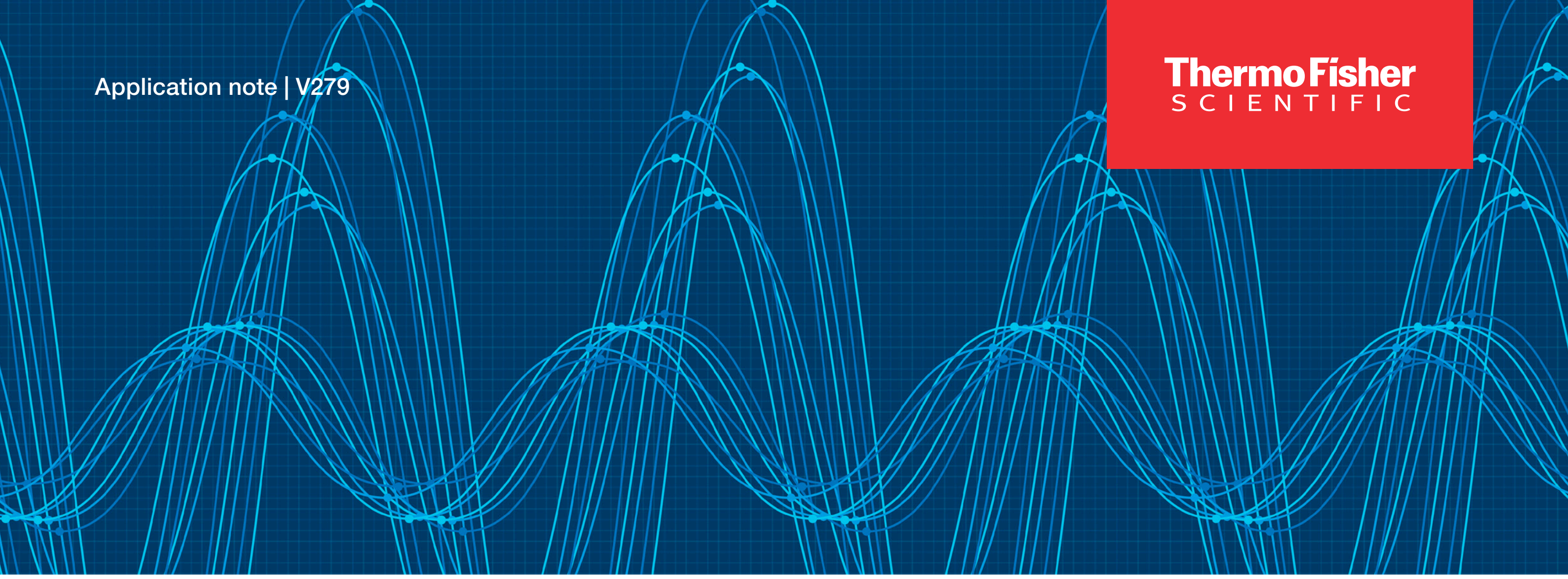


Application note | V279

Performing rheological tests in oscillation with the HAAKE Viscotester iQ Rheometer

Author

Fabian Meyer, Thermo Fisher Scientific, Karlsruhe, Germany

Keywords

Rheology, QC rheometer, Oscillatory testing, Mechanical bearing, Viscoelastic behavior, Linear-viscoelastic range, Curing reactions

Abstract

Rheological tests in oscillation mode are used to determine not only the viscous but also the elastic properties of a material. One of the key benefits of oscillatory tests, compared to rotational experiments, is the fact that, when performed in the linear-viscoelastic range, they are considered to be non-destructive. The microstructure of a sample is not disturbed or destroyed by the applied forces during the experiment. This is why oscillatory tests are the preferred method for investigating the storage behavior and shelf life stability of complex materials. In addition phase transitions, crystallization and curing processes can be investigated by oscillatory tests. However, dynamic oscillatory tests require rheometers with a low-friction bearing system, a low instrument inertia and a highly dynamic motor concept. Therefore, this type of test is usually reserved exclusively for air bearing rheometers. In the following study the oscillatory capabilities of a robust, but still highly dynamic, rotational rheometer with a mechanical bearing, are demonstrated. The results of different types of oscillatory tests for various materials are presented.

Introduction

During rheological tests in oscillation, a sample is exposed to a continuous sinusoidal excitation of either a deformation (controlled deformation mode, CD) or a shear stress (controlled stress mode, CS). Depending on the type of excitation, the material will respond with a stress (in CD mode) or a deformation (in CS mode). When the amplitude values of the applied stress or deformation signal is low, the response of the sample will also show a sinusoidal shape. This range is called the linear-viscoelastic range, and tests that are performed in this range are considered non-destructive, meaning that the applied forces are too low to alter a material's microstructure. Depending on the type of sample, the applied sinusoidal signal and the response of the sample will show a phase shift, delta δ, between 0° and 90°. A phase shift of 0° indicates that the sample shows no viscous response and is considered purely elastic. Examples of materials that exhibit this behavior would be steel or a thermoset polymer. Consequently a phase shift of 90° implies that a material is behaving as purely viscous with no elastic response. Water and low viscosity mineral oils would be examples for samples with this behavior. In real life, most complex materials show both, viscous and elastic behavior,

Figure 1: Thermo Scientific™ HAAKE™ Viscotester™ iQ Rheometer with Peltier temperature control unit and parallel plate geometry.

also known as viscoelastic behavior. Oscillatory measurement techniques are ideal to quantify the amount of viscosity and elasticity hidden in a ma terial's structure. When performed in the non-destructive, linear viscoelastic range, oscillatory tests can be used to study the shelf life stability of a material or to investigate different kind of phase transitions, which include melting, curing or crystallization that may occur under different conditions. Different measurements become available when an oscillatory excitation force is applied to a sample.

These measurements include:

- **Oscillatory Amplitude Sweep**—The frequency of the exciting sinusoidal signal (stress or deformation) is kept constant while the amplitude is increased gradually until the microstructure breaks down and the rheological material functions are not independent of the set parameter anymore. Amplitude sweeps are mainly used to determine the linear-viscoelastic range of a material. However, they can also be used to derive a yield stress.
- **Oscillatory Frequency Sweep**—The amplitude of the sinusoidal excitation signal (stress or deformation) is kept constant, while the frequency is increased or decreased gradually. Frequency sweeps show whether a sample behaves like a viscous or viscoelastic fluid, a gel-like paste or fully cross-linked material.
- **Oscillatory Time Sweep**—Amplitude and frequency of the sinusoidal excitation signal (stress or deformation) are kept constant. The rheological material properties are monitored over time. Time sweeps are used to investigate structural changes that can occur during curing and gelification reactions as well as drying and relaxation processes.
- **Oscillatory Temperature Sweep**—Amplitude and frequency of the sinusoidal excitation signal (stress or deformation) are kept constant, while the temperature is increased or decreased. Due to the thermal expansion of the measuring geometry during a temperature sweep experiment, an automatic lift control is required. Therefore, this type of test cannot be performed with the HAAKE Viscotester iQ Rheometer in combination with either cone and plate or parallel plates measuring geometries.

This application note demonstrates the possibilities as well as limitations for performing different kinds of oscillatory experiments with a robust, mechanical bearing Quality Control (QC) rheometer.

For more information about rheological tests in oscillation mode, please take a look the literature reference (1).

Materials and methods

All tests were performed with a HAAKE Viscotester iQ Rheometer with Peltier temperature control (Figure 1). This compact rotational rheometer is equipped with a highly dynamic, Electronically Commutated (EC)-motor that allows for rotational rheological experiments in Controlled Stress (CS) as well as in Controlled Rate (CR) mode. Despite the fact that the bearing of this instrument is mechanical, and thus the bearing friction as well as the total system inertia is much higher compared to an air bearing rheometer, oscillatory tests in CS mode as well as in Controlled Deformation (CD) mode are possible within certain ranges of frequency, angular deflection and torque. The rheometer can be equipped with various types of measuring geometries, ranging from coaxial cylinders over vane type rotors to parallel plates and cone & plate fixtures. This flexibility allows for testing a broad range of different samples. In rotational mode, this includes materials from low viscous fluids to stiff pastes. In oscillatory mode, medium to high viscous samples can be tested. The specifications/ measuring range for oscillation tests are listed in Table 1.

Table 1: Specifications of the HAAKE Viscotester iQ Rheometer for oscillatory experiments.

	Values
Minimum torque (CS and CD mode)	0.2 mNm
Maximum torque (CS and CD mode)	100 mNm
Minimum deflection angle (CS and CD mode)	10 µrad
Maximum deflection angle (CS and CD mode)	∞
Minimum oscillatory frequency	0.1 Hz
Maximum oscillatory frequency	20 Hz

As a Newtonian standard fluid, a certified mineral oil provided by the German Calibration Service (Deutscher Kalibrierdienst, DKD, Braunschweig, Germany) was used. As a non-Newtonian reference material, a polyisobutylene dissolved in 2,6,10,14-tetramethyl-pentadecane provided by the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) was used.

Results and discussion

Standard materials

To confirm the oscillatory measuring capabilities of the HAAKE Viscotester iQ Rheometer, two certified standard materials were tested first. Figure 2 shows the results of frequency sweeps performed with a Newtonian DKD standard fluid at different temperatures. All tests were performed with a 35 mm parallel plate geometry. The measuring gap was set to 0.5 mm. With decreasing temperature the material becomes more viscous and the measuring range is extended towards lower frequencies. Only data above the minimum instrument torque of 200 µNm is shown. The obtained complex viscosity data is compared with the certified values for the dynamic viscosity provided by DKD in Table 2. It can be seen that the deviation from the certified viscosity is less than 7.5 % for all measured data.

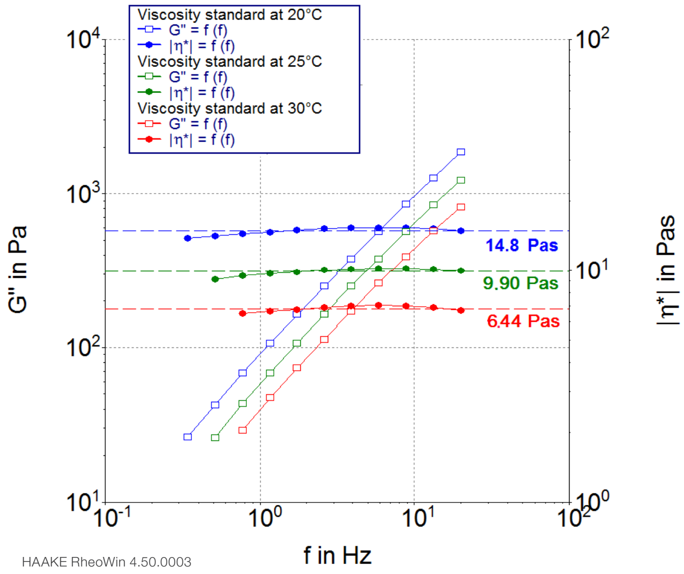


Figure 2: Loss modulus G" and complex viscosity Iη*I as a function of the frequency f for DKD Newtonian standard fluid at three different temperatures.

Table 2: Results of frequency sweeps with DKD Newtonian standard fluid at different temperatures.

	Test temperature		
	20 °C	25 °C	30 °C
Average measured complex viscosity	14.9 Pa·s	9.90 Pa·s	6.44 Pa·s
Max. deviation from average	6.9 %	7.3 %	5.5 %
Certified value for dynamic viscosity	14.7 Pa·s	9.36 Pa·s	6.11 Pa·s
Max. deviation to certified value	6.0 %	6.5 %	6.8 %

Figure 3 shows the results of the amplitude sweep performed with the HAAKE Viscotester iQ rheometer on the non-Newtonian standard material provided by NIST. The test was performed with a 60 mm parallel plates geometry. The measuring gap was set to 0.5 mm. For comparability the same material was also tested with a high-end air bearing rheometer equipped with a 35 mm parallel plates geometry. The measuring gap was set to 0.5 mm.

The results obtained with the HAAKE Viscotester iQ Rheometer show good agreement with the results obtained with the air bearing rheometer. For both, G' and G", the maximum difference between the two instruments is below 5 %. The modulus data clearly allows differentiation between the linear and the non-linear viscoelastic range of the tested standard sample.

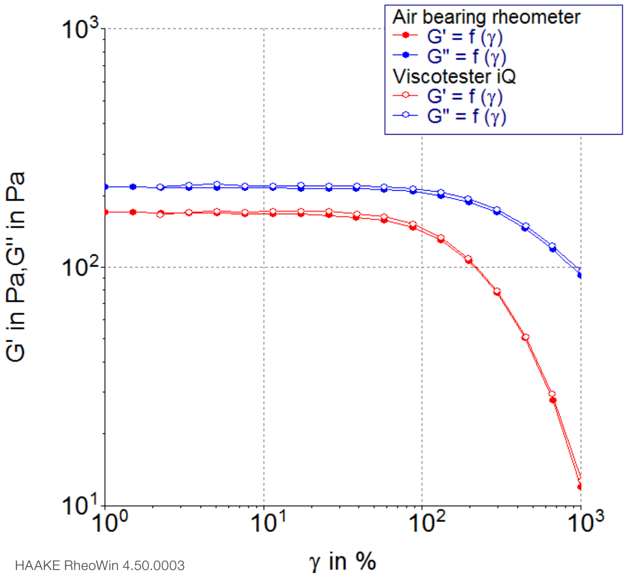


Figure 3: Storage modulus G' and loss modulus G'' as a function of the deformation γ for NIST non-Newtonian standard material at 25 °C.

The information obtained from the amplitude sweep allowed for performing frequency sweeps within the linear viscoelastic range. For this test a deformation of 10 % was select ed. For the frequency range, the maximum available range of the HAAKE Viscotester iQ Rheometer from 0.1 to 20 Hz was selected. The results as well as the certified data provided by NIST are shown in Figure 4. For comparison, the rheological data is displayed as a function of the angular frequency ω. A good agreement between measured and certified values can be observed in Figure 4. The cross-over point of storage (G') and loss modulus (G") was calculated in both cases by the same interpolation method provided by the Thermo Scientific™ HAAKE™ RheoWin™ rheometer operating software. Results from the frequency sweep shown in Table 3 indicate less than 7 % difference between the two calculated modulus values.

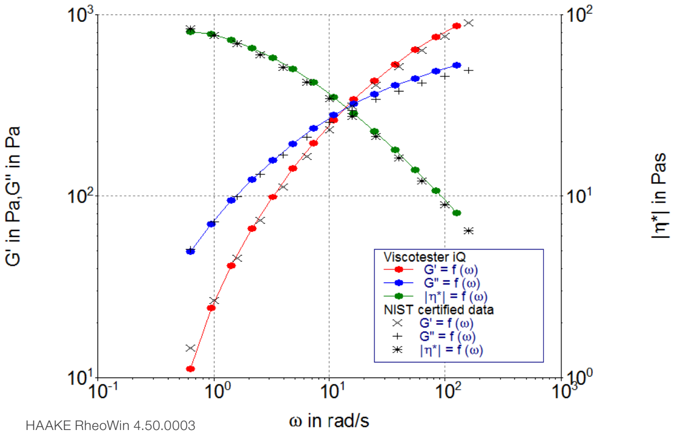


Figure 4: Storage modulus G', loss modulus G" and complex viscosity Iη*I as a function of the angular frequency for the NIST non-Newtonian standard sample at 25 °C..

Table 3: Results of frequency sweeps with non-Newtonian viscosity standard at 25 °C.

	Crossover frequency	Crossover modulus (G'=G")
Calculated cross-over from measured data	13.4 rad/s	300 Pa
Calculated cross-over from certified data	13.5 rad/s	281 Pa

Consumer products

After confirming the performance of the oscillatory measuring mode in the HAAKE Viscotester iQ Rheometer, several consumer products were tested. Amplitude sweeps were performed in order to determine the linear-viscoelastic range of the various materials. The results of the amplitude sweeps are shown in Figure 5. For the tests with the body lotion and the dishwashing detergent, a 60 mm parallel plates measuring geometry was used. The high-viscous skin care cream was tested with a 35 mm parallel plates setup. For all tests the measuring gap was set to 0.5 mm. The test temperature was 20 °C.

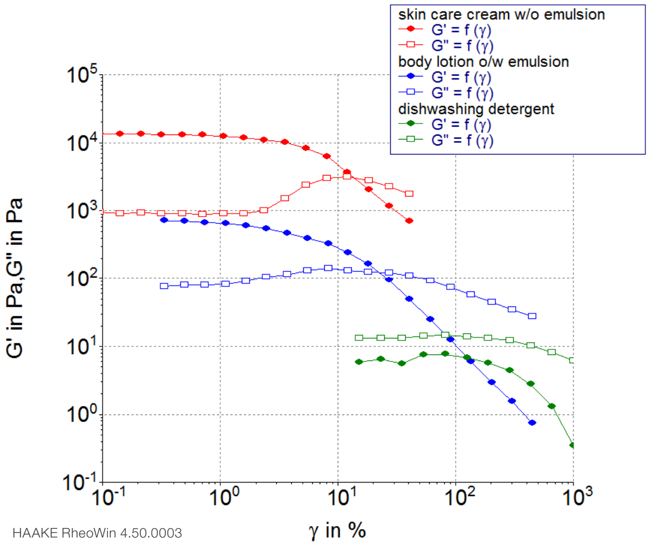


Figure 5: Storage modulus G’ and loss modulus G” as a function of deformation γ of different consumer products at 20 °C.

It can be seen in Figure 5 that the available deformation range depends on the viscosity of the material. Because of the lower torque limitation due to the mechanical bearing, materials with a low overall viscosity cannot be tested at very low deformation. With increasing viscosity the measuring range is extended towards lower deformations. All displayed data points were acquired above the minimum torque value of 200 µNm. Despite the torque limitations, the end of the linear-viscoelastic range can be identified for all three samples. Therefore, frequency sweeps were performed using the following values for the deformation amplitude.

- Skin care cream w/o emulsion: 1 %
- Body lotion w/o emulsion: 1 %
- Dishwashing detergent: 100 %

Figure 6 shows the results of the frequency sweeps. All tests were performed over the entirely available frequency range of the HAAKE Viscotester iQ Rheometer. However, only data acquired above the minimum torque of 200 µNm is displayed.

As expected for this type of material, both cosmetic emulsions do show a predominantly elastic behavior over the entire available frequency range. The bigger difference between G’ and G” for the skin care cream compared to the body lotion indicates a higher storage stability and a lower tendency towards phase separation. The dishwashing detergent shows a crossover point in the investigated frequency range. This material is predominantly viscous at lower frequencies and more elastic at higher frequencies. The data in the range of lower frequencies does not indicate any kind of yield stress behavior.

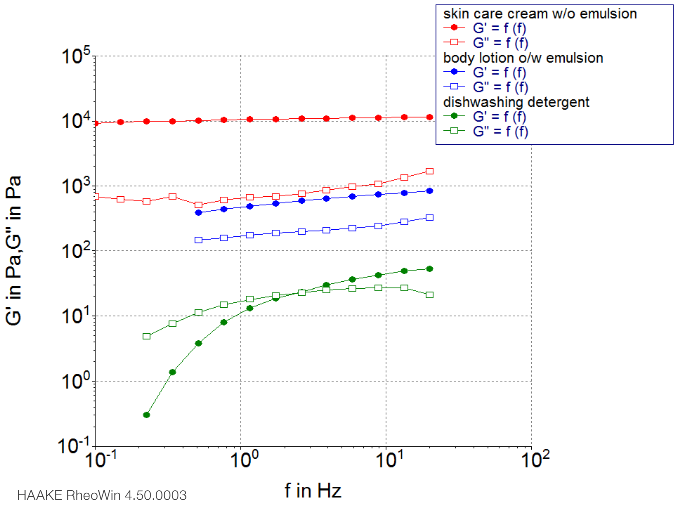
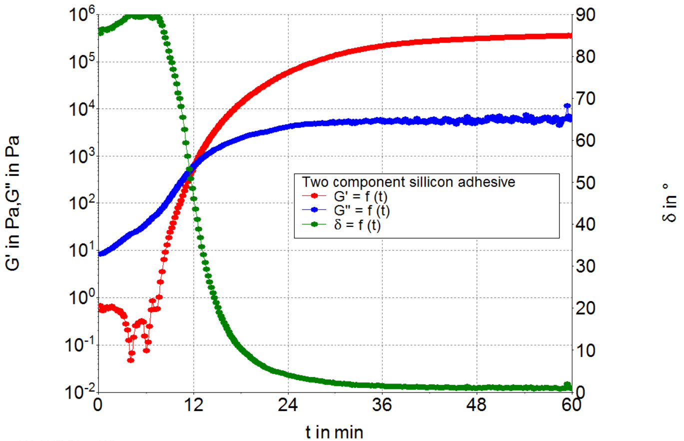


Figure 6: Storage modulus G’ and loss modulus G” as a function of frequency f for different consumer products at 25 °C.

Curing reactions

Oscillatory tests are also used quite frequently for investigating curing reactions, where the sample is going through a liquid to solid phase transition. Parameters like curing time, final strength as well as the gel point (cross-over of G’ and G”) can be obtained from these rheological tests. Figure 7 shows the rheological data of a curing reaction performed with a two-component silicon adhesive. After mixing the two components, the sample was loaded on the bottom plate of the rheometer and an oscillatory time sweep experiment was started right after the measuring gap was set to 0.5 mm. The test was performed with a 35 mm parallel plates geometry in CS oscillation mode. The applied shear stress was 100 Pa and the test temperature was 70 °C.

The tested two-component system shows a phase transition from a more liquid to a more solid like behavior. In the first minutes of the experiment, G” is dominant. With ongoing reaction time, both moduli are increasing while G’ is increasing more rapidly. After 12 minutes a cross-over between G’ and G” can be observed. From then on the sample is behaving predominantly elastic and the slopes for both moduli are decreasing again. After 60 minutes the moduli are constant and the mechanical behavior of the material does not change anymore.



HAAKE RheoWin 4.50.0003

Figure 7: Storage modulus G', loss modulus G" and phase angle δ as a function of time t for a two-component silicon adhesive at 70 °C.

Conclusion

It was demonstrated that oscillatory experiments can be performed with a mechanical bearing rotational rheometer in CD as well as in CS-mode using the HAAKE Viscotester iQ Rheometer. Though the measuring range is limited compared to a high-performance, low-friction and low-inertia air bearing rheometer, the results allow for the identification of linear- and non-linear-viscoelastic behavior of various materials. Frequency sweeps in the linear-viscoelastic range reveal details of the microstructure for the given material and allow for predictions about shelf life and stability. In addition, oscillatory test methods can be used to monitor curing reactions and other liquid to solid (or solid to liquid) phase changes.

Reference

1. Schramm G., "A practical approach to Rheology and Rheometry", 2nd Edition 2004, Thermo Electron Karlsruhe.

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