Understanding the rheology of yield stress materials

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1 Introduction

1.1 Yield stress materials

Materials can be classified in a very general way into elastic solids and Newtonian liquids. The former is a material that will deform when a force is applied to it, but returns to its initial shape after the force is removed. For the latter material, there is a constant shear viscosity \((\eta)\) that represents its mechanical properties; however, this is temperature and pressure dependent [1].

In addition, many everyday materials are neither elastic solids nor Newtonian fluids. For example, there are shear-thinning fluids [2–12] for which the shear viscosity decreases with increasing deformation rate, and shear-thickening fluids [2, 3, 7, 8, 13–19] for which the viscosity increases with increasing deformation rate. In addition to these, there are materials that respond elastically to small applied stresses \((\sigma)\) but flow once a threshold stress is exceeded [20]; this threshold is called the yield stress \((\sigma_y)\) and these type of materials are called yield stress materials. Classical examples of yield stress materials are paints, foams, wet cement, cleansing creams, mayonnaise and toothpaste.

Yield stress materials are widely used in industrial, pharmaceutical and cosmetic applications. Therefore, the physical and flow properties of this type of materials are important for their formulation and handling [21]. In this sense, it is extremely
important to know the yield stress, as this is the stress at which the material starts to flow.

The classical description of yield stress materials was initiated by Bingham [22], who captured the phenomenological behavior of these in the following way:

\[
\sigma = \sigma_y + f(\dot{\gamma}) \quad \text{if } \sigma > \sigma_y
\]

and

\[
\dot{\gamma} = 0 \quad \text{if } \sigma \leq \sigma_y
\]

(1.1)

where \(\sigma\) is the shear stress, \(\sigma_y\) the yield stress and \(f(\dot{\gamma})\) some function of the deformation or shear rate \(\dot{\gamma}\). Thus, if \(\sigma < \sigma_y\) there is no flow, and if \(\sigma \geq \sigma_y\) the stress is a monotonically increasing function of \(\dot{\gamma}\) [23].

The most commonly used model for describing yield stress materials is the Herschel-Bulkley model [24], which presupposes a well-defined yield stress:

\[
\sigma = \sigma_y + K \cdot \dot{\gamma}^n
\]

(1.2)

where \(K\) and \(n\) are adjustable model parameters. After the yield stress is overcome, if \(n = 1\) the material flows with a constant viscosity, if \(n < 1\) the viscosity decreases with \(\dot{\gamma}\) (shear-thinning behavior), and if \(n > 1\) the viscosity increases with \(\dot{\gamma}\) (shear-thickening behavior).

1.1.1 Problems when dealing with yield stress materials

The main problem encountered by scientists and engineers dealing with yield stress materials is that the yield stress of a given material is very difficult to determine [23, 25–28]. Indeed, it has been demonstrated that variations of more than one order of magnitude can be obtained depending on the way the yield stress is measured [29–33].

Because it is necessary to define a yield stress value for use in engineering design and operation of processes, it was proposed to work with two yield stresses—one static and one dynamic—or even with a range of yield stresses (see Mujudumdar et. al. [26]): 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 [34].

The second problem is that when yield stress materials are made to flow, most of the time shear banding occurs: part of the material flows but another part remains quiescent.

In addition to the above-mentioned problems, it has been shown that yield stress materials can exhibit thixotropy [34, 35], i.e., the shear viscosity decreases continuously over time when a sample that has been previously at rest is made to flow.

Yield stress materials that have been widely studied are emulsions, foams and gels, because of their wide applicability; therefore, I use these materials as model systems for studying the flow behavior of yield stress materials (Figure 1.1).
1.2 Emulsions

An emulsion is defined, according to the International Union of Pure and Applied Chemistry IUPAC, as “a dispersion of droplets of one liquid in another one with which it is incompletely miscible” [36]. The dispersed liquid is normally called the internal or dispersed phase, and it is in the form of spherical droplets with a diameter that varies between 1-100 µm (in some special cases, between 0.1-500 µm [37]). The liquid in which the droplets are dispersed is normally called the continuous phase. Examples of emulsions are mayonnaise, margarine, milk, coffee whiteners, cosmetic and pharmaceutical creams and cortisol cream.

Emulsions are thermodynamically unstable, due to the large positive interfacial free energy of the dispersed system, which decreases with the reduction of the interfacial area [38]. Therefore, the dispersed droplets eventually coalesce, leading to separation of the constituent liquids.

Drop coalescence is controlled by adding emulsifiers, normally surfactants; these are amphiphilic materials that adsorb at the drop interface and produce some interdrop repulsion according to a variety of static and dynamic phenomena [39]. In addition, certain solid nanoparticles and polymers can be used as emulsifiers, as they also adsorb at the liquid-liquid interface, reducing drop coalescence [40–43].

1.2.1 Emulsions and yield stress

The flow properties of emulsions are determined by several variables, such as viscosity of the liquids, type and concentration of emulsifier, temperature and drop size of the dispersed droplets. A parameter of paramount importance is the dispersed phase content, normally called internal volume fraction (φ) given by the ratio of the volume of the dispersed phase to the total volume of the emulsion.

When φ is higher than a critical value (φc), the dispersed droplets jam and a yield stress appears, due to the short-range repulsive forces between the droplets [34, 44, 45]. Thus, for φ > φc emulsions will not flow unless the yield stress is overcome. The value of φc ≈ 0.64, but it is highly dependent on the polydispersity of the emulsion [46–48]. In addition, it has been reported that by adding clays or by increasing the concentration of surfactant, it is possible to induce attractive
forces between the droplets, which leads to thixotropy [34, 35, 49, 50], making the determination of the yield stress complicated.

On the one hand, after emulsions with $\phi > \phi_c$ are made to flow, they behave like shear-thinning fluids, and the viscosity decreases with increasing shear rate. On the other hand, emulsions with $\phi < \phi_c$ behave either like Newtonian liquids at low shear rates or like shear-thinning fluids at high shear rates [45].

1.3 Foams compared to emulsions

Foam is defined, according to the International Union of Pure and Applied Chemistry, as “a dispersion in which a large proportion of gas by volume in the form of gas bubbles, is dispersed in a liquid solid or gel. The diameter of the bubbles is usually larger than 1 $\mu$m” [36].

The mechanical behavior of foams is similar in many aspects to that of emulsions. At small stresses, foams and emulsions behave as viscoelastic solids, while above the yield stress they flow [1, 47]. For foams, the yield stress is also given by the repulsive interactions between the bubbles [51].

1.4 Carbopol

Carbopol are crossed linked acrylic acid resins that form small “sponges” when dispersed in water. These sponges swell in water under neutral pH, so that concentrations of carbopol higher than approximately 0.035 %wt are sufficient for the particles to jam; thus a yield stress arises [52]. People refer to carbopol suspensions as carbopol ‘gels’; however, when carbopol shows yield stress behavior, it is not a gel in the sense that there is no percolating network of polymers connected by chemical bonds, but rather a concentrated suspension of sponge-like particles [25].

Emulsions, foams and carbopol ‘gels’ behave in a similar way in that they exhibit a yield stress when the amount of dispersed phase is high enough. In addition, they do not exhibit thixotropic behavior, which makes them excellent model systems for studying the flow properties of yield stress materials.
Chapter 1

1.5 Scope of this thesis

This thesis focuses on the study of the flow properties of yield stress materials. To this aim, I use model systems such as emulsions, foams and carbopol ‘gels’, together with rheological measurements and flow visualization techniques. This thesis is divided as follows:

- **Chapter 2**: in this chapter I describe the experimental techniques and the preparation protocols of the materials studied in this thesis.

- **Chapter 3**: this chapter compares a ‘simple’ yield stress material with a thixotropic yield stress material. It is shown that for a ‘simple’ yield stress material the yield stress is a well defined value, while for the thixotropic one the yield stress is ill-defined.

- **Chapter 4**: in this chapter I show the different types of shear banding that can occur in both a ‘simple’ and a thixotropic emulsion. For both of them, shear banding manifests if the shear stress is inhomogeneous or due to wall slip; in addition, the thixotropic emulsion exhibits shear banding when sheared below a critical shear rate value.

- **Chapter 5**: in this chapter I use a transparent emulsion to show that wall slip can be controlled by modifying the wettability of the shearing walls. This enables the disentanglement of two effects leading to gap-dependent viscosities: wall slip and cooperative effects.

- **Chapter 6**: in this chapter I use emulsions with different internal volume fractions to show that the entire mechanical behavior below and above jamming can be understood in a way analogous to a phase transition. In addition, a two-state model is proposed to describe the transition between jammed and unjammed states.

- **Chapter 7**: in this chapter I compare different methods for measuring the yield stress of emulsions, foams and carbopol gels, providing a physical explanation of what each of these methods measure.

- **Chapter 8**: in this chapter I show partial results of topics that deserve more research, such as rheological behavior of mayonnaise and margarine, and
stored stress in yield stress materials. In addition, I suggest experiments, with the aim of improving our current understanding regarding the mechanical behavior of yield stress materials.

References


Chapter 1


