more reliable production of adhesive coatings.

Interpretation

In the example shown in Figure 17, all samples have identical 'Brookfield' viscosities. This would be expected as the viscosities are all the same below 1000 s^{-1} , however, the high shear rate viscosities are significantly different. Sample A exhibits the lowest viscosity at 10^5 s^{-1} , indicating that it should have better transfer properties.

| Test Conditions | |
|-------------------------------|---|
| Samples | Pressure-sensitive adhesives for high-speed coating application |
| Geometry | Cone and plate system CP 0.5° / 40 mm |
| Gap | 15 μm |
| Temperature | 20°C |
| Toolkit_V001 Shear Rate Table | 0.1 - 20,000 s^{-1} Up Linear |

In the case of sample C, a sharp rise in viscosity is seen at shear rates $>5 \times 10^3 \text{ s}^{-1}$, this is where the sample has become mechanically unstable. Mechanical instability is often due to shear-induced aggregation of the latex base if pH or additives have diminished the sample's electrical double layer (1). In this case, the sample shows a sharp jump in viscosity at higher shear rates.

Conclusion

Properties affecting high-speed coating, application and end use can be measured using modern rheometers that are unattainable using simpler conventional measurement devices. Good rheological design of intermediate and finished products makes production more reproducible and efficient. In new product development, rheometers can eliminate many wasteful pilot scale trials and identify genuinely good formulations at minimal cost.

(1) Husband, J.C. (1993) : MSc Thesis: Shear-induced aggregation of carboxylated polymer latices, University of Manchester.

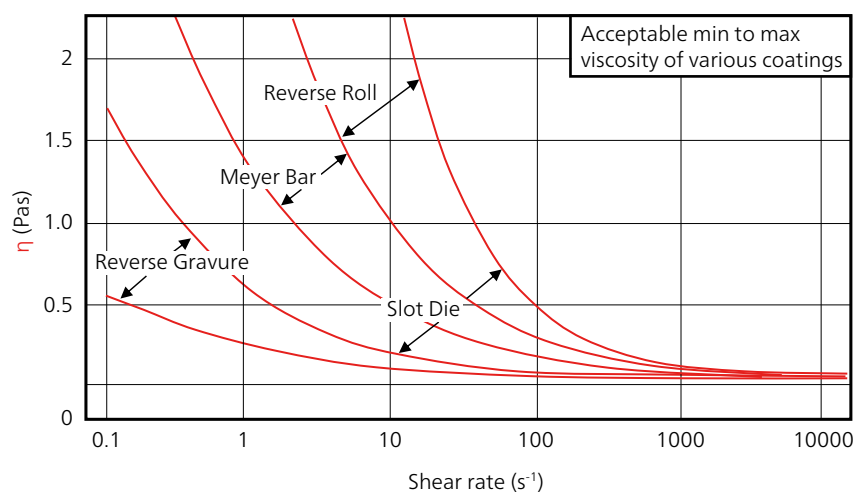


Figure 16. Viscosity vs. shear rate. Running a variety of dilutions of a sample in various processes can be useful to determine the maximum and minimum acceptable viscosities for the process. (Data shown is just for illustrative purposes and may not be accurate for some materials)

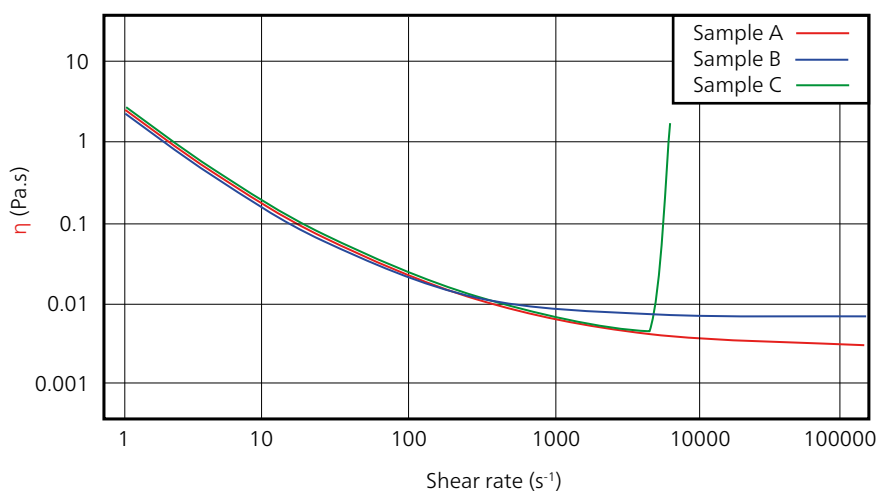


Figure 17. Viscosity vs. shear rate. Unstable samples often exhibit sudden shear thickening above a specific shear rate – a phenomenon known as 'shear induced aggregation'.

Paints, Coatings and Inks

Adhesive Film 'Leakage'

Introduction

When rolls of adhesive or resin coated material are stored, the coating can often creep slowly from the ends of the roll: a phenomenon known as leakage. Similarly, the rolls can develop flat areas when not stored vertically or where they touch other rolls. The response of the adhesive at a very low frequency can indicate how it will behave in storage conditions. The oscillation frequency sweep test will therefore show whether the adhesive will be viscously dominated at low frequencies and hence be able to flow, or elastically dominated and hence be less able to flow.

| Test Conditions | |
|---|--|
| Samples | Pressure-sensitive adhesives |
| Geometry | Cone and plate system 4° / 40 mm with a solvent trap |
| Toolkit_O002 Frequency Sweep (Strain Control) | 10 - 0.1 Hz |
| Strain | 0.010 |

Interpretation

The frequency sweep results in Figure 18 show that Sample B is viscous at all frequencies and that it is unlikely to become elastic at very low frequencies. This means that although the adhesive may mix-up and apply quite satisfactorily, the reel of adhesive film is likely to give some leakage at the ends. Sample A has a frequency sweep profile where at very low frequencies, it is elastically dominated and therefore has a gel-like structure. This material will therefore resist seeping at low shear rates.

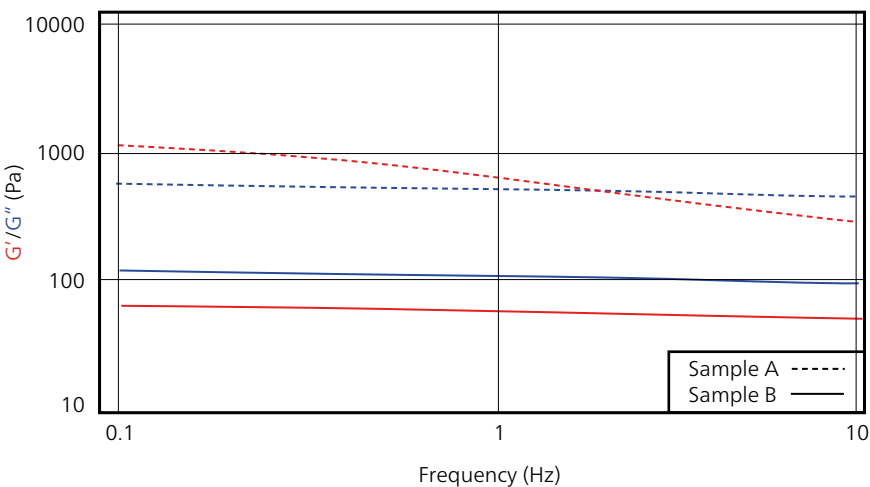


Figure 18. Elastic (G') and viscous (G'') moduli vs. frequency. Sample A is more elastically natured at low frequencies and will therefore resist creeping out over time, whereas sample B is viscously natured and will flow with time.

Creep Testing

Introduction

Using the creep method, we can apply the same stress as would be applied in the reel of adhesive and actually see whether the sample will flow or not at that stress.

Using a concentric cylinder model as shown in Figure 19, we can approximate the stress at the center of the adhesive for one roll of the coated film. The internal pressure can be calculated from the tension of the film and dimensions of the roll:

$$\rho = \frac{T}{r.L.}$$

ρ = Internal pressure (N.m⁻²)
 T = Tension force of the film when wound (N)
 L = Length of the roll (m)
 r = Outer radius of the roll (m)
 f = film thickness

The leakage stress on the adhesive (σ_1) will be a maximum at the wall and will be:

$$\sigma_1 = \frac{f.\rho}{2} \quad \text{or} \quad \frac{f.T}{2. r.L.}$$

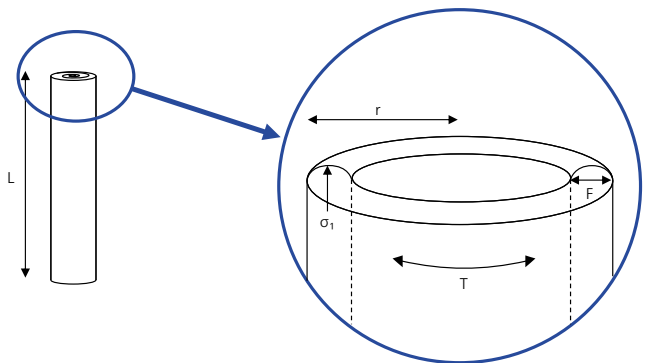


Figure 19. Model of a roll of adhesive of film thickness (F) and tension (T). The squeezing pressure on the material is σ_1 .

Test Conditions Creep Testing

| | |
|--|--|
| Geometry | Parallel plate 20 mm system with a solvent trap (gap = 1 mm) |
| Temperature | 23°C |
| Creep time | 600 seconds |
| Creep Stress (Toolkit_C001 Creep and Recovery) | As calculated from the roll tension as shown below |

For multiple layers all under the same tension the effect can be approximated as cumulative in the worst case for each layer of adhesive film. So the worst situation would be taking the center of the roll. The leakage stress in this case would be:

$$\rho_c = \frac{T}{r_1.L} + \frac{T}{r_2.L} + \dots$$

where
 ρ_c = Cumulative pressure inwards (N.m⁻²)
 T = Tension of the film when wound (N)
 L = Length of the roll (m)
 r_n = Outer radius of layer n (m)

If the inner and outer most diameters of 'n' layers of tape are similar, the cumulative pressure can be approximated to be:

$$\rho_c = \frac{2n.T}{L.(r_n + r_1)}$$

where
 r_n = Outmost radius (m), r_1 = Innermost radius (m)

So, the cumulative stress will be approximately

$$\sigma_c = \frac{f.n.T}{L.(r_n + r_1)}$$

If we apply this stress in the creep experiment, we can see whether the adhesive will start to leak or not. The creep test shown here runs for approximately ten minutes, but could be extended if required. As the rheometer can measure such exceedingly small shear rates, it is possible to measure leakage that would occur over several months in minutes.

Paints, Coatings and Inks

Interpretation

The results in Figure 20 show that when the stress was applied, sample A stretched initially but then came to rest after approximately 350 seconds. This indicates that the sample is solid-like in nature unlikely to leak under the tension of the reel. Conversely, sample B continued to flow indefinitely, indicating that it is viscous in nature and will show signs of leakage in time.

Conclusion

The creep test can be used to quickly identify good and bad formulations without the need for extensive storage testing. An adhesive can be reformulated and evaluated in the laboratory by addition of suitable modifiers, to provide an elastically dominated end product that will not cause leakage problems.

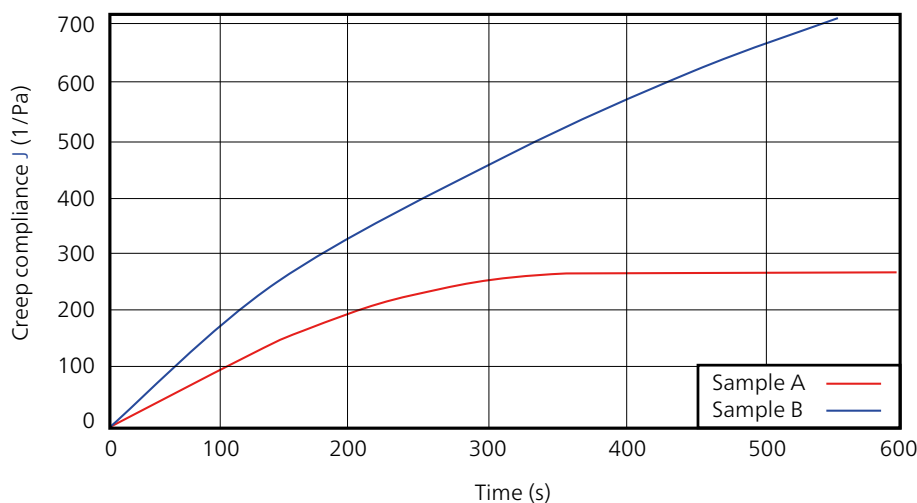


Figure 20. Creep tests at the calculated cumulative stress will show whether the adhesive will flow over a period of time (as sample B) or not (as sample A)



Paints, Coatings and Inks

Assessing the Printing Performance of Screen Inks

Background

Screen inks are printed by squeezing the ink through a nylon sheet that has holes describing the image. The size and density of holes per square inch determines the ink properties required. The ink should resist flowing through the screen before the squeegee is passed over the mesh, which requires a high viscosity at low shear stresses. The ink should also have a reasonably quick rebuild time so that the ink doesn't drip after printing, or give too much absorption resulting in dot gain.

Conversely, if the high shear viscosity is too high or the ink rebuilds too quickly, the ink may give dot loss, as it will not absorb sufficiently onto the substrate, see illustration to the right.

The following two experiments show how we can quickly characterize the flow curve and the rebuild time for these inks.

Viscosity Flow Curve

Introduction

The ink should resist flowing through the screen before the squeegee is passed over the mesh, which requires a high viscosity at low shear stresses. However, the high shear viscosity needs to be low enough so that it can wet the substrate and adhere.

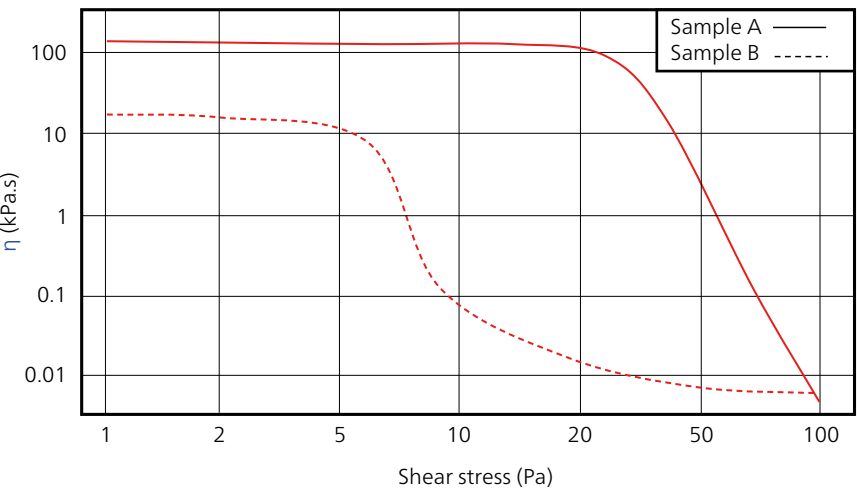
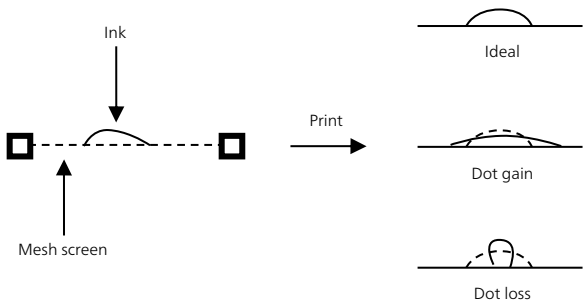


Figure 21. Viscosity vs. shear stress. The zero shear viscosity shows how well the ink will resist flowing before and after the squeegee has passed over the mesh. Sample B is more likely to show dripping than sample A.

| Test Conditions | |
|--|---|
| Samples | Screen-printing inks |
| Geometry | Parallel plate system PP40 and a solvent trap cover |
| Gap | 500 μm |
| Temperature | 200°C |
| (Viscometry_0004 – Table of shear stresses with Ellis model fit) | 1 - 200 Pa Up Log |



Interpretation

Ink A (in Figure 21) showed a much higher zero shear viscosity than Ink B, suggesting that it is more likely to resist flowing before and after the squeegee has been passed over the mesh, eliminating drips and smudges. Sample B exhibited a much lower low shear viscosity, indicating that it may drip through the printing screen before and after squeegeeing.

At high shear, the viscosities became asymptotic indicating that both inks would be sufficiently low viscosity to pass through the mesh and give some coating of the substrate.

Characterizing the Rebuild Time of Inks by Pre-Shear Oscillation

Introduction

A screen ink should have a reasonably quick rebuild time so that the ink doesn't drip after printing, or give too much absorption into the substrate resulting in dot gain. However, if the ink rebuilds too quickly, the ink may give dot loss, as it will not absorb sufficiently onto the substrate.

Interpretation

The pre-shear simulates the printing process, whereas the oscillation simulates the static time on the substrate. The structure breakdown during the pre-shear can be assessed as described on page 8. Figure 22 shows that the structure in Sample A rebuilds very quickly after the pre-shear, almost returning to its original elastic modulus (as defined from a precursor amplitude sweep experiment). Sample B however has broken down significantly more than sample A, and is

| Test Conditions | |
|--|---|
| Samples | Screen inks |
| Geometry | Parallel plate system 40 mm with a solvent trap |
| Gap | 500 microns |
| Pre-shear | Shear rate: 500 s ⁻¹ Shear time: 30 seconds Equilibrium time: 1 second |
| Single Frequency Oscillation rSolution_0001 Monitoring structure rebuild (thixotropy) following extrusion from a bottle, tube or spray head.rseq | Stress: 1 Pa Frequency: 2 Hz |

still rebuilding after 400 seconds. This indicates that sample B is likely to continue flowing after printing and therefore exhibit dot gain.

Conclusion

Inks may be formulated quickly with the aid of the rheometer to show which formulations are likely to work successfully. Where a current formulation is satisfactory, these two tests may be used to characterize that ink, and provide an insight into the 'ideal behavior' for other formulations.

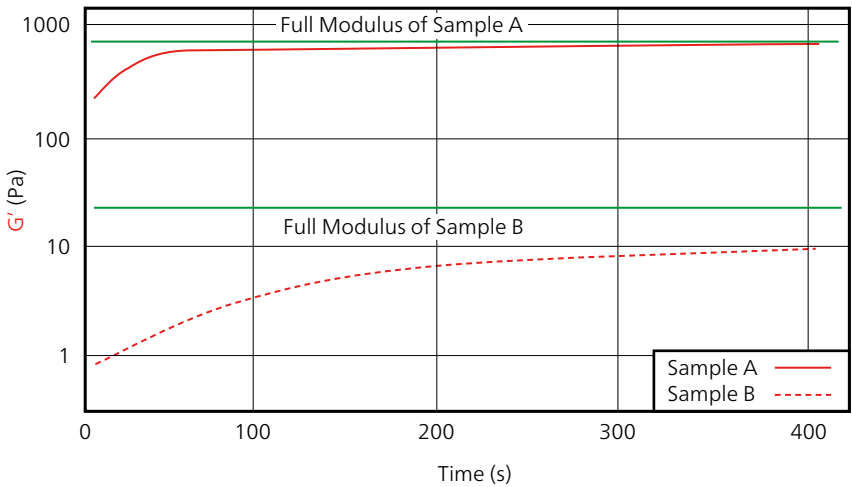


Figure 22. Elastic modulus (G' – red) vs. rebuild time. The full moduli of the respective samples is shown by the green lines.

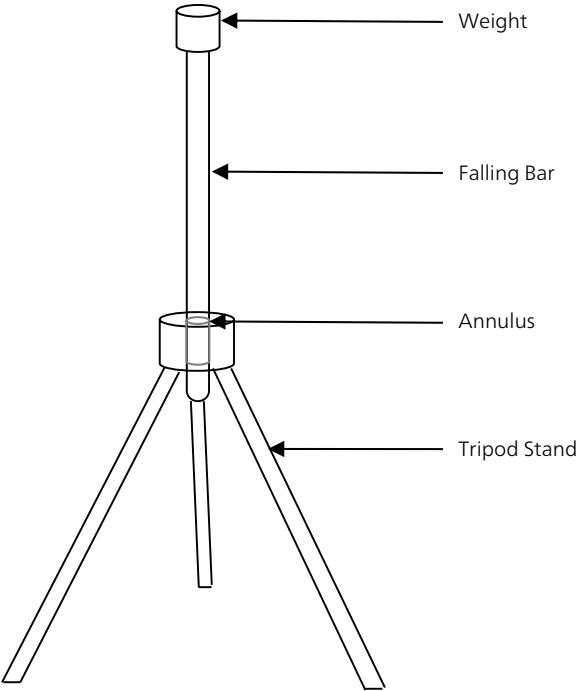
Paints, Coatings and Inks

An Alternative Test to the Falling Bar Viscometer Test ASTM D4040 – 10(2019)

Introduction

In the failing bar viscometer, the sample is pasted around a vertical cylindrical bar. A predefined weight (usually one of three sizes) is placed on the top of the bar, and the bar is timed while it falls through an annulus.

| Test Conditions | |
|--|--|
| Samples | Lithographic inks |
| Geometry | Cone and plate system 1°/20 mm |
| Temperature | 20°C |
| Gap | 30 microns |
| Pre-shear | Shear rate: 200 s ⁻¹ Shear time: 5 seconds Equilibrium time: 10 seconds |
| Table of shear rates (Toolkit_001 Frequency Table of Shear Rates) | 10 - 200 s ⁻¹ Up Linear |



The time of falling (s) can be plotted against the weight applied (g) and this can be loosely equated to show the shear stress against shear rate. A graph of 3-4 points of shear stress is then extrapolated to zero shear rate (as shown below in green). The intercept indicates a yield stress value (YV) and the gradient a plastic viscosity (PV). The results can be variable depending on the amount of sample applied to the bar, the shearing history from applying the sample to the bar, the temperature and accuracy of the timing.

Using the NETZSCH rheometer, we can run a pre-shear to simulate application of the sample onto the bar and then a flow curve to show the behavior with the different weights attached. A model can then be fitted to the results curve of 100 points or more, as shown in Figure 23.

Interpretation

The shear rates applied on the rheometer simulate a series of weights applied to the rod, each giving a different shear stress. The experiment may be carried out in controlled stress, however, empirically it has been seen that the controlled shear rate method gives better correlation with the falling bar method.

The completed flow curve from the rheometer is then fitted with a Bingham or Casson model to give the Yield stress and Plastic viscosity values from the formula:

The Bingham Model

$$\sigma = \sigma_0 + \eta\dot{\gamma}$$

The Casson Model

$$\sigma^2 = \sigma_0^2 + (\eta\dot{\gamma})^2$$

Where:

σ = Shear stress

σ_0 = Yield Stress (YV)

η = Plastic Viscosity (PV)

$\dot{\gamma}$ = Shear Rate

Conclusion

Falling bar measurements often vary between operators, depending on how the sample is mixed and taken with the spatula, the amount of sample placed on the bar and the time taken before starting the test (if the material is thixotropic). This subjectivity can lead to anomalous and misleading results, and gives a poor basis for formulating inks, whereas the correct use of a rheometer gives accurate and reproducible results with a minimum of mess and considerable time saving. The rheometer test gives better temperature control more precise sample loading and absolute viscosity results. The rheological data may also be saved for quality control and reference purposes.

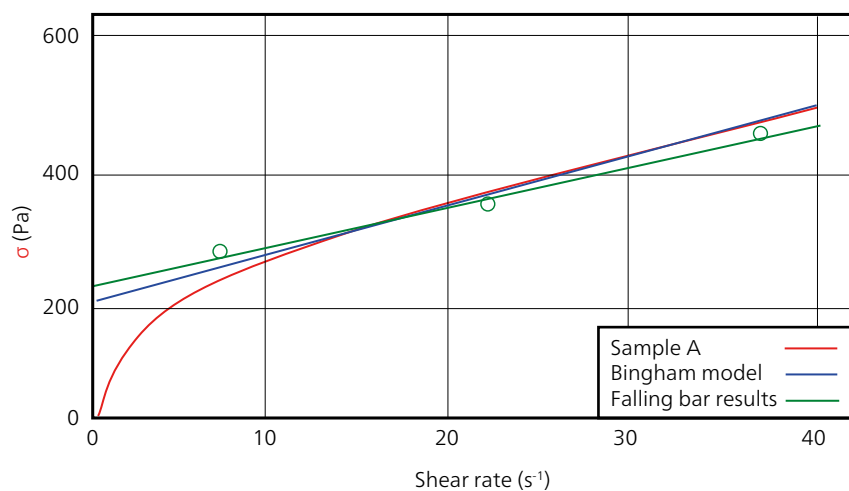


Figure 23. Shear stress vs. shear rate. The three different weights used in the falling bar test equate to three different stresses.

Paints, Coatings and Inks

Characterizing Ferro-Magnetic Inks – Low Shear Viscosity

Introduction

Ferro magnetic inks are used extensively in the printing of 'best before' dates on beverage tins, numbers at the bottom of bank checks and strips on car park tickets. The number printed is then readable with an electromagnetic reader. The low shear viscosity of an ink is critical to giving good print sharpness and a sufficiently thick film (where magnetic strips are printed). The differences in the low shear viscosity are due to differences in the microstructure of the inks, which may be caused by variations in the raw material properties, or non-reproducible production of the ink dispersion.

Interpretation

In the measuring range of a simple viscometer, at medium to high shear rates, the viscosity of both samples is asymptotic (see Figure 24). However, below 0.1 s^{-1} the viscosity values deviate considerably from each other. As sample A has the higher viscosity, it is likely to give a thicker printed layer and may show sharper print edges than sample B.

| Test Conditions | |
|--|--|
| Samples | Ferro-magnetic inks |
| Geometry | Cone and plate system $4^\circ / 20\text{ mm}$ |
| Temperature | 20°C |
| Gap | 150 microns |
| (Measure_0005 – Table of shear stresses) | 5 - 200 Pa Up Log |

Conclusion

The NETZSCH rheometer can be used to quickly identify differences in the printing quality and ink thickness of ferro-magnetic inks. Formulations can therefore be developed and optimized without the need for extensive printing trials.

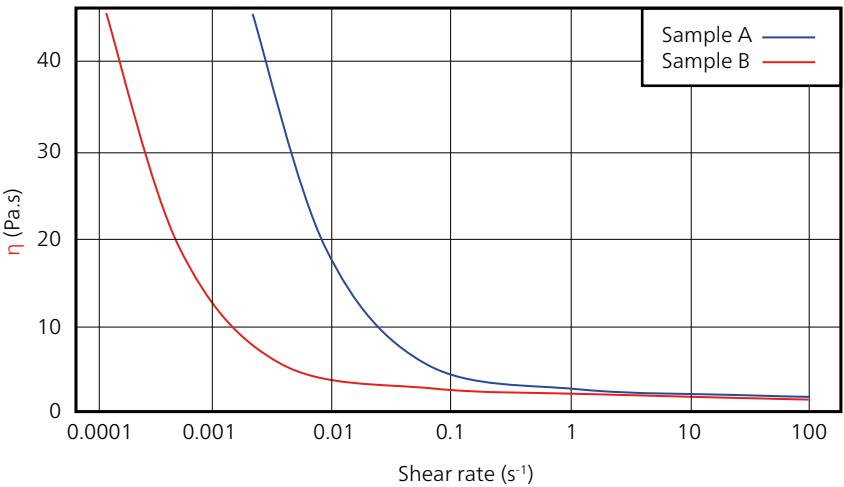


Figure 24. Viscosity vs. shear rate. The shear thinning part of the flow curve shows whether the sample thins easily (sample B) or less easily (sample A) upon shearing. Sample A is likely to give a higher definition print than sample B.

Assessing the Dispersion of Ink Pigments

Introduction

In this experiment, the sample is oscillated with an increasing stress known as an amplitude sweep and the storage and loss moduli are plotted against the shear stress. The moduli initially are independent of stress, giving a plateau known as the linear viscoelastic region (LVR). The length of the linear viscoelastic region shows how far the material can be deformed before the onset of structure breakdown.

Interpretation

Figure 25 shows sample A possessed a shorter linear viscoelastic region (LVR) than sample B and will therefore break down more easily with vibrations and small movements. A long LVR indicates that the sample is more stable to oscillation stresses, and therefore strong associations have been formed between the particles. **For any single formulation, this therefore gives an indication of how well dispersed the pigment is.** From the results above, it can be seen that sample A is not as well dispersed as sample B.

Test Conditions

| | |
|--|---|
| Geometry | Cone and plate system 4° / 40 mm with solvent trap system |
| Temperature | 20°C |
| (Oscillation_0001 – Amplitude sweep shear stress controlled with LVER determination) | 0.1 - 100 Pa Up Logarithmic |

Conclusion

A relatively quick amplitude sweep experiment can indicate the degree of dispersion of an ink, and be used to optimize the dispersant dose and method. Unstable formulations can also be eliminated without the need for storage testing.

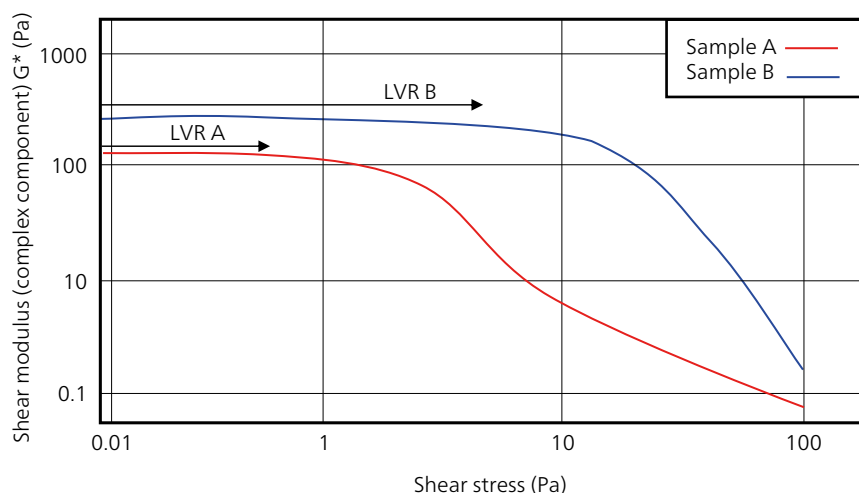


Figure 25. Shear modulus (complex component) vs. shear stress. The length of the linear viscoelastic region (LVR) indicates how well dispersed the sample is.

Polymers





Polymers

Cure Analysis of Composites

Introduction

Rheology is used in the composites industry to monitor cross linking during curing. The sample's flow behavior during the cure reaction dictates an essential part of the processing parameters for manufacturing composite materials. For example, composite parts are often assembled out of 'pre-preg', which consists of some substrate material such as graphite, metal, ceramic or glass fiber coated with a reaction pre-polymer such as an epoxy.

The pre-preg material is typically 'laid up' by softening and forming the material around a form or mandrel. The material is then cured in an autoclave by subjecting the sample to a programmed temperature and pressure cycle. Key elements in the process are the temperature ramp rate and the time required to apply the pressure. If the ramp is too fast, the epoxy will become fluid too quickly and run off the substrate. If the application of pressure is not coincident with the softening point of the resin, then compaction between the layers does not occur and the part may have voids and consequently, poor mechanical strength. Once the material is cured, it cannot be reprocessed. Consequently, a lack of understanding of the particular cure characteristics of a batch of pre-preg can be costly.

| Test Conditions | |
|------------------------------|---|
| Samples | Epoxy 'pre-preg' laminates (1.5 mm disks stacked) |
| Geometry | Disposable PP 15 mm and Kinexus High-Temperature Cell HTC |
| Single frequency oscillation | Toolkit_0004 Single Frequency Temperature Ramp(Strain control)) <ul style="list-style-type: none">Strain: 0.001Frequency: 1 HzTemperature: -40 - 200°C at 1.5 K/min |

A NETZSCH rheometer can heat the pre-preg whilst applying a constant strain oscillation and so measure the viscosity throughout the cure cycle. This enables the manufacturer to select the ideal temperature ramp rate and pressure time to give optimum results.

With a Kinexus, the rheometer can also control the normal force (downward pressure) applied to the sample. With this facility, laminates with a very high thermal expansion can be tested and the rheometer will adjust the gap to retain constant pressure conditions. This prevents the polymer from being squeezed out of the substrate.

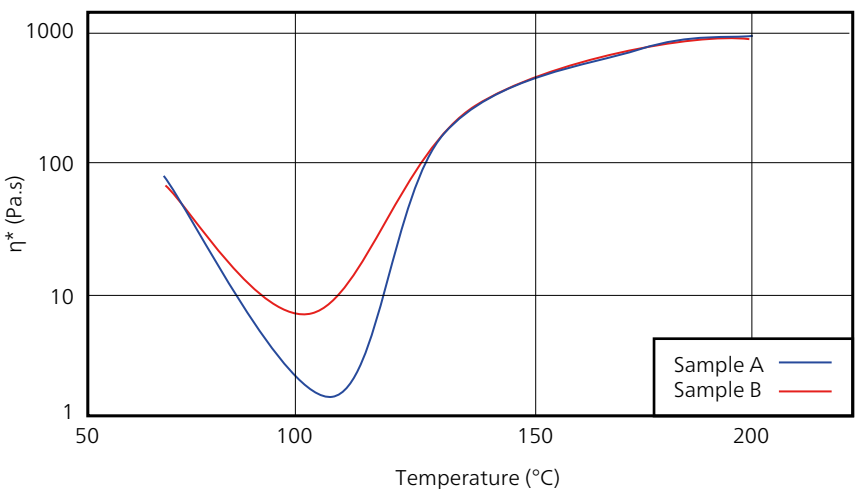


Figure 26. Shear viscosity (complex component) vs. temperature. The minima in the heating ramp test shows how well the prepreg layers will adhere together and also whether they will slip out of place before curing.



Interpretation

The results in Figure 26 show two variations of pre-preg tested using disposable plates or regular plates coated with a release agent. The minimum viscosity of curve A is much lower than curve B. This could result in resin run-off and a bad part made from resin A. The process could be modified by using a slower ramp rate so that as the resin softens, it reacts sufficiently to inhibit runoff. Note that the time to cure as indicated by the plateau in the complex viscosity is similar for both samples A and B.

Definition Crosslinking and Curing

Crosslinking is the general term for the process of forming relatively short sequences of chemical bonds to join two polymer chains together. The term curing refers to the crosslinking of thermosetting resins, such as unsaturated polyester and epoxy resin. Crosslinking boosts the thermal stability and mechanical properties of the polymer.

Conclusion

Using the standard conditions, sample A may become too low in viscosity before curing and so potentially form a defective part. The rheological data can be used to optimize the process to produce strong parts.



Polymers

Using the High-Temperature Cell to Measure the Melting Point or Peltier Cylinder with Torsional Fixtures to Measure the Glass Transition of Solid Samples

Melting Point Analysis

Introduction

Melting point analysis of polymers can be difficult to carry out with standard melting point apparatus, because polymers soften over a wide temperature range, rather than at a specific point as with a highly crystalline compound. The results are often subjective to an individual's judgement and can therefore be inaccurate. Oscillation data shows how the polymer softens over an extended temperature range. The modulus or complex viscosity can be used to determine actual extrusion or compounding conditions at all of the relevant temperatures. The mean melting point can be quoted as where the viscosity curve is steepest.

Interpretation

Figure 27 indicates that the sample softened dramatically between 97°C - 103°C. The point of inflection of viscosity could be quoted as the precise melting point at 101°C. This is a very accurate measure of melting point and also shows the effect of small temperature changes on the modulus of the polymer around the melting point. The crystallinity of a polymer may be assessed from a hysteresis loop between the melting point measured during heating and the freezing point during cooling. Temperature should be ramped sufficiently slowly for the sample to be near thermal equilibrium throughout the test.

| Test Conditions | |
|---|--|
| Samples | Solid polymers and compounds (data is for LD Polyethylene) |
| Geometry | Parallel plate 20 mm and HTC |
| Single Frequency Oscillation Toolkit_O004 Single Frequency Temperature Ramp(Strain control) | Strain: 0.1 Frequency: 1 Hz Temperature: 90 - 350°C |

Conclusion

The rheological behaviour of a polymer melt can be characterized using NETZSCH rheometers over a wide temperature range.



Melting Point Determination

The melting point of a substance is the temperature at which it changes from solid (crystalline) to liquid (isotropic melt). Melting effects can easily be determined as endothermal processes with a high degree of both reliability and accuracy by means of differential scanning calorimetry (DSC, e.g., NETZSCH DSC 214 Polyma).

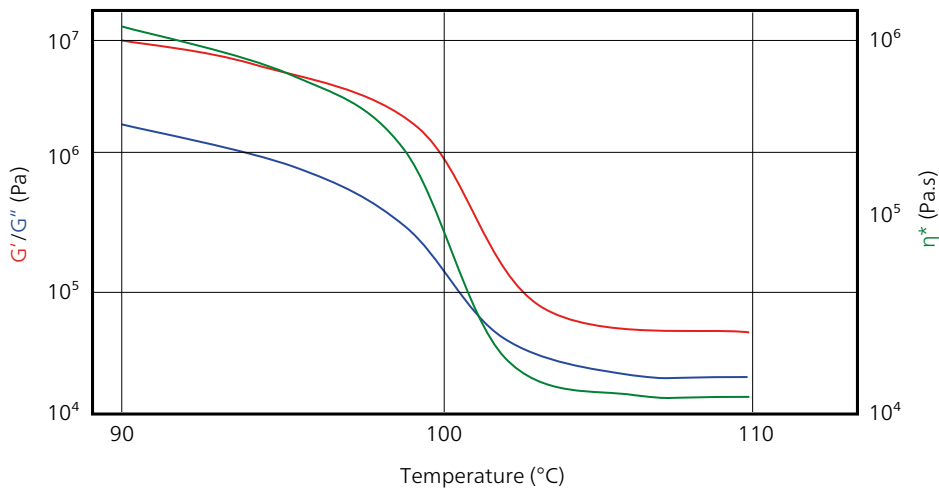


Figure 27. Elastic (red), viscous (blue) moduli and shear viscosity (complex component, green) vs. temperature from an oscillation temperature ramp test

Glass Transition Temperature Analysis

Introduction

On cooling, polymers stiffen until the modulus reaches a plateau of $\approx 2 \text{ GPa}$ ($2 \times 10^9 \text{ Pa}$) known as the glassy region. At this temperature and below, the polymer is very brittle and cannot be worked without fracturing, and hence the glass transition temperature (T_g) is critical for some plastics users. T_g analysis of polymers can be carried out by several methods, such as classical dynamic mechanical analysis (DMA) or differential scanning calorimetry (DSC). By using the solids strip fixtures with the Peltier cylinder, the modulus of many materials can be measured, such as steel, inorganic glasses or glassy polymers, at temperatures down to -30°C with a chiller attached to the Peltier cylinder.

Interpretation

The oscillation results in Figure 28 show how the T_g is evident from the peak of the $\tan \delta$ curve at -18°C . This mechanically assessed T_g is likely to be around 10°C higher than that measured by differential scanning calorimetry (DSC) measurement, because T_g is frequency dependent. Good

| Test Conditions | |
|------------------------------|--|
| Samples | Solid polymers and polymer compounds (example is for LD Polyethylene) |
| Geometry | Solid strips fixtures and Peltier cylinder |
| Single Frequency Oscillation | Strain: 0.0001 Frequency: 1 Hz Temperature: -20 to -30°C |

correlation can be obtained between DSC and DMA if a low frequency oscillation is used, for example 10^{-3} Hz . Determination of T_g by dynamic mechanical methods has a number of advantages over calorimetry since a direct determination of engineering (elastic) mechanical properties are made simultaneously. Molecular mobility can be assessed via the energy dissipating processes observed as peaks in G'' and $\tan \delta$.

Conclusion

The melting point and glass transition temperatures can be accurately measured for a wide range of polymers and composites using NETZSCH rheometers.

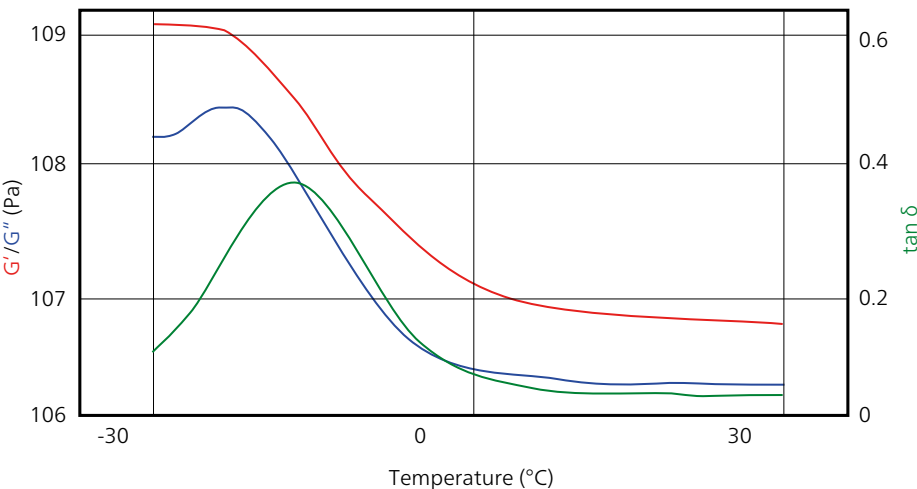


Figure 28. Elastic (red), Viscous (blue) moduli and $\tan \delta$ (green) vs. temperature from an oscillation temperature ramp test

Polymers

Mold Filling Characterization

Introduction

The flow characteristics of a compounded plastic are critical when being injection molded. If the viscosity at low shear rate is too high, the part may show poor mold filling characteristics and so fine details and acute corners could be omitted. Using the NETZSCH rheometer it is possible to accurately quantify the flow characteristics in the relevant shear region and so simulate molding.

Interpretation

The pre-shear in this test simulates the high shear rate extrusion, and the flow curve simulates the mold filling into the fine detail areas of the mold. The lower the low shear viscosity, the better the compound fills the corners and details of the mold. Figure 29 shows that sample B may give better mold filling characteristics than sample A.

| Test Conditions | |
|----------------------------------|---|
| Samples | Polymer-melt compounds |
| Geometry | CP 2.5° / 40 |
| Pre-conditioning | 100 s ⁻¹ for 10 seconds, 1 second equilibrium |
| Toolkit_V001 Shear rate table | Shear rates: 0.12 - 10 s ⁻¹ / (down) Temperature: 160°C (or normal molding temperature) |

Conclusion

The NETZSCH Kinexus rheometer can be used to accurately quantify mold-filling characteristics of polymers and polymer compound melts.

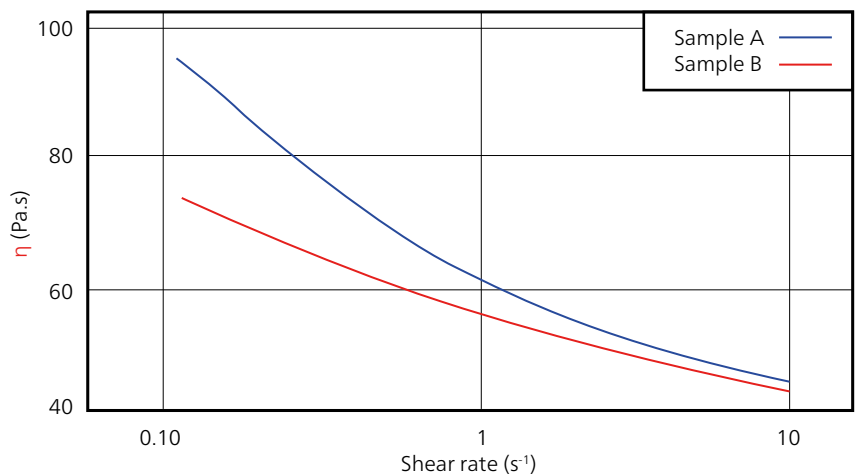


Figure 29. Shear viscosity vs. shear rate

Determining Extrusion Performance

Introduction

When a plastic is extruded to give a certain section, it can sometimes exhibit die swell or melt fracture resulting in a poorly dimensioned part or an unattractive rough surface. This oscillatory test simulates the lower end of the high shear rates seen in extrusion. The lower the complex viscosity, the more easily the polymer will be extruded, the smoother the surface and if the extrudate is under tension, the section will be thinner.

Interpretation

The results in Figure 30 show that sample A has a lower viscosity than sample B and so will extrude more easily and probably with a smoother surface.

If the rheological data of a product can be correlated with its performance in an extruder, any unacceptable formulations can be eliminated without the need for extrusion trials. This dramatically cuts down on wasted time and product. The effect of temperature on the viscosity during the extrusion process can be studied by running this test with a table of temperatures. This allows us to determine the acceptable temperature limits for the process.

| Test Conditions | |
|--|---|
| Samples | Polymer melt compounds |
| Geometry | CP 2.5° / 40 |
| Frequency sweep Toolkit_O002 Frequency Table (Strain control) | Frequency range: 1 - 50 Hz / up/log Temperature: 160°C (or normal extrusion temperature) Strain: 0.05 |

Conclusion

The NETZSCH Kinexus rheometer can be used in conjunction with the lab and pilot scale extruders to formulate high-quality polymer melt compounds. Another NETZSCH product, the Rosand capillary rheometer is ideal for actually simulating the extrusion of polymers to measure die swell and surface roughness of the extrudate under different temperatures and shears.

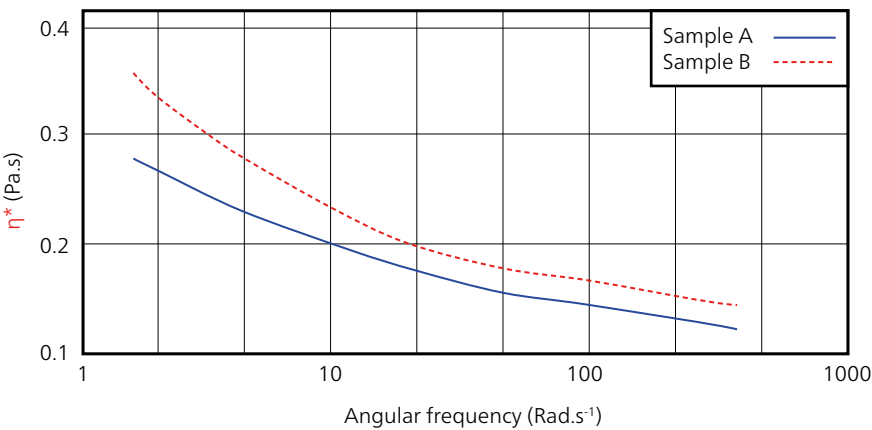


Figure 30. Shear viscosity (complex component) vs. angular frequency for the two polymer melt samples

Polymers

Determining and Measuring Thixotropy in Sealants

Determination of Thixotropy

Introduction

Thixotropy is 'time dependent shear thinning behavior', i.e., when sheared, the sample decreases in viscosity and upon cessation of shear, the viscosity **slowly** rebuilds to return to its original value. If the viscosity reduces and **immediately** returns after shearing, the material is said to be 'shear thinning' (or 'pseudoplastic'). This 'hysteresis loop test' is a simple method for determining whether a sample is thixotropic, see page 11).

Interpretation

Figure 31 indicates that Sample A exhibits a high degree of thixotropy, so on acceleration the sample initially gave a high stress, but as the sample's structure was broken down, the response was not linear. On the down ramp, the sample showed a lower stress than it did at the same shear rate on the UP curve. This indicates that its structure had not recovered from the shearing at 100 s⁻¹ and so it must be thixotropic. Sample B appears to be less thixotropic, as the UP and DOWN curves do not encompass such a large area.

| Test Conditions | |
|---|--|
| Samples | Sealant materials |
| Geometry | Cone and plate system 4° / 20 mm |
| Temperature | 25°C or as desired |
| Measure_0027 – Shear rate ramp up and down linear | 1 - 100 s ⁻¹ up/down linear |

Conclusion

If the sealant is found to be thixotropic, this should be taken into account when carrying out subsequent tests. Sample application will need to be carried out in a reproducible way, or the samples should be pre-sheared so that they all have the same shear history. To quantify the thixotropy accurately, the following test can be carried out.



Thixotropy

This phenomenon can be observed in various gels which become fluid when disturbed (as by shaking). Certain substances, including some types of mayonnaise, are normally thick gels, but can be liquified by shaking or stirring and take a time to rebuild.

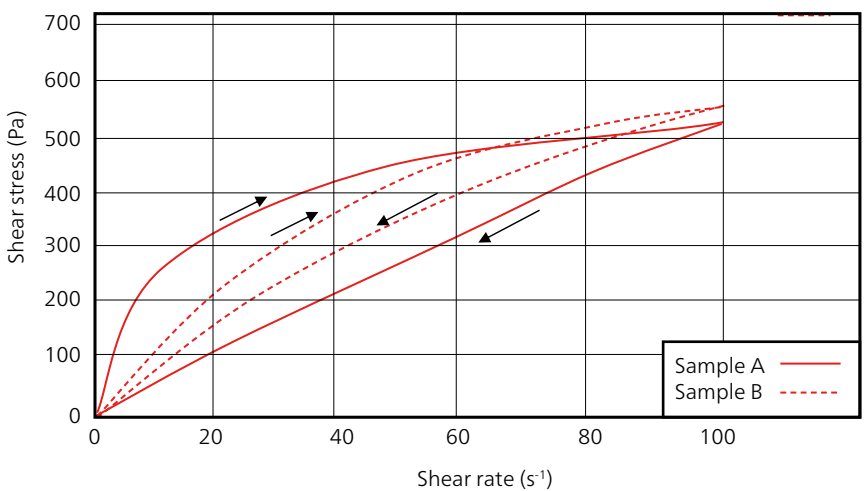


Figure 31. Shear stress vs. shear rate results from a thixotropic loop test

Quantifying Thixotropy

Introduction

In this test, the sample's structure is broken down by a pre-shear to simulate extrusion of the sealant from a gun or application of the sealant. The material is then subjected to small strain oscillation so that the structure can be monitored whilst the sample recovers. In an oscillation test, the elastic and viscous components of a sample can be identified separately, this allows determination of whether the material is elastically or viscously dominated at any time. Whilst the material is viscously dominated ($G'' > G'$), the sealant is likely to be able to flow and hence slump, however, when the elastic modulus becomes strongly dominant ($G' > G''$), sagging should stop. If the test is run for long enough, the moduli will reach a plateau where the sealant has fully recovered.

Interpretation

The results in Figure 32 show that after the pre-shear the material became a viscous liquid for ≈ 80 s. The full recovery of structure took ≈ 600 s and from the ratio of the initial modulus to the final modulus, we can see that the structure had broken down to $\approx 20\%$ of its full value after the pre-shear.

To check that the material has fully recovered after 600 s, we can compare the final modulus with the modulus of the

| Test Conditions | |
|--|---|
| Samples | Sealants |
| Geometry | Cone and plate system 4° / 20 mm |
| Temperature | 25°C or as desired |
| Pre-shear | Shear rate: 100 s ⁻¹ Shear time: 10 seconds Equilibrium time: 1 second |
| Oscillation_0005 | Strain: 0.005 |
| – Step shear strain | Frequencies: 1 Hz |
| – Shear strain profile with rebuild analysis | |

unsheared material. The crossover point of the elastic and viscous moduli indicates when the structure becomes predominantly elastic and hence the sealant will not flow. Formulations with an earlier crossover would therefore show reduced sagging.

Conclusion

The thixotropic nature of a sealant can be accurately quantified, so a suitable pre-shear and equilibrium time can be used in subsequent tests. This will then allow all samples to be assessed either after they have fully recovered, or at least with the same 'shear history', allowing comparable and reproducible results.

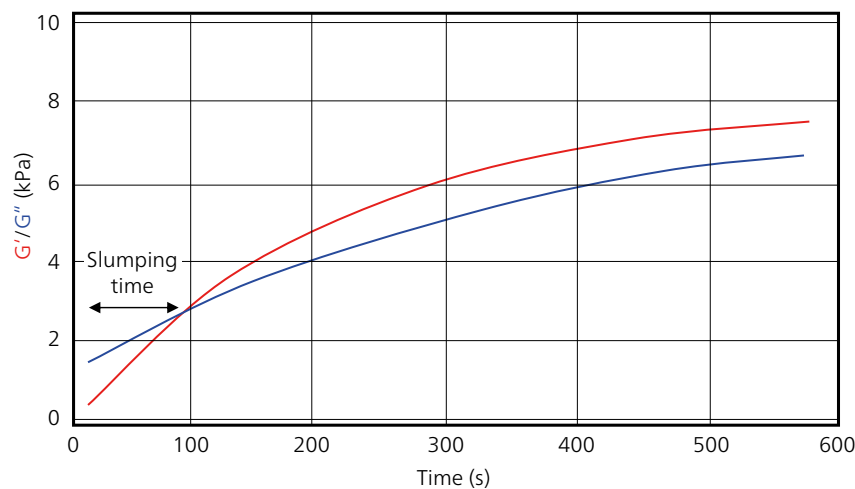


Figure 32. Elastic (red) and viscous (blue) moduli vs. time from an oscillation rebuild test

Polymers

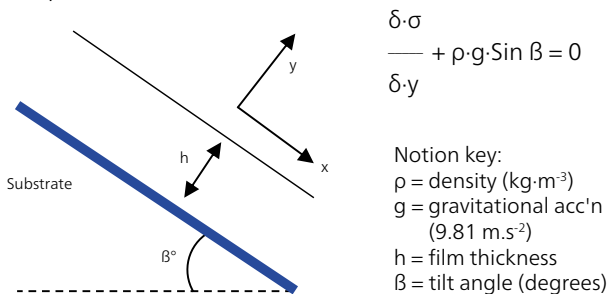
Simulation of the Slump Test (for Sealants) by Pre-Shear Creep

Introduction

In a creep test, the rheometer applies a constant stress and the strain is measured with time. The results are normally plotted as compliance (i.e., strain/stress) against time. In this test, the sample's structure is broken down by a pre-shear to simulate extrusion of the sealant from a gun or application of the sealant. A creep stress simulating gravity on a 1cm thick bead (for a sealant of density 1600 Kg.m⁻³) is then applied to the material, so that the slump can be monitored while the sample recovers. If the correct creep stress is applied to simulate the application, the compliance at any time will indicate the slump of the sample.

Slump Resistance

Since slumping flow does not involve acceleration, a balance exists between the gravitational forces and the stress in the sample.



| Test Conditions | |
|-------------------------------------|---|
| Samples | Sealants |
| Geometry | Cone and plate system 4° / 20 mm |
| Temperature | 15°C |
| Pre-shear | Shear rate: 100 s ⁻¹ Shear time: 10 seconds Equilibrium time: 1 second |
| Measure_0042 – Creep end by time | Stress: 160 Pa (depending on layer thickness required) Creep time: 300 seconds |

This gives the maximum shear stress σ_{\max} as: $\sigma_{\max} = \rho \cdot g \cdot h \cdot \sin \beta$ i.e., sagging will not occur for sealants with yield stresses greater than σ_{\max} .

Interpretation

The sample was seen to slump initially after the pre-shear, as shown by the rise in creep compliance (J_c) (see Figure 33). After 150 seconds the sample had recovered sufficiently to stop slumping.

Conclusion

The traditional channel slump test for sealants is time consuming, messy and the results can vary depending on how much the product is worked prior to the channel being filled. Rheological testing is accurate and reproducible, giving a precise value for the slump. This enables the formulator to optimize the quantity of thixotropes and fillers added.

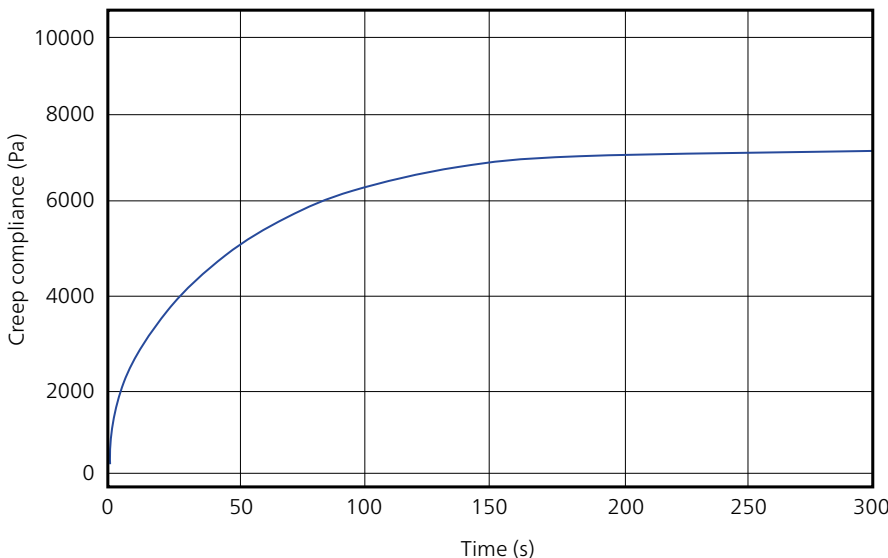


Figure 33. Creep compliance ($J(t)$) vs. time. The creep following a short period of shearing can show whether a material will continue to flow (and so slump) immediately after extrusion.

End Use Evaluation of Sealant Materials

Introduction

A sealant needs to have a high yield stress to prevent sagging, but also a lower high shear rate viscosity, so that it can be extruded easily and the bead will have a smooth surface. This test simulates extrusion shear rates on applying the sealant material. To obtain a reproducible extrusion size and characteristics, it is necessary to maintain a constant viscosity, by adjustment of the filler content. The low shear viscosity will also indicate the sag resistance of the sealant.

Interpretation

The results in Figure 34 indicate that both materials would be expected to produce a similar extrusion profile since the viscosity at high shear rates is the same. Sample A will resist sagging much more than sample B because the viscosity at low shear rates is higher. The rheology of a freshly made batch of sealant often changes over the first few days, as the filler components absorb more of the liquids in the mixture. It may also therefore be necessary to quantify the change over a week, so that immediate viscometry results can be related more accurately to the end use.

N.B. It is important to check for thixotropy (as described above) in sealant materials, as the shear history can strangely influence the data.

| Test Conditions | |
|----------------------------------|--|
| Samples | Sealants |
| Geometry | Cone 2° / 20 mm |
| Toolkit_V001 shear rate table | Shear rates: 0.1 - 100 s ⁻¹ up/log Delay time: 15 seconds proportional to strain Temperature: 20°C (for normal working temperature) |

Conclusion

Rheological evaluation is a valuable aid to good sealant formulation and can be used to predict the end-use characteristics of products without extensive sag and extrusion testing.

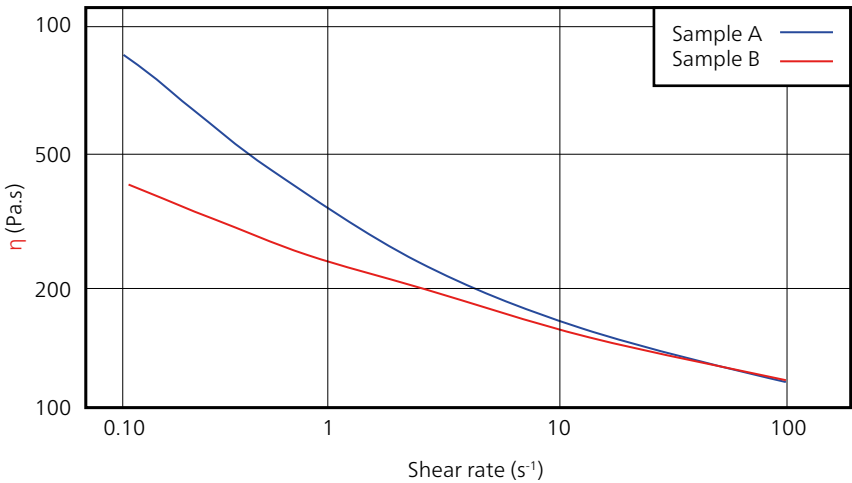


Figure 34. Viscosity vs. shear rate. Flow curve results for two sealants showing their pumpability (from the high shear viscosity) and their resistance to flowing from the low shear viscosity.

Polymers

Determination of Molecular Weight Distribution, Molecular Weight Average and Long Chain Branching

Introduction

Differences in the large-scale architecture of a polymer, such as mean molecular weight (MW), MW distribution, and long-chain branching (LCB) can be determined at low stresses by creep testing. Figure 35 shows that initially the elastic character (J) of the polymer melt dominates the response. At long times, no further elastic deformation occurs and viscous response (η) is dominant. Creep measurements offer the advantage that the elastic and viscous responses are easily distinguished as they are separated in time. Zero shear viscosity (η_0) can be measured from running a series of successively lower stress creep tests as described on Page 64.

Zero Shear Viscosity & Creep Testing

Figure 36 (below) shows how the viscosity changes with shear rate as a function of molecular weight for polystyrene melts. As molecular weight increases, the plateau in viscosity at low stresses, called the 'zero shear viscosity' (η_0) occurs at successively lower rates. Observing differences in the zero shear viscosity allows differentiation between samples with different molecular weight. If possible, viscometry is used to find the zero shear viscosity plateau, as described below, however, where the shear rates involved are too low to give good viscometric data, creep testing is used as described on Page 64.

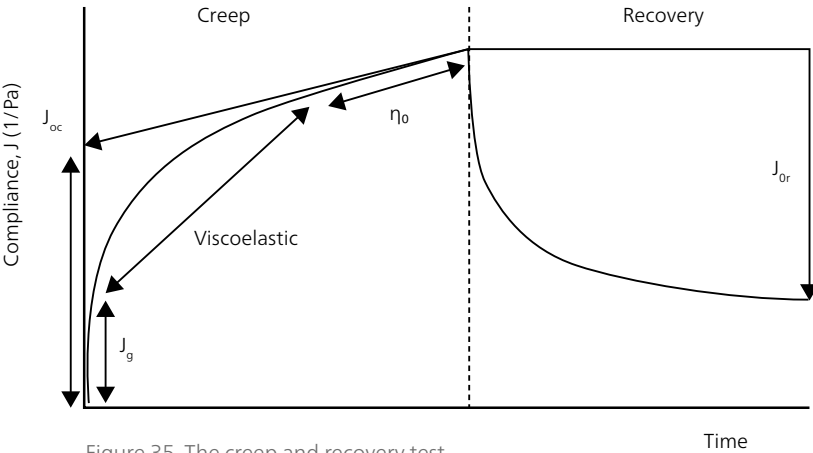


Figure 35. The creep and recovery test

Kuhn-Mark-Houwink-Sakurada Equation:

$$\eta_0 = K \times (MW)^a$$

where a is around 3.4 for polymer melts

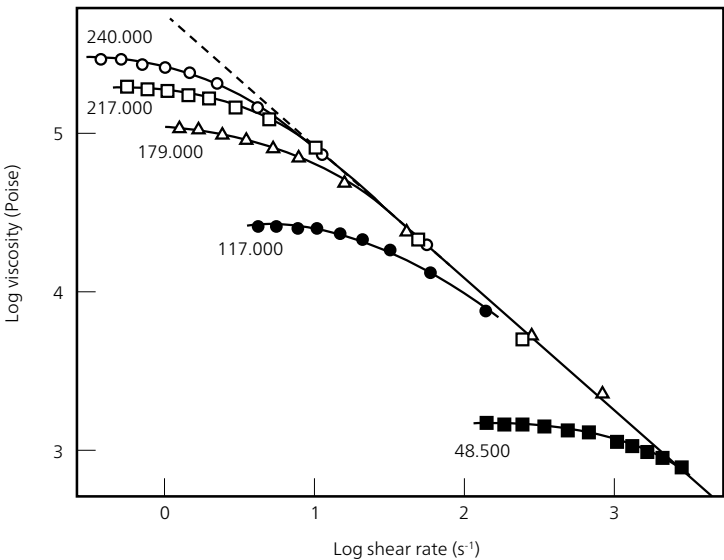


Figure 36. Viscosity of different MW polystyrenes against shear rate

Note: Measuring Zero Shear Viscosity by Viscometry

For high molecular weight polymers, zero shear viscosity is best measured by creep testing since the shear rates necessary to determine the Newtonian plateau viscosity may be too low for reliable viscosity data to be measured.

Interpretation

We can interpret the results in Figure 37 to say that sample A has a higher molecular weight than sample B as it has the highest zero shear viscosity. This relationship is linear below a critical value of MW and is determined by the polymer structure. Above the critical MW of the polymer, the viscosity increases by the molecular weight to the power of ≈ 3.4 and so measurement of the zero shear viscosity is a sensitive means of ranking samples according to their molecular weight.

A calibration curve of zero-shear viscosity and molecular weight could in principle be constructed by reference to the data obtained by gel permeation chromatography. Measurement of melt viscosity has significant advantages compared with GPC as sample preparation is simple and rheological properties of high molecular weight materials are

| Test Conditions | |
|---------------------------------------|---|
| Samples | Polymer melts materials |
| Geometry | Disposable PP25 with High Temperature Cell |
| Measure_005 – table of shear stresses | Shear stress: 1 - 50 Pa, down/log, but plot results as Viscosity vs. Shear Rate Gap: 1 mm Temperature: melt point +20°C (as a starting point) |

easily discriminated, whereas GPC has considerable difficulty in differentiating elution values of these types of materials.

Visco-elastic data derived from oscillatory tests can also be used to determine molecular properties of polymers qualitatively by examination of cross-over moduli and frequency when $G'=G''$ or by advanced analysis routines that relate polymer visco-elastic responses to molecular mobility.

Conclusion

Rheological evaluation of polymer melts can be used to elucidate much information about the molecular weight and structure of the material. Samples are easily prepared and analysis is relatively fast.

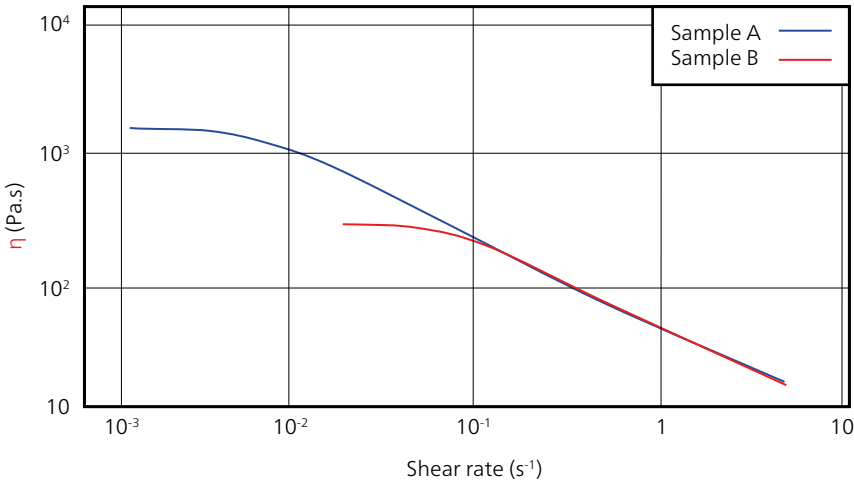


Figure 37. Shear viscosity vs. shear rate for two polymer melt samples

Polymers

Creep Testing to Find Zero Shear Viscosity

Interpretation

At successively lower stresses, if a material has a zero shear viscosity plateau, creep compliance curves will start to overlay, as shown at 8 and 10 Pa in Figure 38. When this occurs and the test is run until the sample is at steady state, the viscosity value given in the creep results box (in the NETZSCH software) is the zero shear viscosity. It may be necessary to renew the polymer sample if it starts to degrade during testing, however, the sample life may be extended by purging with nitrogen gas around the measuring system.

Please note:

If the zero shear plateau is inaccessible even with creep testing, as with very high molecular weight polymers, the temperature can be increased by 10°C and the experiment repeated. The degradation rate of the polymer is likely to increase dramatically with increased temperature, and hence lower temperatures are tried first.

For many commercial polymer-melts, it is generally accepted that the elasticity measured during creep, J_{eo} , is related to

| Test Conditions | |
|--|---|
| Samples | Polymer melt materials |
| Creep_0004 – Multiple creep end by time with increasing stress | At appropriate stresses (from the LVER) to give steady state flow |
| Gap | 1 mm |
| Creep time | ≈600 seconds |
| Temperature | Temperature melt point +20°C (as a starting point) |

molecular weight distribution, independent of molecular weight. In contrast, it is also generally accepted that the zero shear viscosity is only a function of weight-average molecular weight (for unfilled polymers). J_{eo} and η_0 are material functions and can be used to characterize the sample structure. For many commercial polymers, creep measurements are the only way to define the zero shear response of the material. Multiple creep tests can be sequenced allowing the whole test series to be run over night without intervention.

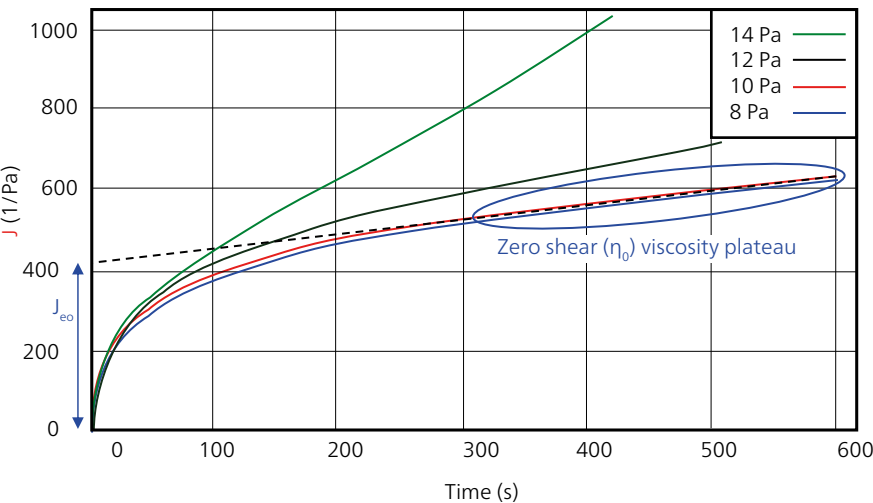


Figure 38. Creep compliance vs. time. Repeating creep tests with lower and lower stresses, we can determine the viscosity in the linear visco-elastic region.

Determination of Long Chain Branching

Long-chain branched polymers often resemble materials with a very broad molecular weight distribution. One way to differentiate branching from a wide molecular weight distribution is to measure activation energy at the zero shear viscosity. The activation energy is a factor describing how the polymer's zero shear viscosity changes with temperature. Over moderate ranges in temperature, viscosity follows an Arrhenius-type relationship of the form:

$$\eta_0 = \eta_\infty \exp (H_{\text{act}}/RT)$$

This activation energy (H_{act}) can be determined easily by plotting the $\ln(\eta_0)$, versus T^{-1} (see Figure 39). The gradient will

be H_{act}/R (where R is the gas constant of $8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$). The more LCB present, the less the zero shear viscosity is affected by temperature. Therefore, polymer melts of equivalent molecular weight exhibit a larger activation energy if significant LCB is present, in contrast to samples with only differences in molecular weight distribution, which would give similar activation energy.

Conclusion

Rheological evaluation of polymer melts can be used to elucidate much information about the molecular weight and structure of the material. Samples are easily prepared and analysis is relatively fast.

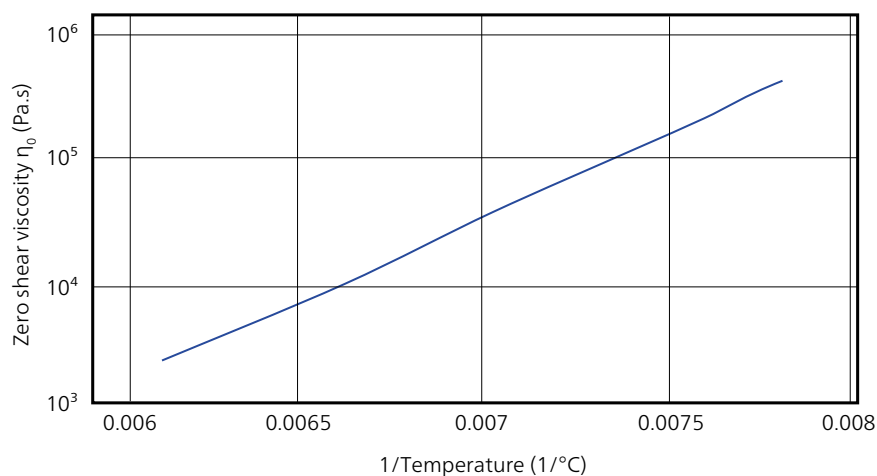


Figure 39. Zero shear viscosity vs. reciprocal temperature gives the gradient as H_{act}/R

Polymers

Impact Resistance of Polymer-Blended Compounds

Introduction

Impact resistance is related to a compound's ability to absorb energy, and this has been correlated with the quantity of mobile components present. $\tan \delta$ gives an indication of the damping characteristics of a polymer at any particular temperature. The area of the $\tan \delta$ peak below ambient temperature indicates the degree of mobility of the polymer and therefore its impact resistance. By running a temperature sweep from 30°C below the $\tan \delta$ peak to around 30°C above the $\tan \delta$ peak, and plotting $\tan \delta$ against temperature, the impact strength of the sample can be estimated from the area under the curve. This empirical relationship is useful for comparing different compound mixtures prepared from the same polymer.

Interpretation

Figure 40 shows the area of $\tan \delta$ below 30°C was greater for sample B than for sample A, indicating it would be able to absorb energy more easily and therefore have a higher impact resistance. Sample B also showed a slightly higher loss modulus (G'') and lower storage modulus (G') than sample A, meaning it would be slightly less rigid.

| Test Conditions | |
|-------------------------------|--|
| Samples | Solid polymers and polymer compounds |
| Geometry | Solid strips fixtures and Cylinder Peltier |
| Single Frequency Oscillations | Toolkit_0004 Single Frequency Temperature Ramp(Strain control) <ul style="list-style-type: none">■ Strain: 0.001■ Frequency: 1 Hz■ Temperature range: from 30°C below to 30°C above the T_g of the sample |

Conclusion

The NETZSCH rheometer can be used to evaluate formulations of polymer compounds to screen out brittle products prior to manufacture. It may also be possible correlate this method with others, such as a falling weight impact tester.

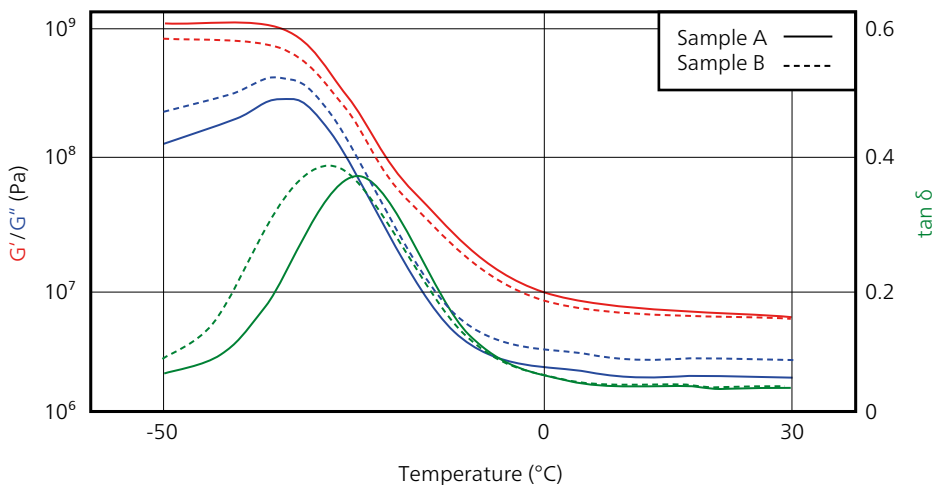


Figure 40. Elastic (red), viscous (blue) moduli and $\tan \delta$ (green) vs. temperature. The peak in $\tan \delta$ (along with a large drop in modulus from $2 \cdot 10^9$ Pa) shows the glass transition temperature.



Food





Overcoming 'Slippage' When Characterizing Concentrated Suspensions

Introduction

A common problem when measuring concentrated suspensions, such as tomato ketchup, as shown here, is that instead of shearing in the normal laminar way, the sample starts to slip. Slip can occur at both the upper and lower surfaces, as shown in Figure 41.

The slip is either due to the material undergoing a local stress induced phase change, e.g., ice melting at the surface, the liquid phase separating from the bulk of the sample to form a slip plane, or by boundary concentration depletion of particles near the surface of the plates¹. By using roughened or serrated measuring systems, we can reduce and often completely eliminate slip. The serrations allow the stress to be applied over a larger area of sample and provide voids to accommodate any separating liquids.

| Test Conditions | |
|--|--|
| Samples | Tomato ketchup |
| Geometry | Smooth PP40 and serrated PP 40 systems |
| Measure_0005 Table of shear stresses log. rseq Table of Shear Stresses | Shear stresses: 10 -150 Pa / up/log (plot viscosity vs. stress) Gap: 1 mm |

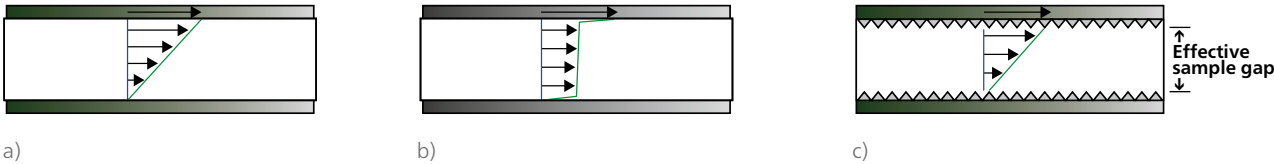


Figure 41. Illustration of a) Normal laminar flow, b) Slip that can occur with smooth geometries and c) Elimination of slip with serrated plates

¹Barnes Howard A.m A handbook of elementary rheology (2000) p. 134

Interpretation

The flow properties of the sample are first measured using a regular parallel plate measuring system. The resulting curve (see Figure 42) shows a 'double knee' (two individual drops in the red viscosity curve), indicative of sample slippage. This is because the ketchup undergoes some separation under shear and the water comes out from the solid fibers, and the plate surface slips on the layer of water. Re-running the sample with serrated plates, allows the water to be accommodated in the grooves without allowing the sample to slip. The viscosity curve no longer contains the double knee and a more conventional shear thinning profile is produced. The

effective surface is now the peaks of the serrations for gap setting purposes. If only the upper plate is serrated, then the slippage can easily continue at the lower plate instead, therefore both serrated upper and lower plates should be used.

Conclusion

Slippage can occur in fibrous suspensions, concentrated particulate suspensions and materials susceptible to shear induced melting. When slip is suspected, a roughened or serrated measuring system should be used to test the sample. If the results from both the roughened and smooth plates were identical, no slippage would be occurring.



Serrated PP40



Measurement Tip

When slip is suspected, a roughened or serrated measuring system should be used to test the sample.

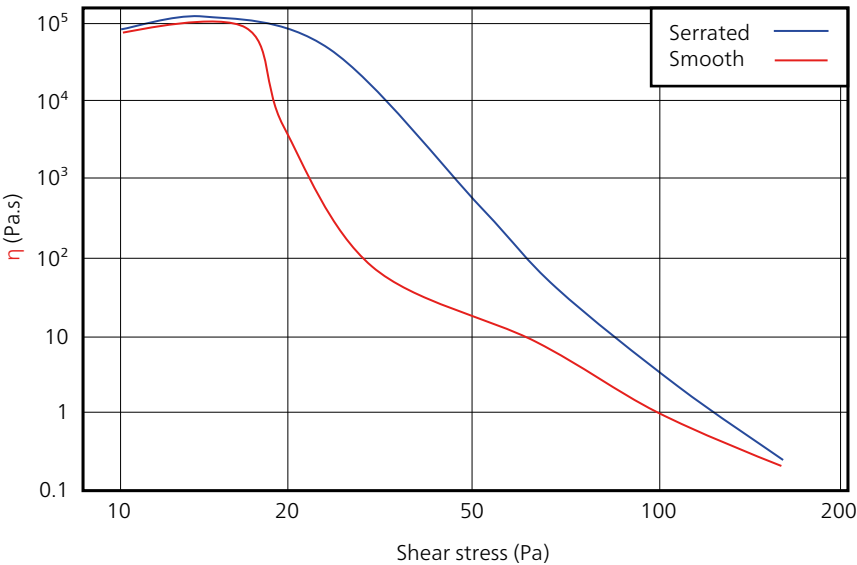


Figure 42. Shear viscosity vs. shears stress graph showing a sample that is slipping (red) and the same sample tested with serrated plates (blue).

Determining 'Stand-up' Characteristics of Caramel and Chocolate

Introduction

This test is to determine the low shear rate viscosity which is a measure of the caramel's or chocolate's stand-up properties. The higher the viscosity at low shear rate, the more firmly the material will retain any particular profile and resist slumping. In confectionery, this is useful to produce the shapes as seen in Walnut Whips™, or the profile on the top of a Mars™ bar. To obtain a reproducible extrusion size and shape, it is necessary for the chocolate to maintain a constant viscosity throughout the process. The viscosity of chocolate can be adjusted by using different emulsifier, dosing and tempering conditions.

Interpretation

From the example given in Figure 43, it can be seen that sample A's low shear viscosity is much higher than that of sample B and therefore, it is more likely to possess better stand-up characteristics. This test could also be used to reduce stand-up for samples such as margarines and other similar materials that can be problematic in container filling.

| Test Conditions | |
|-----------------------------------|---|
| Samples | Caramel and chocolate |
| Geometry | Cone and plate system 4° / 20 mm |
| Toolkit_V001 Table of Shear Rates | Shear rates: 0.1 - 100 s ⁻¹ / up/log Delay time: 15 seconds proportional strain Integration time: 5 seconds Temperature: 40°C (or normal working temperature) |

Conclusion

The NETZSCH Kinexus rheometer can be used to assess the 'stand-up' characteristics of foods very simply, making it an ideal tool to assist formulation without the need for extensive production trials.

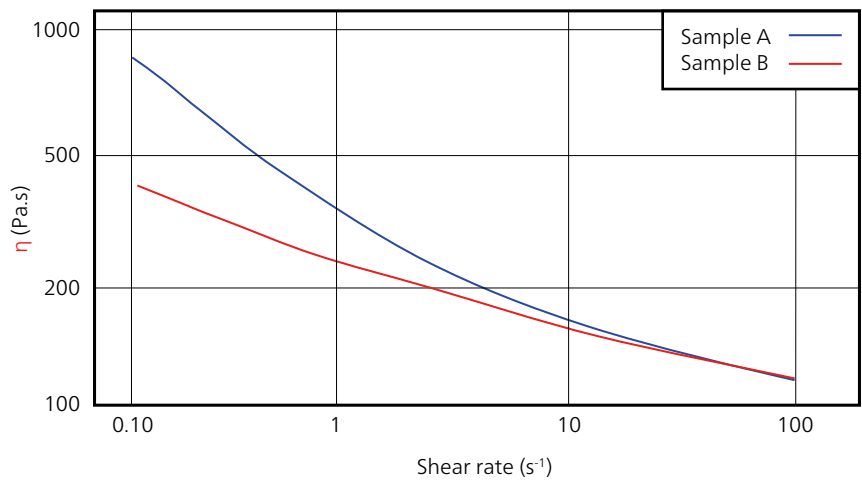


Figure 43. Shear viscosity vs. shear rate curve of two melted chocolate samples showing different viscosities at low shear rates

Characterizing Gelation Time and Strength

Quantifying Thixotropy

Introduction

The gelation time of foods containing a gel can be dramatically affected by other ingredients in the formulation. The gelant dosing can be adjusted to maintain the same gelling time despite formulation changes. Steady shear viscometry can be used to measure the structure building, however, the shearing action inherently retards the structure growth. Using a NETZSCH Kinexus rheometer, we can apply small oscillations to the sample and monitor the structure build-up without hindering the process. In this experiment, the sample is pre-sheared initially to give a common starting point for all samples. As no gelation has taken place at this stage, the results are not affected.

Interpretation

Carrageenan gelation is temperature induced, so the sample 'sets' when the temperature is cooled down. The temperature at which the gelation occurs will depend on the ionic and gelant concentrations of the mixture as well as the pH. In the results shown in Figure 44, the sample was initially a thin liquid and the viscous modulus was dominant over the elastic modulus. The crossover point of the elastic and viscous moduli indicates when the sample has reached a 'gel point', as shown below at around 90 s. Thereafter, the structure

| Test Conditions | |
|---|---|
| Samples | Carrageenan gels, xanthan gums or similar |
| Geometry | 60 mm parallel plate system, stainless steel/ titanium |
| Temperature | 80 to 20°C (temperature ramp down) at 3°C/minute, hold at 20°C |
| Pre-shear | Shear rate: 100 s ⁻¹ Shear time: 10 seconds Equilibrium time: 1 second |
| Measure_0029 – Single frequency controlled with temperature ramp | Strain: 0.005 Frequencies: 1 Hz Delay time: 1 second Wait time: 0 seconds |

becomes predominantly elastic and hence the sample will not flow. Formulations with an earlier crossover would therefore show less flow before gelation. If the test is run for long enough, the moduli will reach a plateau where it has fully reacted.

Conclusion

A NETZSCH Kinexus rheometer can be used to accurately quantify the gelation times of foods. The formulation can therefore be optimized with regard to gelant dosing in the minimum of time.

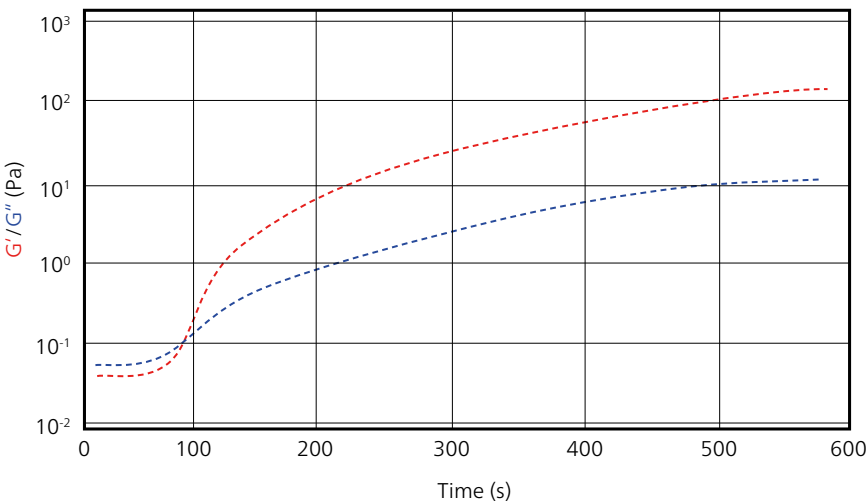


Figure 44. Elastic (red) and viscous (black) moduli versus time. The oscillation temperature cooling ramp results show precisely when the material starts to gel and at what emperature.



Determination of Butter 'Spreadability' and Fat Components

Introduction

The interest in the spreadability and manageability of dairy products has brought about much rheological investigation. Formulation can be greatly simplified by using rheology to show the effect of different fats and emulsifiers in a mixture, as well as the effect of changing the processing conditions. In this test, the spreadability of butter can be related to the complex viscosity at low temperatures.

Interpretation

The experiment in Figure 45 shows how the butter softened with increasing temperature, but more specifically, we can see the two fat components melting at different temperatures. The peaks in the $\tan \delta$ (tangent of the phase angle) curve indicate that components are melting at 17°C and 23°C. By addition of a component with a lower melting point or with a less temperature dependent viscosity, the butter will become more spreadable. The spreadability of the butter straight out of a refrigerator could be taken as inversely proportional to its viscosity at approx. 5°C.

| Test Conditions | |
|--|---|
| Samples | Spreadable dairy products |
| Geometry | 15 mm parallel plates (stainless) with fluids immersion cell |
| Temperature | 10 to 35°C at 2.5°C per minute |
| Measure_0029 –Single frequency strain with temperature ramp | Strain: 0.001 Frequency: 1 Hz Delay time: 2 seconds Wait time: 5 seconds |

In Figure 46 the NETZSCH immersion cell is used because it allows accurate temperature control for materials that have poor thermal conductivity, such as the amorphous solids tested here. In the immersion cell shown on the next page, the sample and both upper and lower measuring systems are immersed in the temperature controlling fluid. This gives unprecedented temperature control, with temperature gradients of <0.1°C through the sample.

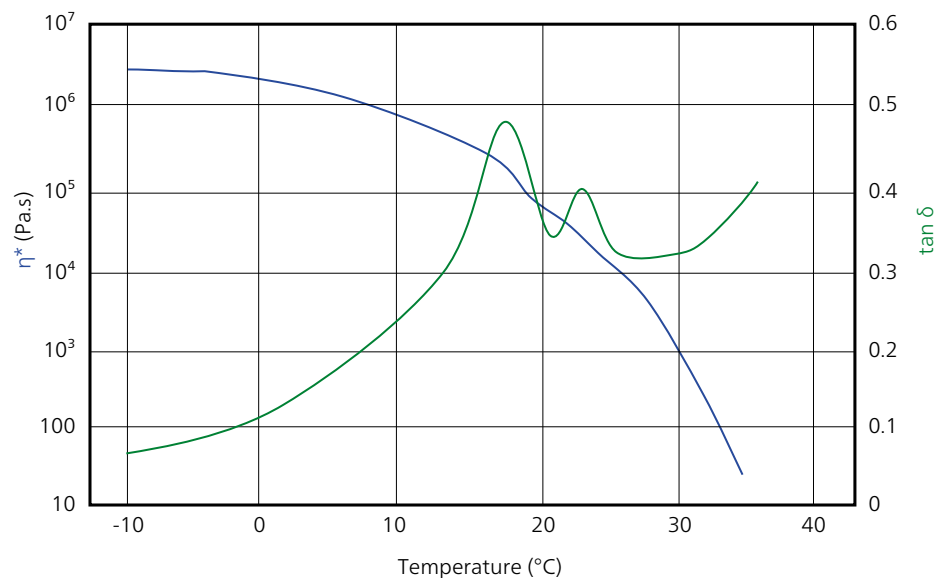


Figure 45. Shear viscosity (complex component) and $\tan \delta$ versus temperature. The oscillation temperature heat ramp results show precisely when the material starts to soften and $\tan \delta$ shows the inflection point (where each component melts).

The graph below shows how the viscosity of the sample decreased when the immersion cell was drained to simulate a parallel plate system with lower plate heating only.

It can easily be seen that the low-temperature results would be falsely low using one-sided thermally controlled parallel plates, as the sample doesn't reach thermal equilibrium.

Conclusion

The spreadability of butter and margarine products can be easily assessed by measurement of its complex viscosity at

different temperatures. The temperature at which each component melts can also be detected from peaks in the plot of $\tan \delta$ against temperature. Obviously, the higher the viscosity, the less spreadable the material will be. This test can be used to aid formulation of spreadable foods, so that they have the correct viscosity over their working temperature ranges.

The use of the immersion cell is paramount for true viscosity measurements and melting characteristics. If a one-sided thermally controlled parallel plate system is used, only one broad peak in $\tan \delta$ is seen, as the sample has a larger temperature gradient between the two plates.



Immersion Cell

- Allows samples, e.g., hydrogels and tissue samples, to be tested while immersed in water or buffer
- Prevents drying
- Controls temperature, ionic strength and can simulate in-vivo situations

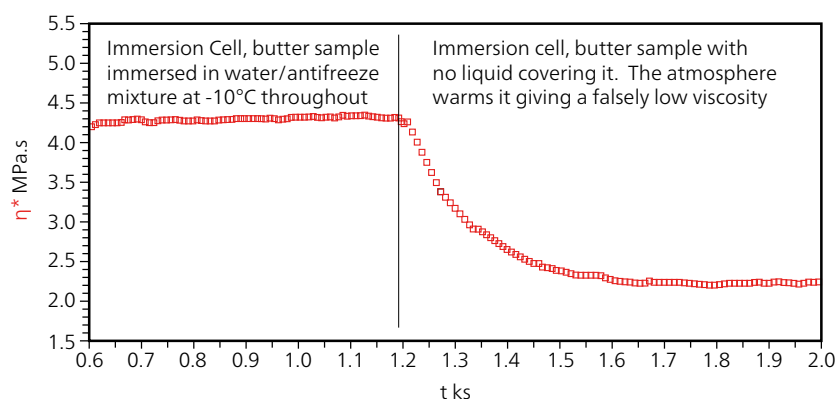


Figure 46. Phase angle vs. frequency. When the phase angle trends down toward zero with reducing frequency (red), this indicates an elastic solid structure, whereas when the phase angle trends up at lower frequencies (blue), this indicates an elastic liquid structure (without a yield stress).

Formulation of Soup Mixtures to Resist Settling of Solid Components

A. Prediction of Yield Stress Using Oscillatory Techniques

Introduction

Soups and other food suspensions such as sweet and sour or stir fry sauces often need to be formulated so that they have a degree of 'body' to inhibit sedimentation of the vegetable components. This body can be characterized by measuring the yield stress of a sample. The yield stress is the lowest stress required to start the sample flowing. We can describe the sample with physical and mathematical models known as Voigt units. The sample's viscous component can be described by a dashpot. A dashpot behaves like a piston filled with oil, with a hole in it so that it will flow on application of stress, but rest wherever it is left. The elastic components, such as cross-linked polymers or branched systems can be described as springs. A spring will extend when a stress is applied and retract when the stress is removed.

| Test Conditions | |
|--|--|
| Samples | Canned soups, stir fry sauces or similar |
| Geometry | Cone and plate system 4°/40 mm with a solvent trap |
| Temperature | 25°C |
| Strain | 0.005 (or in linear region) |
| Toolkit_0002Frequency Table (strain control) | 10 - 0.1 Hz down, 10 points |

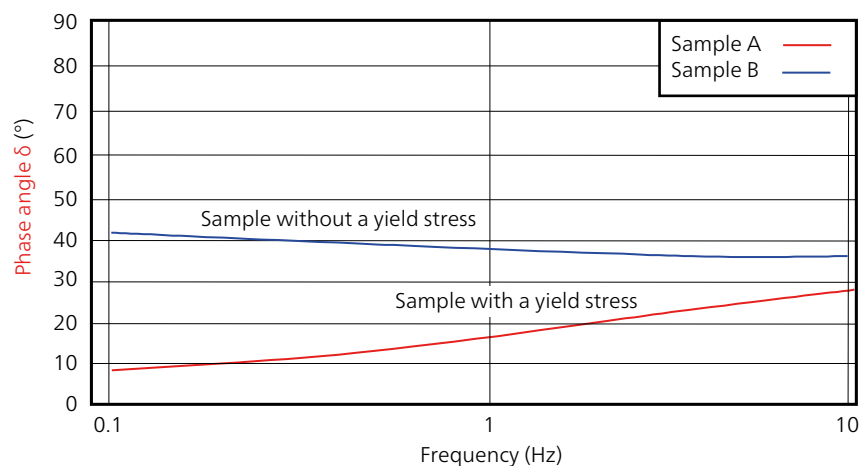


Figure 47. Phase angle vs. frequency. When the phase angle trends down toward zero with reducing frequency (red), this indicates an elastic solid structure, whereas when the phase angle trends up at lower frequencies (blue) this indicates an elastic liquid structure (without a yield stress).

Interpretation

In oscillation testing, the phase angle shows whether a material is viscously or elastically dominated. The lower the phase angle, the more elastic a material is and the higher, the more viscous. The frequency sweep results of the sample indicated by the blue line show that the material's phase angle falls slightly with increasing frequency. This means that the material is exhibiting more elasticity at high frequencies. From the models described below (Figure 48), it can be shown that in the case of a Maxwell system, the spring is not appreciably damped by the dashpot component over short timescales. Figure 47 shows that sample (sample B) will exhibit dominant elasticity at high frequency. At lower frequencies, the viscous component has time to flow, masking some of the elasticity. Therefore, we can see that this material has a zero shear viscosity rather than a yield stress.

Alternatively, the Kelvin (also known as Voigt) model has a

spring in parallel with a dashpot and in this case, the elasticity can be shown to be more prevalent at low frequencies than at high. Therefore, the material shown by a red line is similar to the Voigt model and may therefore act as if it has a yield stress rather than a zero shear viscosity.

Conclusion

For practical purposes, using the shape of the phase angle curve in a frequency sweep, it is possible to predict whether the sample has a yield stress or a zero shear viscosity.



Zero Shear Viscosity

is measured at very low shear rate. It shows the material's viscosity at rest.



Yield Stress

is defined as the stress applied to the sample before it starts to flow.

Below the yield stress, the sample will deform elastically (like stretching a spring), above the yield stress, the sample will flow like a liquid.

Larson, R.G (1999), The Structure and Rheology of Complex Fluids



A Maxwell material, also called **Maxwell** fluid, is a viscoelastic material having the properties of both elasticity and viscosity.

The elasticity manifests over short timescales, whereas the viscosity manifests over longer timescales due to the in-series nature of the spring and dashpot. It is named after James Clerk Maxwell who proposed the model in 1867.

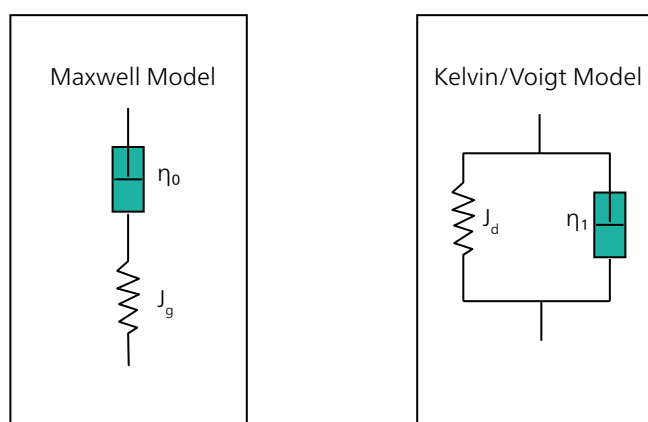


Figure 48. Maxwell and Kelvin/Voigt models of visco-elastic materials

B. Yield Stress Measurements of Soup by Stress Ramp

Introduction

On application of stress, a sample with a yield stress initially acts as an elastic solid. The instantaneous viscosity appears to increase, as the more stress that is applied to the sample, the more the sample resists flowing. When the yield stress is reached, the sample starts to flow and the measured viscosity falls rapidly. In this case, the corresponding stress at the peak of the viscosity curve therefore can be used to describe the yield stress of the sample.

Nominally, a user can say that sample A (see Figure 49) showed a yield stress of 35 Pa and will therefore resist settling much more effectively than sample B which showed a yield stress of 12 Pa. There is, however, a more mathematical approach given below. Settling is due to the difference in density of the solid food particle and the bulk sauce; this gives a resultant stress under gravity. When the particle is static, a balance exists between the gravitational forces and the stresses in the fluid:

$$\delta_{gravity} = \frac{r \cdot g \cdot (d - \rho)}{3}$$

r = particle radius
g = gravitational acc'n
 ρ = fluid density
d = particle density

| Test Conditions | |
|--|--|
| Samples | Canned soups, stir fry sauces or similar |
| Geometry | Cone and plate system 4°/40 mm with a solvent trap |
| Temperature | 25°C |
| Shear stress sweep Toolkit_V003 Yield Stress (Stress Ramp) | 1 - 100 Pa up linear |
| Ramp time | 60 seconds |

Thus, if the material has a yield stress greater than $\sigma_{gravity}$, then one would not expect sedimentation to occur, providing the structure isn't broken down considerably in canning or transportation.

Conclusion

The yield stress can be used to calculate whether a sample is likely to settle in-situ, or whether it will be difficult to start pumping or stirring. Good rheological product design will dramatically enhance processing and end use.

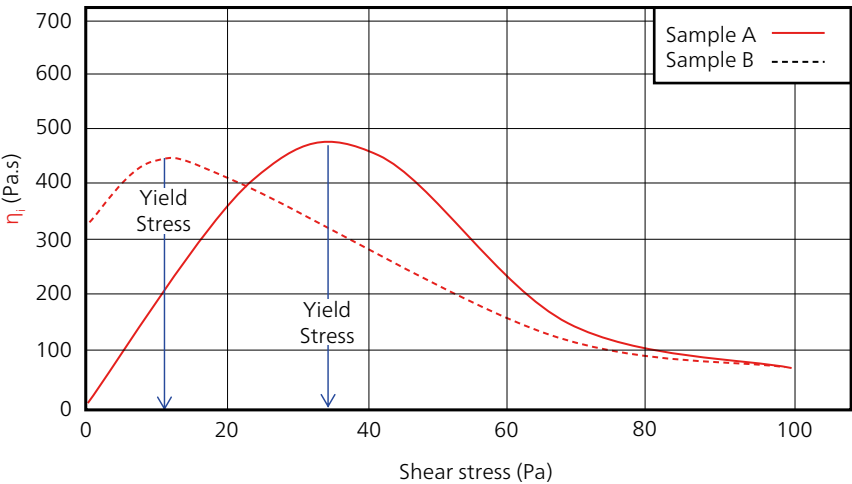


Figure 49. Shear viscosity vs. shear stress. The peak viscosity from a stress ramp indicates the yield stress of the material.

C. Yield Stress Determination by Creep Test

Introduction

After a period of equilibration (at least 5 minutes), sequential creep measurements are made (see Figure 50) at selected stress increments. The starting stress is typically a factor of two below the yield stress value as defined by the previous stress ramp experiment.

At the stress values where the sample is not flowing (below the yield stress, 12 Pa in this case), curves overlay and tend to plateau. The sample's behavior can be described as being 'linear' below the yield stress. Strain increases proportionally with the applied stress values, so the modulus and compliance are constant.

At stresses above the yield stress (>12 Pa), the sample produces a non-linear response and the compliance values now increase with increasing stress steps. In this experiment, the yield stress would be determined as a value between 10 Pa and 12 Pa. For a more accurate determination of the yield stress, smaller stress increments should be made in this range.

| Test Conditions | |
|---|--|
| Samples | Canned soups, stir fry sauces or similar (sample B from above shown) |
| Geometry | Cone and plate system 4°/40 mm with a solvent trap |
| Temperature | 25°C |
| Creep_0004 Multiple creep end by time with increasing stress.rseq | 6, 10, 12, 14 Pa (or small steps in the yield stress region) |

Conclusion

The yield stress can be measured by several methods as shown above. The stress ramp is a fast and reasonably accurate method, however, for the best accuracy or to determine whether something will flow over a long period of time, the creep test is best. The yield stress value may then be used to calculate whether a sample is likely to settle in-situ, or whether it will be difficult to start pumping or stirring. Good rheological product design will dramatically enhance processing and end use.

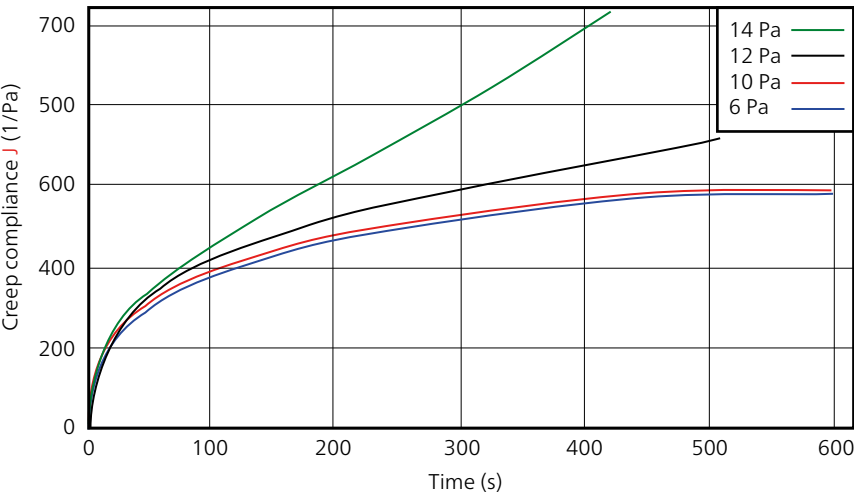


Figure 50. Creep compliance vs. Time (action). Repeated creep tests at small stress increments can clearly elucidate a samples yield stress, In the data above it can be seen that the sample starts to flow between 10 and 12 Pa, where the creep compliance doesn't plateau.

Pharmaceuticals & Cosmetics





Pharmaceuticals & Cosmetics

Determining Yield Stress in Toothpastes

Introduction

On application of stress, a sample with a yield stress initially acts as an elastic solid. The instantaneous viscosity appears to increase, as the more stress that is applied to the sample, the more the sample resists flowing. When the yield stress is reached, the sample starts to flow and the measured viscosity falls rapidly. The peak of the viscosity curve therefore indicates the yield stress of the sample.

Interpretation

Figure 51 shows that sample A exhibited a yield stress of 100 Pa and will therefore resist pumping or flow much more than sample B, which showed a yield stress of 60 Pa.



| Test Conditions | |
|--|--|
| Samples | Toothpaste |
| Geometry | Cone and plate system 4°/40 mm with solvent trap |
| Temperature | 25°C |
| Shear stress sweep Viscometry_0010 – Table of shear rates 1 - 200 Pa, up linear with Power law model fit | |
| Ramp time | 30 seconds |

Conclusion

The yield stress can be used to calculate whether a sample is likely to be difficult to start pumping or stirring. Consumer perception is also an important factor, if the bead of toothpaste appears to be 'runny' because of a very low yield stress, it may be perceived as less effective, or dilute. Good rheological product design can dramatically enhance processing and consumer perception.

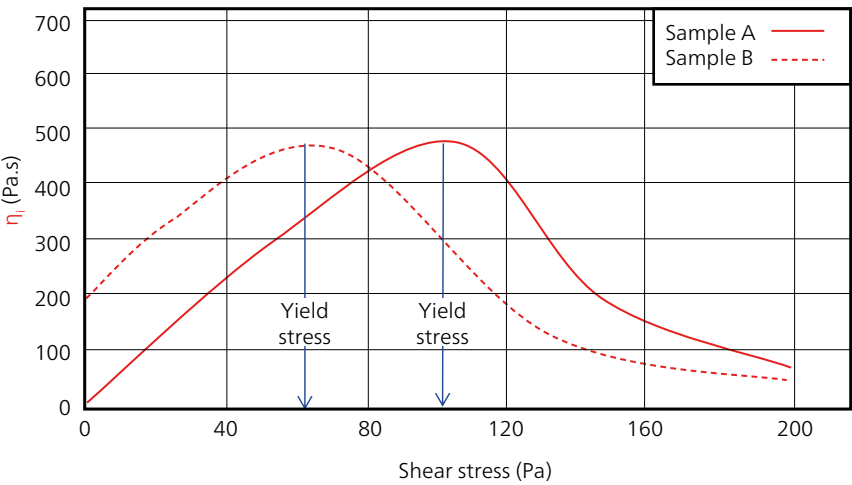


Figure 51. Shear viscosity vs. shear stress. Yield stress can be seen from the peak in the viscosity curve if the sample is significantly elastic.

Measuring the Flow Characteristics of Hand Cream and Absorbing Body Lotions

Introduction

Hand creams are generally formulated to have a high viscosity at low shears and a low viscosity at high shears. The high viscosity at low shears gives the cream a good 'stand-up' appearance in the pot, inferring a rich creamy product. If the lotion has a low viscosity when at rest, it may be unstable with storage, giving separation. A low viscosity at high shear rates allows the product to be absorbed into the skin when rubbed.

Interpretation

The results in Figure 52 show that sample A has a very high viscosity at low rates, indicating that it may resemble a firm, well-bodied product. However, its viscosity fell dramatically at higher rates to become a thin liquid. Sample A would therefore probably be absorbed into the skin easily as well, making it an ideal hand cream.

Sample B's viscosity at low shear rates was insufficiently high to give it good stand-up properties. Similarly, its high shear viscosity may not be low enough to allow it to absorb into the skin well.

| Test Conditions | |
|--|--|
| Samples | Hand cream |
| Geometry | Cone and plate system CP 0.5°/40 mm and a solvent trap cover |
| Gap | 30 µm |
| Temperature | 27°C (~ body surface temperature) |
| Table of stress Viscometry_0010 – Table of shear rates 0.1 - 200 s ⁻¹ up log with Power law model fit | |
| Single Frequency Oscillation | Strain: 0.005 Frequencies: 1 Hz |

Conclusion

Viscosity profiles of body lotions can influence the product stability and end use. The viscosity profile will also dictate how the material can be pumped and its appearance when at rest.

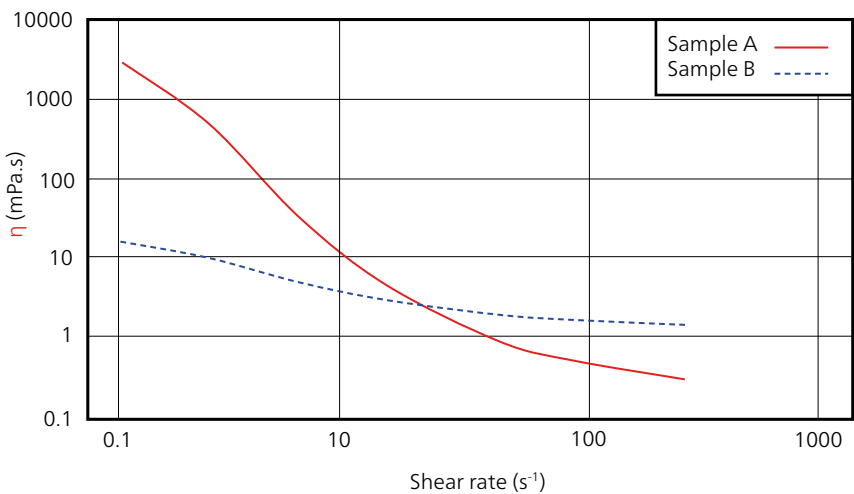


Figure 52. Shear viscosity vs. shear rate (s⁻¹)

Pharmaceuticals & Cosmetics

Absorption Characteristics of Nasal and Throat Sprays

Introduction

The absorption of a nasal spray as with many other pharmaceutical sprays is dependent on how well it remains on the affected area of skin. Research has indicated¹ that addition of thickeners such as microcrystalline methoxy cellulose or dispersed cellulose can dramatically increase the efficacy of the spray, as they impart a higher low shear rate viscosity. A large diameter cone was used for the measurements to enhance sensitivity at low stress, as in this case the low stresses more closely simulate the application.

Interpretation

The results in Figure 53 show that sample A exhibited a viscosity almost four times that of sample B in the stress range that might be expected for an in-vivo situation. This would indicate that sample A is likely to remain in place after application and therefore be more effective than sample B.

Test Conditions

| | |
|---|---|
| Samples | Pharmaceuticals sprays |
| Geometry | Cone and plate system 2°/55 mm acrylic/solvent trap |
| Gap | 70 µm |
| Temperatue | 37°C |
| Table of stresses Measure_0005 Table of shear stresses log. rseq | 0.01 - 2 Pa UP log |

Conclusion

The rheology of pharmaceutical sprays can dramatically affect their in-vivo effectiveness. This test was able to accurately characterize the nasal sprays and could therefore be used to determine the optimum dosing of thickeners.

¹ Journal of Pharmaceutical Sciences, p405, vol 77, no. 5. May 1988

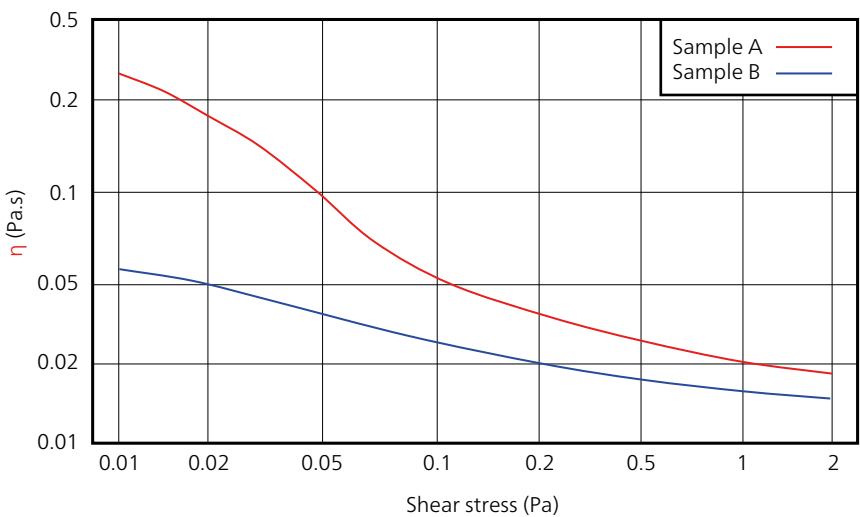
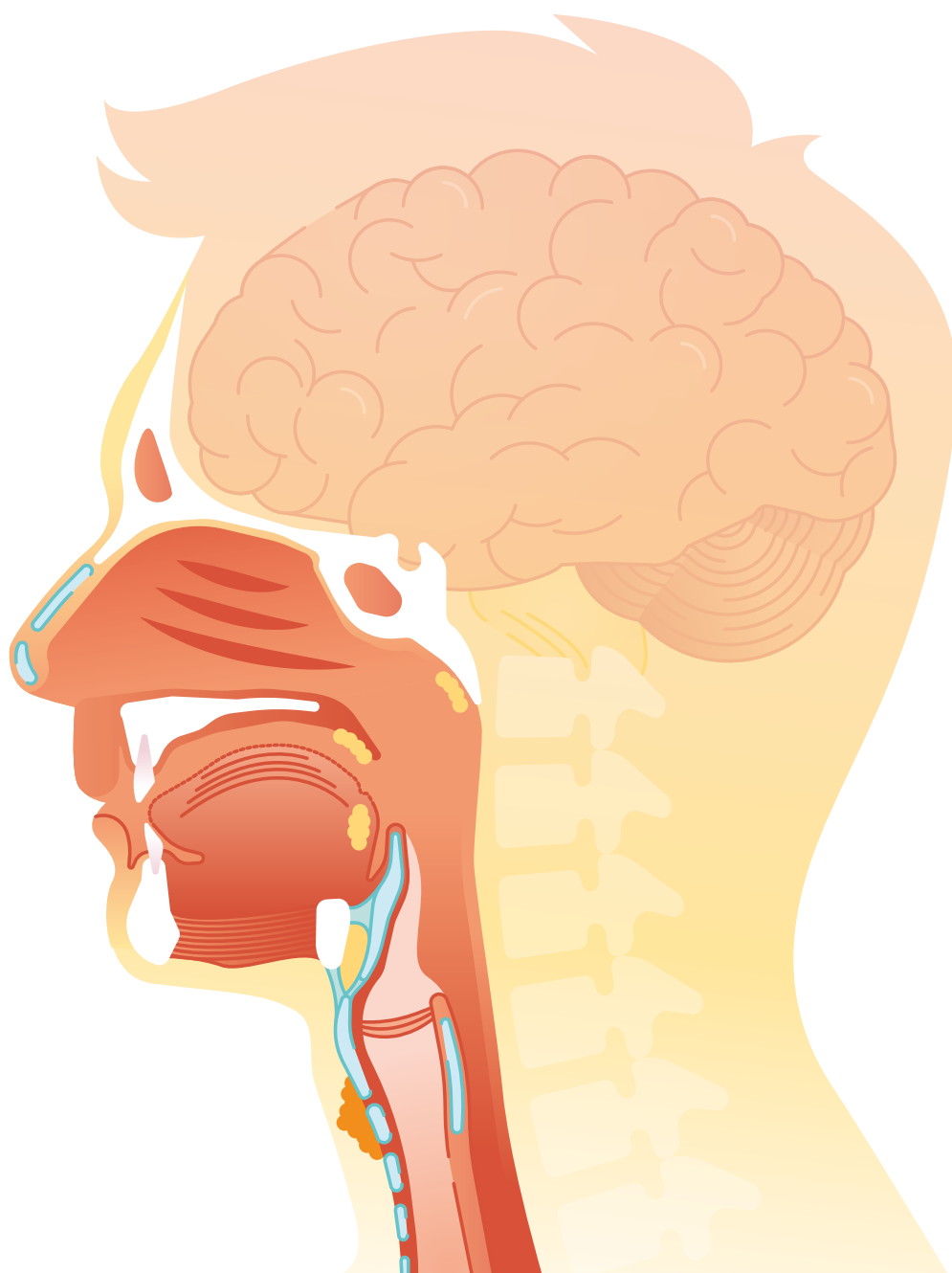


Figure 53. Shear viscosity vs. shear stress. Visometry flow curve at lower stress can show the resistance to flowing under gravity.



Pharmaceuticals & Cosmetics

Characterizing Gel Samples

Gelation Time Measurements

Introduction

Dental molding systems need to have a fixed working time after mixing and then gel quickly to form a resilient structure. Ideally, the gel will not be adversely affected by conditions in the mouth and must only contain orally acceptable components.

Interpretation

The results in Figure 54 indicate that the sample is initially liquid-like as the viscous modulus (G'') is dominant over the elastic modulus (G'). The crossover point of the elastic and viscous moduli indicates the gel point and thereafter when the structure becomes predominantly elastic, the sample will not flow. For stiffer gels, the elastic modulus may start higher than the viscous modulus, and both increase with time. In both cases, the moduli will reach a plateau when the reaction is complete.

Conclusion

The NETZSCH rheometer may be used to accurately characterize gelation properties and so can be used to optimize current formulations and create new products.

| Test Conditions | |
|--|--|
| Samples | Liquid systems that gel with time, e.g., dental molding gels |
| Geometry | Cone and plate system 1°/40 mm stainless steel |
| Temperature | 37°C (or whatever required for the gelation to take place) |
| Pre-shear | 100 s ⁻¹ |
| Single frequency oscillation Toolkit_O033 Single Frequency (strain control) | Strain: 0.005 Frequency: 1 Hz |



Elastic Modulus G'

$$G' \text{ (Pa)} = \frac{[\text{Stress}] \cdot \cos \delta}{|\text{Strain}|}$$



Viscous Modulus G''

$$G'' \text{ (Pa)} = \frac{[\text{Stress}] \cdot \sin \delta}{|\text{Strain}|}$$

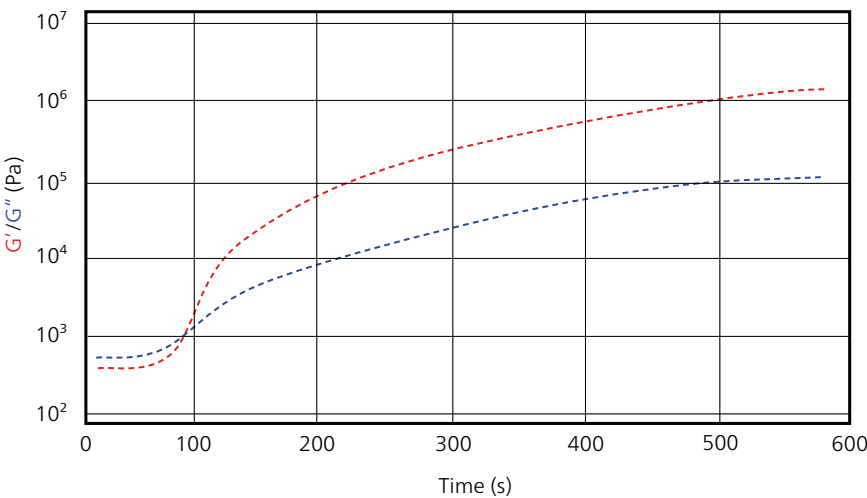


Figure 54. Viscous (blue) and elastic (red) moduli (Pa) vs. time (s). The crossover of the moduli indicates when the sample becomes elastically dominated. For materials that had very little elasticity initially, this is often used as a gel point.

Gelation Strength Determination

Introduction

Both samples are subjected to a sinusoidally increasing stress (see Figure 55). Whilst the sample's structure is maintained, the complex modulus G^* remains constant. However, when the gel's intermolecular forces are overcome by the oscillation stress, the sample breaks down and the modulus falls.

Interpretation

Sample A gave a much shorter linear viscoelastic region than sample B and will therefore break down much more easily with vibrations and small movements. The length of the linear viscoelastic region is also a good indication of the stability of the gel to resist syneresis, where a layer of liquid forms on the surface of the gel.

| Test Conditions | |
|--|---|
| Samples | Wound healing gels, toothpaste gels, etc. |
| Geometry | Cone and plate system 4°/40 with a solvent trap |
| Temperature | 25°C |
| Stress amplitude sweep | |
| Measure_0030 | 0.1 - 100 Pa up logarithmic |
| Amplitude sweep stress controlled.rseq | |

Conclusion

A relatively quick amplitude sweep experiment can indicate the strength of a gel and its modulus. This can therefore be used to optimize dosing of gelation agents and other components.

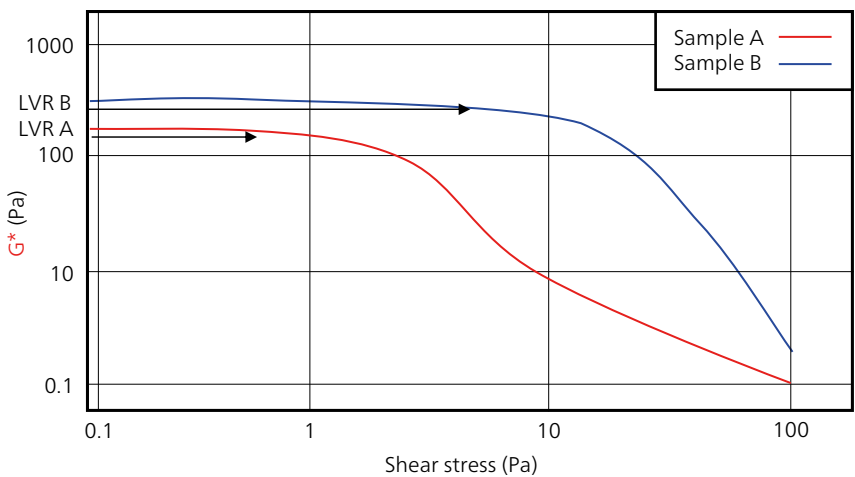


Figure 55. Shear modulus (complex component) vs. shear stress. The length of the linear viscoelastic region in stress gives a good indication of the stability of a dispersion.

Characterizing Gels Using Oscillation Frequency Sweeps

Interpretation

A frequency sweep in the sample's LVR can be used to characterize the nature of a gel or solution. Where a material has strong intermolecular associations, such as sample A (see Figure 56), it will give a gel like structure and the elastic modulus is dominant over the viscous modulus. A gelled system is characterized by little change in the viscoelastic properties with frequency, as shown for sample A.

In a viscous material such as sample B, the viscous modulus is dominant over the elastic modulus, and both show frequency dependence. It is also possible to get a reversible network, which gives elastic properties at one extreme of frequency and viscous at the other. These systems can be described by the Maxwell and Kelvin models (see page 14), or more complex derivatives of these. If a material is required to give good storage stability, it will generally need to be elastically dominated at low frequencies. Similarly, if a material is to be sprayed, it should not be too elastic at high frequencies, or it may exhibit undesirable properties such as 'cobwebbing'.

| Test Conditions | |
|--|--|
| Samples | Gels or gel-like solutions |
| Geometry | Cone and plate system 4°/40 mm with a solvent trap |
| Frequency sweep | 10 - 0.1 Hz |
| Strain Toolkit_O002 Frequency Table (strain control) | 0.010 (or in LVER as found from amplitude sweep experiment before) |

Conclusion

A relatively quick frequency sweep experiment can indicate the strength of a gel, its modulus and its processing characteristics. This data can therefore be used to determine suitable gelation agents and optimize formulations.

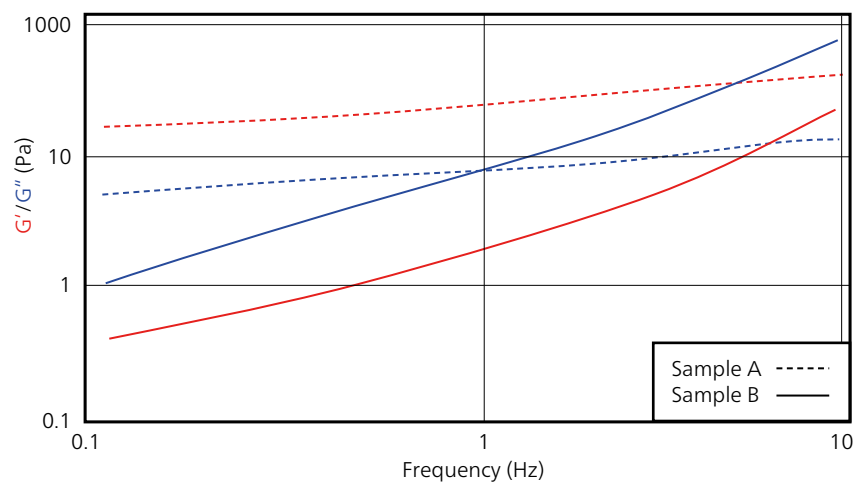


Figure 56. Elastic (red) and viscous (blue) moduli vs. frequency. The sample results shown in a dashed line indicate an elastically dominated structure, whereas the sample results shown as solid lines show the viscous modulus is dominant and therefore a viscously natured structure.

UV Curing Analysis of Dental Filling and Enamel Pastes

Introduction

For obvious reasons, the curing properties of dental fillings and enamels must be tightly controlled. Using a NETZSCH rheometer, we can measure the curing properties in a controlled environment and with specified light dosing by using the UV cell. In this cell, the lower plate is a removable quartz disk. The UV light source is placed underneath and illuminates the sample, initiating the cure reaction. In this test, the sample is subject to microscopic oscillations that will not inhibit the cure reaction. The storage and loss (elastic and viscous, respectively) moduli may be studied throughout the reaction.

Interpretation

Initially, the sample is viscously dominated and so the loss modulus (G'') is higher than the storage modulus (G') (see Figure 57). The crossover of these moduli at around 98 s below indicates the gel point and thereafter, the structure becomes predominantly elastic and the sample will not flow. The moduli will reach a plateau when the reaction is complete.

If the elastic modulus is higher right from the start of the test (as the sample is thickened), an inflection point may be used

| Test Conditions | |
|---|--|
| Samples | Dental fillings and enamel pastes |
| Geometry | Parallel plate 25 mm disposable and UV curing cell |
| Gap | 1 mm |
| Temperature | 30°C |
| Single Frequency Oscillation UV_VIS0002 Single Frequency Strain Controlled UV-VIS. resq | Strain: 0.002 Frequency: 1 Hz |

as a curing time. Alternatively, another technique is to oscillate at three different frequencies repeatedly and determine the point in the cure when the phase angle becomes independent of frequency which is considered the true gel point in such cases.

Conclusion

Cure times can be easily measured using NETZSCH's UV curing cell, making it a good formulation aid.

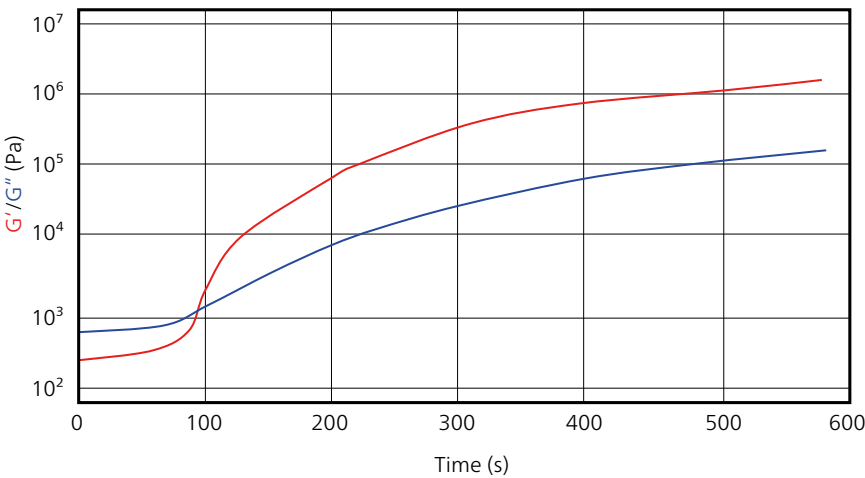


Figure 57. Elastic (red) and viscous (blue) moduli vs. Time. The crossover point of the G' and G'' can indicate a gelation time for initially viscously dominated samples.



Bitumen, Petrochemicals & Miscellaneous





Bitumen, Petrochemicals & Miscellaneous

Determining the Viscosity Temperature Dependence on Engine Oils

Introduction

Engine oils and lubricants need to provide a good layer thickness by having sufficient viscosity, without giving significant frictional effects from the viscosity being too high. The ideal viscosity range of an engine oil is therefore quite narrow. Mineral oils generally have a very temperature dependent viscosity and so need to be modified. Viscostatic oils (can be created by adding polymeric compounds that open up their conformation at higher temperatures. When heated, the increase in viscosity of the polymer additive counteracts the fall in viscosity of the oil. In this experiment, we can measure the viscosity of the oil at all working temperatures and determine whether it will be sufficiently 'thin' when cold, for say, an engine to start, or sufficiently 'thick' to lubricate well when hot.

| Test Conditions | |
|------------------|--|
| Samples | Oils and lubricants |
| Geometry | Parallel plate 40 mm |
| Shear rate | 10 s ⁻¹ |
| Gap | 1 mm |
| Temperature ramp | Range of interest (e.g., 20°C - 90°C at 3 K/min) |

Viscosity is dependent on the temperature!

Interpretation

The results show in Figure 58 that sample A's low temperature viscosity is much higher than that of sample B and therefore, it will be much more difficult to circulate in an engine on start-up. Conversely, sample B showed a higher viscosity than sample A when hot, indicating that it would give more lubrication when up to temperature.

Conclusion

The temperature dependence of a lubricant is one of the most important factors in determining its efficacy. Using a NETZSCH rheometer, the viscosity can be accurately measured over a wide temperature range. Results are also referenced against nationally recognized standards.

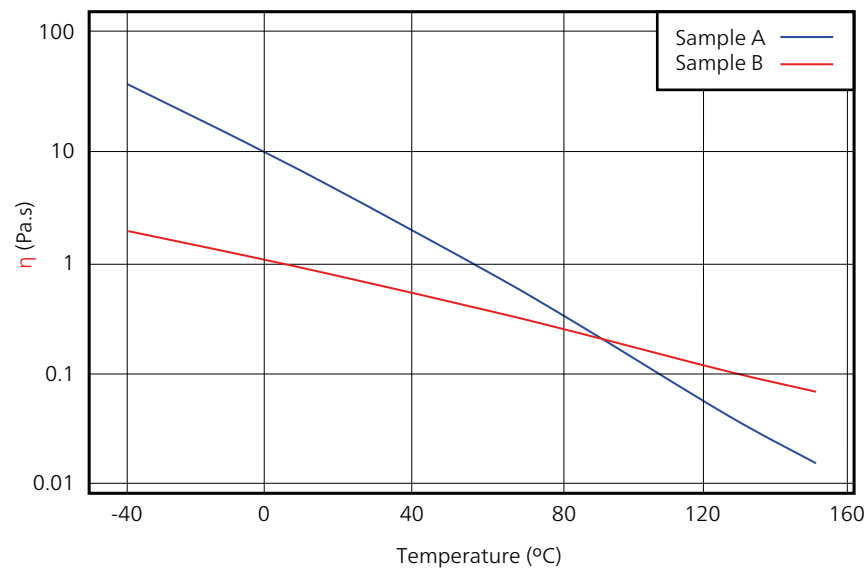


Figure 58. Shear viscosity vs. temperature. Sample B (red) has been formulated to be less temperature dependent than sample A, both easing cold start conditions and increasing lubrication performance when hot.



Bitumen, Petrochemicals & Miscellaneous

Measuring Yield Stress in Sooty Engine Oil

Introduction

Sooty engine oils will develop a microstructure of carbon particles when left to rest, imparting a slightly gel-like nature. If structure forms quickly, then the oil will be immobilized on the engine surface in-situ when the engine is stopped and this can form immediate lubrication again on start-up, thus reducing wear. Some oils actually are formulated to contain magnetic particles to reduce start up wear this manner. However, if the structure becomes too strong, the oil may be inhibited from flowing around the smaller channels. This resistance to flowing is called a 'yield stress'.

On application of stress, a sample with a yield stress initially acts as an elastic solid. In this case, the instantaneous viscosity appears to increase as more stress is applied. The sample is effectively absorbing energy and as a result resists flowing. When the yield stress is reached, the sample starts to flow and the measured viscosity falls rapidly. The peak of the viscosity curve can be used to indicate the yield stress of the sample.

| Test Conditions | |
|--|--|
| Samples | Sooty engine oil |
| Geometry | Cone and plate system 4°/40 mm with a solvent trap |
| Shear stress sweep Toolkit_V003 Yield Stress (Stress Ramp) | 0.03 Pa - 1 Pa up linear |
| Ramp time | 60 seconds |
| No. of samples | 30 |

Interpretation

Nominally, a user can say that sample A (see Figure 59) showed a yield stress of 0.35 Pa and will therefore resist flowing much more effectively than sample B which showed a yield stress of 0.12 Pa. There is, however, a more mathematical approach given on the next page.

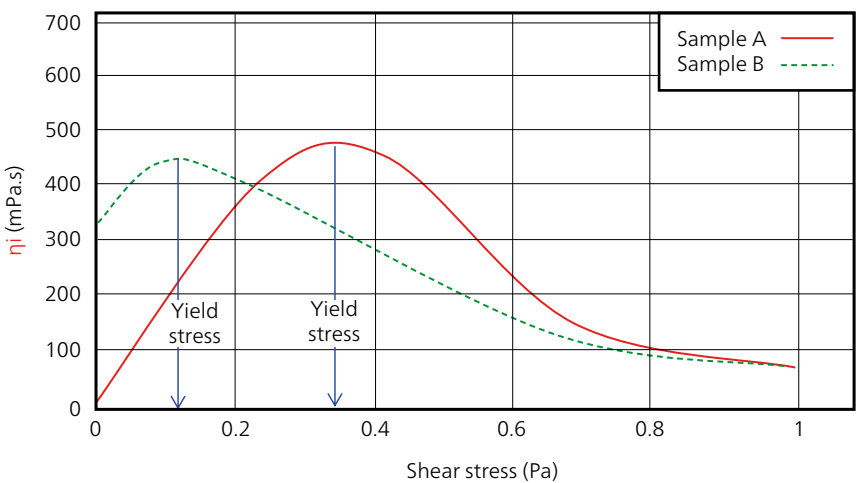


Figure 59. Shear viscosity vs. shear stress. The yield stress is indicated by a peak in the viscosity curve. Below this point the material exhibits elastic behavior, and above, a combination of viscous flow and some elastic behavior.

Film Thickness

The maximum equilibrium film thickness deposited on a surface will be dependent on the yield stress of the oil, the gravitational forces and the angle of inclination. The equilibrium state can be modelled as:

$$\sigma_{\text{yield}} = \rho \cdot g \cdot h \cdot \sin \beta$$

ρ = density ($\text{kg} \cdot \text{m}^{-3}$)

h = film thickness

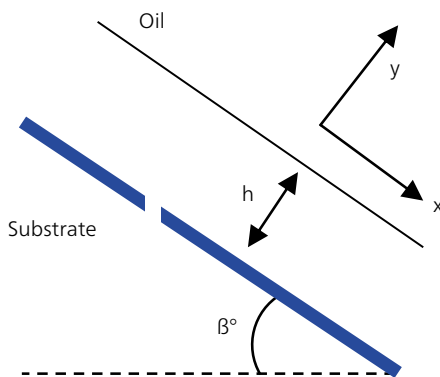
g = gravitational acc'n ($9.81 \text{ m} \cdot \text{s}^{-2}$)

β = tilt angle (degrees)

Conclusion

The yield stress can be used to calculate the maximum oil film thickness that can remain on an inclined surface, as well as whether it will be difficult to start pumping. Good rheological product design will dramatically enhance processing and end use performance.

Resistance to Pumping



A coating's resistance to start pumping will also be proportional to its yield stress. It can be seen that the shear stress (at the wall) of a fluid running through a pipe (ignoring entrance and exit effects) is:

$$\sigma_w = \frac{D \cdot P}{4L}$$

D = diameter of the pipe

p = min. pressure through the pipe

L = length of the pipe

If the pipe pressure exceeds $4L \cdot \sigma_o / D$, then the sample will start to flow in the pipe, where σ_o is the yield stress.

Bitumen, Petrochemicals & Miscellaneous

Grade Determination of Asphalts (SHRP Method)

Introduction

One of the key factors in making a durable road surface is the nature of the asphaltic cement. Asphalt is a bituminous product taken from the residue of cracked crude oils and is largely viscous in nature unless modified¹. The two main problems that occur in asphaltic concrete (tarmac) surfaces are that wheel ruts are formed when the material is too soft or that the surface cracks when too hard (see Figure 60).

The viscosity of asphalt is highly temperature dependent, and so any road surface needs to be constructed from a suitable grade of asphalt for the climate in that region. In the Strategic Highway Research Program (SHRP, USA), methods were optimized to assess and grade asphalts so that they could be valued and sold appropriately as SUPERPAVE™ products. The SHRP testing regime contains several steps, this being only one of them.

| Test Conditions | |
|-----------------|--|
| Samples | Asphalt cement |
| Geometry | PP 25 mm for original binder for pressure aging vessel sample, with Kinexus Active Peltier |
| Temperature | As described in the AASHTO ² method T315 (46, 52, 58°C ...) |
| Shear strain | 12% for original binder, 1% for pressure aged vessel |
| Frequency | 10 rads/s |
| Delay time | 6.25 seconds |



Figure 60. A cracked road surface due to too hard an asphalt binder being used. Another common problem (not shown here) is the rutting seen when too soft a binder is used.

¹ ASTM special publication: The influence of asphalt composition on rheology. No 294, 1960

² AASHTO Provisional standard TP5: Standard test method for determining the rheological properties of asphalt binder using a Dynamic Shear Rheometer

³ AASHTO Provisional standard MP1: Standard specification for performance graded asphalt binder

Asphalt is a particularly difficult material to assess rheologically, as it is highly temperature dependent; the viscosity varies by 20% for 1°C temperature change! Also it is highly viscous, has a poor thermal conductivity, and polymer modified bitumen can be thixotropic. These problems were investigated by the SHRP team and a specific set of methods was designed to give optimally reproducible data. These are now available as pre-written sequences with the Kinexus DSC range of instruments.

Also, the poor thermal conductivity of the sample required the development of a specialized cell for enhanced temperature control. This cell heats the atmosphere all around the sample, as well as the geometry above and the lower plate that it is loaded onto. This gives unprecedented temperature control, with temperature gradients of <0.1°C through the sample. This cell now forms part of the standard asphalt testing method in the AASHTO system.

Interpretation

The SHRP testing regime is quite complicated and too long to describe in detail in this book, however, the complete analysis is according to AASHTO T315^{2,3}.

In the results presented in Figure 61 (original binder), sample A showed a $G^*/\sin \delta$ value exceeding 1 Kpa at 58°C, and so this product would qualify to become paving grade PG58, e.g., (and PG52) (specifications taken from the references given).

This test is initially carried out on the original binder and then on rolling thin film oven test (RTFO) residue and the pressure aged vessel (PAV) binder, each with different temperatures and pass criteria.

Conclusion

The grade of asphalts can be accurately quantified using a NETZSCH KINEXUS rheometer an active hood Peltier controller or with a NETZSCH DSR rheometer.

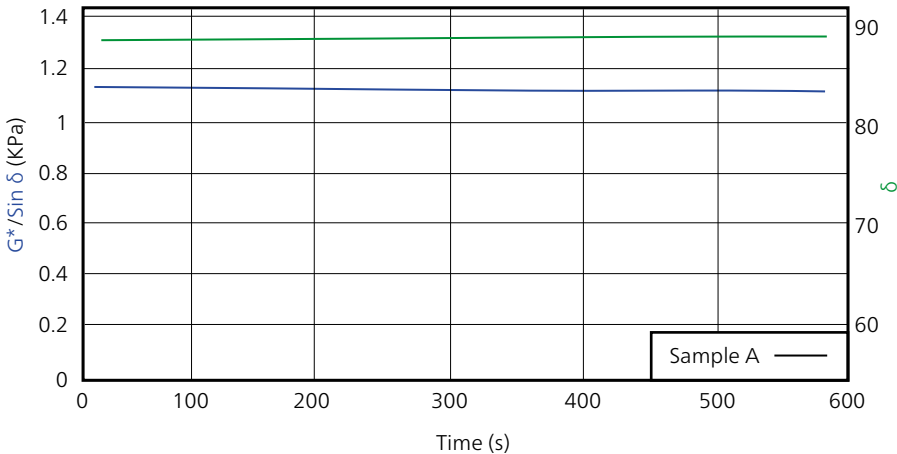


Figure 61. $G^*/\sin \delta > 1$ KPa in the original binder indicates that the asphalt binder is likely to be stiff enough to resist rutting when first laid on the road. For the Rolling Thin Film Residue (a treatment which evaporates a similar quantity of volatiles as the mixing and layout process), the binder needs to have a $G^*/\sin \delta$ value of >2.2 KPa.

Bitumen, Petrochemicals & Miscellaneous

Producing a 'Black Curve' for Bitumen Products

Introduction

Black curves are a plot of phase angle (δ) vs. complex modulus (G^*), containing no reference to temperature or frequency. Consequently, they are very easy to produce. Individual data points from the frequency sweeps at all the temperatures are simply plotted on the same graph; it is even possible to use data from a fixed-frequency temperature sweep, since temperature errors do not affect the plot.

Elimination of temperature and frequency from the data can be useful. A series of bitumen differing in penetration but not temperature susceptibility (penetration index) will give a single Black curve. Deviation from this curve is caused by errors of measurement, changes in composition, or variation in structure. Effects caused by processing, ageing, or polymer addition are highlighted by this form of presentation.

Interpretation

In the results shown in Figure 62, sample A is a polymer modified bitumen and generally has a lower phase angle than an unmodified product, sample B. The lower the phase angle, the more elastic-natured the asphalt binder will be and so it is less likely to form wheel ruts on a road in hot weather (modulus shown $<10^5$ Pa). At very low temperatures (modulus $>10^7$), the polymer modified sample has a higher phase angle than the unmodified material, indicating that it is still somewhat viscous (although elastically dominated)

| Test Conditions | |
|---|---|
| Samples | Asphalt cement |
| Geometry | PP 25 mm for original binder or PP8 for pressure aging vessel sample, with an active hooded Peltier |
| Temperature | 90 - 10°C at 1.5 K/min |
| Frequency | 10 rads/s |
| Delay time | 6.25 s |
| Measure_0036 Single frequency strain controlled temperature ramp.rseq | 12% for original binder, 1% for pressure aged vessel |

and is less likely to show cracking. Photographs cracking are shown on page 96 At very high temperatures (modulus 10^1), the binder softens enough to become viscous so that it can be easily mixed and laid in position.

Conclusion

The viscoelastic nature of the asphalt is able to be easily and quickly determined using the NETZSCH KINEXUS rheometer with an active hooded Peltier controller, or with a NETZSCH DSR rheometer. This makes these instruments ideal tools in formulation and chemical modification of asphalts.

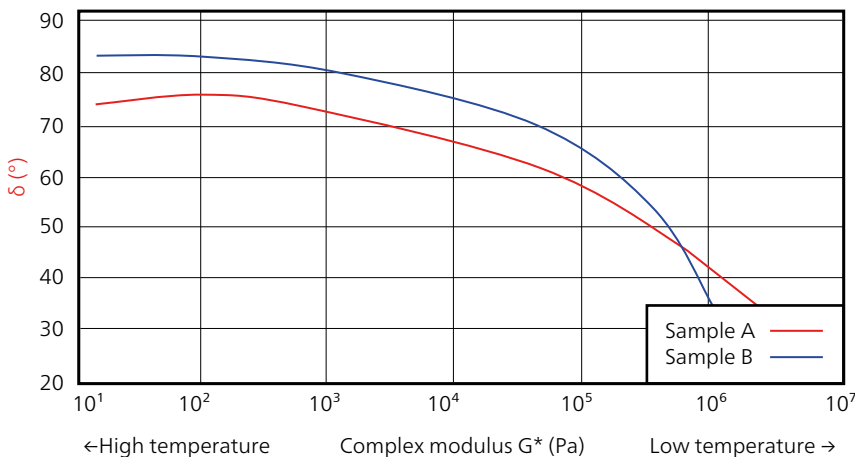


Figure 62. Phase angle vs. shearmodulus (complex component). This blacks space curve indicates how viscous or elastically natured the asphalt binder will be at different moduli (and hence temperatur

Finding Temperature Transitions in Grease

Introduction

Lubricating products can be used at extremely low temperatures such as farming equipment in Siberia, or vehicles used at the South Pole (-40°C or lower). When cooled, the different fractions in the grease will freeze up individually and a corresponding peak should be evident in the $\tan \delta$ value. In parallel with the $\tan \delta$ peak, the complex viscosity (η^*) will, of course, increase.

Interpretation

The oscillation results in Figure 63 clearly show the freezing points of each component from the peaks of the $\tan \delta$ curve at approximately -10°C and -50°C. The viscosity also showed two individual 'drops' tying in with the phase changes. The sample's workability at any particular temperature can therefore be seen from the complex viscosity.

This mechanically assessed phase change is likely to be around 10°C higher than that measured by differential scanning calorimetry (DSC), because the phase change is frequency dependent, and a DSC sample is at rest. However, as most lubricant manufacturers need to determine the working range of a grease material at low temperatures, the T_g (or freezing point) measured by rheometry is often much more pertinent.

| Test Conditions | |
|------------------------------|--|
| Samples | Grease and high modular weight lubricants |
| Geometry | PP15 serrated and active hooded Peltier controller with a chiller bath |
| Single frequency oscillation | Strain: 0.005 Frequency: 1 Hz Temperature range: 40°C to -40°C |

Conclusion

The melting point and glass transition temperatures can be accurately measured for any grease or lubricant compound using the NETZCH Kinexus where the transition occurs between -40°C and 200°C.



Complex Viscosity, η

is used to identify the minimum viscosity the resin achieves at elevated temperature prior to the cure commencing. However, when plotted as a function of angular frequency, for some materials, it can be correlated to shear viscosity as a function of shear rate (Cox-Merz relationship) which enables the generation of effective viscosity/shear rate profiles from oscillation frequency sweeps for those materials which are impossible to test under shear using traditional techniques.

<http://www.rheologyschool.com/advice/rheology-glossary>

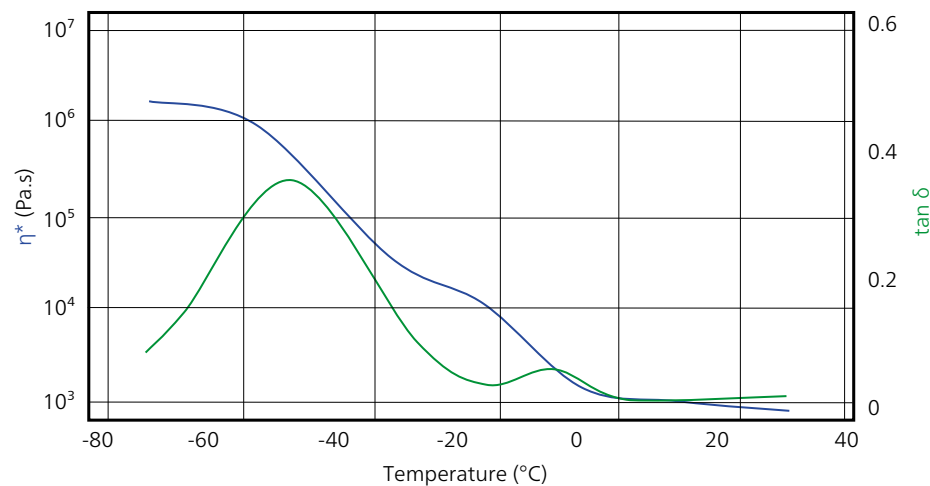


Figure 63. Shear viscosity (complex component) and $\tan \delta$ vs. temperature. The drops in viscosity overlap with the peaks in $\tan \delta$ at any given temperature and indicate where components are undergoing phase transitions.

Bitumen, Petrochemicals & Miscellaneous

Use of the Vane Tool for Yield Stress Measurements on Cement Pastes

Introduction

The slump resistance and levelling properties of cement pastes are critical to their performance in use. The 'yield stress' is the maximum stress that the sample can resist before it starts to flow. This therefore shows the cement's ability to resist flowing when applied to a vertical surface, or conversely its resistance to leveling when applied to a floor, etc.

The yield stress of a mortar could be measured using a parallel plate system with a wide gap (due to the large size of sand particles), however, results are often noisy due to the particles moving over one another, however, a vane tool usually gives excellent results. The vane tool measuring geometry is also ideal for yield stress determinations of other difficult materials such as slurries, red mud, concentrated coal dispersions, etc. as it has a very wide gap and also eliminates any slip at the geometry surface.

In this test, the vane tool is introduced vertically into a pre-formed sample in the cup. This means that the yield stress can be measured without the sample's micro-structure being disturbed whilst loading. The yield stress results are very reproducible and accurate. More information about the Boger Vane Method can be found in the Journal of Rheology 27(4), 321, 1983.

| Test Conditions | |
|---|----------------------------|
| Samples | Cement paste / mortar |
| Geometry | V14 (4 blade) in a C25 cup |
| Temperature | 2.3°C |
| Toolkit_V003 Yield Stress (Stress Ramp) | 0.1 - 700 Pa up |
| Ramp time | 120 s |
| No. of samples | 60 |



Vane tool

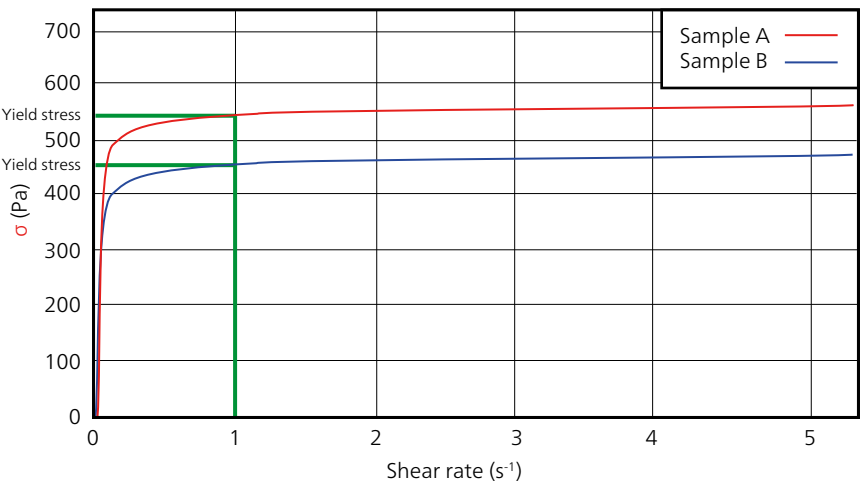


Figure 64. Shear stress vs. shear rate. In this stress sweep we are using an arbitrary nominal shear rate of 1 s⁻¹ to indicate when the samples are starting to flow slowly, however other shear rates may be used as desired.

On application of stress, a sample with a yield stress initially acts as an elastic solid, just deforming slightly, but not actually flowing. In this case, the shear rate will be around zero until the stress applied becomes higher than the sample's yield stress. A plot of shear stress against shear rate clearly shows when the material starts to flow.

Interpretation

The yield stress is often taken as the stress point where the shear rate exceeds 1 s^{-1} . Figure 64 indicates that sample A showed a yield stress of 540 Pa and will therefore resist flowing much more effectively than sample B, which exhibited a yield stress of 450 Pa. There is, however, a more mathematical approach, given below.

Slump Resistance

The slumping force of a mortar on a surface can be calculated with the following formula if the density and film thickness are known:

$$\sigma_{\text{yield}} = \rho \cdot g \cdot h \cdot \sin \beta$$

ρ = density ($\text{kg} \cdot \text{m}^{-3}$)
 h = film thickness

g = gravitational acc'n ($9.81 \text{ m} \cdot \text{s}^{-2}$)
 β = tilt angle (degrees)

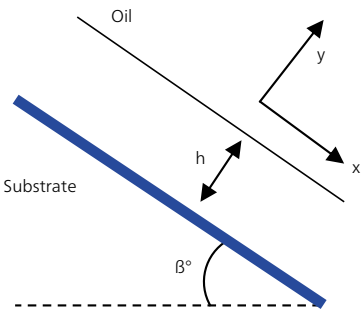


Figure 65. Model of an inclined surface can be used to calculate the sagging stresses that a cement will experience.

If the slumping stress exceeds the sample's yield stress, then the sample could be expected to flow and hence slump when applied.

Conclusion

The yield stress can be used to evaluate mortar formulations to predict whether they will be fit for an application. Higher yield stress materials will give good slump resistance, but poor leveling properties and vice versa.



Glossary of Terms

| <i>Term</i> | <i>Definition</i> | <i>Unit</i> |
|----------------|---|----------------|
| AASHTO | American Association of State Highways Testing Organizations | - |
| ASTM | American Standard Test Method | - |
| CP | Cone and Plate | - |
| DMTA | Dynamic Mechanical Thermal Analysis | - |
| DSC | Differential Scanning Calorimetry | - |
| HTC | High-Temperature Cell | - |
| G^* | Complex modulus (oscillatory stress/oscillatory strain) | Pa |
| G' | Storage (or elastic) modulus ($G^* \cdot \cos \delta$) | Pa |
| G'' | Loss (or viscous) modulus ($G^* \cdot \sin \delta$) | Pa |
| Hz | Hertz – frequency in oscillations per second | - |
| LVER | Linear Viscoelastic Region | - |
| OB | Original Binder | - |
| PAV | Pressure Aging Vessel | - |
| PP | Parallel Plate | - |
| RTFO | Rolling Thin Film Oven | - |
| SHRP | State Highways Research Program | - |
| UV | Ultra Violet | - |
| $\dot{\gamma}$ | Shear rate (shear strain/shearing time) | s^{-1} |
| γ | Shear strain (deformation/height of sample) | - |
| δ | Phase angle – a lag between the applied function and measured function in oscillating testing | ° (degrees) |
| η | Viscosity (shear stress/shear rate) | Pa.s |
| η^* | Complex viscosity (osc' shear stress/osc' shear rate) | Pa.s |
| ρ | Density | $Kg \cdot m^3$ |
| σ | Shear stress (force/area) | Pas |

NETZSCH-Gerätebau GmbH
Wittelsbacherstraße 42
95100 Selb
Germany
Tel.: +49 9287 881-0
Fax: +49 9287 881 505
at@netzsch.com

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