

Practical course Rheology

Bachelor

Introduction

Rheology is the science of flow and deformation of matter. In general, it is studied how materials respond to mechanical forces in terms of stress-strain relationships. Most materials in everyday life are either fluid or solid. However, this lab class is intended to show that all materials are described by both, an elastic and a viscous component at the same time. The degree to which materials appear viscous or elastic depends on the rate of deformation, as well as the magnitude of deformation. The theory of visco-elasticity provides a proper description of the mechanical properties. In the limit of linear visco-elastic response the material is elegantly captured by equivalent networks of simple springs and dash-pots. In this practical course, you shall learn how to determine the viscoelastic properties using a plate-rheometer, where materials are sheared between to plates.

Basic principles

Hookean solid

The simplest form of deformation, when a material is loaded by a force, is the uniaxial extension (**Fig.1**). We measure the relative elongation, $\varepsilon = \Delta L/L$, called "strain", as a function of applied force, F_{\perp} , per cross-sectional area, A , which is called "stress", $\sigma_{\perp} = F_{\perp}/A$. Robert Hooke observed that for many materials there is a linear relation between force and extension (*ut tensio, sic vis*, "as the extension, so the force; *Lectures de Potentia Restitutiva* in 1678) and hence

$$\sigma_{\perp} = E \cdot \varepsilon$$

The proportionality constant E is called the elastic modulus or "Youngs-modulus". Materials that exhibit a linear stress-strain relation are called "hookean" and behave like an elastic spring, $F = k \cdot \Delta L$, with spring constant, $k = A \cdot E/L$.

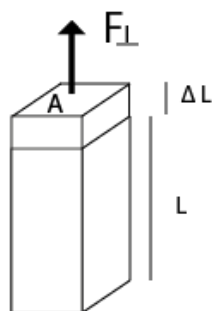


Fig. 1: Hookean solid. A material is extended uniaxial by the applied force F_{\perp} per cross-sectional area, A , resulting in the relative elongation $\varepsilon = \Delta L/L$.

Shearing is the deformation of a material/substance, in which parallel surfaces are sheared past one another (**Fig. 2**). By moving the upper plate by a force F_{\parallel} the sample under the area A is *sheared*.

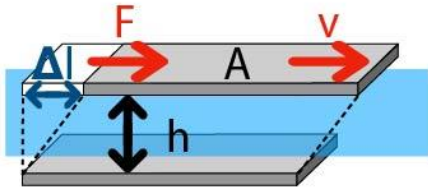


Fig. 2: Two-plate-model of shear rheometry: A sample (blue) in the gap of height h is placed between two plates (grey). The upper plate (shear area A) moves with shear force F . The effective velocity v shows the resistance of the sample. This leads to a displacement Δl of the upper plate.

We measure the shear angle $\gamma = \Delta x/y$ ($\gamma = \Delta l/h$), i.e. the displacement over the plate separation, y , as a function of shear stress.

$$\sigma_{\parallel} = G \cdot \gamma$$

The corresponding modulus G is called the shear modulus. For homogenous material the Youngs modulus and shear modulus are related by

$$G = \frac{E}{2(1 + \mu)}$$

Where μ denoted the Poisson ratio, $\mu = (\Delta d/d)/(\Delta L/L)$, i.e. the ratio of relative lateral thinning to relative extension.

Note that both, elongation and shear, represent linear elastic deformations that can be presented as spring-like behaviour. The deformations are proportional to force, when load is applied and do not change as long as the strain stays the same. The material returns instantly to its original state, when the load is released. Energy is stored and fully recovered.

Non-linear deformation

As described above is the linear-elastic behaviour described by the hookean law. However, specific materials such as rubbers show a non-linear behaviour. Here, the strain does not depend linearly on the deformation. This called rubber elasticity describes the mechanical behaviour of many polymers, especially those with cross-links. A deformation of a polymer leads to an extension of macromolecules or segments of it, that return reversible to the previous state as soon as the strain is released. If the deformation is irreversible, we have a plastic deformation (**Fig. 3**).

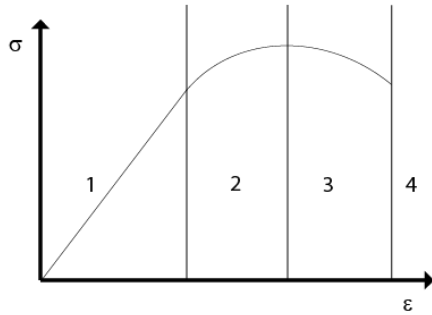


Fig. 3: Stress-strain diagram: 1) Linear-elastic deformation (Hookean). 2) Plastic-deformation. 3) Constriction. 4) Rupture.

Newtonian Fluid

The resistance to motion, when fluids are deformed, was first described by Sir Isaac Newton. He called it *lack of slipperiness* between fluid particles in his book *Philosophiae Naturalis Principia Mathematica*. It is stated that the required force F to keep a steady motion of two planes relative to each other is proportional to the relative velocity, u , between the two surfaces.

$$F = A \cdot \eta \cdot \frac{u}{h}$$

The relation defines the dynamic viscosity, η . Since the ratio of velocity to plate distance is equal to the strain rate $\dot{\gamma} = d\gamma/dt = u/h$, the constitutive equation of viscosity reads

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

Note that the viscosity is also dependent on the concentration of the substance:

$$\eta = \eta_0 + [\eta]c$$

with η_0 the viscosity of pure water, $[\eta]$ the intrinsic viscosity of the substance and c the concentration of the substance.

For polymers this linear relationship does not hold. Here, at small polymer concentrations we find a linear dependency of the viscosity on substance concentrations. However, further increasing the concentration leads to a strong increase in viscosity. This observation can be explained on the basis of the behaviour of the molecules in solution. At dilute solutions, the polymer chains are separate from one another and exist as individual coils. As concentration increases, the polymers overlap and entangle. This concentration is called the coil overlap concentration c^* for polymer solutions. Beyond the overlap concentration, the viscosity increases dramatically (**Fig. 4**).

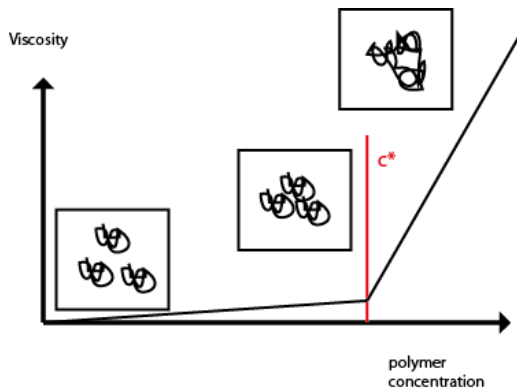


Fig. 4: Viscosity increases non-linearly for polymers in solution. Red line indicates the coil overlap concentration c^* .

Non-linear flow behaviour

It is shown that a material can respond differently depending on the deformation time. Elasticity means that the substance instantly returns to its original shape, whereas viscous deformation is observed when the shape of the object changes due to the applied force. The substance is then plastically deformed. There are several types of flow behaviour depending on the observed fluid (**Fig. 5**) that are discussed in the following.

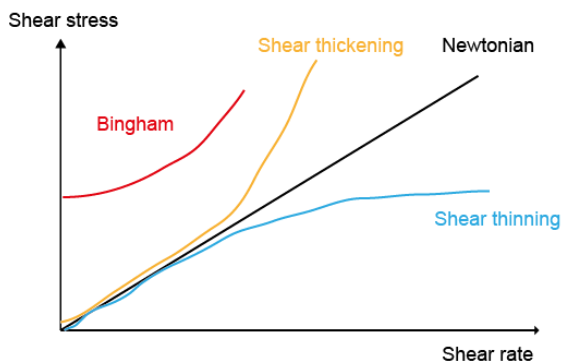


Fig. 5: Non-linear response of fluid-like materials. A Newtonian fluid shows a linear response. Hence, viscosity is independent on the shear rate. If the molecular structure of a fluid breaks down with increasing shear rate, this property is called shear thinning. The opposite is called shear thickening or dilatancy. A Bingham plastic has a yield stress and for higher shear rates a viscosity independent of the shear rate.

Newtonian Behaviour

Newtonian fluids have a direct proportionality of shear rate and shear stress. This means, that the viscosity is independent on the shear rate over a wide range of shear rates. Examples are water, oil, glycerol or honey.

Shear thinning

Shear thinning happens due to the breakdown of the molecular structure in a sample, because there are hydrodynamic forces generated during shear. Hence, an increasing shear rate means a less than proportional increase in shear stress. Consequently, the viscosity decreases with the shear rate. Examples: Shower gel, yoghurt, toothpaste, styling gel, marmalade.

Shear thickening

Shear thickening happens due to an increase of size (dilatancy) or amount of structural units within the substance because of shear. An increasing shear rate means a more than proportional increase in shear stress. Consequently, the viscosity increases with the shear rate. Example: starch dispersions.

Yield stress

For some materials, there is no flow until a specific threshold. The yield stress has to be exceeded or the substance behaves like a solid. Due to the yield stress, the viscosity is dependent on shear rate also for low shear rates (Bingham-Plastic).

Thixotropic Behaviour (Time dependent)

When the viscosity of a material decreases over time while the shear rate is kept constant, it is called thixotropic. Here, the molecules in the fluid are linked together at weak forces. At high shear rates, or if shear stress is present over a longer time, these inter-molecule linkages are broken. This results in a disruption of the structural units, which weakens the resistance to flow during shearing. Thixotropy can be measured when you analyse the viscosity with rising shear rate and directly afterwards with a falling shear rate. When the first curve shows larger values for the viscosity than the second one, the substance is called thixotropic (**Fig. 6**). Examples: paint, salad dressings, soft cheeses. The opposite of thixotropic behaviour is antithixotropic. Here, viscosity increases at a constant shear rate with time. This is due to intermolecular interactions causing increasing friction over time, when a steady shear stress is applied. Example: printing ink.

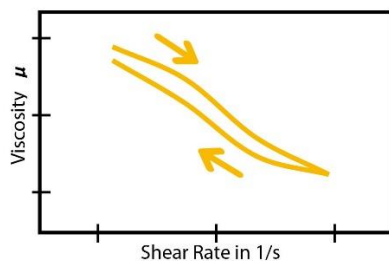


Fig. 6: Thixotropic behaviour. When measuring the viscosity of a substance with rising shear rates and immediately afterwards with falling shear rates, the second curve is lower.

Linear visco-elasticity

In linear visco-elasticity we combine elastic and viscous behaviour in one material, but consider only linear response in both elasticity and viscosity. The combination is best represented by so-called equivalent models, where elastic and viscous components are represented by combinations of springs and dash-pots.

The Hookean solid is represented by a spring as described above. Since in the following we are only concerned with shear deformation, we represent the material property of the spring by the shear modulus G .

The Newtonian fluid is presented schematically by a dashpot, because an ideal fluid flows with the input of deformation energy. A dashpot consists of a cylinder filled with

liquid. In there, a piston is immersed and does not touch the walls of the cylinder (**Fig. 7**). The extension of a dashpot is irreversible and it therefore resembles the deformation of a fluid. The added energy dissipates completely, which means that it is converted to heat. This makes it impossible for a dashpot to return to its original state. The rate of deformation is proportional to the applied force.

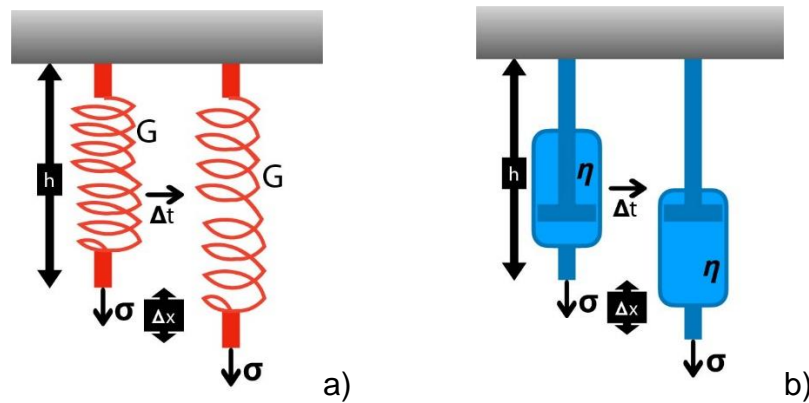


Fig. 7: The Hookean solid is represented by a spring (a) and the viscous fluid by a dash-pot (b). a) The spring as a schematic model for the elastic component of a sample. It has a modulus G and an initial height h . The result of a force σ over time Δt is a displacement Δx . b) The dashpot as a schematic model for Newtonian flow behaviour. It is filled with a fluid of viscosity η and has an initial height h . The result of a force σ over time Δt is a displacement Δx .

Maxwells Model of Viscoelasticity

James Maxwell argued in his paper *On the Dynamical Theory of Gases*, that a material could exhibit simultaneously both fluid and solid reactions when deformed. A material of this type can be depicted by a dashpot and a spring connected in series (**Fig. 8**). When you externally apply a load and remove it, part of the deformation energy is used to get back to the original state, while the other part is lost, which means converted to heat energy. Real materials are called viscoelastic, because they combine these two components.

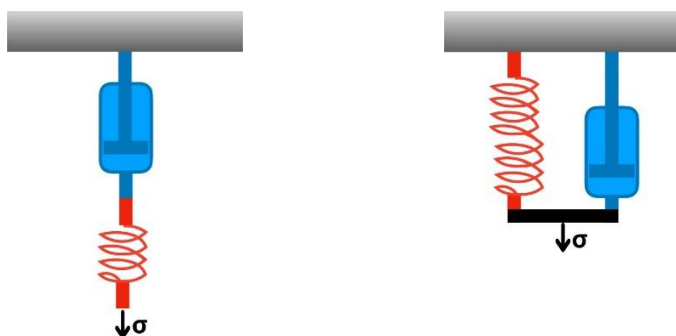


Fig. 8: Maxwell and Voigt Model. Left) A dashpot and a spring connected in series as an illustration of the Maxwell model. Right) A dashpot and a spring connected in parallel as an illustration of the Voigt model.

The force σ leads to a mixture of both the dashpot's and spring's behaviour.

In the Maxwell model the stress σ applied to both viscous and elastic element of the material is equal $\sigma = \sigma_\eta = \sigma_G$, while the total strain γ is the sum of the fluid and solid strains: $\gamma = \gamma_\eta + \gamma_G$. Hence the strain rate of the Maxwell model is a linear superposition

$$\frac{d\gamma}{dt} = \frac{d}{dt} (\gamma_\eta + \gamma_G) = G^{-1} \frac{d\sigma}{dt} - \eta\sigma$$

For the particular case of an instantaneous strain deformation, i.e. a strain jump in time, $\gamma(t) = \gamma_0\Theta(t)$, the differential equation is solved by the following time dependent stress function

$$\sigma(t) = G\gamma_0 \cdot \exp(-t/\lambda)$$

Hence the Maxwell model builds up stress due to the elastic element, but the stress relaxes exponentially with relaxation time $\lambda = G/\eta$ due to the viscous flow element. Obviously at large time scales the Maxwell model behaves like a fluid and viscoelastic fluids are often presented in the form of the Maxwell model.

Voigt Model

The Voigt Model is used to describe viscoelastic solids, which return to the original shape when deformed. In order to describe the behaviour of viscoelastic solids a description was introduced that corresponds to a dashpot and a spring connected in parallel (**Fig. 8**). The connection in parallel allows for a complete recovery to the original state.

Viscoelastic properties

In order to address viscoelastic properties, one typically carries out an oscillation test, where a substance is subjected to a stress or strain input of a frequency in a range of about 0.1 Hz to 10 Hz. The strain or stress response is then measured.

Let us consider an oscillatory strain.

$$\gamma(t) = \gamma_0 \sin(\omega t)$$

Then the resulting time dependent stress, which is measured in the transducer, will show the same frequency, but depending on the material, might exhibit a phase shift

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

Decomposing the phase shifted oscillation into sin and cos terms, the stress is seen to contain a component which is in phase with the strain and another component which is in phase with the strain rate, $\dot{\gamma}(t) = \gamma_0 \cos(\omega t)$. By definition it follows

$$\sigma(t) = \sigma_0 (\cos(\delta) \sin(\omega t) + \sin(\delta) \cos(\omega t)) = G \cdot \gamma(t) + \eta \cdot \dot{\gamma}(t)$$

This relation is more elegantly written as a complex stress-strain relation:

$$\sigma(t) = \gamma_0 (G' \sin(\omega t) + G'' \cos(\omega t)) = G^* \cdot \gamma(t)$$

where the shear modulus, G^* , is now a complex quantity constituted by a real and imaginary part:

$$G^* = G' + iG'' = \frac{\sigma_0}{\gamma_0} (\cos(\delta) + i \sin(\delta))$$

G' is called the storage modulus and G'' the loss modulus. The storage modulus describes the elastic component of the material. The name refers to the fact that elastic deformation can store mechanical energy. The loss modulus represents the viscosity $\eta = G''/\omega$ and refers to the dissipation of energy in viscous fluids. The ratio of loss modulus to storage modulus is called the loss factor, $\tan(\delta) = G''/G'$. For an elastic solid the loss factor is 0, for a viscous fluid it is ∞ . A loss factor of 1 means the substance is at a transition between a liquid and a solid state. This transition point is called the gel point.

Schematic diagrams of a shear strain input γ with the resulting shear stress response σ are shown in **Fig. 9**. A perfectly elastic sample (Hookean solid) has a phase angle of zero between strain input and stress response. An ideal fluid under oscillatory strain shows a stress response σ proportional to the strain rate $\dot{\gamma}$. This corresponds to a phase angle of $\delta = \pi/2$ in the response.

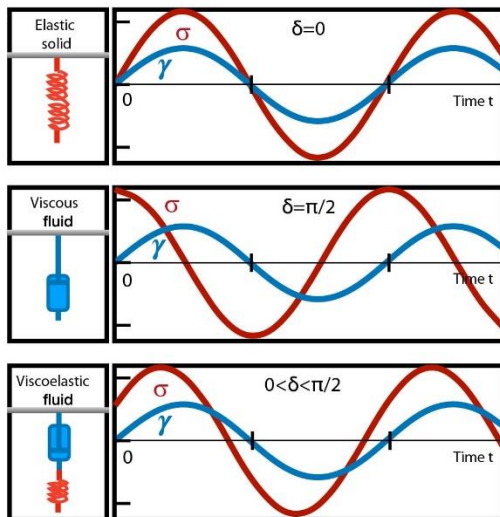


Fig. 9: Oscillation shear experiments.

Schematic diagrams of shear strain γ (blue curve) with the resulting shear stress response σ (red curve).

For a phase angle of $\delta = 0$, the sample is an elastic solid.

For a phase angle of $\delta = \frac{\pi}{2}$ the sample is a viscous fluid.

A viscoelastic fluid shows a phase angle between 0 and $\frac{\pi}{2}$.

Basics of the experiment

The instrument used to study the viscoelastic properties of a material is a rheometer. There are several types of rheometers that one can use depending on the substance and the objective (sliding plate rheometer, a rotational rheometer, a capillary rheometer, extensional rheometer). Here, we will use a rotational rheometer (**Fig. 10**). Here, the sample is loaded between two plates. By applying a torque (a rotational shear stress) to the upper plate, the resulting strain, strain rate or shear rate is measured.

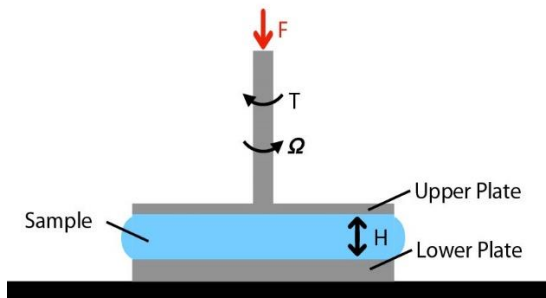


Fig. 10: The rotational plate-plate rheometer. The sample (blue) is put between two plates (grey). The applied angular velocity Ω results in a torque T under consideration of the total normal force acting on the fixed plate F .

Here, we use the KINEXUS ultra+ rheometer by Malvern Panalytical. You will find a handout describing how to use the instrument next to the rheometer in the lab. During the course, you will perform different types of rheological experiments that are described shortly in the following.

Viscosity versus shear rate

You measure the viscosity of your sample as a function of the shear rate. The range of the shear rate of a typical experiment is 10^0 to 10^2 (1/s). To characterize the sample, the dependence can be described by a power law. The viscosity of a Newtonian fluid does not depend on the shear rate (**Fig. 11**). A gel shows a slope of $-1/2$ and a viscoelastic solid has a slope of -1 .

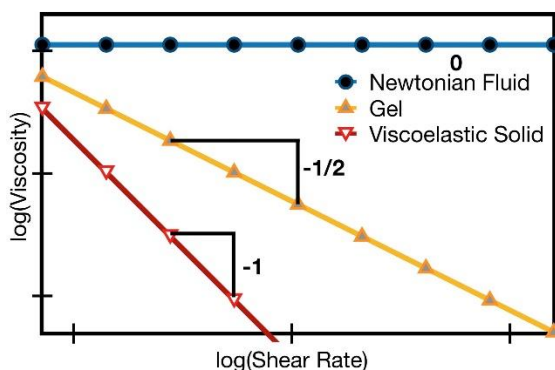


Fig. 11: The power law as a first characterization of a sample. Newtonian fluid (blue), gel (yellow) and viscoelastic solid (red).

Oscillatory experiment: Amplitude sweep

Here, an oscillatory shear strain is applied to a sample. Over time, the shear strain amplitude rises at a fixed frequency (**Fig. 12**). The interesting measured values of this experiment are the storage modulus G' and the loss modulus G'' (**Fig. 12**). A constant plateau of G' (or G'') indicates a linear viscoelastic region. At a specific shear rate G' decreases. Here, the relation between the shear rate and G' is no longer linear and the sample softens. If $G'' > G'$ in the linear regime, the dominating loss modulus indicates a fluid behaviour. If $G' > G''$, you have a solid or gel-like substance. If G' crosses G'' , the sample starts to flow. This is the yield point. This type of experiment is needed to determine the linear viscoelastic region. The corresponding shear strain is later on used for a frequency sweep.

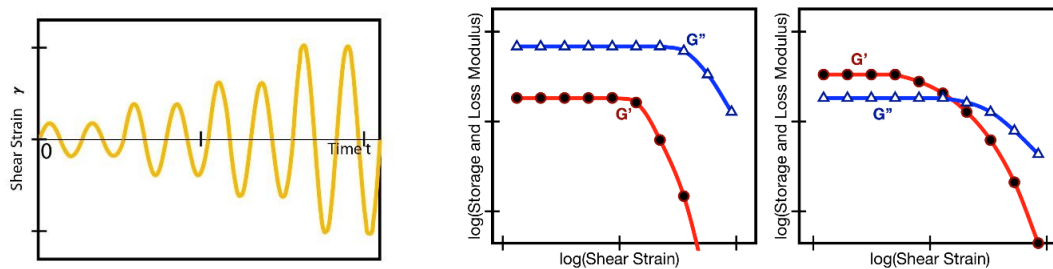


Fig. 12: Amplitude sweep: Left: the shear strain applied to the sample increases step-wise over time at a selected frequency. Middle: Exemplary result of an amplitude sweep of a viscoelastic fluid. Right: Exemplary result of an amplitude sweep of a gel.

Oscillatory experiment: Frequency sweep

It is also possible to change the frequency at a constant shear strain as an oscillatory experiment (**Fig. 13**). The applied shear strain should be chosen according to the previous amplitude sweep, so that the shear strain lies in the above described linear viscoelastic region. In this experiment, again G' and G'' are determined. If $G' < G''$ at low frequencies, the sample is a viscoelastic liquid. In some cases, G' crosses G'' at higher frequencies. Here, the so-called critical stress is reached. If $G' > G''$ without a frequency dependence, your substance is gel-like (meaning it has more structure). For high frequencies G'' might exceed G' . This is the yield point, at which the sample starts to flow.

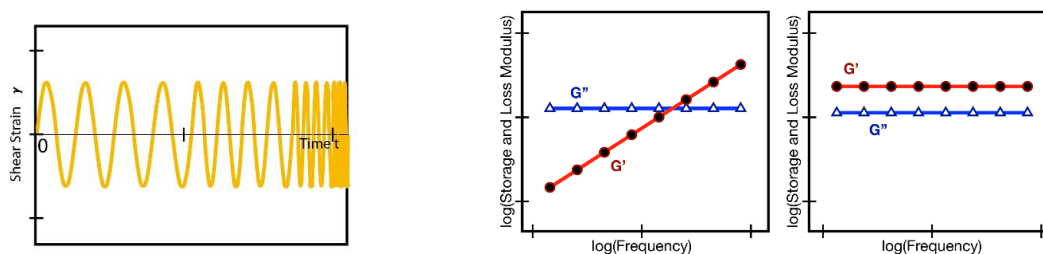


Fig. 13: Frequency sweep. Left: The frequency applied to the sample increases step-wise over time at a selected shear rate. Middle: Exemplary result of a frequency sweep for a viscoelastic fluid. Right: Exemplary result of a frequency sweep for a gel-like substance.

For polymers such as guaran G' crosses G'' at a specific frequency. The polymer goes from a viscous behaviour to an elastic one at this frequency. In general, one can determine four regions for a polymer melt shown in **Fig. 14**.

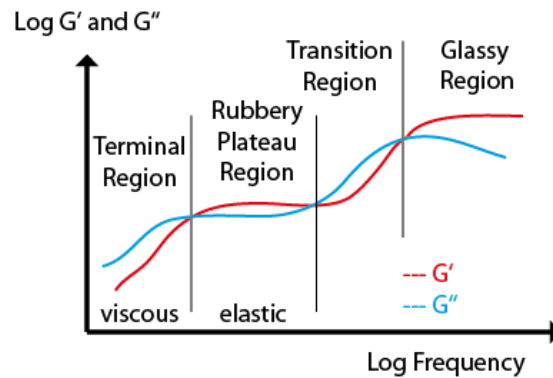


Fig. 14: The viscoelastic spectrum of a polymer melt

Your experiments

Detailed instructions on how to use the instrument, you will find in the handout lying next to the instrument. You will perform two experimental series:

Water-sucrose

Sucrose also termed Saccharose is a disaccharide containing the single sugars fructose and glucose.

- Prepare the following solutions: 0%, 10%, 20% and 40% sucrose-water solution.
- Investigate the viscosity versus the shear rate (Program: Shear Rate Table for Waterlike Samples, choose 10^0 to 10^2 shear rate, 25°C , 5 samples per decade, Tskip after 1 min)

Answer the following questions in your protocol:

- Plot viscosity versus shear rate (double log plot). Determine a power law relation from the slope in the double log plot.
- Plot shear stress versus shear rate (double log plot). What type of flow behaviour do you observe?
- Plot the viscosity versus sucrose concentration. What dependency do you find? Determine the intrinsic viscosity.
- Interpret all your results: Are your results in line with your expectations?

Guaran

Guaran, also called guar gum, is a polymer. In detail it is a galactomannan polysaccharide extracted from guar beans that has thickening and stabilizing properties useful in food, petroleum or paper industry.

- Prepare the following solutions: 0%, 0.25%, 0.5%, 1%, 1.4%, 2% and 2.3% Guaran-water solution. Add directly into water and stir immediately.
- Please perform the following experiments:
 - A) Viscosity versus shear rate (Program: Toolkit_V001 Shear rate Table, choose 10^0 to 10^2 shear rate, 25°C, 5 samples per decade, Tskip after 1 min).
 - B) Frequency sweep (Program: Toolkit_O002 Frequency table (strain control), choose 0.01 to 200 Hz, 25°C, 5 samples per decade, shear strain 0.5%, Tskip after 1 min).

Answer the following questions in your protocol:

A)

- Plot viscosity versus shear rate (double log plot). Determine a power law relation from the slope in the double log plot.
- Plot shear stress versus shear rate (double log plot). What type of flow behaviour do you observe?
- Plot the viscosity versus Guaran concentration. What dependency do you find? Determine the coil overlap concentration c^* .
- Interpret all your results: Are your results in line with your expectations?

B)

- Plot G' and G'' versus frequency
- Determine the frequency at which the polymer transits from a viscous behaviour to an elastic one.
- How many regions of the viscoelastic spectrum of the polymer have you been able to determine?
- Interpret all your results: Are your results in line with your expectations?