Rheological methods for characterization of liquid soaps and detergents

Elling-Olav Rukke and Reidar Barfod Schüller

Norwegian University of Life Sciences, Faculty of Chemistry, Biotechnology and Food
Science, P. O. Box 5003, N-1433 Ås, Norway

ABSTRACT

In this introductory study, several rheological methods were used to investigate and characterize the texture and viscosity of some commercially available liquid soaps and detergents. Viscosity and rheology play a crucial role in the performance of these products both as household products and as cleaning agents in various industries.

For the food industry it is important to have knowledge about these products behavior in the factory; for example, during automatic CIP-wash of pipelines and process equipment. Rheological measurement equipment like a high -performance rheometer is important for the industry that require quick and reliable methods for characterization and control of shear conditions and viscosity regarding different mixing, pumping and temperature regimes.

The tests employed in rotation were shear rate sweeps including low shear rates and hysteresis tests to detect thixotropic behavior. The results were fitted to the Herschel-Bulkley model. Conventional start-up tests were also performed.

Amplitude sweeps were performed in oscillation to determine stiffness, strength and limiting strain if the fluids formed a structure.

The results exhibit variations in rheological behavior and show that some of the products show signs of a yield stress, some were Newtonian while other were pseudoplastic. Some of the products also revealed clear thixotropic behavior.

INTRODUCTION

The main objective with this work was to investigate which measurement methods that are suitable to characterize the texture and rheological properties of liquid soaps and detergents. It was also of interest if it was possible to detect eventually differences of different rheological measurement methods regarding mixtures in the recipes.

Many of these rheological measurement methods are also of interest when producing the different liquid soaps and detergents. It may be of interest to predict flow of soaps and detergents through pumps and pipelines. Or predict finished products properties regarding rheology, stability, appearance etc[1].

In recent years it has also been focused on the environmental implications of these products. Soap is designed as a product to be used once. Then it is flushed down the drain. In addition, there are also environmental implications linked to the manufacturing of the products. There are at least three main areas of concern [2,3]:

1. Safe transport and containment of raw materials
2. Minimization of losses during manufacture
3. Air pollution aspects of detergent processing

Liquid detergents are gaining momentum in the market and are, by and by replacing the powder detergents. Hand dishwashing liquid detergents are used for manual washing up and are frequently used on almost daily basis like many other household cleaning products. The surfactants of soaps are compounds with a dual property: One part interacts with water, the other part interacts with dirt, oil and microbes on our skin, Fig 1.

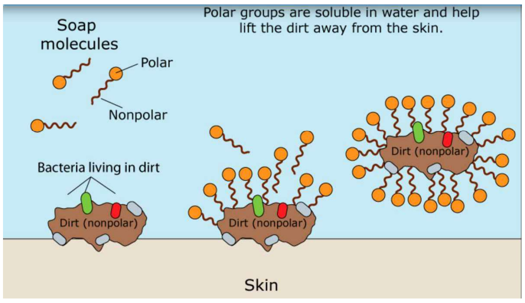

Figure 1: How soap works and interacts with dirt. Soap molecule graphic by Michael Gerhardt for UNESCO Science Communications.

Surfactants like soaps, are molecules that consist of hydrophilic head groups and hydrophobic tails. When dissolved in water above their critical micellar concentration, they can spontaneously self-assemble into larger aggregates called micelles. However, unlike polymer chains, which are covalently bonded along their backbones, these micelles are only held together by relatively weak physical attractions. These attractions or repulsions can break and reform under Brownian motion. The dynamics of this ongoing and reversible breakup and reformation process is a strong function of surfactant and salt concentration, salinity, temperature, flow etc. Investigations of the extensional rheology of some of these micelle solutions under unlike conditions are reported[4].

Soaps and detergents are essential to personal and public health. Soaps and detergents found in our homes can be grouped into four general categories: Personal cleaning, Laundry, Dishwashing, and household cleaning[5].

These properties are also frequently exploited in the ongoing pandemic. COVID-19, an "enveloped" virus surrounded by a lipid, or fatty acid membrane, is reported as an easy mark for the soap's surfactants, which are effective at dissolving the membrane and "kills" the virus[6].

A part of the study was also trying to determine if the rheological measurement methods used, could help to divide the different products into distinct groups.

MATERIALS AND METHODS

The soaps and detergents

The selection of soaps and detergents is shown in Fig. 2.

Table 1: Test sample description

Name	pH
Zalo	6.75
Comfort Sensitive tøymykner (Softener)	3.30
Milo tøyvask (laundry)	7.56
Klar tøyvask (laundry)	8.53
Klar håndvask (hand soap)	5.23
Lano håndvask (hand soap)	4.93

Figure 2: The selected detergents; Zalo, Comfort Sensitive tøymykner, Milo, Klar tøyvask, Klar håndvask and Lano håndvask.

pH- measurements

pH in the beverages was measured directly at 20°C. Each sample rested for 30 minutes before pH measurement (Thermo Scientific PH meter, Orion Star A 211, SN X25276, Indonesia).

Rheometer setup

The following tests were run in the MCR301 rheometer from Anton Paar fitted with a Titanium CC27 bob/cup measuring system:

- Shear rate sweeps in rotation from 0.001 1/s to 2 1/s.
- Slow shear rate tests varying shear rate from 1e-3 to 1e-6 1/s.
- Hysteresis test for thixotropic behaviour from 2.5 1/s to 50 1/s and back down to 2.5 1/s.
- Amplitude sweeps in oscillation from 0.01 to 100% strain at 10 rad/s to investigate stiffness, strength, and strain limit.
- Start-up test in rotation at a constant shear rate of 0.1 1/s.

Analysis

The shear rate sweep data were fitted to the Herschel-Bulkley model[7] expressed by Eqn. 1.

$$\tau = a + b\dot{\gamma}^{p} \qquad (1)$$

RESULTS

Rheometer results

The results from the shear rate sweep measurements were fitted to the Herschel-Bulkley model using a least squares method in MATLAB. The results are shown in Fig. 3, Fig. 4, and Fig. 5.

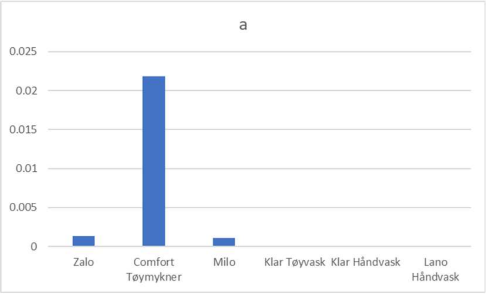

Figure 3: Herschel-Bulkley parameter a.

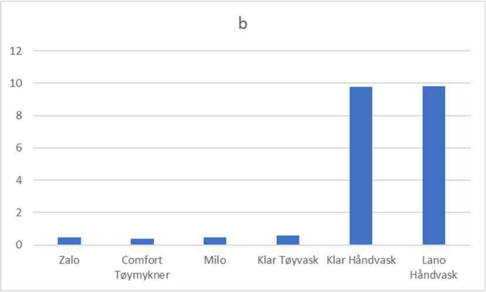

Figure 4: Herschel-Bulkley parameter b.

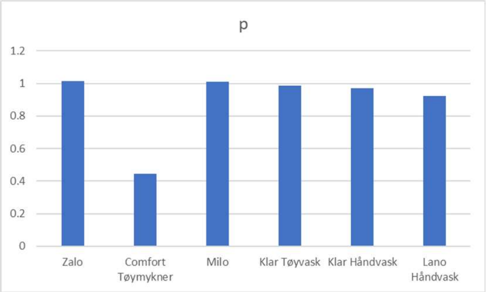

Figure 5: Herschel-Bulkley parameter p.

The results from the low shear rate tests are shown in Fig. 6.

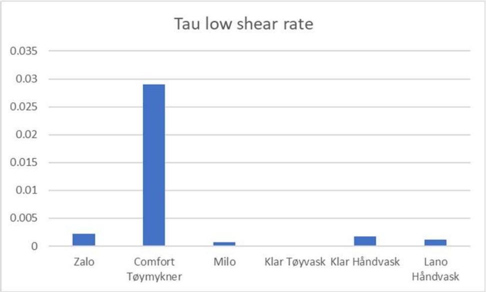

Figure 6: Limiting shear stress at low shear rate.

The results from the start-up tests are all shown in Fig. 7, and the hysteresis results are shown in Fig. 8. Finally, the results from the amplitude sweeps are shown in Fig. 9.

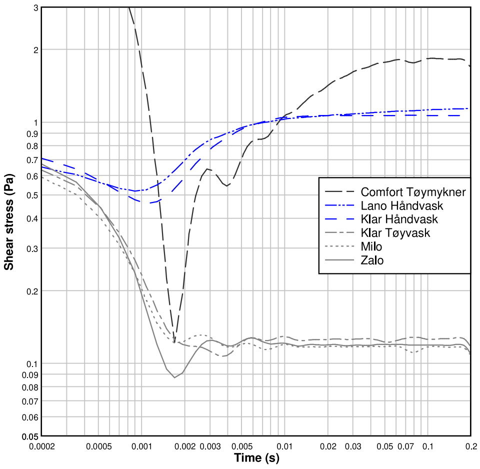

Figure 7: Results from start-up test with shear rate of 0.1 1/s.

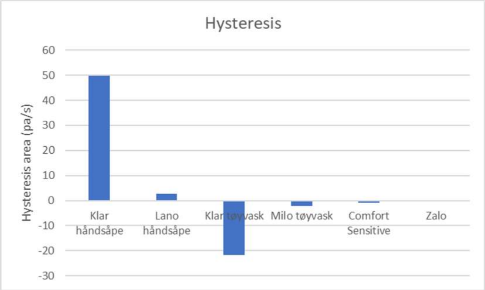

Figure 8: Hysteresis area from shear stress versus shear rate diagram. Positive value indicates recovery, a negative value indicates degradation.

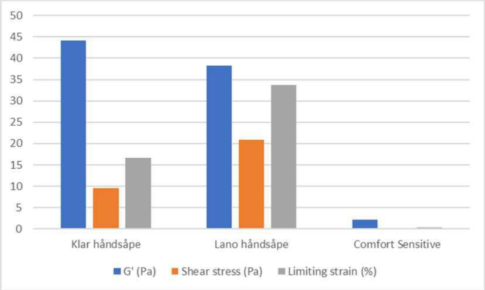

Figure 9: Stiffness, strength and limiting strain from amplitude measurements.

DISCUSSION

The Herschel-Bulkley parameters show that Comfort Sensitive tøymykner exhibits a clear yield stress, and Zalo and Milo show signs of a yield stress (Fig. 3).

Fig. 4 shows that the hand wash soaps have a much higher viscosity that the other samples. Fig. 5 shows that most of the samples are almost Newtonian, except Comfort Sensitive tøymykner that is clearly pseudoplastic.

The limiting shear stress at low shear rates, shown in Fig. 6, shows that Comfort Sensitive tøymykner has a yield stress as previously was seen in Fig. 3.

The start-up tests, shown in Fig. 7, show that the samples exhibited three different types of responses. The Comfort Sensitive tøymykner started with a high value, dropped to a low value and increased back to a high steady value. The hand soap showed similar behaviour, first a small reduction in shear stress followed by a significant increase in shear stress. Klar tøyvask, Milo and Zalo all showed a significant decrease in shear stress with time.

Fig. 8 shows that some of the samples exhibited a thixotropic behaviour. The Klar hand soap has a strong positive value, indicating structure recovery, while the Klar tøyvask exhibited a strong negative value, indicating structure degradation. The remaining samples did not show clear thixotropic behaviour.

The amplitude sweep results in Fig. 9 show that the hand soaps have a structure. Also, the Comfort tøymykner showed a sign of structure.

CONCLUSIONS

The conclusions from this study can be summarized as follows:

- The results exhibit variations in rheological behavior and show that some of the products show signs of a yield stress, some were Newtonian while other were pseudoplastic.

- Some of the products also revealed clear thixotropic behaviour.

REFERENCES

1. Guida, V. (2009), “Rheology modelling of multiphase detergent processing”, *Comsol Conference, Milano, October 14-16.*

2. Cowan-Ellsberry, C., Belanger, S., Dorn, P., Dyer, S., Mcavoy, D., Sanderson, H., Versteeg, D., Ferrer, D. and Stanton, K. (2014), “Environmental Safety of the Use of Major Surfactant Classes in North America”, *Critical Reviews in Environmental Science and Technology,* 44:1893–1993, DOI: 10.1080/10739149.2013.803777

3. Phelps, Jr. A.H. (1967), “Air pollution aspects of soap and detergent manufacture”, *Technical information report from the T1-2 Committee, Journal of the air pollution control association, Vol 17, N 8.*

4. Bhardwaj, A., Richter, D., Chellamuthu, M. and Rothstein, J.P. (2007), “The effect of pre-shear on the extensional rheology of wormlike micelle solutions”, *Rheol Acta* 46:861–875 DOI 10.1007/s00397-007-0168-9

5.Cowdhury, D. (2013), “Consumer behavior of soaps and detergent with reference to Thanjavur District, Tamilnadu”, *International Journal of Advancements in Research & Technology,* Volume 2, Issue 4, 79 – 83, ISSN 2278-7763

6. Reed, C. (2020), “How Soap kills covid-19 on hands”, UNESCO Science Communications Consultant 06.04.2020.

7. Steffe, J. F., “Rheological Methods in Food Process Engineering”, 2^{nd} ed. 1996, Freeman Press, East Lansing, Michigan, USA. 317-339, ISBN: 0-9632036-1-4