Understanding the rheology of yield stress materials
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Understanding yield stress fluids
Part I: Two types of yield stress materials

3.1 Problems when determining the yield stress

As mentioned before, yield stress materials respond elastically to small applied stresses, but flow once a threshold stress is exceeded; this stress is the yield stress. It is of no doubt that these materials are particularly important because they are widely used in both cosmetic and industrial applications; classic examples are paints, foams, wet cement and cleansing creams. Therefore, over the past 25 years a relatively large number of methods have been developed for measuring the yield stress [1–5]. The problem we want to address here is that the yield stress of a given material has turned out to be very difficult to determine. Indeed it has been demonstrated that a variation of the yield stress of more than one order of magnitude can be obtained depending on the way it is measured [4, 6, 7]. The variable nature of yield stress measurements has even led to the suggestion that an absolute yield stress is an elusive property [8, 9]. One method that has been frequently used for characterizing yield stress materials is to work with two yield stresses, one static and one dynamic [10–12]. The static yield stress would be the stress above which the material turns from a solid state to a liquid one, while the
dynamic yield stress is the stress where the material turns from a liquid state to a solid one. The fact that these are usually found to be different poses a problem. All of these difficulties have resulted in lengthly discussions of whether the concept of the yield stress is useful and how it should be defined and subsequently determined experimentally [13].

In this Chapter, I show that in order to understand the discrepancies in the determination of the yield stress of a given material, one needs to distinguish between two types of yield stress materials, thixotropic and ‘simple’ ones [14–16]. A ‘simple’ yield stress material is one for which the viscosity depends only on the shear rate (or shear stress), while for thixotropic materials the viscosity depends also on the shear history of the sample. The rheological behavior is then determined by the competition between a spontaneous build-up of some microstructure at rest—aging—and its breakdown by flow—shear rejuvenation—[14].

3.2 Simple vs. thixotropic yield stress materials

To study the properties of yield stress materials with variable thixotropy I use emulsions, which allow having both simple and thixotropic yield stress materials in a single system. Samples consist of a silicone oil-in-water emulsion and a castor oil-in-water emulsion, both with an internal volume fraction $\phi = 0.8$. The thixotropic character of the samples is controlled by adding bentonite clay to the formulations [17].

3.2.1 Rheological measurements

Rheological measurements were done using cone-plate geometries with roughened surfaces in a controlled-shear-stress rheometer (CSS), Anton Paar MCR 300 and in a controlled-shear-rate rheometer (CSR), Rheometrics ARES. It is well know that working with roughened surfaces is an efficient method to avoid wall slip when performing rheological measurements [9, 18].

A first test consisted in performing up-and-down stress and up-and-down shear rate sweeps (Figure 3.1). The flow curve of the pure emulsions is completely reversible upon increasing and decreasing of the stress or the shear rate. Conversely, when
bentonite is added, a clear hysteresis in the flow curves is observed, which becomes more pronounced as the clay content increases; this is the hallmark of thixotropic behavior [14, 16]. Therefore, with this simple test it is demonstrated that the normal emulsions are simple yield stress materials, while the emulsions loaded with bentonite behave like thixotropic yield stress materials, which become more thixotropic with higher clay contents.

To demonstrate that in simple yield stress materials the shear stress tends to a plateau for low shear rates, two different test are performed; in one test the shear stress is imposed—using the CSS rheometer—and in the other test the shear rate is imposed—using the CSR rheometer. These experiments allow obtaining steady-state flow curves. To reach the steady state, values are only taken after the viscosity changes by less than 3% (roughly the rheometer resolution). Figure 3.2 (a,b) shows that the normal emulsions have the behavior of a simple yield stress material, i.e. the shear stress tends to a plateau and the flow curve is typical of that of a Herschel-Bulkley-type fluid [19]: $\sigma = \sigma_y + K\dot{\gamma}^n$, where $\sigma$ is the shear stress, $\sigma_y$ is the yield stress, $\dot{\gamma}$ is the shear rate; $K$ and $n$ are adjustable model parameters. Conversely, the flow curves corresponding to the loaded emulsions (Figure 3.2 (c,d)) show a plateau only when the CSR rheometer is used. Under an imposed stress, the steady-state value of the viscosity jumps discontinuously to infinity at a critical shear stress. Therefore, when the stress is imposed, there exists a critical shear rate, $\dot{\gamma}_c$, below which no stable flows are possible.
Figure 3.2: Steady state flow curves - shear stress vs shear rate - for: (a) castor oil-in-water emulsion, (b) silicone oil-in-water emulsion, (c) castor oil-in-water emulsion with 5% wt clay and (d) silicone oil-in-water emulsion with 1% wt clay. The empty symbols correspond to measurements performed with the CSR rheometer and the filled symbols to measurements performed with the CSS rheometer. The red lines are fits of the flow curves to the Herschel-Bulkley model: for the castor oil-in-water emulsion (a) \( \sigma = 29.9 + 14\dot{\gamma}^{0.46} \) and for the silicone oil-in-water emulsion (b) \( \sigma = 39.59 + 6.28\dot{\gamma}^{0.72} \). The critical shear rates are for the loaded castor oil-in-water emulsion (c) \( \dot{\gamma}_c \approx 0.58 \text{s}^{-1} \) and for the loaded silicone oil-in-water emulsion (d) \( \dot{\gamma} \approx 1 \text{s}^{-1} \).

The thixotropic character of the loaded emulsions and the existence of this critical shear rate is best demonstrated by the viscosity bifurcation experiment [15], which is shown in Figure 3.3. In this experiment, a fixed stress is imposed using the CSS rheometer and the shear rate (or viscosity) is followed in time until a steady state is reached. The same procedure is repeated for different stress levels. For the pure emulsions there is a continuous family of curves, implying that all shear rates are possible when imposing the stress (Figure 3.3 (a,b)). However, for the loaded emulsions this is not the case (Figure 3.3 (c,d)).
Figure 3.3: Viscosity bifurcation experiments - time evolution of shear rate for different imposed stresses - for: (a) castor oil-in-water emulsion, (b) silicone oil-in-water emulsion, (c) castor oil-in-water emulsion with 5 %wt clay, and (d) Silicone oil-in-water emulsion with 1 %wt clay.

On the one hand, above a critical shear stress ($\sigma_c$) the thixotropic emulsion liquefies and flows rapidly, i.e. it flows with a viscosity that decreases in time towards a constant value in steady state. Therefore, at stresses above $\sigma_c$ shear rejuvenation overcomes aging. On the other hand, for stresses below $\sigma_c$, the shear rate is observed to decrease, indicating that aging overcomes shear rejuvenation. Because the stress is fixed, this corresponds to an increase of viscosity in time or “aging”; the steady state reached by the material is in fact one without flow at all. This feature is clearly shown in Figure 3.3 (c), from which it is obvious that for the castor oil-in-water emulsion loaded with bentonite $\dot{\gamma}$ decreases gradually in time, as soon as the imposed stress is smaller than the critical one; eventually $\dot{\gamma}$ becomes so small that it can no longer be measured. In addition, Figure 3.3 (d) shows that for the loaded silicone oil-in-water emulsion, the microstructure is quickly recovered, which is the reason why as soon as the shear stress is below $\sigma_c$, the shear rate
rapidly decreases; indeed, the measured $\dot{\gamma}$'s lie within the rheometer's detection limit and the signal is very noisy.

Figure 3.1 shows that the hysteresis loop for the loaded castor oil-in-water emulsion is bigger than for the loaded silicone oil-in-water emulsion. Therefore, it is not surprising that the loaded silicone oil-in-water emulsion recovers faster than the loaded castor oil-in-water emulsion, which is confirmed by the viscosity bifurcation experiment.

The transition between a material that flows and one that does not flow is therefore discontinuous in the stress; this is the viscosity bifurcation \cite{20, 21}. It also implies the existence of a critical shear rate ($\dot{\gamma}_c$) that is the lowest shear rate for which a homogeneous flow is still observed; this happens at the critical stress ($\sigma_c$).

The existence of a critical shear rate poses the question: how does this relate to shear banding? This is discussed in the next Chapter.

### 3.2.2 Attractive vs repulsive forces

The presence of clay particles in a loaded emulsion leads to a material that behaves like a thixotropic yield stress material. It has been suggested that in emulsions, clays induce thixotropy thanks to the formation of links between neighboring droplets \cite{17}. This would lead to flocculation of the droplets, in a way similar to a colloidal gel \cite{14}. In order to visualize this effect, a pure and a loaded castor oil-in-water emulsion, for which a fluorescent dye was added to the oil (Nile red), were diluted with water. Figure 3.4 shows that isolated droplets are observed in a normal emulsion, whereas for a loaded emulsion, the sample shows large aggregates of droplets. Therefore, while the yield stress in a normal emulsion is due to repulsion between the dispersed bubbles, the yield stress in a thixotropic emulsion is due not only to the repulsion between the droplets, but also due to the attractive forces induced by the clay particles. However, how clays induce 'attraction' between the droplets remains an open question. Do clays form a continuous network around the oil droplets? Do they induce aggregation of droplets via colloidal particle links? Or do they induce depletion interaction between the droplets?

It has been reported that for emulsions, the micelle concentration increases with the concentration of surfactant, enhancing the depletion forces and leading to
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Flocculation of the dispersed droplets. When the concentration of surfactant is high enough, an excess of osmotic pressure pushes droplets together, due to the formation of micelles that do not adsorb at the interface and that are excluded from between the surfaces of two neighboring droplets, meaning that high surfactant concentrations induce depletion interaction between the droplets [22–24].

Figure 3.4: Confocal imaging of castor oil-in-water emulsions. The images were taken after dilution of concentrated emulsions down to an oil volume fraction of 1 % and ×100 magnification. (a) Pure emulsion. (b) Emulsion with 3 %wt clay.

3.3 Conclusions

This chapter shows that it is necessary to make a careful distinction between simple and thixotropic yield stress materials [4, 6, 8–14, 16, 25]. Thixotropy is due to the existence of a microstructure that confers elasticity and hence a yield stress to the material. However, such structures are modified by the flow, leading to an apparent yield stress that depends on the (shear) history of the sample. Conversely, for ‘simple’ yield stress materials, such as foams, emulsions and cabopol gels [8, 9, 18, 26, 27], the yield stress is due to repulsions between bubbles, droplets and swollen microgel particles, respectively; there is no percolated structure in these materials that is destroyed by the flow. If follows that for ‘simple’ yield stress materials, static and dynamic yield stresses are the same, as is evident from the coincidence of the up-and-down stress (shear rate) sweeps in Figure 3.1; hence, there is no problem in defining the yield stress. For thixotropic yield stress materials, the static yield stress will depend on time, due to the aging of the microstructure.
The dynamic stress, on the other hand, is a material parameter: the up-and-down stress sweep of Figure 3.1 corresponds to the steady states of the curves of Figure 3.2 and hence do not depend on time. The observation that a steady state is reached, immediately implies that the competition between shear-induced breakup and spontaneous buildup of the microstructure at rest results in a steady-state structure that is independent of the (shear) history of the sample, in agreement also with the results of a number of model calculations and simulations on glassy systems [28–30]. The dynamic yield stress is then the lowest stress for which such a steady state can be reached, and is then a time- and preparation-independent material parameter. Thus, although indeed there is a problem defining a static yield stress for thixotropic systems, the dynamic yield stress appears to be a well-defined material property.

References


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