Understanding the rheology of yield stress materials
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Understanding yield stress fluids
Part II: Three types of shear banding

4.1 Flow of yield stress materials - Is it always homogeneous?

I have already mentioned that yield stress materials are particularly important because they are widely used in both cosmetic and industrial applications; therefore, the physical and flow properties of this type of materials must be taken into account for their formulation and handling [1]. One of the main issues when dealing with the flow of yield stress materials in practice is that, when they are made to flow, most of the time shear banding occurs: part of the material flows, but another part remains quiescent; this is the problem I want to address here.

For yield stress materials, a heterogeneous flow may result as a consequence of heterogeneous stress [2]. However, in practice, when a typical yield stress material such as a concentrated emulsion is made to flow, the material may also fracture or exhibit wall slip. This again has been an area of intense debate, and although some issues have been clarified [3–6], a general view on shear banding in these materials has been lacking.
Additionally Chapter 3 shows that in a very general way, yield stress materials can be classified into ‘simple’ and thixotropic. For a ‘simple’ yield stress material the viscosity depends only on the applied shear rate or shear stress; therefore, measuring the yield stress in a ‘simple’ yield stress material is, in principle, an easy task. Conversely, when a material exhibits thixotropy, the viscosity decreases continuously over time when a sample that has been previously at rest is made to flow; this implies that for a thixotropic yield stress material the yield stress increases when the sample is left at rest and decreases when sheared before the measurement, i.e. it depends both on time and on the shear history of the sample.

In this Chapter, I ask the question: What does the distinction between the two types of yield stress materials mean for the homogeneity of the flows of such materials?

Regarding the flow of thixotropic systems, a number of models have been developed [1, 5–9], which consider yield stress and thixotropy together, as both of them are related to the microstructure [8]. One explicit model that takes the structure into account is that of a fractal colloidal gel developed by Møller et al. [5]. This model takes into account the aging and shear rejuvenation processes by assuming that the fractal network builds up at rest, and is partially destroyed under flow, which corresponds to structuring and destructuring of the network of the particles, respectively [6, 7]. For my discussion here, the main outcome of the model is that, for thixotropic systems, there exists a critical shear rate below which shear banding happens. Therefore, by comparing for instance the Herschel-Bulkley model for simple yield stress materials to the fractal gel model, the former suggests that, for a constant imposed stress, for all shear rates homogeneous flows are possible in the material [8]. However, the second model predicts that, for thixotropic yield stress materials, there exists a critical shear rate below which no stable flow can be achieved, leading to shear banding [1, 7].

In this Chapter, I investigate the different types of shear localization that can be present in a ‘simple’ and in a thixotropic yield stress material. Considering that it has been well understood and reported that shear localization obviously occurs when stress heterogeneities are present [6–8], I perform experiments in a cone-plate (CP) geometry that for Newtonian fluids corresponds to a homogeneous stress situation. The rheological measurements are performed on two types of emulsions that behave either like ‘simple’ or like thixotropic yield stress materials. Velocity profiles of the flowing emulsions within the gap of the CP cell are obtained by
means of a confocal laser scanning microscope (CLSM) attached to a rheometer. For this, the emulsion is made both transparent and fluorescent.

4.2 Rheological characterization and velocity profiles

I study the shear localization of normal and thixotropic emulsions using a silicone oil-in-water emulsion with $\phi \approx 0.8$. A thixotropic emulsion is prepared by adding bentonite clay to the formulation in such a proportion that the final clay concentration is 1 %wt with respect to the total amount of emulsion obtained.

The macroscopic rheological characterization of both the simple and the thixotropic emulsions is shown in Chapter 3, namely, the up-and-down shear rate sweeps (Figure 3.1 (b)), the steady-state flow curves (Figure 3.2 (b,d)) and the viscosity bifurcation experiments (Figure 3.3 (b,d)). These measurements clearly show that the normal emulsion behaves like a ‘simple’ yield stress material, while the emulsion loaded with clay behaves as a thixotropic yield stress material.

For acquiring the velocity profiles of the flowing emulsions a controlled-shear-stress rheometer (Anton Paar DSR 301) equipped with a 6 mm radius $2^\circ$ CP geometry with roughened cone mounted on a CLSM (Zeiss Pascal Live) was used. The plate of the CP geometry consisted of a glass cover slide through which the confocal images were taken. Figure 4.1 shows a schematic representation of the confocal microscope coupled to a rheometer. Since a fluorescent dye in the sample was necessary for performing these experiments, Nile Red was added to the dispersed phase of the emulsions (silicone oil) and images were obtained using a laser wavelength of 532 nm. Measurements started after the shear rate was imposed for 900 s and it took around 2400 s to get a complete velocity profile. From the confocal ‘movies’, velocity profiles could be reconstructed by simply following the speed of a number of individual bubbles in a slice, averaging and plotting the average as a function of the height at which the confocal slice was made.
4.3 Shear banding in normal and thixotropic emulsions

4.3.1 Smooth plate: wall slip

Wall slip is a phenomenon that is frequently observed during rheological tests as a discontinuity in shear rate near the wall [10]. Most of the times the slip is localized in a thin layer (whose thickness may depend on the shear stress at the wall) and occurs in addition to some bulk flow [11–13]. Additionally, it has also been reported [14–16] that, if wall slip is present, at low shear rates the shear localizes in a small region with high local shear rate, while the remaining part of the fluid behaves like a solid. A recent study using microgel pastes shows that wall slip can be controlled by controlling the chemistry of the shearing surfaces (see [17]); however, roughened surfaces are usually employed to prevent wall slip [11, 18].

In order to study the influence of surface roughness on wall slip, velocity profiles of the normal and the loaded emulsion at different $\dot{\gamma}$’s were first obtained using a
smooth glass cover slide, which in a CP geometry is equivalent to using a smooth plate and roughened cone. Velocity profiles (Figure 4.2) show that, for both the normal and the thixotropic emulsion, the velocity close to the cover slide is much higher than it would be for a Newtonian fluid, while the rest of the material moves like a solid at the speed of the cone. This implies that there is a very large velocity gradient very close to the wall. Perhaps the most important observation is that there is very little difference between the two systems.

One possible explanation of the wall slip in such systems could be a decrease of the concentration of oil droplets close to the plate [10, 19]. If there is a thin layer of a low-viscosity fluid (e.g. water) between the wall and the emulsion, one would expect a very large velocity gradient in that layer, because of the constant stress and the low viscosity in the layer. However, in this case the velocity profiles were obtained by means of direct visualization of the emulsions flow and it was possible to directly count the number of density of emulsion droplets close to the wall and in the bulk, to see whether a difference exists. From doing so, the conclusion is that no droplet depletion occurs close to the wall to within the experimental accuracy.
Figure 4.3: Confocal laser scanning images of the thixotropic emulsion under an imposed shear rate $\dot{\gamma} = 0.5$ s$^{-1}$ at 0.12° from the bottom (approximately 5 µm from the plate) and 63× magnification. The upper figures show microscopy images of the emulsion droplets using a smooth plate at $t = 0$ s and at $t = 1.56$ s. The lower figures show microscopy images of the emulsion droplets using a roughened plate at $t = 0$ s and $t = 2.25$ s. The white bar is equivalent to 20 µm. Black and white circles are just referential for showing the flow/no-flow condition.

Figure 4.3 shows that close to the smooth plate, the material is flowing, but there is no evidence for gradients in droplet concentrations close to the wall; the system remains homogeneous and consequently the wall slip must have a different origin. Figure 4.3 also shows the situation at the wall when the plate is roughened (procedure is shown later); in this case, the sample does not flow at all close to the plate, i.e. wall slip near the plate is avoided.
4.3.2 Rough walls: shear localization

Wall slip was suppressed by applying a very thin layer of low-viscosity instant glue (Loctite \textsuperscript{®}4062) with precision wipes (Kimberly-Clark \textsuperscript{®}) on the glass cover slides. This treatment enabled the creation of a roughness of the order of the drop size, avoiding wall slip, and still having a transparent bottom plate to be able to do the confocal experiments looking through the plate.

Experiments with the confocal microscope coupled to the rheometer consisted in imposing shear rates between 1 and 0.05 s\(^{-1}\), using the CP geometry with roughened surfaces. Velocity profiles (Figure 4.4) reveal that when the roughened plates are used, the sample does not flow at all close to the plate, i.e. wall slip near the plate is avoided (see also Figure 4.3).

![Figure 4.4](image)

**Figure 4.4:** Velocity profiles at different globally imposed shear rates for a normal emulsion (a) and loaded emulsion (c). Fluid velocity normalized by the cone velocity at different imposed shear rates for a normal emulsion (b) and a loaded emulsion (d). All velocity profiles are obtained using roughened plate and cone.
Figure 4.4(a,b) also shows that, for the normal emulsion, the flow is homogeneous even for the lowest imposed shear rates. Conversely, for the thixotropic emulsion (Figure 4.4 (c,d)), as the applied shear rate is below the critical one ($\dot{\gamma}_c \approx 1 s^{-1}$, see Chapter 3), localization is clearly observed.

In agreement with a previous study carried out using magnetic resonance imaging [5] in the thixotropic emulsions, as soon as shear banding occurs, one part does not flow and another part flows at a shear rate that is equal to the critical shear rate. In addition, the fraction of the sheared material increases with the imposed shear rate.

### 4.4 Conclusions

Using a CLSM coupled to a rheometer, velocity profiles of optical transparent emulsions were obtained, which enabled the investigation of shear banding in a CP geometry of ‘simple’ and thixotropic yield stress materials. For a normal emulsion—a ‘simple’ yield stress material—the only type of shear localization that was observed, corresponds to wall slip when using a smooth plate. Conversely, for a loaded emulsion—a thixotropic yield stress material—besides wall slip when using a smooth plate, the system also exhibits shear banding when the imposed shear rate is below a critical value ($\dot{\gamma}_c$). Considering that wall slip is similar for the normal and the thixotropic emulsions, it can be said that for the system studied here, wall slip depends only on the surface roughness. Combining these measurements with earlier ones in Couette geometries [2], it can be concluded that there are three types of shear banding that may happen, due either to stress heterogeneities, the existence of a critical shear rate—for thixotropic yield stress materials—or wall slip. The different types of shear banding in yield stress materials are summarized in Table 4.1.

From Table 4.1, the following conclusions are done:

(a) **Heterogeneous stress**: if stress is heterogeneous, part of the sample may be below, and another part above, the yield stress; this immediately leads to shear localization [7]. Therefore, there is an important difference between a situation in which the stress is homogeneous throughout the sample (e.g. in a CP geometry that for Newtonian fluids corresponds to a homogeneous
Three types of shear banding

Table 4.1: Different types of shear localization in ‘simple’ and thixotropic yield stress materials.

<table>
<thead>
<tr>
<th>Type of yield stress fluid</th>
<th>Normal</th>
<th>Thixotropic</th>
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<tbody>
<tr>
<td>Shear localization due to:</td>
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stress) and those where it is not (e.g. in a Couette geometry, where the stress decreases when going from the inner to the outer cylinder). This means that stress heterogeneities are directly associated with the geometry used.

(b) **Critical shear rate**: considering thixotropic yield stress materials, another type of shear localization may be present when the sample is sheared below a critical shear rate [6].

(c) **Wall slip**: strong localization of the flow in the near-wall region may lead to wall slip [11–13]. When wall slip is present, the viscosity will depend on the gap of the measurement geometry for a Couette or plate-plate cell [10, 22, 23], or the opening angle of the cone for a CP geometry. This seems to be an acceptable definition of wall slip that allows us to distinguish it from case (b): any situation in which the apparent viscosity depends on the gap is automatically called wall slip.

Thus, shear banding in yield stress fluids has mainly been considered as a consequence of either the existence of a stress heterogeneity in the flowing material or as a consequence of wall slip. Additionally, in thixotropic materials a third type of shear localization may arise when these are sheared below a critical shear rate. This hopefully clarifies the situation somewhat. As more research was and is needed on the exact conditions under which wall slip occurs, in Chapter 4 I study this phenomenon and I show how wall slip affects macroscopic measurements of the viscosity, especially using CP geometries.
References


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