Understanding the rheology of yield stress materials

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Citation for published version (APA):

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2

Experimental techniques and materials

2.1 Experimental techniques

The main experimental techniques used in this thesis are rheological measurements and flow visualization; the former were performed using rheometers and the latter using a confocal laser scanning microscope. These techniques and the corresponding measuring methods are described in this chapter.

2.1.1 Rheology

Rheology is a scientific discipline dedicated to the study of the deformation and flow of matter [1]. The easiest way of introducing basic rheological terms is by considering a material between two parallel plates of area \( A \) and separation \( h \), moving in opposite directions, due to the application of a external force \( F \), as shown in Figure 2.1. If the upper plate moves a distance \( d \) with respect to the lower one, the material will be deformed and the following terms can be defined:
(i) **Shear stress** ($\sigma$): is the tangential force $F$ per unit area:

$$\sigma \equiv \frac{F}{A} \quad (2.1)$$

(ii) **Shear strain** ($\gamma$): is the constant of proportionality between $h$ and $d$:

$$\gamma \equiv \frac{d}{h} \quad (2.2)$$

(iii) **Shear rate** ($\dot{\gamma}$): is the rate of deformation:

$$\dot{\gamma} \equiv \frac{d\gamma}{dt} \quad (2.3)$$

For an elastic solid, the shear stress is proportional to the shear strain, following Hooke’s law:

$$\sigma = G' \cdot \gamma \quad (2.4)$$

where $G'$ is called the shear elastic modulus.

Conversely, for a Newtonian fluid, the shear rate is proportional to the shear stress, and the constant of proportionality is called shear viscosity or simply viscosity ($\eta$):

$$\sigma = \eta \cdot \dot{\gamma} \quad (2.5)$$

By plotting the shear stress as a function of the shear rate, it is possible to quantify the flow properties of fluids; this type of plots are called *flow curves*, and from them it can be seen if a fluid is, for example, Newtonian, shear-thinning or shear-thickening (Figure 2.2).
2.1.1.1 Rheometers and measuring geometries

Rheological measurements are carried out using rheometers, which allow the determination of the flow properties of fluids. Rheometers are devices that impose a torque along the axis of a rod that is free to rotate and measure the resulting angular motion, or that control the angular motion and measure the resulting torque [2, 3] (Figure 2.3). Using the appropriate mathematical relations—depending on the measuring geometry—the torque and the angular displacement can be transformed into a shear stress and a shear rate, respectively.

The measuring geometries used for performing the experiments shown in this thesis are represented in Figure 2.4, for which the shear rate and the shear stress is calculated according to the following equations [2–5]:

Figure 2.2: Representation of flow curves of different types of fluids: Newtonian, shear-thinning and shear-thickening.

Figure 2.3: Schematic representation of a rheometer. The material is between two plates and the rheometer imposes a torque, which induces movement of the upper plate, while the lower plate remains static.
(i) **Cone-plate geometry**, with a homogeneous shear stress. In this geometry, the cone rotates and the plate remains static, or vice versa.

\[
\dot{\gamma} = \frac{\omega}{\sin(\alpha_c)} \tag{2.6}
\]

\[
\sigma = \frac{3M}{2\pi R_c^3 \sin^2(\alpha_c)} \tag{2.7}
\]

where \(\omega\) is the angular velocity, \(\alpha_c\) is the angle of the cone, \(M\) is the torque and \(R_c\) is the radius of the cone.

(ii) **Plate-plate geometry**, for which the measuring gap, \(h\), can be varied. In this geometry one of the plates rotates and the other remains static.

\[
\dot{\gamma} = \frac{R_p \omega}{h} \tag{2.8}
\]
where \( R_p \) is the radius of the plate. The shear rate given by (2.8) represents the shear rate at the rim, and this value is used for interpreting experimental data for torsional flow [1].

(iii) **Vane-in-cup geometry**, in which the vane rotates and the cup remains static. The material between the vanes moves as a solid block, making this geometry similar to the Couette geometry (two concentric cylinders).

\[
\dot{\gamma} \approx \frac{\omega (R_i + R_o)/2}{R_o - R_i} \quad (2.10)
\]

\[
\sigma = \frac{M}{2 \pi h_c R_i^2} \quad (2.11)
\]

where \( R_i \) is the radius of the vane, \( R_o \) is the radius of the cup and \( h_c \) is the length of the vane.

### 2.1.1.2 Rheological measurements

The rheological characterization of materials used in this thesis were performed using the rheometers shown in Figure 2.5:

(i) **Rheometrics ARES**: a controlled-shear-rate rheometer, in which the angular velocity is imposed and the corresponding torque is measured.

(ii) **Anton Paar MCR 300/301 and DSR 301**: controlled shear-stress rheometers; in this case, the torque is imposed and the angular velocity is measured. The DSR 301 rheometer was coupled to the confocal laser scanning microscope.

(iii) **Stresstech**: a controlled shear-stress rheometer.

Rheological measurements consisted of (steady) shear, viscosity bifurcation, oscillatory, creep, and stress growth experiments.
Figure 2.5: Rheometers used in this thesis: Rheometrics ARES (a), Anton Paar MCR 300/301 (b), Anton Paar DSR 301 coupled to a confocal microscope (c), and Stresstech (d).

(Steady) shear experiments
These experiments consisted in performing shear rate and shear stress sweeps. The former involve measuring the shear rate while imposing shear stresses from 1 Pa until 100 Pa. The latter involves a similar procedure, but instead the shear rate is varied within certain range. In some cases, the shear stresses (or shear rates) were imposed for a time that was long enough to reach a steady state. In other cases, I was interested in the quick response of the material, and the shear stresses (or rates) were imposed for short times.
Viscosity bifurcation experiments
The viscosity bifurcation experiments consisted in imposing a shear stress and measuring the evolution of the shear rate or the shear viscosity in time. These experiments were useful for testing if a yield stress material is thixotropic or not. For thixotropic materials if stresses below a critical value ($\sigma_c$) are imposed, then the shear viscosity of the sample increases in time until the flow is halted together. Conversely, at stresses only slightly above $\sigma_c$, the viscosity decreases with time towards a low steady value. For non-thixotropic yield stress materials, as soon as a stress above the yield stress is imposed, the material flows [6, 7].

Oscillatory measurements
These measurements consisted in imposing an oscillatory shearing, allowing the determination of the storage ($G'$) and loss ($G''$) moduli, of yield stress materials. $G'$ is a measure of the storage of elastic energy, while $G''$ is associated with the viscous energy dissipated per cycle of deformation [3, 8].

Consider a sinusoidal shear strain $\gamma$ of small amplitude $\gamma_0$ and frequency $\omega$, given by $\gamma = \gamma_0 \sin \omega t$. The shear stress $\sigma(t)$ produced by a small-amplitude deformation is proportional to, but out of phase with $\gamma$:

$$\sigma(t) = \sigma_0 \sin(\omega t + \delta) = \gamma_0 [G'(\omega)\sin(\omega t) + G''(\omega)\cos(\omega t)]$$

(2.12)

where $\delta$ is the phase angle difference between the applied strain and the stress response, and $G'$ is in phase with the strain and $G''$ is in phase with the deformation rate, $\dot{\gamma}$.

For a perfectly elastic material, $G'' = 0$ and $\delta = 0$, whereas for a viscous fluid $G' = 0$ and $\delta = 90^\circ$. In yield stress materials, both $G'$ and $G''$ are nonzero and $0^\circ < \delta < 90^\circ$.

Creep experiments
These measurements consisted in imposing a shear stress and recording the strain response in time. At stresses lower than the yield stress, yield stress materials behave like elastic solids, therefore the strain increases in time toward a constant
value. Conversely, at stresses higher than the yield stress, the strain increases indefinitely with time and a constant shear rate indicates that the material is indeed flowing [9].

**Stress growth experiments**

These experiments consisted in imposing a low shear rate and measuring the shear stress in time. The obtained curves for yield stress materials (shear stress vs time or strain), consist of an initial linear portion representing the elastic behavior, followed by a nonlinear region and ultimately a constant shear stress value [8].

### 2.1.2 Confocal laser scanning microscopy

For visualizing the flow behavior of emulsions I used a Confocal Laser Scanning Microscope (CLSM), Zeiss Pascal Live (Figure 2.6). This device incorporates two principal ideas: rejection of out-of-focus light and point-by-point illumination of the sample.

CLSM is a technique that allows the acquisition of images with better contrast and definition and greater vertical and lateral resolution compared to traditional optical microscopes. The main advantage of this device is that optical sections of the samples are obtained, which allows the reconstruction of three-dimensional images [10, 11].
This device was used for obtaining “movies” of flowing emulsions, from which it was possible to reconstruct velocity profiles, showing the variation of the velocity along the line perpendicular to the direction of the flow. For this aim, the CLSM was coupled to the DSR 301 rheometer.

In addition, the CLSM was used for the observation of the interaction of emulsions with different surfaces.

2.2 Materials

2.2.1 Emulsions

The emulsions used for this thesis are castor oil-in-water and silicone oil-in-water emulsions. Both emulsions were stabilized using Sodium Dodecyl Sulfate (SDS, from Sigma Aldrich), which is a surfactant molecule with the molecular formula: $CH_3(CH_2)_{11}SO_4Na^+$. SDS is an anionic surfactant, as it dissociates to yield a surfactant ion whose polar group is negatively charged [12].

2.2.1.1 Castor oil-in-water emulsion

Castor oil-in-water emulsions were prepared in the following way:

(i) Continuous phase: was prepared by dissolving SDS in ultra-pure water (Milli-Q ®), obtaining a solution with 1 wt% SDS concentration.

(ii) Dispersed phase: consisting of Castor oil (Sigma-Aldrich).

(iii) Emulsification: the aqueous phase was added to the oil, subsequently both phases were emulsified using a IKA T18 emulsifier at 24,000 rpm for 5 minutes. The internal volume fraction was $\phi = 0.8$.

(iv) Emulsion with lower $\phi$: were prepared by diluting the original emulsion ($\phi = 0.80$) with the 1 wt% SDS solution.

Thixotropic systems were prepared by manually mixing already-prepared emulsions with Bentonite clay (from Steetley bentonite & Absorbents Limited). The
Chapter 2

final clay concentration was 2 or 5 wt% with respect to the total amount of emulsion.

2.2.1.2 Silicone oil-in-water emulsion

Silicone oil-in-water transparent emulsions were prepared in the following way:

(i) Continuous phase: consisted of a solution of 46.2 wt% ultra-pure water (Milli-Q ®) and 53.8 wt% glycerol (99 % GC, from Sigma-Aldrich). SDS (Sigma-Aldrich) was dissolved in the water-glycerol solution, in such a proportion that the SDS concentration in the continuous phase was 1 wt%.

(ii) Dispersed phase: consisted of Silicone oil (Rhodorsil ®47 V 500); this phase was dyed with Nile red (Sigma-Aldrich). For each 100 ml of oil, around 2 ml of a saturated solution of Nile red dissolved in the oil were added.

(iii) Emulsification: the aqueous phase was added to the oil, subsequently both phases were emulsified using a IKA T18 emulsifier at 24,000 rpm for 5 minutes. The internal volume fraction was $\phi = 0.8$.

(iv) Centrifugation: in order to remove air bubbles from the samples, these were centrifuged at 2,500 rpm for 30 minutes. The final system was a transparent emulsion.

Thixotropic systems were prepared by adding Bentonite clay (from Steetley Bentonite & Absorbents Limited) to the formulation before emulsification. The final clay concentration was 1 or 3 wt% with respect to the total amount of emulsion.

2.2.2 Carbopol ‘gels’

Carbopol ‘gels’ were prepared by mixing Carbopol (Ultrez U10 grade) and ultra-pure water for one hour, in such a proportion that the Carbopol concentration was 2 wt%. Sodium hydroxide (NaOH, from Sigma-Aldrich) was dissolved in water to obtain a 18 wt% NaOH solution, which was used to adjust the pH of the carbopol-water mixture to approximately 7: for each 500 g of carbopol-water mixture, 20 mL of the 18 wt% NaOH solution were added. The resulting mixture was vigorously
shaken and left to rest for one day. Samples with lower concentration of carbopol were prepared by diluting the 2 wt% Carbopol sample with ultra-pure water.

### 2.2.3 Foam and hair gel

Foam used in this thesis is a commercially available foam (Gillette regular). Additionally, hair gel is also commercially available (Albert Heijn), and basically is a carbopol gel in which the pH is stabilized using triethanolamine instead of NaOH.

### References


Chapter 2

