

Comprehensive Rheology Guide

Abstract

Have you ever wondered why it is, that sunscreen stays inside the bottle when turned upside down, but spreads smoothly when applied on skin? It all has to do with the rheological behavior of a specific material. In this paper we will explore the basics of rheology, how different instruments can measure different aspects of a fluid's behavior and examine the differences between relative and absolute measurement systems by looking at various practical examples.

Table of Contents

1	Introduction	1
1.1	Basics of Rheology	1
2	Rheometry.....	4
2.1	Flow cups.....	4
2.2	Bubble Viscometers	4
3	Rotational Viscometers	4
3.1	Couette Viscometers.....	5
3.2	Searle Viscometers.....	5
3.2.1	Stormer Viscometers.....	5
3.2.2	Rotational Spindle Viscometers.....	7
3.3	Absolute Measurement Systems.....	8
3.3.1	Cone and Plate viscometers	8
3.3.2	Rheometers	11
4	Conclusion	11
5	Literature:.....	11

1 Introduction

1.1 Basics of Rheology

Rheology, from Greek “*rhéō*” or “flow” and “*-logia*” or “study of”, is the science of matter's flow behavior and describes deformation and flow under applied forces. It applies to pure liquids like water or complex mixtures and suspensions like polymers or biological materials like blood. Rheology also describes the deformation behavior of solid substances. Scientifically the field of rheology operates between two extremes, perfectly flowing fluids and ideal elastic solids. A low viscous mineral oil and a steel ball are good examples of these extremes. In reality, every fluid will have a viscous as well as an elastic deformation component and will therefore be called viscoelastic substances. A glue for wall papers can be considered a viscoelastic fluid

and a rubber eraser can be considered a viscoelastic solid. Since this is an article about the measurement of fluid viscosities, we will focus on this aspect of rheology.

Closely related to rheology is viscosity. From the latin word “viscum” or (literal translation: mistletoe). It stems from a viscous glue derived from the mistletoe berry. It is a measure of a liquid’s resistance to deformation at a given rate. This can be described as the force needed to overcome friction between adjacent layers of fluid.

In general, liquids can be categorized in two different ways: Non-Newtonian fluids and Newtonian fluids.

Newtonian fluids, coined by Isaac Newton in 1687, are fluids, whose shear stress is proportional to the shear rate.^[1] This means, that an ideal Newtonian fluid will have a constant viscosity at varying shear rates. **Non-Newtonian fluids** exhibit viscoelastic tendencies, and their viscosity will vary depending on the shear rate or shear stress as well as possibly time. In practice ~~reality~~, every fluid will have some degree of non-Newtonian behavior, and it is the task of the rheologist to determine the influence of this behavior for the specific test environment.

To further illustrate this, Figure 1 shows the differences in the flow curves between two parallel plates for Newtonian and two non-Newtonian fluids. If in the case of Newtonian fluids, ~~if we plot~~ the shear stress is plotted as a function of the shear rate, a straight line is obtained, corresponding to the viscosity. However, for non-Newtonian fluids, we will obtain a non-linear function. That means, that for non-Newtonian fluids more than one measurement point is needed to determine the viscosity. In the case of (b), the viscosity increases with increasing shear rate. An example of this is a mixture of cornstarch in water. For (c), the viscosity decreases with increasing shear rate. This is called pseudoplastic or shear thinning behavior, and it occurs for example in most wall paints.^[2]

The most important takeaway from this is that the **viscosity is not an absolute value, but a function of the shear rate.**

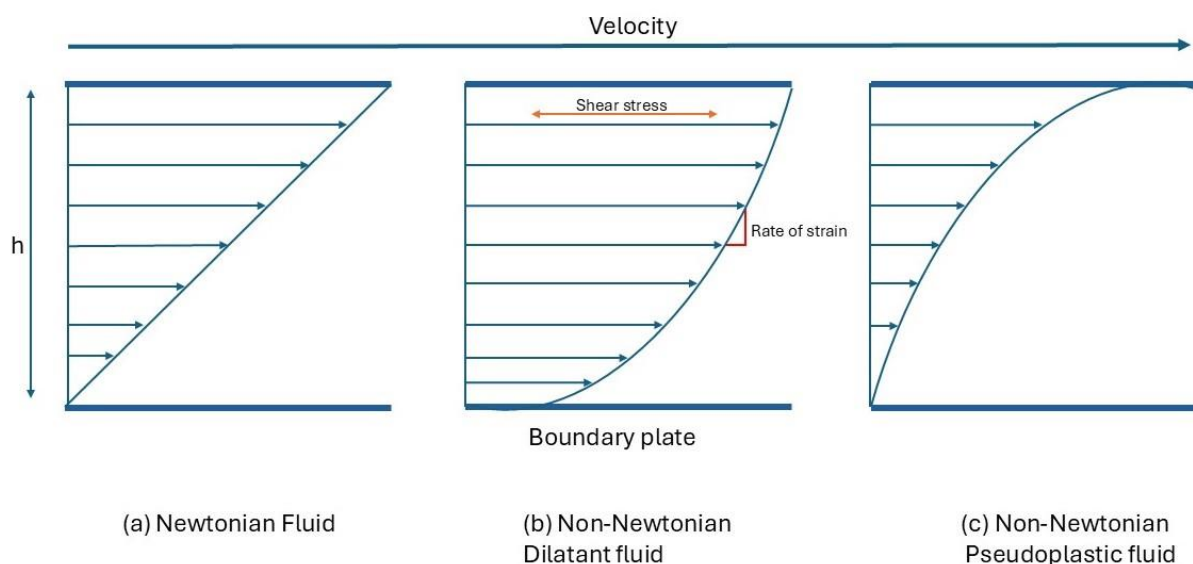


Figure 1: Friction between adjacent (Newtonian) fluid layers in relative motion. The force, that is required to move the upper layer is the shear stress, a measure of the fluids viscosity, while the speed of this deformation is the applied shear rate. h = distance between moving plates; v_s = velocity of the shear movement.

It is also common for substrates to exhibit a yield value. This means, that the fluid will only flow, when a certain amount of force is applied on it. To get back to our example in the beginning, this corresponds to the tube of sun screen not flowing out until squeezed.

For some substances, the viscosity is not only dependent on the shear rate, but also on time. This time dependent behavior is called **thixotropy or rheopexy** for shear thinning and shear thickening substances respectively. This can be attributed to the destruction of agglomerates and structured solutes inside the analyte which take time to reform after shear stress was induced into the sample. Common examples for thixotropic substances are gels and colloid dispersions. **To measure this behavior, a stress ramp can be utilized** (Figure 2). The sample is subjected to an increasing shear rate (t_0 to t_1) until a maximum has been reached and the viscosity is constant (t_1 to t_2). Afterwards the shear rate is decreased again to measure the relaxation time (t_2 to t_3). The shear stress and shear rate can then be plotted with this data and the area inside the resulting hysteresis loop depict the thixotropic behavior.^[3]

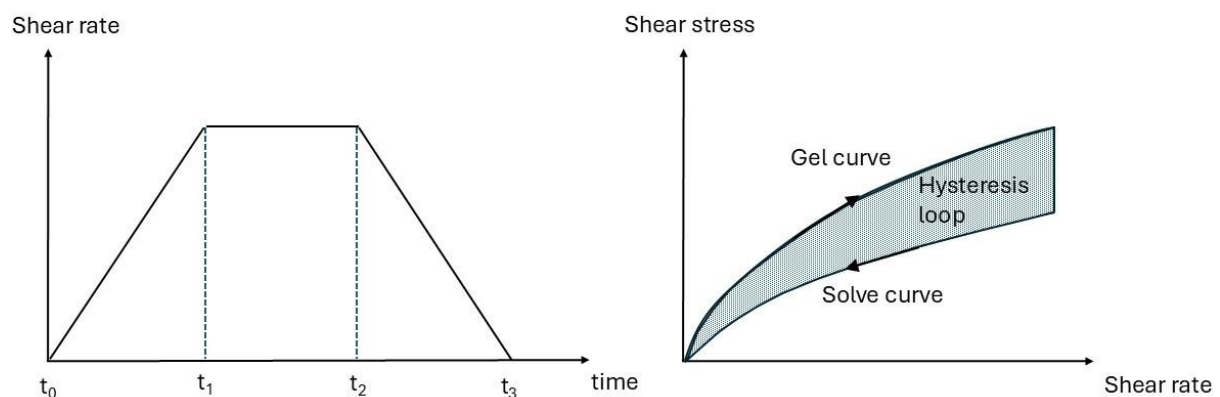


Figure 2: Sample measurement of a thixotropic substance. A stress ramp is being used to determine the thixotropic behavior. The area of the resulting plot of the shear rate and shear stress indicate a hysteresis loop.

To better visualize some of these concepts and to understand what shear rate represents, some typical rates that correspond to some real-world processes and applications can be seen in the following Table 1.^[4] Sometimes, depending on the stage in the production process chain, different shear rates are used, and therefore, if one wants to test their product thoroughly, it has to be tested at different steps in the process. For example, a wall paint needs to be tested at a low shear rate to determine the particle sedimentation behavior. In addition, it needs to be tested at high shear rates to determine the behavior during application with a roller.

Table 1: Overview over different processes, their approximate shear rates and the real-world application of these processes.

Process	Shear rate [s ⁻¹]	Application
Particle Sedimentation	0.001 to 0.01	Dispersion Paints
Gravity Flow	0.01 to 0.1	Dispersion Paints
Extrusion	1 to 100	Polymer Melts
Blending	100 to 1000	Roller Application
Spraying	1000 to 10000	Spray paints
Rubbing	10000 to 100000	Creams
Machine Lubrication	1000 to 1000000	Mineral Oils

The industry has therefore developed a range testing tools that are more or less suitable for different applications. In the following section we will discuss several of these instruments, their measurement principles and their advantages and disadvantages.

2 Rheometry

Rheometry is the science of measuring (from Greek “metron” or “to measure”) flow. This field has developed in unison with rheology to measure and verify the evolving theories. It is important for quality and process control applications as well as for process modelling.

2.1 Flow cups

Flow or efflux cups are simple devices that measure viscosity by the time (efflux) it takes for a known volume of fluid to flow from a hole in the bottom of the cup. Different shapes and nozzle sizes have been defined according to several international standards. These cups are suitable only for the measurement of **Newtonian fluids**, as they do not provide a reliable means of controlling the shear rate inflicted on the sample, since this depends on the fill volume which decreases during the measurement.^[5]



Figure 3: Overview over different types of available flow cups: DIN Cup – Ford Cup – ISO Cup.

2.2 Bubble Viscometers

Bubble viscometers consist of calibrated glass tubes which are filled with a defined amount of sample liquids, closed with a stopper and inverted. The resulting air bubble rises through the sample to the top of the tube. The time it takes for this bubble to reach the top is related to the sample's viscosity. By comparing the sample time to calibrated standards, the viscosity can be narrowed down. This method is by its very nature, a relative measure and should only be used for simple quality control checks.^[6]

3 Rotational Viscometers

A coaxial rotational spindle viscometer consists of a measurement body and a measurement vessel. Many different variants are known, but they can be broadly characterized into two operational modes.^[7]



Figure 4: An array of different bubble reference tubes with a sample tube in the middle.

3.1 Couette Viscometers

Couette viscometers are defined by the rotation of the measurement vessel while the body stays static. This method does not produce Taylor vortices but needs to be tempered separately. Due to technical limitations this can prove difficult. In order to achieve reproducible results, the tests need to be run in a temperature-controlled room which is why they are less common.

3.2 Searle Viscometers

Searle viscometers are defined by the rotation of the measurement body, while the measurement vessel remains static. This is the most common form of a rotational viscometer. The downside to this method is, that at high shear rates Taylor vortices may develop in low viscous samples.

3.2.1 Stormer Viscometers

A Stormer viscometer is a rotational spindle viscometer that is mostly used for simple QC testing in the paint and coatings industry according to ASTM D562. The spindle possesses two paddles that rotate directly inside of the sample can at a fixed speed of 200 rpm. The measured torque is directly displayed in Krebs-Units (KU). The viscosity cannot be described in absolute units, as the instrument does not operate under defined geometries and therefore, does not have or apply constant shear rate.[7]



Figure 5: Stormer Viscometer with the corresponding paddle spindle. An attachment for the secure measurement inside of paint cans is attached at the bottom.

3.2.2 Rotational Spindle Viscometers

Rotational Spindle viscometers consist of a rotating shaft to which a spindle is attached. The spindle is rotated inside the sample and the measured torque of this rotation is translated into the viscosity. They are ideal for quickly measuring a wide range of sample viscosities. Several types of spindles are available depending on the viscosities of the samples. An example of these instruments with an array of available spindles is shown in Figure 6. The shear stress for these instruments is given by the geometry of these spindles and is fixed, the shear rate, however, is not. This is because the gap between the spindle and the edges of the sample container is not defined, and the shear rates are not constant.



Figure 6: A rotational spindle viscometer with several spindles for low viscosities.

To compensate this, containers and spindle combinations with defined gaps are available as adapters for these viscometers. They describe a cylindrical spindle with a container according to ISO 3219. In the following Figure 7 this is illustrated. At sufficiently small gaps, the shear rate is almost constant while bigger gaps, induce a degree of non-linearity.

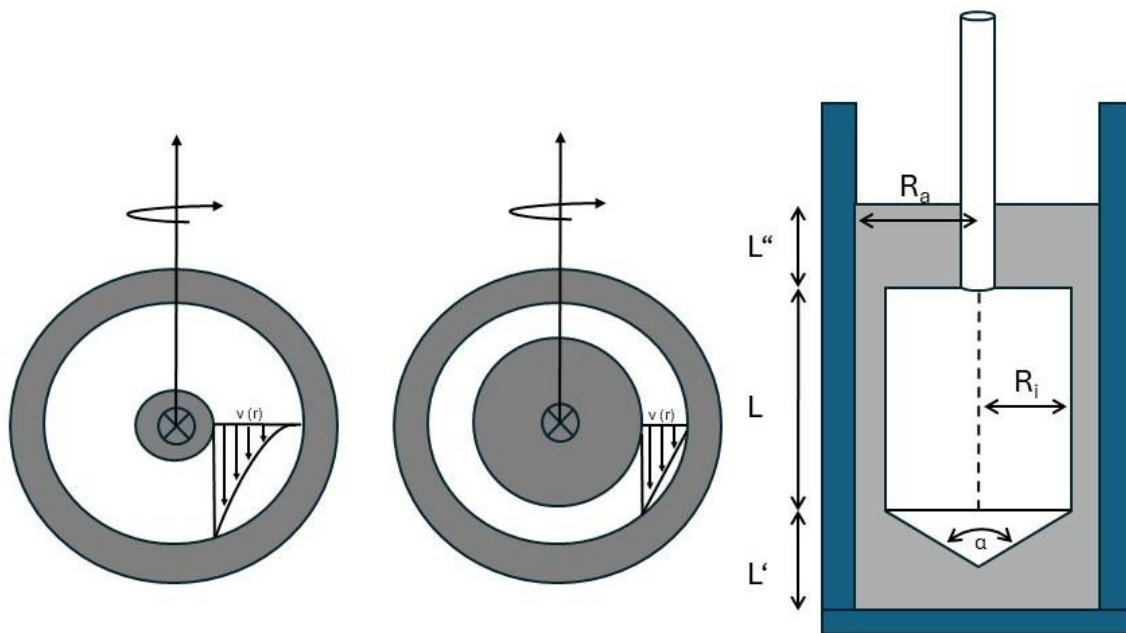


Figure 7: Example of non-linear flow (left), almost constant flow at sufficiently low gap size (middle) and an example of an ISO 3219 container (right). Note, that the ratio of the lengths and radii is given by the standard.

They can be used for low viscous substances and can be tempered using double walled cylinders. At high shear rates however, Taylor vortices can occur. Also In addition, the samples must be highly homogenous and require a minimum amount of sample, typically around 10 to 20 mL.^[8]

3.3 Absolute Measurement Systems

These measurement systems are defined by their use of absolute geometries in the measurement environment. This ensures constant shear rates throughout the whole sample and allows for the application of high shear without the generation of Taylor vortices. The most commonly used types are Cone / Plate and Plate / Plate geometries.

3.3.1 Cone and Plate viscometers

A Cone and Plate viscometer consists of a thermally controlled base plate and a cone with a defined geometry that is centered on the base plate. The base plate is typically equipped with a thermocouple, capable of heating and / or cooling (Figure 8).



Figure 8: Cone and plate viscometer with a cone and a thermally controlled base plate.

For operation, a small amount of test liquid is placed between the cone and the base plate. The cone's tip is set at a precise angle, usually around 1-2 degrees, creating a defined gap for the liquid. As the cone spins at a constant speed, the liquid resists the motion, creating a shear stress proportional to the fluid's viscosity (see Figure 9).

The shear stress [Pa] is the force applied parallel to the surface, while shear rate [s^{-1}] represents the rate of change of the fluid's layers adjacent to the surfaces. These two variables are used to calculate a sample's viscosity. The relationship between these parameters can be expressed using Equation 1.[9]

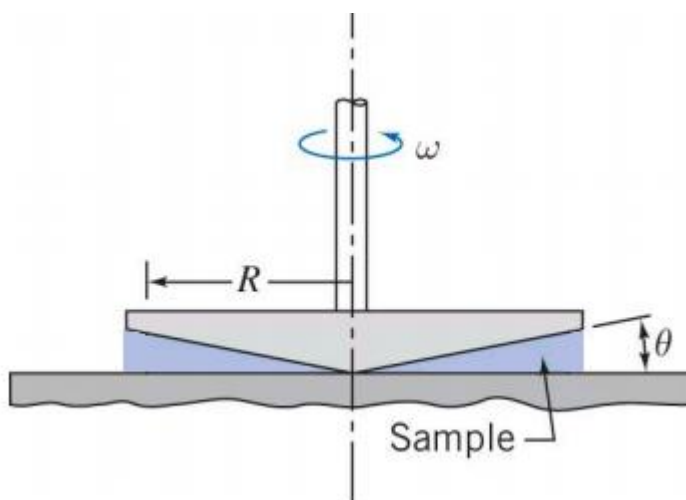


Figure 9: Schematic representation of a cone and plate viscometer during a measurement. R = radius of the cone [cm]; θ = cone angle [°]; ω = rotational speed of the cone [rad/s]. Shear rate = $\frac{\omega}{\tan \theta}$ where $\omega = \frac{2\pi}{60} \times \text{rpm}$.

Equation 1: Relationship between shear stress, shear rate and viscosity.

$$\text{Shear Stress} = \text{Shear Rate} \times \text{Viscosity}$$

As the shear rate is known, which is defined by the geometry and the rotational speed of the cone, and the measured torque value of the instrument is proportional to the viscosity of the sample, we can easily determine the shear stress. The radius of the cone affects the sensitivity of the measured torque of the instrument.

This allows for accurate and reliable data collection about a fluid's viscosity under controlled conditions. As previously said, this method allows for the application of high shear rates up to 12.000 s^{-1} which make it suitable to simulate processes like spray applications. It should be noted, that for shear rates above 10.000 s^{-1} shear heating of the analyte can occur which has to be considered. For extremely high shear rates of $\geq 10^6$ high pressure capillary viscometers should be used.^[10]

The big advantage of cone and plate viscometry is the constant applied shear rate throughout the sample which makes the results very accurate. Another advantage is, that because of the small amount of sample used, it is cost efficient to use as well as easier to clean than other methods. However, dispersions with large particle sizes can induce inaccuracies. The fill volume of the cone also has an influence on the results and filling should always occur according to the manufacturer's instructions. An example of a properly filled, overfilled and underfilled cone can be seen in Figure 10. The most important thing to note is, firstly, not to overfill the cone and secondly, to use the same amount of sample for every subsequent measurement to assure reproducibility.

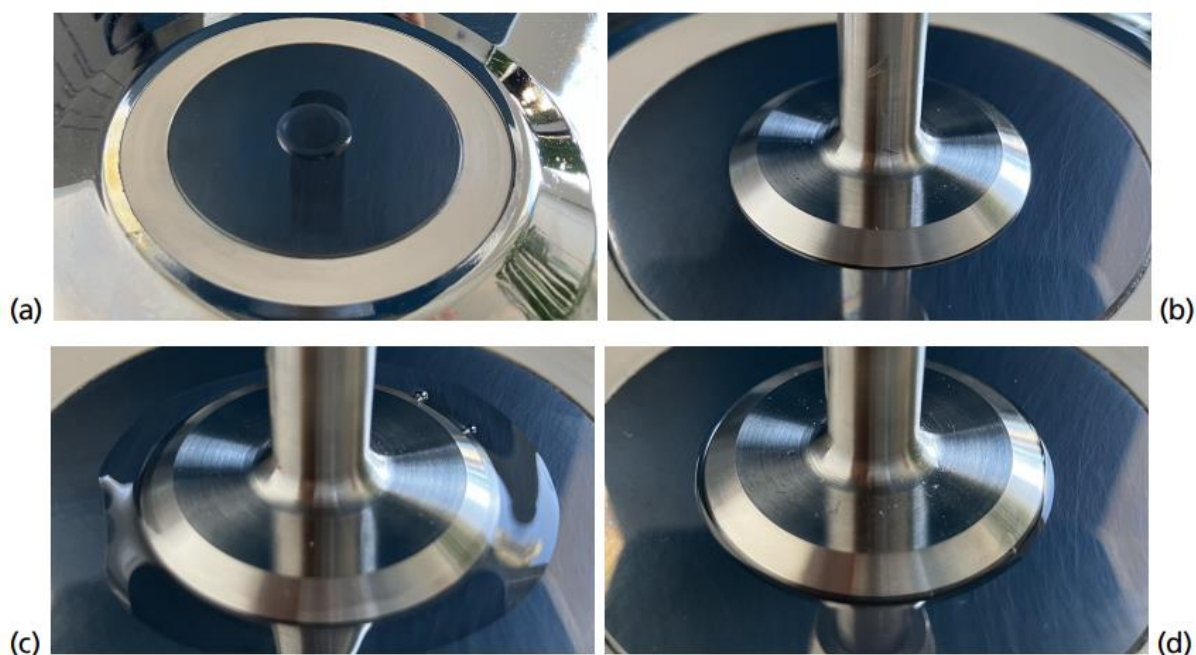


Figure 10: An example of how to fill the cone of a cone and plate viscometer. First, apply a defined amount of sample onto the base plate (a), then lower the cone. The different fill cases are (b) not enough sample, (c) too much sample and (d) perfect amount of sample.

Several international standards describe the use of cone and plate viscometers at specific shear rates. For ISO 2884 the shear rate must be between 5000 and 20000 s^{-1} , while for ASTM D4287 it is fixed at 12000 s^{-1} . ASTM D7395 describes a low shear rate method for the determination of viscosities. The shear rate is fixed at 500 s^{-1} .^[11-13]

3.3.2 Rheometers

Rheometers are scientific instruments that can measure the full range of a substances rheologic behavior. They can measure from very low shear rates to very high shear rates in small intervals. They usually utilize cone and plate, plate / plate or cone / cone geometries with the ability to control the gap between the cones (and / or plates) precisely and possess very sensitive step motors. Due to this sensitivity, full rheometers are the most accurate to measure rheological behavior, but need high level of expertise to operate.

4 Conclusion

We can see that it is crucial to select the right tools for the right applications. Each instrument, such as cone and plate viscometers, rotational viscometers, and flow cups have their unique strengths and are suited for specific types of materials and conditions. Therefore, it is essential to carefully select the appropriate technique that aligns with your particular needs and objectives. By doing so, you can ensure accurate and relevant results, ultimately enhancing the efficiency and effectiveness of your work.

5 Literature

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