Understanding the rheology of yield stress materials
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In this chapter I present some interesting topics that deserve more research. For some of them, I already carried out some experiments, but in all cases I give recommendations that would (hopefully) help improving our current understanding regarding yield stress materials.

### 8.1 Behavior of structured materials: Mayonnaise vs. Margarine

Margarine and mayonnaise are common dietary products. Mayonnaises are oil-in-water emulsions, in which the dispersed phase consists of a vegetable oil and the continuous phase of vinegar. Egg yolk is added to stabilize the emulsion, together with thickening agents and flavoring materials [1–4]. The actual trend is to substitute regular foods for low-calorie versions, increasing the interest in fat substitutes and in new formulations with lower oil content; therefore, the production of dietetic mayonnaise implies the decreasing of the dispersed phase and the use of additives to stabilize the emulsion and to increase the viscosity of these foodstuffs [5].
Margarines are water-in-oil emulsions, in which the aqueous phase consists of water, salt and preservatives, while the oil phase is a blend of partially hydrogenated oil. These water-in-oil emulsions are stabilized by the use of lecithin and monoglycerides [6, 7]; however, any substance approved by the FDA can be used as surfactant [8]. The firmness of margarines is basically given by the crystallization of the oil phase [8–10], which consists of a hydrogenation process by which liquid oils are changed into solid fats due to the formation of saturated and trans fatty acids [11]; however, these acids have numerous negative health effects, such as increased incidence of heart disease or high cholesterol [12]. Therefore, the trend is to limit the amount of trans-fatty acids in foods.

The common challenge when developing new mayonnaises and margarines is to obtain products with a ‘texture’ similar to that to which consumers are used to. In this context, “... texture encompasses all the rheological and structural (geometrical and surface) attributes of a food product perceptible by means of mechanical, tactile and, when appropriate, visual and auditory receptors”[13]. Thus, different formulations can be compared by measuring their rheological properties, which may give a quantitative contribution to texture characterization and control [5].

8.1.1 Rheological characterization of Mayonnaise

Two commercially-available mayonnaise samples were characterized, one regular mayonnaise (Calvé Mayonaise from Unilever) and one light mayonnaise (Calvé Licht en Romig, from Unilever), whose composition is shown in Table 8.1. To perform the rheological measurements two rheometers with cone-plate geometries and roughened surfaces were used: a controlled-shear-stress rheometer (CSS, Anton Paar MCR 301) and a controlled-shear-rate rheometer (CSR, Rheometrics ARES). Measurements consisted in shear stress sweeps and shear rate sweeps; each shear stress sweep was performed twice using the same sample.

The stress sweep experiments show that the regular mayonnaise exhibits thixotropy and that the microstructure responsible of this behavior is built—aging—and destroyed—shear rejuvenation—very quickly, as the different stress sweep cycles superimpose (Figure 8.1 (a)). Different works have shown the existence of thixotropy in mayonnaises and other foodstuffs, considering only the breaking-up of the microstructure with shear (see e.g. [3, 14, 15]). Nevertheless, it has been
Table 8.1: Nutritional values and ingredients of Calvé Regular and Calvé Light

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Calvé Regular</th>
<th>Calvé Light</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fat</td>
<td>70 g</td>
<td>27 g</td>
</tr>
<tr>
<td>from saturated fat</td>
<td>6 g</td>
<td>2.5 g</td>
</tr>
<tr>
<td>Carbohydrates</td>
<td>3.5 g</td>
<td>9 g</td>
</tr>
<tr>
<td>from sugars</td>
<td>3.5 g</td>
<td>5 g</td>
</tr>
<tr>
<td>Proteins</td>
<td>0.9 g</td>
<td>0.6 g</td>
</tr>
<tr>
<td>Salt</td>
<td>0.9 g</td>
<td>1.4 g</td>
</tr>
</tbody>
</table>

1 Ingredients: Rapeseed oil, water, vinegar, egg yolk 5%, sugar, mustard (water, mustard seed, vinegar, salt, spices, flavor), salt, flavor, thickeners: xanthan gum, antioxidant E385; color: β-carotene.

2 Ingredients: Water, rapeseed oil 35%, sugar, modified corn starch, egg yolk 2.8%, mustard (water, mustard seed, vinegar, salt, sugar), salt, flavor, citrus fiber, concentrated lemon juice, acidifier: lactic acid, preservative: sorbic acid, stabilizers (xanthan gum, guar gum), antioxidant E385, color: β-carotene.

shown that, under shear, mayonnaise has both a reversible and an irreversible structural breakdown; the reversible structural breakdown has been associated with a flocculation-deflocculation process and the irreversible one with the coalescence of the oil droplets [16–18]. Considering that by loading our sample in the measuring geometry, its microstructure could have been partially destroyed [3], then our measurements confirm that there is a structure, for which the breakdown is reversible.

Interestingly, Figure 8.1 (b) shows that the light mayonnaise seems to have an initial structure that is irreversibly destroyed after the first increasing shear stress sweep is performed. The sample recovers partially, showing that also for light mayonnaise there seems to be a structure that breaks reversibly. However, more experiments are needed in order to confirm that the remaining structure after shearing ages and shear-rejuvenates, in a fashion comparable to the behavior exhibited by the regular mayonnaise.

In addition, the shear rate sweeps allow us to obtain the steady-state flow curves shown in Figure 8.1 (c,d), which can be fitted to the classical Herschel-Bulkley model [19]. It is worth mentioning that by the end of the experiments, changes in the color of the samples were observed, which can be an evidence of phase separation.
8.1.2 Rheological characterization of Margarine

As done with the mayonnaise samples, two margarine samples were studied: a regular margarine (Becel Gold, from Unilever) and a light margarine (Becel Light, from Unilever), whose composition is given in Table 8.2. The measurements consisted again in performing shear stress and shear rate sweeps.

Figure 8.2 (a,b) shows that both the regular and the light margarine have an initial structure that is destroyed after the first increasing shear stress sweep experiment is performed, i.e. the fat crystal network is destroyed. This structure is not recovered; nevertheless, the remaining structure seems to behave like a thixotropic material, which corresponds to the remaining water-in-oil emulsion. New research is needed
### Table 8.2: Nutritional values and ingredients of Becel Gold and Becel Light

<table>
<thead>
<tr>
<th></th>
<th>Becel Gold 1</th>
<th>Becel Light 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>content pr. 100 g</td>
<td>content pr. 100 g</td>
</tr>
<tr>
<td>Proteins</td>
<td>&lt; 0.5 g</td>
<td>0.9 g</td>
</tr>
<tr>
<td>Carbohydrates</td>
<td>0.6 g</td>
<td>3 g</td>
</tr>
<tr>
<td>Saturated fat</td>
<td>16 g</td>
<td>6 g</td>
</tr>
<tr>
<td>Mono-unsaturated fat</td>
<td>17 g</td>
<td>8 g</td>
</tr>
<tr>
<td>Poly-unsaturated fat</td>
<td>36 g</td>
<td>16 g</td>
</tr>
<tr>
<td>Omega 6 (linoleic acid)</td>
<td>29 g</td>
<td>12 g</td>
</tr>
<tr>
<td>Omega 3 ((\alpha)-linolenic acid)</td>
<td>7 g</td>
<td>3.9 g</td>
</tr>
<tr>
<td>Trans fat</td>
<td>&lt; 1 g</td>
<td>&lt; 1 g</td>
</tr>
<tr>
<td>Dietary fiber</td>
<td>&lt; 0.5 g</td>
<td>&lt; 0.5 g</td>
</tr>
<tr>
<td>Sodium</td>
<td>0.01 g</td>
<td>0.02 g</td>
</tr>
<tr>
<td>Vitamin A</td>
<td>800 (\mu)g</td>
<td>800 (\mu)g</td>
</tr>
<tr>
<td>Vitamin D</td>
<td>7.5 (\mu)g</td>
<td>7.5 (\mu)g</td>
</tr>
<tr>
<td>Vitamin E</td>
<td>9 (mg)</td>
<td>9.4 (mg)</td>
</tr>
</tbody>
</table>

1 Ingredients: Vegetable oils and fats, water, dry milk solids, emulsifiers (mono- and diglycerides from fatty acids, sunflower lecithin), acidifier (citric acid), flavor, vitamins A and D, color (\(\beta\)-carotene).

2 Ingredients: Vegetable oils and fats, modified starch, gelatin, emulsifiers (lecithin, mono- and diglycerides from fatty acids), preservative (potassium sorbate), acidifier (citric acid), vitamins A and D, flavor, color (\(\beta\)-carotene).

To better understand the interactions between emulsifiers and fat crystals, as well as, the origin of the thixotropy behavior of the remaining emulsion after breaking up of the fat crystal network [12].

Conversely, for the light margarine, with the second increasing shear stress sweep, the sample fractures, making it impossible to obtain valuable rheological data. Previous works using commercial margarines have also shown instability phenomena and wall slip when performing rheological measurements [12].

Additionally, as done with the mayonnaise samples, shear rate sweeps were carried out using the margarine samples, which allow us to obtain the steady-state flow curves shown in Figure 8.2 (c,d). The steady-state flow curves were fitted to the Herschel-Bulkley model. By comparing the stead-state flow curves, we can observe that the viscosity values of the regular and the light margarine in the shear rate range \(10 \text{ s}^{-1} \lesssim \dot{\gamma} \lesssim 50 \text{ s}^{-1}\) are very different. This shear rate range is the typical one for spreading butter on bread [20]; if we consider that the consumer expects that a light and a regular margarine behave in a similar way, then improvements in the formulation of light margarines need to be made.
Figure 8.2: Flow curves obtained by performing shear stress sweeps (a,b) and steady-state shear rate sweeps (c,d). (a) and (c) show results corresponding to the regular margarine. (b) and (d) show results corresponding to the light margarine. In (a) and (b) empty squares correspond to the first increasing shear stress sweep and the filled squares correspond to the first decreasing shear stress sweeps; empty and filled circles correspond to the second increasing and decreasing shear stress sweeps, respectively. In (c) and (d) the lines correspond to the fits to the Herschel Bulkley model, which for the regular margarine (c) is $\sigma = 11.1\text{Pa} + 1.4\text{Pa.s}^{0.88} \cdot \dot{\gamma}^{0.88}$, while for the light margarine (b) is $\sigma = 40.1\text{Pa} + 6.7\text{Pa.s}^{0.73} \cdot \dot{\gamma}^{0.73}$.

Regarding the appearance of the samples by the end of the experiments, I observed that while the regular margarine had a more creamy-like aspect, the light margarine seemed to phase separate as shown in Figure 8.3.

8.1.3 Mayonnaise, Margarine and Future Work

Even when for mayonnaise more rheological studies have been performed than for margarines (see e.g. [2–5, 16, 21, 22]), a complete rheological characterization considering the microstructures of these materials is lacking. This information will
be useful in quality control of commercial production, knowledge and design of texture, design of unit operations and understanding of the effects of mechanical processing on the structure of these emulsions [16, 23].

In the spirit of contributing with the improvement of the formulation of margarines and mayonnaises, as well as with the characterization of their rheological properties, I would like to propose the following:

(i) Margarines and mayonnaises exhibit thixotropy. If we compare these systems with the castor oil-in-water and silicone oil-in-water emulsions, for which thixotropy is induced by adding clay to the formulations, then it would be possible to prepare mayonnaises and margarines using food-grade clays. The use of clays for the formulation of margarines will be beneficial, as the use of hydrogenated fatty acids would be reduced or even completely avoided.

(ii) Perform a complete rheological characterization of mayonnaises and margarines, using the experimental techniques described in this thesis: shear rate and shear stress sweeps, steady-state flow curves, viscosity bifurcation experiments, oscillatory measurements to determine the storage (G') and the loss (G'') moduli, creep tests and stress growth experiments. The complete rheological characterization of the commercially-available materials will allow us to compare the mechanical properties and ‘texture’ of new formulations with the existent products.
8.2 Clays and Thixotropy

It was shown in this thesis that clay confers thixotropic properties to oil-in-water emulsions. However, the exact mechanism, due to which this happens, is not fully understood, *Do clay particles gel the continuous aqueous phase, are they a depletion agent or do they form links between neighboring droplets?*

To answer this question, I propose the following:

(i) Following the work of Wang et. al [24] dye hydrophilic clays. The method consists, basically, in using Auramine O or Rhodamine B to dye the clay.

(ii) After dying the clay, transparent emulsion should be prepared (silicone oil-in-water) and the died clay should be added to the formulation.

(iii) The clayey emulsion should be diluted to allow the observation of the role of the clay in the thixotropic character of the system.

(iv) Using the confocal laser scanning microscope couple to the rheometer, the behavior of the clay in the emulsion can be observed during shearing and resting.

By following this simple procedure, it would be possible to reveal the mechanism due to which emulsions become thixotropic when clay is added.

8.3 Stored stress in ‘simple’ yield stress materials

‘Simple’ yield stress materials, are called ‘simple’ because for them the yield stress is a well-defined value, considering that measurements are performed in the same way and that the criterion for defining this value is the same (see Chapter 7). Nevertheless, if shear rate sweeps are performed by turning the measuring geometry in one direction and then the same experiment is performed in the contrary direction, results are different.
I used a controlled-shear-rate rheometer (ARES) for performing rotational experiments, consisting of shear rate sweeps in an emulsion, a carbopol gel and a hair gel. I used a CP geometry with roughened surfaces and performed experiments according to the following protocol:

(i) Pre-shearing of the sample at $100 \text{ s}^{-1}$ for 60s. *Rotation = counterclockwise.*

(ii) Resting for 60 s.

(iii) Shear rate sweep. *Rotation = clockwise.*

(iv) Shear rate sweep. *Rotation = clockwise.*

In all cases, flow curves were fitted to the Herschel-Bulkley model and the yield stress happened to be higher for flow curves obtained just after pre-shearing and resting, than for flow curves obtained in a second measurement carried out just after the first shear rate sweep was performed (See Figure 8.4 (a)).

Interestingly, for each system, the only parameter of the Herschel-Bulkley model that varies is the yield stress; the $K$ and $n$ fitting parameters are approximately the same.

To be sure that the obtained results are not due to a rheometer’s artifact, the same experiments were performed in a silicone oil (Rhodorsil ®47 V 500), observing that...
both shear rate sweeps superimpose, indicating the absence of any artifact (Figure 8.4 (b)).

These results suggest that there is a stored stress in ‘simple’ yield stress materials. More research should be done, involving simulations and experiments, in order to understand this phenomenon. Questions that need to be answered are: In which way do ‘simple’ yield stress materials store stress? Is this phenomenon due to the orientation of the dispersed entities in one direction, and subsequent realignment in a contrary direction?

If these questions are answered, we will be a step closer to fully understand the fascinating rheology of yield stress materials.

References


