Application note | V282

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Investigating the viscoelastic behavior of cosmetic emulsions by performing creep and recovery tests

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Introduction

Understanding the complex flow and deformation behavior of cosmetic emulsions helps to design and optimize final products, to meet the consumer expectations in terms of appearance and behavior during application. Rotational rheometers are the ideal instruments to investigate the rheological properties of liquid and semi-solid formulations. Rheological tests can also be used to simulate processing condition to make production more efficient as well as to assess product stability and shelf life behavior.

For complex materials, like for instance all types of dispersed systems, we differentiate in general between their viscous and elastic properties. Both contribute to the overall flow and deformation behavior and the perception of a material during application. A various number of test methods are available to measure the response of a material to an external mechanical excitation.

Theoretical backround

Creep and recovery tests are the most direct way in rheology to qualify and quantify the elasticity of a material. The experiment is divided into two segments. During the first part, the creep, an instantaneous stress signal is applied to the sample for a defined period of time. In the second part, the stress is removed again and the recovery of the sample is monitored. The response of the sample is a deformation curve with a shape depending on both, the amount of stress applied by the rheometer and the microstructure of the sample. For pure viscous and pure elastic materials the results of a creep and recovery experiment are shown in Figures 1a and b, respectively.

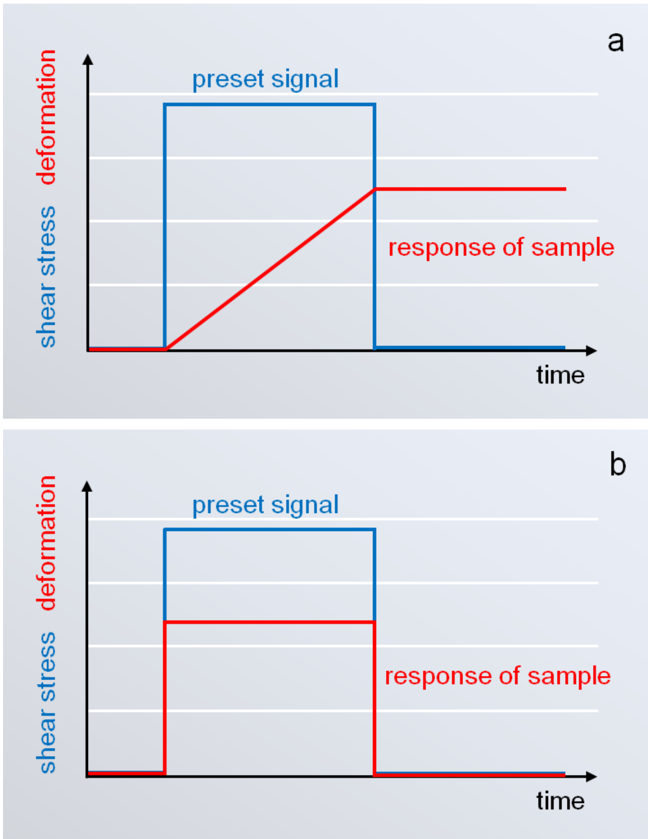

Figure 1: Behavior of a pure viscous (a) and a pure elastic (b) material in a creep and recovery test.

For a pure viscous material the deformation increases linearly over time as long as a constant stress signal is applied. The constant slope of the deformation signal indicates steady shear conditions over the entire creep phase.

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Once the stress is removed from the viscous sample the deformation signal will remain constant and no recoil (reverse motion) is observed (Figure 1a). All kinetic energy brought into the material during the creep phase dissipates into heat energy and is not stored in the material. The viscous material does not show any elastic response. The other extreme behavior is the one of a completely elastic material. When neglecting all effects caused by the instrument and sample inertia, this type of material shows an instantaneous and constant deformation once a step stress is applied.

In the recovery phase the deformation jumps back to zero (Figure 1b). The recoil is a result of the elasticity of the material. All energy is stored inside the material and released again once the external stress is removed.

Most complex materials do not behave like an either purely viscous fluid or a purely elastic solid. They exhibit both, viscous and elastic properties. The degree of the two components depends on the characteristics of the sample as well as the magnitude of applied stress. The possible outcome of a creep and recovery test with a viscoelastic sample is shown in Figure 2.

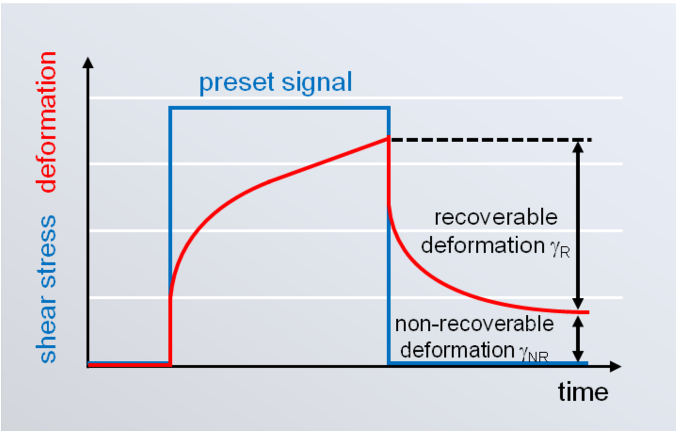

Figure 2: Behavior of an ideal viscoelastic material in a creep and recovery test.

The deformation curve can be divided into different sections. During the creep part the viscoelastic material shows an instantaneous increase in deformation as a first response. This can be assigned to initial elastic stretching of the structural units of the sample. The second part is a delayed viscoelastic response, where first changes to the microstructure are occurring. Once all elastic components are fully stretched, a steady state flow with a linear increase of the deformation signal over time is observed. When the stress is removed an instantaneous elastic recoil, followed by a delayed viscoelastic reversed deformation is observed. After a certain period of time a constant value is reached and the sample is fully recovered again. As shown in Figure 3, the total deformation of the material during the creep phase can be separated into two categories: the recoverable deformation γ_R and the non-recoverable deformation γ_{NR}. The more elastic a material behaves, the more recoverable deformation can be observed during the recovery part. It is important to note that percentage of recoverable deformation (in comparison to the total deformation) for a viscoelastic sample will decrease the longer the duration of the steady state flow during the creep period. A more absolute measure of the total elasticity of a material is the so called equilibrium compliance J_e. The equilibrium compliance is the ratio of the recoverable deformation and the applied stress during the creep phase:

$$J_e = \gamma_R / \tau \qquad [1]$$

Materials and methods

In order to measure the recoverable deformation of a material correctly, a rheometer with a low friction bearing should be used. Instruments with a mechanical bearing will in general show a too low recoverable deformation since some of the energy stored inside the sample is needed to overcome the internal friction of the rheometer. This is especially true for materials that exhibit a very fragile structure and only low elasticity.

The results presented in this report were obtained using the Thermo Scientific™ HAAKE™ Viscotester™ iQ Air Rheometer in combination with a Peltier temperature control unit for parallel plates and cone & plate geometries (Figure 3). Several creep and recovery tests were performed on a commercially available soft cosmetic emulsion. A 60 mm 1° degree cone measuring geometry was used for all measurements. All tests were performed at 20 °C. Creep and recovery tests were performed at different shear stresses during the creep period. Five values have been selected: 4, 6, 8, 10 and 12 Pa. The duration of the creep and the recovery parts was kept constant at 100 s and 200 s, respectively. An example for a job (procedure) setup for a creep and recovery test with the Thermo Scientific™ HAAKE™ RheoWin™ Job Manager Software is shown in Figure 4.

Figure 3: HAAKE Viscotester iQ Air with Peltier temperature control.

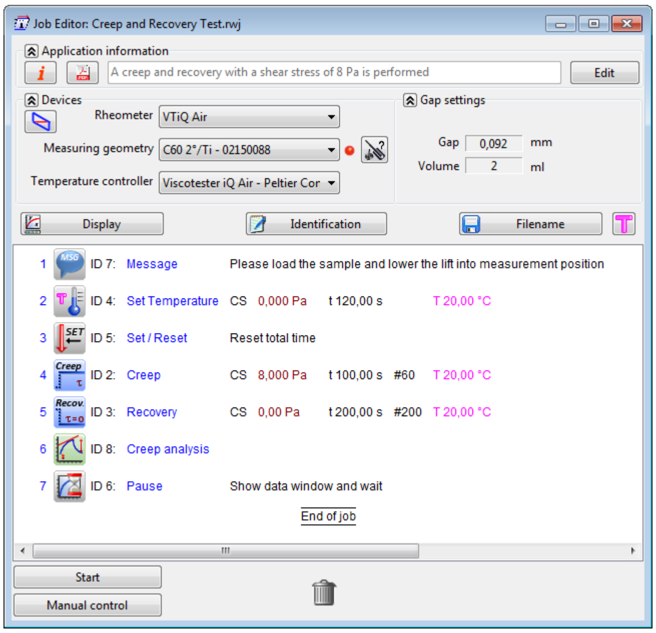

Figure 4: HAAKE RheoWin routine for a creep and recovery test including data evaluation.

Results and discussions

The results of creep and recovery tests with the cosmetic emulsion performed with different stresses are shown in Figure 5. It can be seen, that the sample behaves like a viscoelastic material with an instantaneous deformation (elastic response) once the stress is applied, followed by a delayed viscoelastic deformation. When the stress is removed the sample generates a reverse deformation due to its elasticity and the energy stored during the creep period. It can be seen that the percentage of recoverable deformation is decreasing with increasing shear stress. Table 1 reports the numerical values for percentage of recoverable deformation as calculated by the HAAKE RheoWin Software creep and recovery evaluation routine.

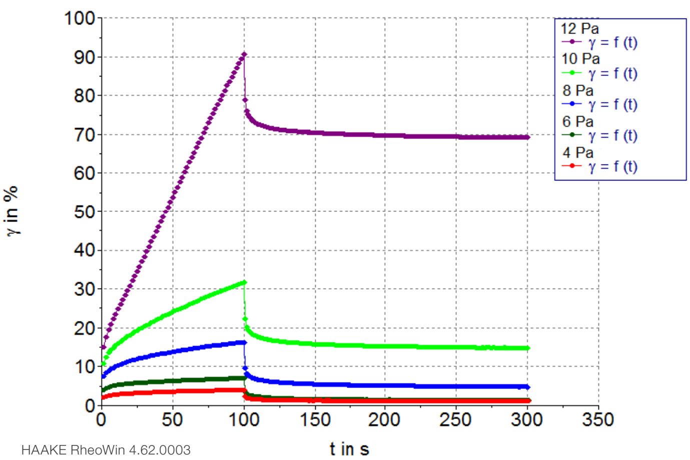

Figure 5: Creep and recovery test with cosmetic emulsion at different shear stress.

For a better comparability of the different runs and to identify major changes in the deformation behavior it is helpful to plot the compliance instead of deformation as a function of time.

Table 1: Percentage of recoverable deformation for different stresses during the creep phase.

Shear stress during creep phase (Pa)	Percentage recoverable deformation (%)
12	23.78
10	53.13
8	70.77
6	79.80
4	76.67

The compliance is defined as the ratio of the deformation, γ and the applied stress, τ:

$$J = \gamma / \tau \qquad [2]$$

Such a plot is shown in Figure 6.

It can be seen that the results of the experiments with a shear stress of 4 and 6 Pa overlay in the compliance versus time plot. This behavior is indicating that the applied stresses in the creep phase are still below the yield stress τ_0 of the tested material. The yield stress is considered the minimum shear stress required to over-come elastic deformation of a material and to generate flow. Above the shear stress of 6 Pa the curves are differing and at 12 Pa a clear linear increase of compliance over time occurs. This is indicating that the yield stress of the sample is exceeded and flow is induced.

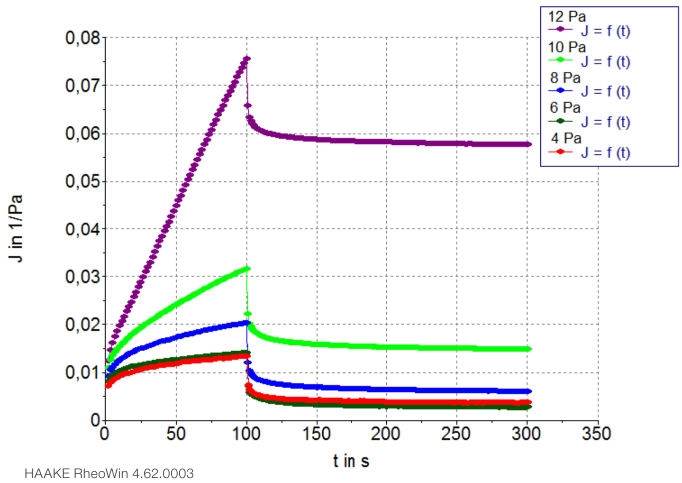

Figure 6: Creep and recovery test with cosmetic emulsion at different shear stress.

The equilibrium compliances values as directly calculated by the RheoWin software are shown in Table 2.

Table 2: Equilibrium compliance for different stresses during the creep phase.

Shear stress during creep phase (Pa)	Equilibrium compliance (1/Pa)
12	0.01683
10	0.01702
8	0.01628
6	0.01156
4	0.01109

At a shear stress of 8 Pa the values of the equilibrium compliance is slightly smaller than for the higher stresses. This is probably due to the fact that at the low shear stress the duration of the creep phase was not long enough to reach the steady state and the elastic components of the sample were not fully stretched yet. On the opposite, at the higher stresses the duration of the creep phase was long enough to reach steady state flow and the calculated values of the equilibrium compliance are, within a certain tolerance, independent of the applied stress.

A standard determination method of the yield stress consists in performing a stress ramp experiment. In this test a linearly increasing shear stress is applied and the deformation of the sample is monitored over time. The result of a stress ramp experiment with the same cosmetic emulsion used for the creep and recovery tests is shown in Figure 7.

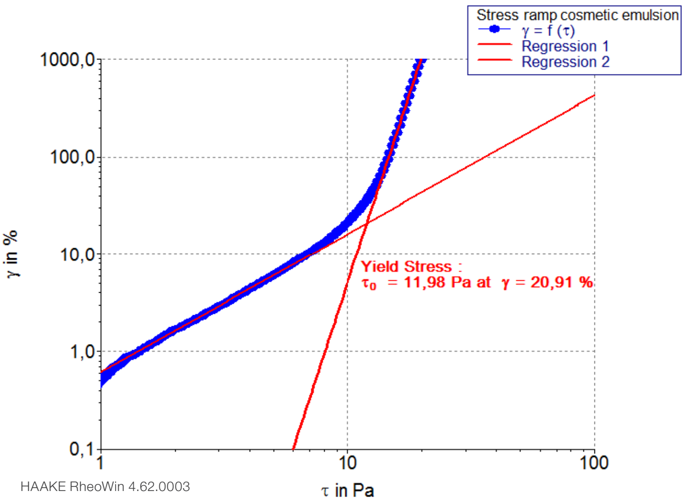

Figure 7: Stress ramp test with yield stress determination according to tangent method for cosmetic emulsion.

The deformation stress curve shows 3 distinct regions. In the first region (i.e. below the yield stress) the sample is deformed elastically by the applied stress. Here the slope of the deformation stress curve is not much larger than 1 in the double logarithmic plot. As the stress increases and approaches the yield stress of the sample, the deformation starts to change more rapidly and the slope increases. At higher shear stresses a second linear region with a higher slope is observed. Here the sample is flowing. A common way to calculate the yield stress using the data collected during a shear stress experiment is the tangent method. The yield stress corresponds to the stress value at the intersection of the tangents to the two linear regions. The yield stress of the cosmetic emulsion according to this method is around 12 Pa. This value is higher than the yield stress estimated from the creep and recovery tests. This difference can be explained by the fact that the intersection of the tangents generates a value which falls into the transition region where the materials behavior is not entirely elastic anymore. The true onset of flow can be obtained when plotting viscosity versus shear stress as shown in Figure 8.

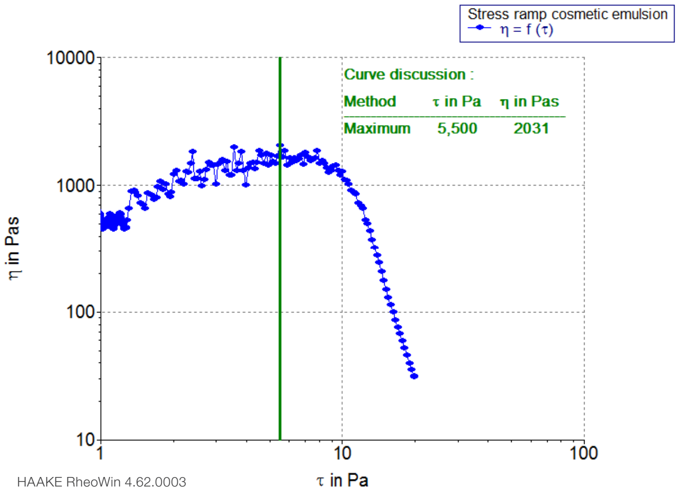

Figure 8: Viscosity as a function of shear stress for cosmetic emulsion with determination of maximum viscosity.

The viscosity curve shows a maximum at 5.5 Pa. In Figure 9 the viscosity data were plotted together with the deformation data on the same graph.

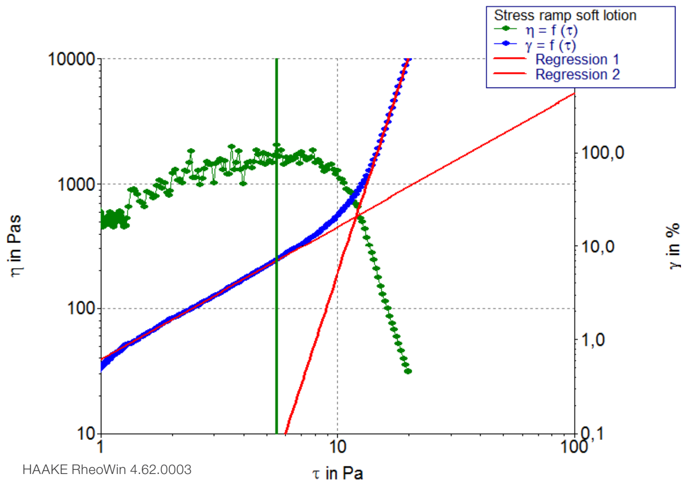

Figure 9: Viscosity as a function of shear stress for cosmetic emulsion with determination of maximum viscosity.

It can be observed that the maximum in viscosity occurs when the deformation enters the transition range. This stress value is in good agreement with a yield stress of 6 Pa derived from the creep and recovery tests.

Conclusion

It was demonstrated that the HAAKE Viscotester iQ Air can be used to perform creep and recovery tests even on weakly structured viscoelastic samples. Creep and recovery tests are not only a useful rheological method to differentiate and quantify the viscous and elastic properties of a material but can also be used to measure yield stresses very accurately.

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