

7 Most Important Test Methods

A variety of measurement methods and instruments are used for rheological characterization of cosmetic emulsions. At low shear rates [62] for detection of the apparent yield stress, stressed-controlled rheometer are used because with this type of instrument the stress is preset and the onset of flow can be determined more or less accurately depending on the quality of the angle resolution of the instrument. Characterization of processing conditions requires measurements at high shear rates with a torsional rheometer or at extremely high shear gradients with a capillary viscometer. The measurement system used is also important and will depend on the product to be measured. Watery fluids need a cylinder system, viscous samples the cone-plate system and all other solid materials the parallel plate system. Modern rheometers are versatile and allow different types of strains and combinations thereof, permitting simulation of many operations in a production process.

One of the first experiments performed with a new, unknown sample is the so-called positive ramp test (Fig. 7.1). Here the applied shear stress is increased continuously with time at a constant temperature. It is also referred to as a stress-time ramp. In this experiment an integral viscosity is obtained as a first estimation of the range in which the actual measurements should be performed. A step test is then performed as the second experiment (Fig. 7.2). In contrast to the first

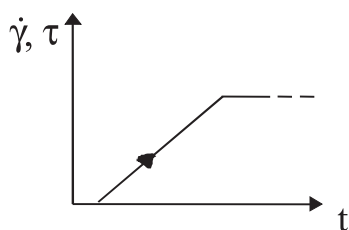


Fig. 7.1. Positive ramp

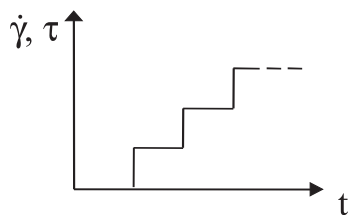


Fig. 7.2. Step test

experiment, here the shear stress is kept constant for a certain time and then increased in several steps. The result obtained is a so-called static viscosity value.

Next the material properties are determined after sudden application (Fig. 7.3) or removal (Fig. 7.4) of a load.

After determining the integral viscosity in a positive ramp test as shown in Fig. 7.1 it is of course also possible to do a negative ramp test (Fig. 7.5) to see whether the sample had been changed by the original positive ramp test. Last but not least, the user is free to choose any combination of these tests (Fig. 7.6) and even change temperatures.

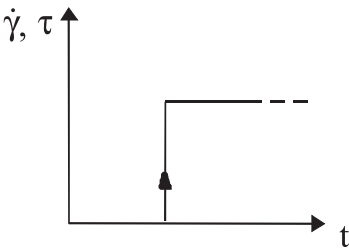


Fig. 7.3. Load jump

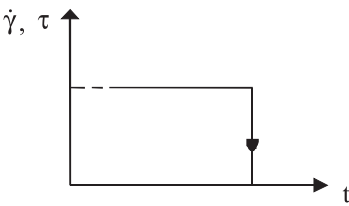


Fig. 7.4. Release jump

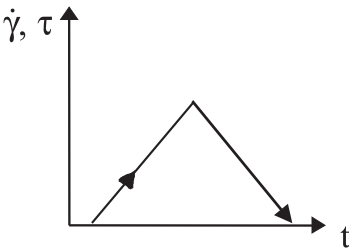


Fig. 7.5. Positive and negative ramp

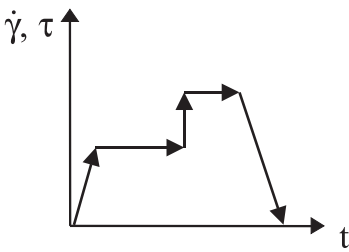


Fig. 7.6. Combination test

7.1 Stress Ramp Test

Now let us take a closer look at the positive ramp or stress ramp test. It is a simple and quick test that can be done with a stress-controlled rheometer. The shear stress is increased continuously within a certain time (Fig. 7.7), the resulting torque measured at discrete time intervals and from this the viscosity calculated. Programming the right stress ramp is crucial. But how can we determine the right ramp? Should it be 20 Pa/min or 100 Pa/min? The experiment provides the answer.

Let us assume that the sample has a yield stress also known as the yield point. This is product-specific and should be determined relatively accurately. A small stress ramp should be programmed for thinner liquids and a larger one for thicker creams. An appropriate number of measurements must be performed to determine if the whole product range can be measured with a single stress ramp.

After programming the stress ramp and performing the measurement the next step is to interpret the resulting curve. Although there are several models available for interpreting measuring curves, they often give rise to relatively large errors because ideal mathematical conditions usually do not exist. Differences already arise from the way in which the results are plotted. If the shear stress is plotted against the shear rate, the curve shown in Fig. 7.8 is obtained. Initially, the force or shear stress applied to the sample does not cause any detectable deformation. In other words, the system remains at rest.

No deformation becomes visible until a critical shear stress has been reached, and a shear rate is determined. Using the mathematical relationship formulated by Herschel–Bulkley:

$$\tau = \tau_0 + K \cdot \dot{\gamma}^n \quad (7.1)$$

the coefficients can be determined and the critical shear stress for the yield stress calculated (corresponding to Fig. 7.8: $C1 = \tau_0$; $C2 = K$; $C3 = n$).

In the tangent method, the abscissa and ordinate are interchanged in the plot (Fig. 7.9). It can be readily seen that the curve shows two linear regions of different

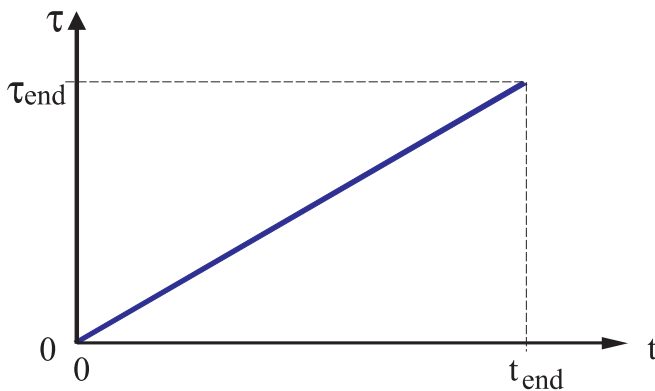


Fig. 7.7. Determination of the apparent yield stress

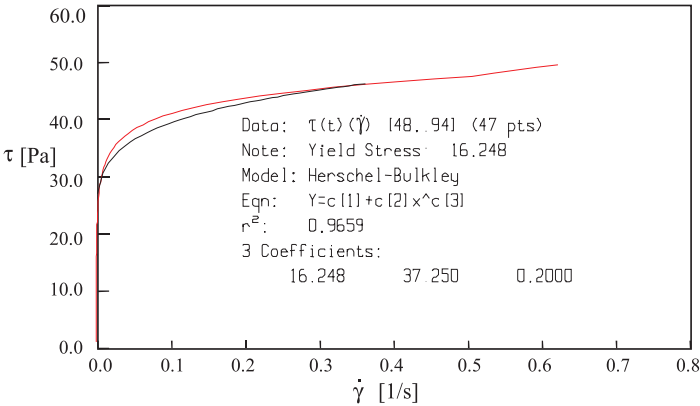


Fig. 7.8. Interpretation of the yield stress according to Hershel Bulkley

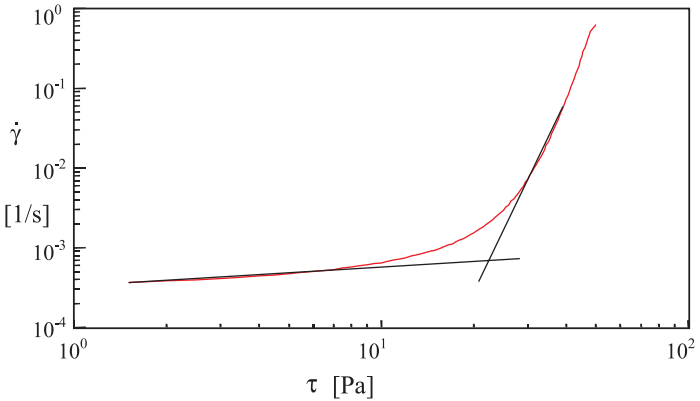


Fig. 7.9. Interpretation of the yield stress according to the tangential method

slope and a transition region. The intersection of the two tangents to the apparent linear regions is interpreted as the yield stress. This method is strongly dependent on the choice of measuring points for each tangent.

A third method for plotting the results [63] of a stress ramp test is the double logarithmic plot of the viscosity vs the shear stress.

In practice, plotting the viscosity as a function of shear stress gives good results. The viscosity initially increases to a maximum (Fig. 7.10) and then decreases again. The stress corresponding to the viscosity maximum is called the critical shear stress $\tau_{critical}$. This is the stress needed to cause the system to flow. Note that the calculated viscosity is an integral of the force over time. Therefore it is the shear stress rather than the viscosity that is the more important parameter for determining the apparent yield stress. In this way, discrete critical shear stresses can be assigned to specific products.

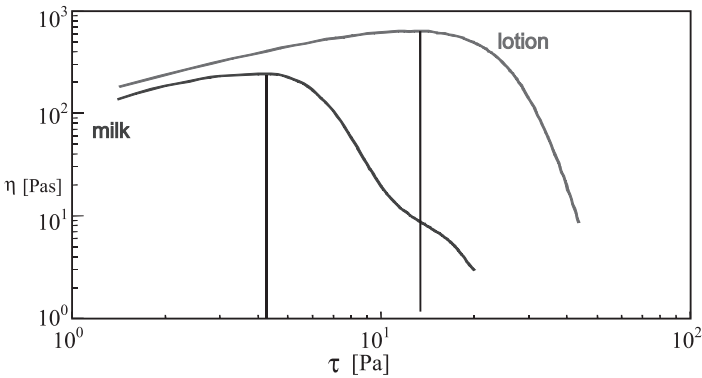


Fig. 7.10. Apparent shear stress of two products

7.2 Newtonian Flow Behavior

Products containing surfactants usually exhibit Newtonian flow behavior (Fig. 7.11). This is typically detected in the lower shear rate range. If flow behavior is Newtonian, the viscosity at constant temperature is independent of the applied stress or the velocity gradient. The value obtained is the mean of the viscosities over the velocity gradient.

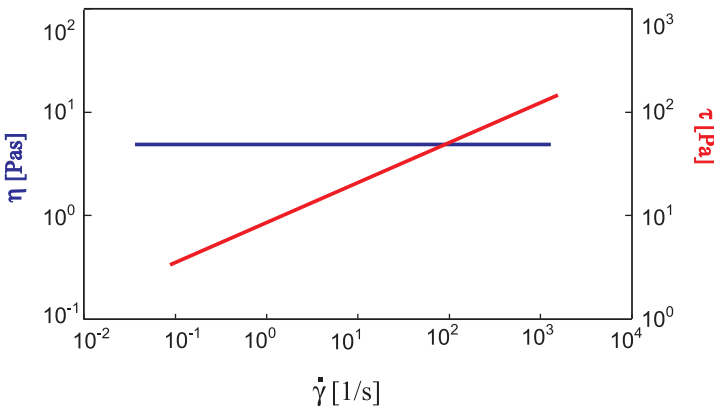


Fig. 7.11. Newtonian flow of a surfactant-containing product

7.3 Creep Test and Creep Recovery

The creep test is a simple and quick test for obtaining initial information on the viscoelastic properties of a sample from viscosity-relevant (as opposed to oscillation measurements) data. In this experiment (Fig. 7.12) a constant force

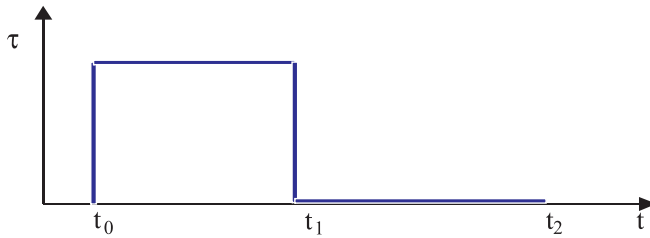


Fig. 7.12. Creep and creep recovery test

(shear stress) is applied to the sample at time t_0 and removed again at time t_1 . The recovery up to time t_2 is recorded.

The sample responds initially to the force applied at t_0 with deformation. In other words, it starts to creep. At t_1 (after removal of the force), the sample recovers again. There are three different types of creep and creep recovery curves.

7.4 The Ideal Elastic Behavior

The first case we will consider is an ideal elastic body as exemplified by a steel spring. If a force is applied to the spring it responds with a deformation but returns to its original state after the force is removed (Fig. 7.13).

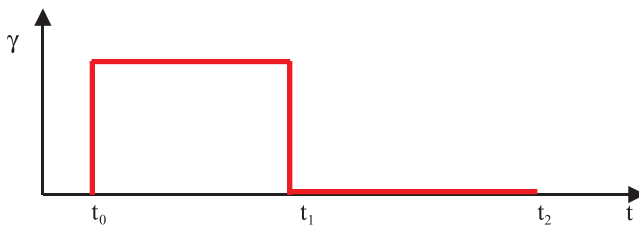


Fig. 7.13. Creep and creep recovery of an ideal elastic body

If the force τ is doubled, the deformation γ also doubles. Ideally, the energy stored in a spring will be recovered 100%. A body with these properties is also known as a Hookean body.

7.5 The Ideal Viscous Behavior

The second case we will consider is water as an example of an ideal fluid. The force τ applied to the fluid causes a linear deformation γ over time. In other words, the sample begins to flow.

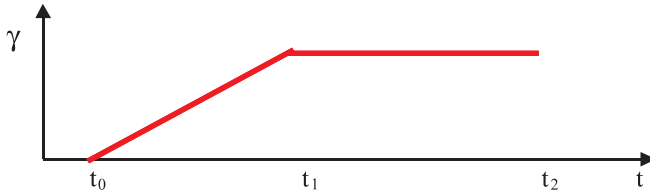


Fig. 7.14. Creep and creep recovery of an ideal viscous body

If the force is removed from the sample (Fig. 7.14), the deformation attained at this time (in our example t_1) is fully retained. The model in this case is the dashpot model according to Newton.

7.6 Real Viscoelastic Behavior

A real body is both viscous and elastic. This means that when a force is applied at the time t_0 deformation begins to take place much more slowly and, if we wait long enough (until t_1), the curve will approach a constant slope.

When the force is removed, part of the energy stored in the body will be released. The result is a recovery of the elastic part γ_e and a permanent deformation (Fig. 7.15) of the viscous part γ_v . A viscoelastic solid will therefore recover after a time lag but it will do so almost completely.

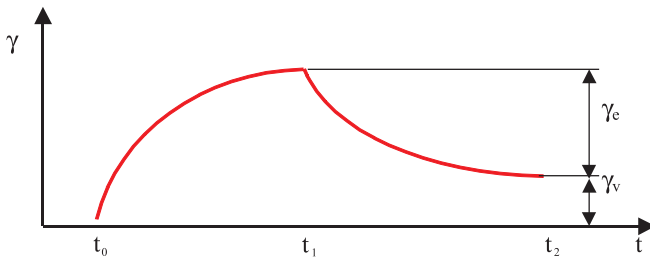


Fig. 7.15. Creep and creep recovery of a real viscoelastic body

7.7 Steady Flow Curve

The best way to measure the viscosity of a non-Newtonian sample at constant temperature and known shear rate is to program a time test. Since both the measuring instrument and the sample need a finite time to reach constant conditions, in other words until the whole system is in equilibrium (Fig. 7.16), it is necessary to wait a certain time before measured values are obtained that can be evaluated.

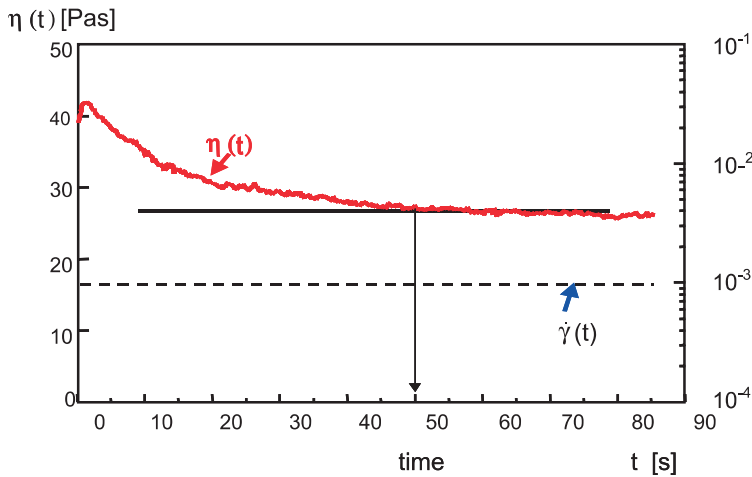


Fig. 7.16. Approach to equilibrium in static measurements

In the extreme example shown in Fig. 7.16, the viscosity increases within the first few seconds at 25°C and a shear rate of 0.001s^{-1} . After passing through a maximum, steady state conditions are not reached until after about 50 s and the viscosity measurement can begin. If several shear rates are applied sequentially in a step test (Fig. 7.2), the following results are obtained.

In the first segment of Fig. 7.17 at a shear rate of $\dot{\gamma} = 0.01\text{s}^{-1}$ steady state conditions had still not been achieved after 150 s. At $\dot{\gamma} = 0.1\text{s}^{-1}$ constant values could not be measured until after 75 s. At $\dot{\gamma} = 1\text{s}^{-1}$ this was already the case after 25 s. Consequently, the greater the shear rate is the sooner steady state conditions

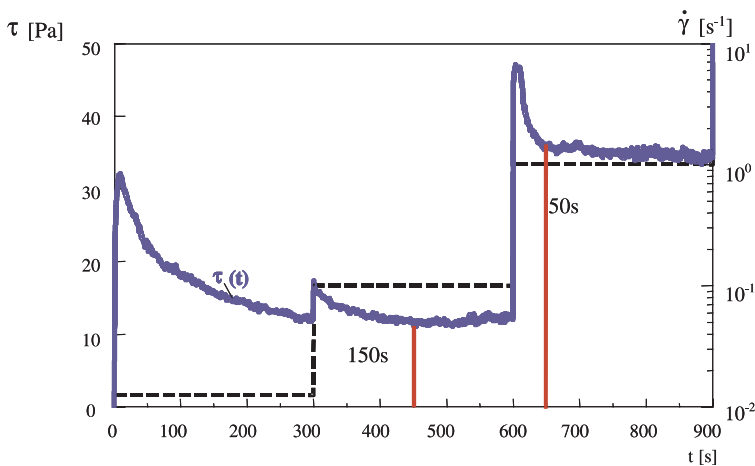


Fig. 7.17. Steady viscosity curve for non-Newtonian samples

will be reached. In other words, the lower the shear rate needed for a measurement the longer the measuring time will be and vice versa.

If we want to measure the static viscosity at higher temperatures with low shear rates, the relatively long measuring time is a considerable disadvantage because the sample can begin to dry out during the measurement (Fig. 7.18).

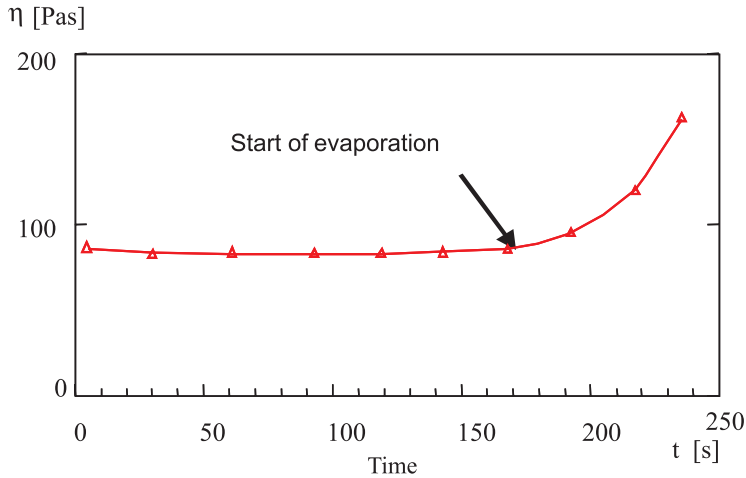


Fig. 7.18. Evaporation at higher temperatures

It is extremely important to keep as many boundary conditions as possible constant when measuring the viscosity because the viscosity depends on many factors including:

- Shear gradient
- Time
- Temperature
- Density
- Solids content
- Molecular weight

This makes it relatively difficult to determine why the viscosity changes during a measurement. Rheological measurements measure the effect and not the cause. Many measurements and the experience gained from them are needed to be able to interpret the data correctly.

7.8 Amplitude Dependence

Now let us consider oscillation measurements. This type of measurement provides information on the structural properties of materials. There are four different measuring variations:

- Amplitude variation
- Frequency variation
- Time dependence
- Temperature dependence

The amplitude variation, also known as the strain test, is performed at constant temperature and frequency (Fig. 7.19). Starting at small amplitudes, the strain is increased in small steps.

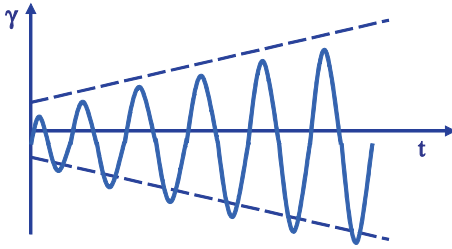


Fig. 7.19. The amplitude or strain test at $T = \text{const.}$ and $\omega = \text{const.}$

Obtained as the response are the two moduli G' and G'' , which run nearly parallel in the lower frequency range. At a product-specific frequency, the response is no longer linear. The linear range is also called the linear viscoelastic range (LVR).

In the example shown in Fig. 7.20 the experiment was run at a frequency of $\omega = 100 \text{ rad/s}$ and $T = 25^\circ\text{C}$. The plots of the moduli G' and G'' vs frequency are double logarithmic. At a strain of approximately $\gamma \approx 0.4\%$ (in this example 100% strain corresponds to 0.5 rad) it can be seen that the storage modulus G' leaves the linear range. Why do we need to perform the measurement in the linear viscoelastic range?

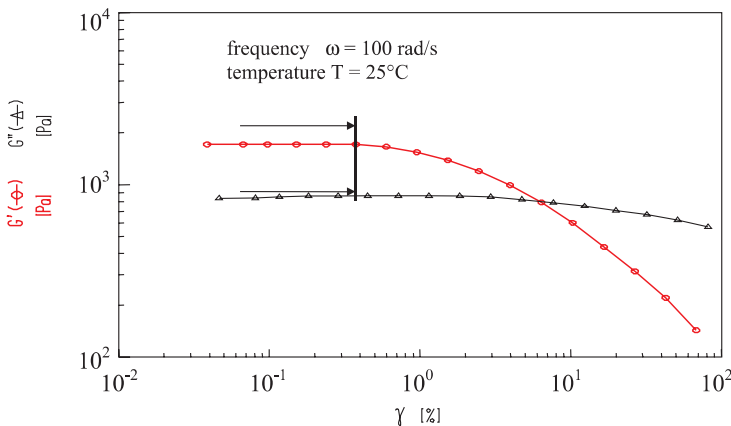


Fig. 7.20. Determination of the linear viscoelastic range with the amplitude test

Rheology Essentials of Cosmetic and Food Emulsions

Brummer, R.

2006, XVIII, 180 p., Hardcover

ISBN: 978-3-540-25553-6