ELEMENTIS

A global specialty chemicals company

Application Leaflet

Rheology in a nutshell - Part 2

Brief overview of rheological characteristics

- Measurement of viscoelasticity
- Oscillatory tests

Enhanced Performance Through Applied Innovation

Introduction

Rheology is the study of how materials deform and flow under the influence of external forces. Understanding the background of this science is essential when formulating modern paint systems.

Rheological additives control the flow characteristics of a system. They do not only “thicken” a liquid, they modify the flow behaviour and structure in a predictable way to control sag resistance, storage stability, application behaviour, spatter resistance, levelling, film thickness and film appearance.

Rheological behaviour can be determined by several different types of measurement, of these **rotational** and **oscillation** are the most important.

It is also important to understand that viscosity can be measured by rotational testing and oscillatory measurements are used to determine the so called viscoelasticity.

Definition viscoelasticity

A purely viscous system, such as water, oil or honey, will strictly obey Newton´s law. It does not store energy and all the deformation energy is dissipated as heat. After deformation has stopped, the fluid has no “memory” of earlier events.

A purely elastic system, such as a steel spring, will recover its stored deformation energy completely independent of the amount and duration of load after an applied force is removed. An ideal elastic system obeys Hooke´s law, where the shear modulus G is defined as the ratio of the shear stress τ over the deformation γ of the material (*Figure 1*).

$$G\ [\mathrm{Pa}] = \frac{\tau\ [\mathrm{Pa}]}{\gamma}$$

Figure 1: Hooke`s law

A *viscoelastic* system shows both viscous and elastic characteristics. Most coating systems are viscoelastic due to their internal structure. The behavior of a viscoelastic liquid can be described with the dashpot-spring (Maxwell) model.

In *Figure 2* the spring represents the elastic part and the dashpot represents the viscous portion in a viscoelastic system (A). When a constant force (F) is applied (B), the spring shows immediate deformation (stretching) up to a constant position proportional to the applied force. Further deflection under the constant force will then be seen as a movement of the piston (C). After the force is removed (D), the piston will remain deflected (cf viscous or loss modulus) whereas the spring will recover to its original position (elastic or storage modulus)

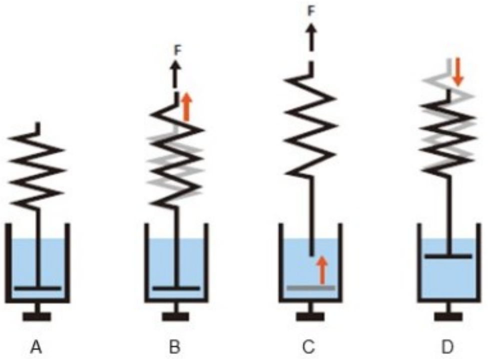

Figure 2: Dashpot-spring model

Viscoelasticity is typically determined in an oscillatory experiment. To carry out such a test, two units, the amplitude (strain) and the frequency, need to be controlled. One of the both units needs to be kept constant (*Figure 3*).

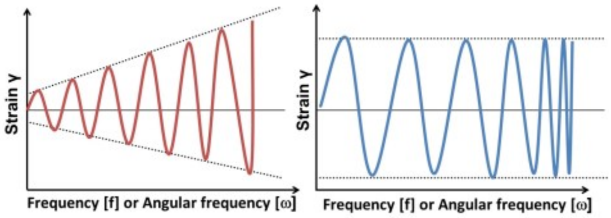

Figure 3: Amplitude and frequency tests

Linear-viscoelastic range

The starting point of such measurement is a so called amplitude sweep and is typically carried out to define the linear-viscoelastic (LVE) range, the yield point as well as the flow point. The LVE range can be defined as the strain range in which the samples structure remains stable.

Practically, in oscillatory experiments, the rheometer is able to differentiate between elastic and viscous behaviour of a sample. The elastic part, the internal structure of a system is described as the storage modulus G`, whereas the viscous part is represented as the loss modulus G”. Two curves for each sample are the result of such measurements (*Figure 4*).

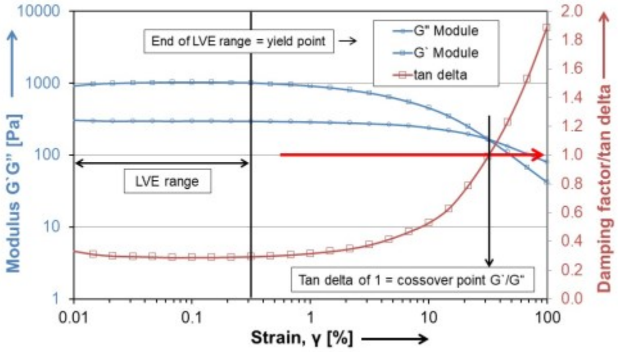

Figure 4: Typical graph aplitude sweep

In case G` acts above G” a dominant elasticity can be concluded for the relevant range of strain. In such case the structure fully recovers to its original level after stress removal without disrupting or changing the internal structure. In the opposite case, G” is acting above G` the viscose character dominates at the applied strain.

Alternatively to G`/G“ the so called damping factor can be utilized (*Figure 4*). This value, often simply called tan delta, is the factor out of G” and G`. In this case only one curve per sample is shown. Damping factors of below 1 indicate dominant elasticity at the relevant strain (dominant G`). If the damping factor is above 1 (dominant G“), the sample displays a fluid character.

The end of the LVE range is defined as the point were the upper, dominant curve starts to decline. This is also visible as an incline of the damping factor curve. The end of the LVE range is also defined as the yield point. In the case of ideal viscous samples, the G” curve is dominant (tan delta above 1). In this case an LVE range but no yield value can be detected.

In case of further strain increase beyond the end of the LVE range, both lines, of G` and G” will cross at a certain strain. This crossover point is the so called flow point so that priorly elastic samples are starting to flow. Alternatively, the flow point is also indicated by a damping factor of exactly 1.

Acting within the linear-viscoelastic range allows to determine the behavior of a material at ultra-low or low stress e.g. to estimate properties such as the storage stability. Also controlled dismantling of the internal structure is possible.

In general, determining the LVE is best carried out when either the moduli (G`; G”) or the damping factor have been plotted as a function of the strain. Alternatively to the strain the shear stress can be plotted on the X axis. This is especially preferred in case of yield/flow point detection.

Amplitude test interpretation

In summary, an amplitude test delivers the following information:

- ♦ Dominant storage modulus G`; damping factor < 1
  - Dominant elastic character
  - System might not be flowable
  - No disruption of structure within LVE range
  - The larger the distance between G` and G” the larger the elastic domination
  - Parallel shift towards higher moduli indicates higher rigidity and stiffness
  - Crossover point G`/G” shifted towards higher strain/shear stress indicates higher stress requirement to initiate flow
- ♦ Dominant loss modulus G”; damping factor > 1
  - Dominant fluid character
  - Disruption of structure
  - Detectable LVE range without yield/flow point
  - The larger the distance between G” and G` the larger the fluid domination
- ♦ Moduli (G`/G”) or damping factor plotted as function of strain for
  - LVE range determination (preset for frequency sweep test)
  - Temperature sweeps
- ♦ Moduli (G`/G”) or damping factor plotted as function of shear stress for
  - Determination of relevant stress level for yield value and flow point detection

Frequency sweep

Measurement of the structural strength is typically carried out with a frequency sweep. The rheometer software will calculate the storage (elastic) modulus G’ and the loss (viscous) modulus G” as a function of the oscillation frequency. The frequency is typically indicated as angular frequency (ш [s^{-1}])

The amount of strain applied (amplitude) has to be held constant within the LVE range (detected in an amplitude sweep). Measuring storage and loss moduli as well as tan delta as a function of frequency can shed light on interactions between various parts in the system and help predict stability (*Figure 5*).

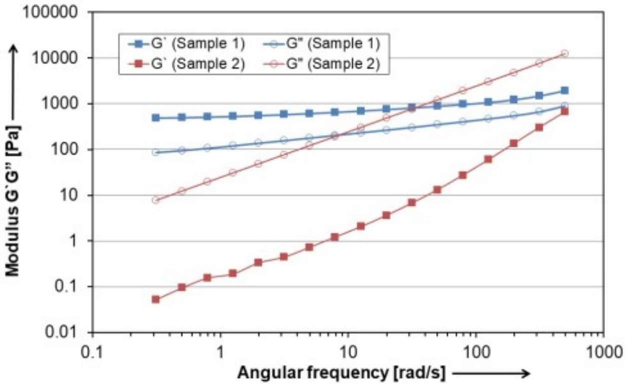

Figure 5: Frequency sweep plotted as moduli G`/G“

The relationship between G´ and G“ at low angular frequencies indicates the behavior of the material under storage conditions. A high G´, storage or elastic modulus, relative to the G”, loss or viscous modulus, is typically desired at low frequencies to keep solids in suspension. In case of sample 1 the G´ acts above G” at all tested angular frequencies which is indicating stable conditions. In case of sample B, G” is well above the G´ at low, medium and high frequencies. Both are inclining parallel with rising angular frequency.

Alternatively, the data can be plotted as the damping factor/tan delta over the angular frequency (*Figure 6*).

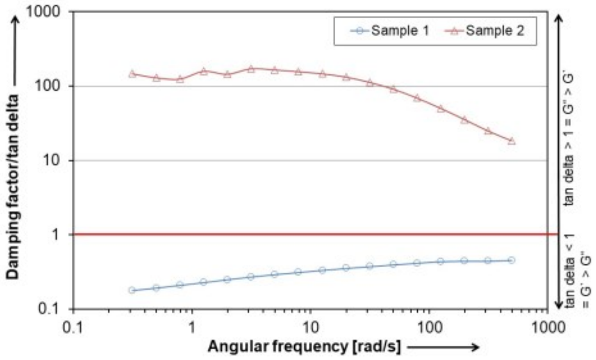

Figure 6: Frequency sweep plotted as damping factor

As mentioned previously, in the case of this type of representation, only one curve per sample is necessary. The data shown for sample 1 are acting below a damping factor of 1 over the entire tested range of frequencies. This describes equal to dominant G` (*Figure 5*) storage stability. Sample 2 displays tan delta values of above 1 over the entire range indicating practically no structure.

Frequency test interpretation

In summary, a frequency sweep delivers the following information:

- ♦ High frequencies represent short term applied stress
  - Short term stability
  - Performance at higher shear rates
- ♦ Low frequencies indicate long term applied stress
  - Long term stability
  - Behavior at lower shear
- ♦ Dominant G`/damping factor below 1
  - Parallel running curves towards low frequencies
    - ◊ Unchanged rheological structure
    - ◊ Long storage stability
  - Increasingly steep slope towards low frequencies with crossover point
    - ◊ Less resistant elasticity, system might show separation or settling
  - Reducing distance between G`/G” at higher frequencies
    - ◊ Reduced short term behaviour
  - Spreading curves at higher frequencies
    - ◊ Better short term stability
  - Large distance between both moduli curves (G` above G”, low damping factor)
    - ◊ Strong dominance of elasticity
    - ◊ Levelling might suffer

Structure recovery

In order to predict the application and post application behavior a time dependent structure recovery test can be utilized. For this typically three steps are carried out.

1. Low frequencies and strain
   - Within the LVE range
   - To simulate intact structure / pre application
2. Larger strain/frequency or oscillation
   - Outside LVE range
   - Structure breakdown
   - Simulation of application step
   - Alternatively high shear rotational step
3. Low frequencies and strain
   - Return to the conditions of step 1
   - Structure recovery
   - Post application behavior

All resulting data are plotted as a function of time.

An example graph of such a test is shown in *Figure 7*. In this case the viscoelasticity in step 1 and step 3 is shown as damping factor. Alternatively, the data can be plotted as moduli G`/G”. In step 2 rotational shear at high shear rates of 1000 s-1 were used. In this case no viscoelastic data was generated.

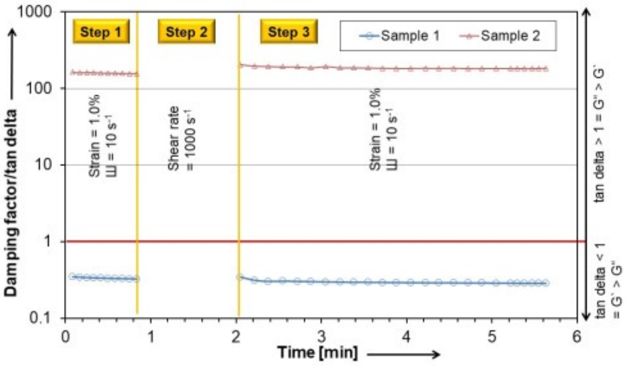

Figure 7: Viscosity recovery

In step 1 the behavior of the samples prior to the application is visualized. Sample 1 shows a very low damping factor (equivalent to strong dominance of G`) which indicates a high amount of structure and elasticity. In sample 2 the damping factor is on the high side (equivalent to strong dominance of G”), indicating practically no structure - the system flows.

In step 2 all structure (if relevant is broken down during application of the material, e.g. by spraying.

Step 3 shows again damping factor values of below 1 directly after finishing step 2. This indicates a quick redomination of the elastic character. This result might be an indication of good sag control. The levelling behavior of sample 1 might not be ideal.

In step 3, sample 2 displays equally high damping factor values. These samples typically demonstrate a very fluid behavior at rest. Due to the missing internal structure no sag control can be expected.

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