Product stability and shelf-life - What rheology has to do with it

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Introduction

Whenever two-phase systems like emulsions, suspensions or foams are used, one of the most important questions is their long-term stability crucially important for example for a product's shelf-life. Depending on how much the two phases differ in density and chemical nature, it takes special preparation steps and/or additives to ensure a stable product.

Phase separation happens when one phase migrates through the other phase e.g. due to gravity or buoyancy. The flow behaviour of both phases is essential for the understanding of this process. A modification of at least one phase's flow behaviour can be used to reduce or suppress phase separation.

In order to avoid sedimentation of solid particles dispersed in a liquid phase, the viscosity at low shear rates has to be high to slow down the sedimentation process. To stop the phase separation completely a yield stress can be introduced into the product either by selecting suitable components or by using suitable additives. Subsequently, rheology is one of the most important methods when formulating a new product or testing an existing one with a focus on its long-term stability.

Methods and materials

Measuring viscosities at low shear rates can be time consuming due to the longer equilibration times at low shear rates. To minimize the time necessary to record a viscosity curve it is important to use a rheometer, which is able to quickly reach the desired rotational speed and keep it constant even at the lowest speeds. Using its fast and precise speed control (Figure 1) combined with its excellent torque sensitivity, the Thermo Scientific™ HAAKE™ MARS™ Rheometer can record viscosity curves over a wide range of shear rates.

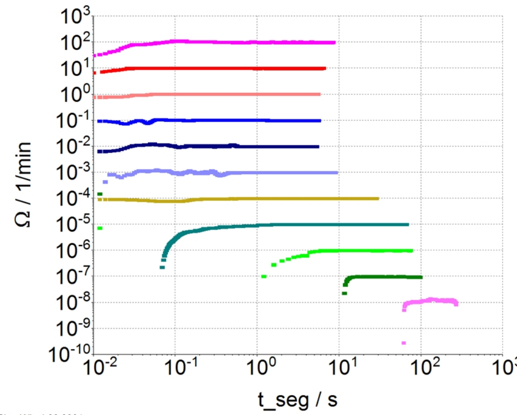


Figure 1: Its modern control loop design allows the HAAKE MARS Rheometer to quickly reach a constant rotational speed even at ultra low rates of 10-8 rpm.

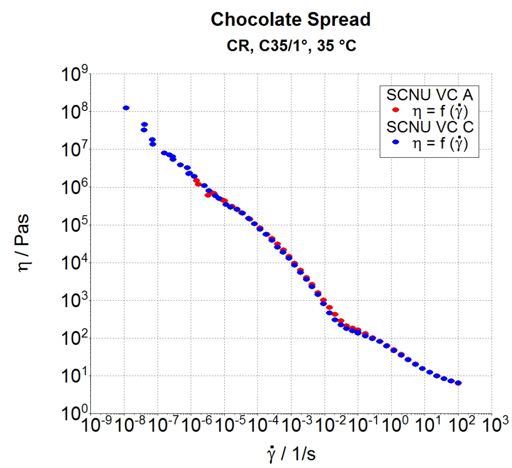


Figure 2: Viscosity curve of a chocolate spread at 35 °C over 10 orders of magnitude in shear rate. The viscosity drops by more than 7 orders of magnitude during the test.

Results and discussion

Figure 2 shows an example for a viscosity curve starting from a shear rate of 10^{-8} s^{-1}. Despite the fact that the shear rate spans a range of 10 orders of magnitude, the curve has been recorded using a single measuring geometry within a single run.

The yield stress τ_0 is the stress level at which a material ceases to behave elastic and starts to flow. While a high viscosity at low shear rates is only able to slow down phase separation, a sufficiently high yield stress can fully prevent any sedimentation. The recommended test method for the yield stress is the stress ramp [1]. During the test, the sample is exposed to a continuously increasing shear stress. Data is collected below and above the yield stress. No extrapolation is needed and it is a sensitive method also suitable for smaller yield stresses.

To determine the yield stress a linear stress ramp is used. The ramping time is selected according to the sample's nature and should be chosen to reach the yield stress 2 – 3 min after its start.

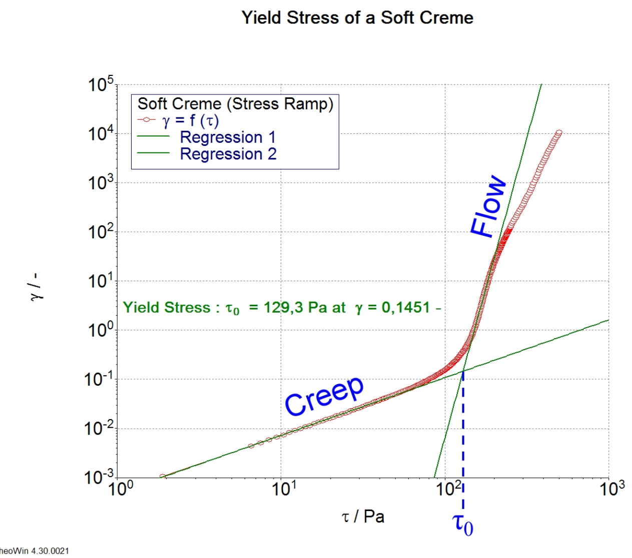
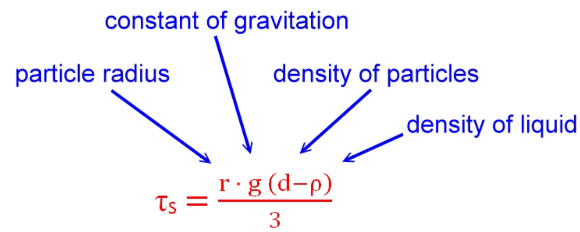


Figure 3: Deformation as a function of stress during a linear stress ramp for a soft crème. The intersect of the curve's slope in the creep regime and the curve's slope in the flow regime marks the yield stress τ_0.

With increasing yield stress a substance is able to bear stronger forces like e.g. the weight force of suspended particles without yielding. Since with increasing yield stress a substance also becomes less flexible it is important to find the optimum value to have a good stability without losing the smoothness needed for the respective application like for a cosmetic emulsion, a lubricant or a specific food product. Figure 3 shows a typical example of a yield stress test result of a cosmetic emulsion. The measuring and evaluation software Thermo Scientific™ HAAKE™ RheoWin™ fits two tangents to the curve's respective creep and flow regime and takes their intersect as the yield stress.

The value obtained can be correlated with the forces trying to destabilize the material like such as the sedimentation stress τ_S that a particle puts on the fluid (Figure 4) to calculate whether sedimentation will occur or not [2].



$$\tau_S = \frac{r \cdot g\,(d-\rho)}{3}$$

$$\tau_S > \tau_0 \Rightarrow \text{sedimentation}$$

$$\tau_S < \tau_0 \Rightarrow \text{no sedimentation}$$

Figure 4: The dedimentation stress τ_S a particle puts on the liquid below it depends on its size and the difference between the particle's density and the liquid's density.

Since some experience is needed for selecting the best parameters and the data evaluation, some users shy away from this test method and look for alternatives. A method, which got some attention due to its simplicity, is to run an oscillation amplitude sweep on the sample and use the end of the linear viscoelastic range (LVR) as a number related to the yield stress (see Figure 5).

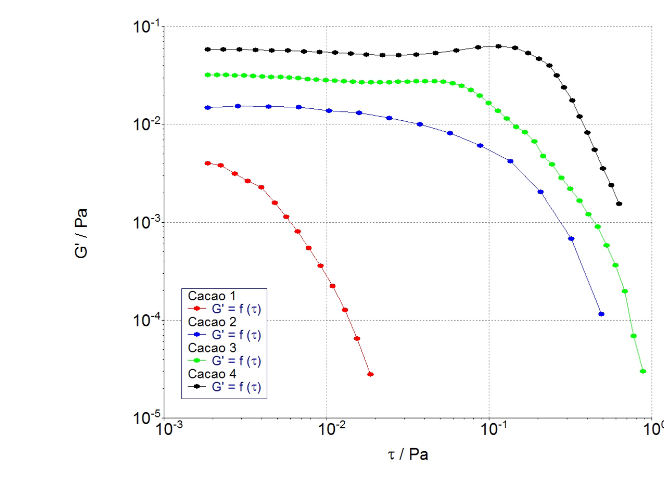


Figure 5: Linear viscoelastic range of different cacao milks. Sample 4 (black curve) is the most stable against sedimentation.

To use this method is tempting because the end of the LVR is usually easily accessible and the results show good reproducibility. Still, it has to be kept in mind that the length of the LVR depends on the oscillatory frequency used and is therefore a relative number only. Even worse, this test does not apply a steadily increasing stress to the sample, which would be the logical consequence of the definition of the yield stress. With an oscillation test, a continuously changing stress is applied for every data point, a completely different way of stressing the sample.

Subsequently the value determined from the oscillation test differs from the yield stress determined with the stress ramp. It is therefore vitally important to agree on a common method before comparing yield stress values.

Conclusion

Rheology is an essential tool when testing the long-term stability of a liquid or paste-like product. The viscosity at low shear rates and the yield stress can be used to reduce or to prevent sedimentation. Due to its torque sensitivity and precise speed control, the HAAKE MARS Rheometer is an excellent choice to determine these parameters with high precision in a very time efficient way.

References

1. DIN Technical Report No. 143 of the NPF/NAB-AK 21.1 "Rheology", Modern Rheological Test Methods - Part 1: Determination of the Yield Point - Fundamentals and Comparative Testing
2. P.B. Laxton and J.C. Berg, Gel trapping of dense colloids. J. Colloid Interface Sci. 285: 152-157 (2005)