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Application Leaflet

Rheology in a nutshell - Part 1

Brief overview on rheological characteristics

- Measurement of viscosity
- Rotational 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 to 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 many coating properties e.g. 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.

Viscosity

Viscosity is the resistance of a material to flow. It is defined as the ratio of shear stress τ to shear rate γ (gamma dot) in accordance with Newton’s law (*Figure 1*).

$$\eta\ [\text{Pas}] = \frac{\tau\ [\text{Pa}]}{\dot{\gamma}\ [\text{s}^{-1}]}$$

Figure 1: Viscosity Newtons law

Newtons law has been defined as the factor out of shear stress τ [tau; Pa] and shear rate γ [gamma dot; s^{-1}]. The derivation and definition of both terms will be explained here.

Shear stress

A simplified theoretical two-plate model made up of very thin (molecular) layers is typically used to illustrate shear stress and shear rate (Figure 2).

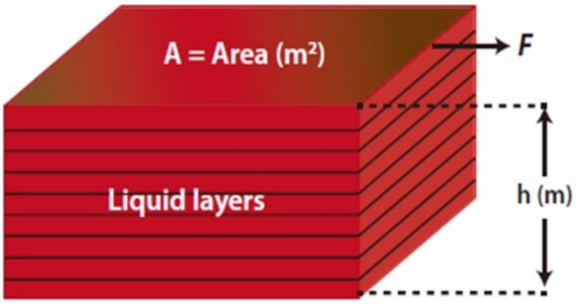

Figure 2: Two plate model

The sample has been positioned in between two plates. The upper plate is mobile whilst the lower plate is stationary. The shear stress is defined as the ratio of a laterally acting force (F [N]) on an area (A [m²]) of the upper plate (*Figure 3*).

$$\tau\ [\text{Pa}] = \frac{F\ [\text{N}]}{A\ [\text{m}^2]}$$

Figure 3: Definition of shear stress

This might result in laminar flow of the layers between the two plates when the force is large enough to overcome the internal structure (*Figure* 4).

Shear rate

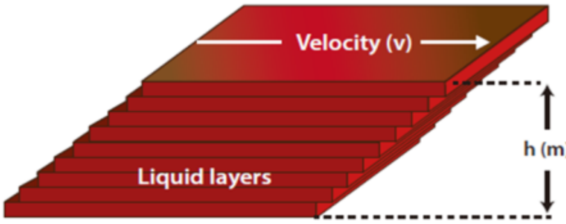

Figure 4: Shear rate in two plate model

The, in the case of flow, resulting velocity (v) is dependant on the internal friction (resistance) of the material between the layers and decreases to zero towards the lower, fixed plate. The ratio of the velocity difference (Λv) between the two layers, to the difference in layer thickness (Λh), which is constant, can be expressed as shear rate (i.e. rate of the deformation of the material, refer to *Figure 5*).

$$\dot{\gamma}\ [\text{s}^{-1}] = \frac{V\ [\text{m/s}]}{h\ [\text{m}]} = \frac{\text{m}}{\text{s}} \times \frac{1}{\text{m}} = \frac{1}{\text{s}}$$

Figure 5: Definition of shear rate

The following fact can be concluded:

- Applying a shear stress does not necessarily result in a movement, detectable as shear rate
- Shear indicates a speed gradient

Strain

The definition of strain (also called deformation) is especially important for yield point and oscillatory measurements (refer to the leaflet “Rheology oscillatory”). To explain this the two plate model can be used again (*Figure 6*).

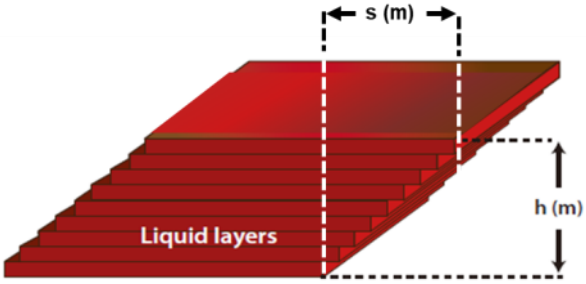

Figure 6: Strain in two plate model

The strain (γ [%]) is the ratio of the maximum length of elongation (s [m]) and the layer thickness of the material in the gap (h [m]). The formula used to calculate strain is shown in *Figure 7*.

$$\gamma\,[\%] = \frac{s}{h} = \frac{m}{m} \text{ x } (^{*}\,100) = \%$$

Figure 7: Definition of strain

Various shear rates

The shear rate applied during the application of the sample material can vary from several hundred up to hundreds of thousands of reciprocal seconds (s^{-1}), depending on the application method used. It is related to the film thickness (or nozzle diameter if spray or extrusion is applied) and to the application velocity or flow rate.

As an example, the shear rates generated during brush application of a paint system is illustrated in *Figure 8.*

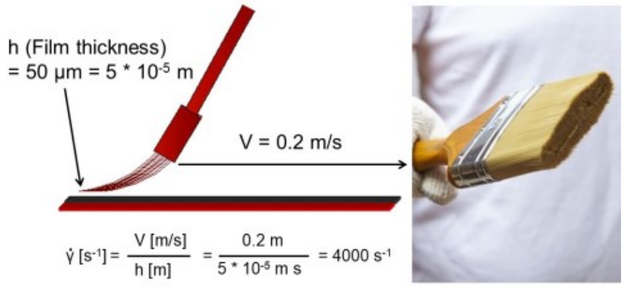

Figure 8: Shear rate calculation of brush application

The energy input by the brushing application is relatively low. However, the total paint volume impacted is very small (note, the value of “h” is very small). As a result, the shear rate is quite high.

Much higher shear rates are typically obtained during the spray application, for example in industrial coatings. As indicated already, the material layer thickness h in this case is defined by the spray nozzles diameter. The speed V of application can be taken from the volume rate applied during a certain time frame (*Figure 9*).

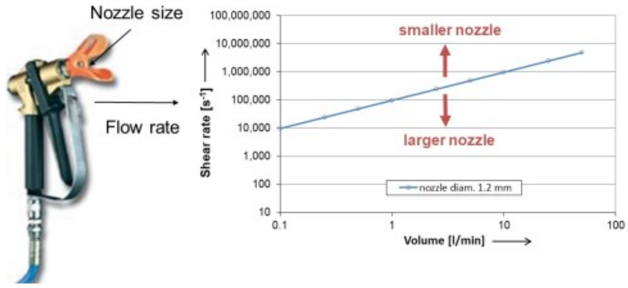

Figure 9: Shear rates for spray application

If the nozzle diameter is 1.2mm, according to the blue curve on the graph, the assumed shear rates start with low volume rates of 0.1 l/min at 10000 s^{-1}, with increasing volume rates shear rate levels of above a million being easily reached. Reducing the nozzle size, will shift the shear rate curve upwards, with smaller nozzle diameters are changing the resulting values in the same way.

During most application methods utilized in the construction market segment the shear rates are noticeably lower. Usually, trowel application finds use in areas like renderings and tile adhesives. Here, the applied layer thicknesses are much higher than with brush or spray applied materials. Also the application velocity might be different (*Figure 10*).

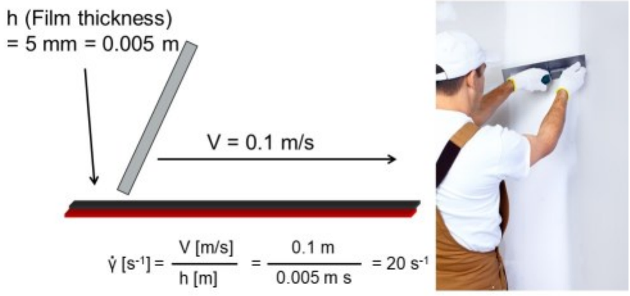

Figure 10: Shear rates from trowel application

The resulting lower shear rates are typically in a range of below 100 s^{-1} for such applications.

Viscosity profiles

A viscosity profile (*Figure 11*) or rheogram shows the dependence of viscosity on the applied shear rate. In such diagrams, the shear rate $\dot{\gamma}$ is plotted the x scale whilst the viscosity η is drawn on the Y scale.

There are a few main time-independent viscosity profiles which are represented by different flow characteristics.

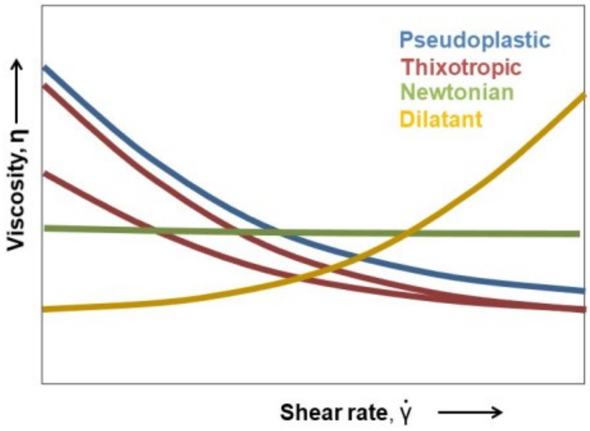

Figure 11: Different flow characteristcs

A viscosity profile (*Figure 11*) or rheogram shows the dependence of viscosity on the applied shear rate. There are three main time-independent viscosity profiles.

The green line in the graph indicates Newtonian flow indicating constant viscosity independent of the applied shear rate (e.g., water or mineral oil).

The yellow curve describes so called dilatant flow in which case the viscosity inclines with increasing shear rate. This behavior can often be seen in highly concentrated cornstarch solutions.

The blue curve displays pseudoplastic or shear thinning flow, where the viscosity decreases with increasing shear rates.

All the three flow characteristics described are time independent. As a consequence the viscosity is exactly defined at any given shear rate.

Thixotropic flow, displayed in the red curve, is time-dependent decrease of viscosity under constant shear or stress. The system will lose its internal structure under shear (mixing, rolling, spraying, etc.) but recover it over a period of time when the shear is removed. This will result in an upper (sheared) and lower (recovery) curve when running a viscosity shear rate profile. In a stable system, the low-shear viscosity will recover to its original value over time.

In *Figure 12* the hysteresis area between the upper and lower curves as a measure of the degree of thixotropy in a system is shown.

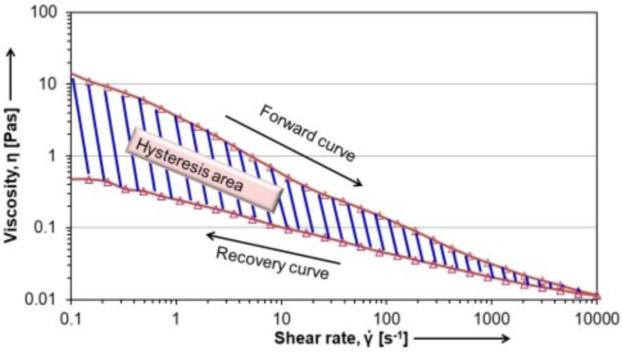

Figure 12: Rheogram - Hysteresis area

However, as the rheogram in *Figure 10* does not allow to determine the exact time for the recovery of the viscosity, another method to evaluate structural recovery is often utilized (*Figure 13*). The viscosity of a material is measured at the lowest possible shear rate until a constant value is achieved. The sample is then subjected to high shear to break down the internal structure (similar to application). The shear rate is then immediately reduced again to the lowest possible level and the recovery of viscosity is measured as a function of time. Recovery to the original viscosity value may take seconds, minutes, or hours, depending on the structure of the system.

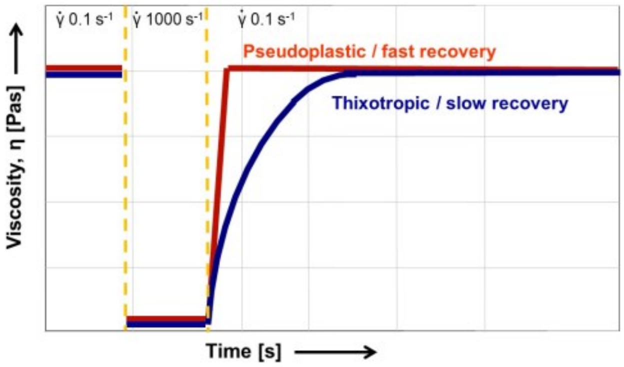

Figure 13: Viscosity recovery

This method can provide reliable information about sag and leveling behavior as it clearly describes the time period of recovery.

Yield values

A yield value is the minimum amount of shear stress required to induce flow. It is a measure of the strength of the internal structure in a system at rest. Once the applied external forces are higher than the internal structural forces, the system starts to flow.

Yield value is not a material constant and depends strongly on the measurement device and the method applied. It is also important to realize that no correlation is seen between viscosity (flow) and yield value (structural strength). Typical examples of yield values are shown in the following.

	Yield value [Pa]	Viscosity [Pas]
Honey	not detectable	11.0
Ketchup	14	0.1
Mayonaise	85	0.6

The most common way to determine the yield value utilizing a rotational method is the so called “tangent cross over” method (*Figure 14*).

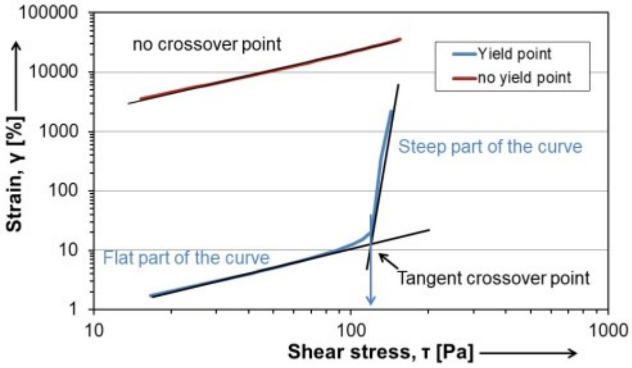

Figure 14: Tangent crossover method

After positioning the test material in the measuring gap of the rheometer, the shear stress is constantly being increased while the strain is detected.

In the case of strongly plastic material with a detectable yield value a certain stress will be required to induce the flow. As a consequence the first part of the resulting blue curve on the graph will be flat. However, in case the stress applied exceeds the internal structure of the sample, the curve suddenly becomes steep. This moment is typically indicated as a characteristic “kink”. Two mathematic regressions, of the flat and of the steeper part, of the curve will be carried out. The tangent crossover point can be taken where the extended regressing curves meet. The yield value can than be read off the shear stress curve in Pa.

A more modern method would be oscillatory. Please refer therefore to the leaflet “Rheology oscillatory”.

Practical relation

Figure 15 illustrates the relationship between shear rate and coatings properties. The way a fluid flows over the entire shear rate range influences certain properties. Therefore every part of a rheogram is important. The success or failure of various systems, e.g. coatings depends on getting the whole rheogram optimized across its entire profile.

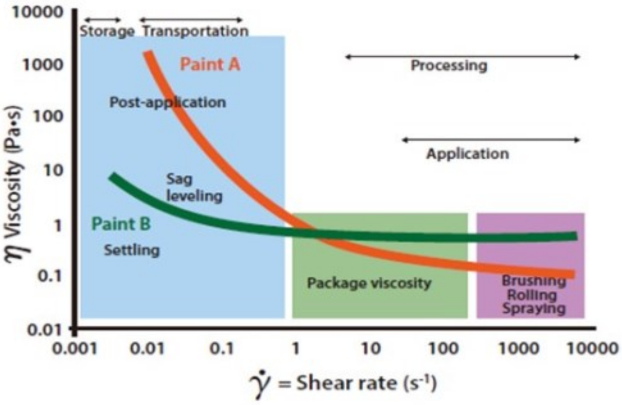

Figure 15: Viscosity recovery

The two curves display paints with equal package or mid-shear rate viscosity but with different rheological profiles. Paint A would probably show better sag control than Paint B, but Paint B would have higher brush drag (and higher film build when brush-applied)

The mid-shear rate range gives information about how a product appears to the user - that is, how it reacts to gentle stirring or shaking - and reflects the aesthetic appearance of the fluid material.

To estimate properties such as post-application behavior and storage stability, the viscosity at the lowest shear rates is of importance. However, modern oscillatory measurements, might show the structural strength (elasticity) of the sample more exactly. This is especially relevant for predicting the storage stability.

Performance under high shear conditions indicates how well a coating will apply. A relatively high viscosity suggests good brush drag or roller resistance whereas a low viscosity indicates good spray properties.

Measurement

Viscometers (such as the Krebs-Stormer, Brookfield, ICI, Flow cup) which typically find use in quality control, measure viscosity in the mid shear rate range only (1-200 s^{-1}). Properties such as settling, sag, leveling, and application properties can not be predicted by this equipment.

Precise measurement of low, medium, and high-shear rate viscosities can be made with more advanced rheometers. These rheometers can work in a controlled shear stress mode (apply known forces/ measure resulting strain), controlled shear rate mode (apply known strain/measure resulting forces), or oscillatory mode. Through continuous or ramped measurement, these instruments follow the change in flow parameters and accurately measure shear rates, shear stresses and viscosities over a wide range of conditions. *Figure 16* gives an indication of the shear rate ranges covered by different equipment.

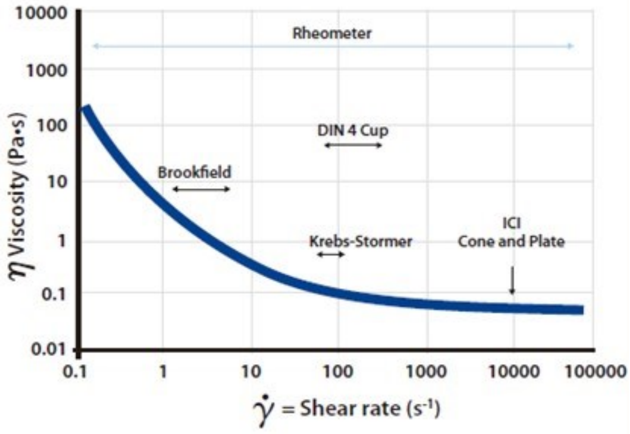

Figure 16: Shear rate relation viscosity measurement

Please contact for technical support:

Techsupport_EMEIA@elementis.com

North America
Elementis
469 Old Trenton Road
East Windsor,
NJ 08512, USA
Tel:+1 609 443 2500
Fax:+1 609 443 2422

Europe
Elementis UK Ltd.
c/o Elementis GmbH
Stolberger Strasse 370
50933 Cologne, Germany
Tel:+49 221 2923 2066
Fax:+49 221 2923 2011

Asia
Deuchem (Shanghai) Chemical Co., Ltd.
99, Lianyang Road
Songjiang Industrial Zone
Shanghai, China 201613
Tel:+86 21 5774 0348
Fax:+86 21 5774 3563

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