



## Rheology solutions for cosmetics and personal care products

Application compendium

## Rheology solutions for cosmetics and personal care products

Rheological testing methods offer a comprehensive toolbox for the cosmetics industry to support new product development. They are particularly useful in improving processing conditions as well as for quality control of intermediates and finished products. Customer expectations and consumer perception towards texture, spreadability and the general flow behavior can be assessed by easily measurable rheological parameters.

Rheological tests allow for the prediction of stability and the establishment of structure/property relationships. This can be even more revealing when rheometry is used simultaneously with complementary analytical methods such as microscopy or molecular spectroscopy.

Understand what to measure in your cosmetic formulation development and quality control and which tools are best to do it. This collection of application notes, whitepapers and articles covers various aspects of optimizing final product properties and processing via rheological measurements.

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## Choosing the right rheometer/viscometer for testing cosmetic/personal care products

From production to application, rheological properties play an important role during the entire life cycle of liquid or semi-solid personal care formulations. Rheological measurements with different types of instruments are performed in the cosmetics industry on a daily base. These include:

- Simple single point viscosity measurements for a fast batch release in production
- Flow curve or yield point measurements in the quality control laboratory
- Comprehensive rheological investigations for the development of new formulations in research and development

Processability, stability and consistency are the attributes determining consumer perception and thus the overall acceptance of the final product. They can be investigated with various rheological test protocols. In the production of personal care products every stage requires different instrument capabilities. Below the different types of instruments are presented with suggestions on how to select the most suitable one according to the particular production stage.



### Handheld spindle viscometers for on-site viscosity measurements at a single rotational speed:

This type of instrument is easy to operate and provides relative viscosity values within seconds with the push of a single button. By using different types of spindles these viscometers can measure a wide range of viscosities. Food products from low viscous juices up to thick doughs can be tested.



### QC rheometers with automatic lift and integrated normal force capabilities for comprehensive rheological investigations:

Our QC rheometers provide extensive flexibility, ensure fast and consistent characterization of a wide range of samples by using Standard Operating Procedures (SOPs) that are easy to create with the rheometer control software. With automatic lift control and the ability to measure and apply axial forces it can perform squeeze, break and tack tests or even tribological measurements.



### Benchtop spindle viscometers for measurements according to the ISO 2555 standard:

Rotational viscometers with multiple rotational speeds for each spindle can identify more complex flow behavior. The obtained viscosity values are still relative for all non-Newtonian materials but allow for comparing different samples.



### Entry level rheometers for absolute viscosity measurements with integrated temperature control:

Rheometers enable the determination of yield stress, thixotropy and viscoelastic properties. These instruments are available with a broad portfolio of different measuring geometries such as parallel plates, cone & plate, coaxial cylinders and vane rotors in various dimensions.



### Research grade rheometers for extended material characterization over the widest measuring range:

The advanced rheometer can be equipped with dedicated measuring cells for specific applications. With automatic lift control and the ability to measure axial forces it can perform squeeze, break and tack tests. It can also be coupled with other analytical techniques such as microscopy or spectroscopy for simultaneous data acquisition.

The following table provides an overview of the measurements that can be performed and of the properties that can be investigated by the different instruments:

	Thermo Scientific™ HAAKE™ Viscotester™ 3	Thermo Scientific™ HAAKE™ Viscotester™ C, D & E	Thermo Scientific™ HAAKE™ Viscotester™ iQ/iQ Air	Thermo Scientific™ HAAKE™ MARS™ iQ/iQ Air	Thermo Scientific™ HAAKE™ MARS™ 40/60
Type of rheometer	Handheld viscometer	Benchtop viscometer	Rotational rheometer	Rotational rheometer	Rotational rheometer
Portable instrument	Yes	Yes	Yes		
Temperature control options			Yes	Yes	Yes
Automatic lift functionality				Yes	Yes
Standalone operation	Yes	Yes	Yes		
Software controlled operation		Limited	Yes	Yes	Yes
Tests in stress controlled (CS) mode			Yes	Yes	Yes
Tests in oscillation mode (CD & CS)			iQ Air only	iQ Air only	Yes
Tests in controlled rate mode (CR)	Yes	Yes	Yes	Yes	Yes
Normal force capabilities				Yes	Yes
Software	No	Yes*	Yes	Yes	Yes
Application specific measuring accessories					
Submersion flow cell				Yes	Yes
Tribology				Yes	Yes
Interfacial rheology					Yes
Hyphenation capabilities					Yes**
Applications and sample types					
Quality control	Yes	Yes	Yes	Yes	Yes
Research & Development			Limited	Limited	Yes
Single-point viscosity	Yes	Yes	Yes	Yes	Yes
Absolute viscosity data		Limited	Yes	Yes	Yes
Flow/viscosity curve		Limited	Yes	Yes	Yes
Viscoelastic behavior			iQ Air only	iQ Air only	Yes
Low viscous samples	Yes	Yes	iQ Air only	iQ Air only	Yes

\*Thermo Scientific™ HAAKE™ RheoWin™ data evaluation software only for model D, HAAKE RheoWin software available for model E

\*\*Rheo-Microscope, Rheo-FTIR, Rheo-Raman

For a more detailed discussion and custom tailored instrument configurations, please contact your local Thermo Scientific Material Characterization representative or <https://www.thermofisher.com/de/en/home/global/forms/industrial/contact-us-rheology-compounding.html?icid=cosmetics-personal-care-products>

Find more information how rheological measurement can support your QC and personal care formulation development in this cosmetics compendium and visit our cosmetics rheology homepage at [www.thermofisher.com/cosmetics](http://www.thermofisher.com/cosmetics).

## Well prepared - good results

### Authors

Cornelia Küchenmeister-Lehrheuer and Klaus Olddörp  
Thermo Fisher Scientific, Karlsruhe, Germany

### Introduction

In recent years the demands regarding the reliability of rheological test results have grown significantly, like for most analytical methods. Only if correct test results can be produced and easily be reproduced they can be used for the reliable characterization or comparison of substances.

Based on correct test results it is e.g. possible for the QC department to compare different incoming materials or different batches from production no matter whether these results have been produced on different instruments or even on different sites. It is nevertheless essential to use a viscometer or rheometer with a measuring geometry, which gives absolute results, like e.g. coaxial cylinders (CC), parallel plates (PP)- or cone and plate (CP)-geometries. Depending on the sample's nature it can also be necessary to agree upon the test routine and data evaluation method.

Every test result contains a certain error, which is the sum of many effects mainly related to the sample, the instrument and the handling. Using the example of PP- and CP-geometries, this report will describe the preparation of a rheological test aiming to show the possible errors and how to minimize them. It is assumed that the rheometer has been installed correctly and is properly levelled.

### Cone or plate? How to choose the right measuring geometry

The classical measuring geometries available for Thermo Scientific™ HAAKE™ rheometers have a notched top (Fig. 1). The motor axis contains a pin, which fits into the notch thus allowing the geometry to be mounted only in always the same position relative to the motor's rotor.



Fig. 1: Classical measuring geometry with a notched cone (left) and a Connect Assist measuring geometry with a mark on its ceramic shaft for defined mounting (right).

The newer Connect Assist measuring geometries have a mark, which can be aligned with a similar mark on the rheometer to achieve the same effect. When a calibration like the MicroStressControl (MSC) [1] is performed to improve the data quality in the low-torque-range (nNm), its results can also be used for later test since the whole setup motor plus measuring geometry is always assembled exactly the same way.

Measuring plates, used as the lower part of PP- or CP-geometries are also designed to be mounted only in one position (Fig. 2) [2].

In a CP-geometry, the shear rate is constant over the whole sample, whereas in a PP-geometry the shear rate decreases from its maximum value at the edge to zero at the centre of the geometry. When non-Newtonian samples are tested with a PP-geometry, viscosity values always contain an intrinsic error because different parts of the sample are exposed to different shear rates. Therefore if possible, a CP-geometry should be used for viscosity tests. Still, due to the bigger flexibility regarding the measuring gap, PP-geometries are the better and sometimes the only choice for many applications. The diameter of the geometry has to be chosen in relation to the sample's viscosity. For water-like samples it is recommended to use cones or plates with the biggest diameter (60 mm). With increasing viscosity smaller diameters have to be used. For e.g. bitumen or hard rubber an 8 mm plate is often the best choice.

For PP- and CP-geometries the correct amount of sample becomes more important for small sample volumes and big edge effects. Therefore to load the correct amount of sample becomes more important for smaller diameters, smaller gaps and higher sample viscosities.



Fig. 2: For our PP- and CP-geometries, measuring plates TMP with the corresponding diameters are available. The notch under the mark on the TMP slides over the pin in the temperature control unit for easy and precise positioning.

## Determination of the zero gap - reference for the measuring gap

Whenever a cone, a plate or the lower measuring plate has been mounted, e.g. after it had to be removed from the instrument for cleaning or when a different geometry has been selected, the axial zero point of the geometry has to be determined. In other words, the axial position where the upper part of the measuring geometry touches the lower part is needed as the reference point for the precise setting of the measuring gap. Any error of the zero gap will auto-matically lead to an increased error of the test results due to a wrong gap size during the test.

The zero gap can be determined manually using the monitor mode in the Job Manager of the Thermo Scientific™ HAAKE™ RheoWin™ rheometer software (Fig. 3). When using an instrument with an automatic lift (e.g. a Thermo Scientific™ HAAKE™ MARS™ rheometer) it is

recommended to include the auto-matic zero gap determination into the HAAKE RheoWin Job (Fig. 4). This prevents forgetting this important step and leads to a user-independent precisely determined zero gap.

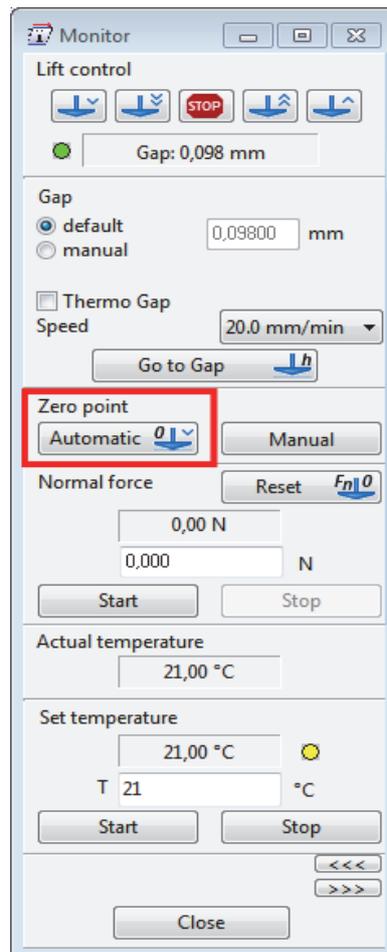


Fig. 3: Automatic determination of the zero gap using the monitor mode.

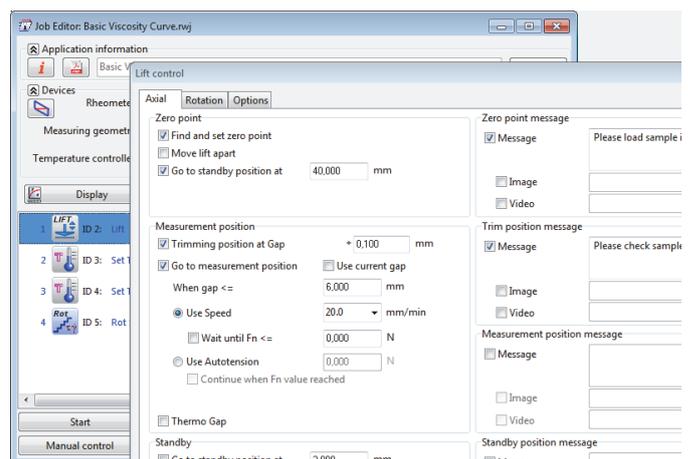


Fig. 4: Automatic determination of the zero gap using the lift control element during a test run. Here a user-defined message has been activated to ask for the sample to be filled into the geometry.

To avoid any error due to thermal expansion or shrinkage of the measuring geometry, the zero gap has to be determined at the temperature, the test is going to be started afterwards. The upper part of the geometry can be put onto the lower measuring plate, which is directly temperature controlled. After the temperature reading remains constant, the upper part of the geometry needs some additional time to adapt to that temperature as well. If

this is done with the upper geometry already mounted, extra care has to be taken that the rheometer's air bearing is not damaged by the expanding geometry for example by setting a small constant normal force. After every part of the measuring geometry has reached the correct temperature, the zero gap can be determined and will be stored as the reference point for the measuring gap.

## Sample history

The pre-treatment or history of the sample can play a crucial role for getting correct and reproducible data. The user has to design the test method keeping in mind that the sample needs to be in thermal and mechanical equilibrium before the rheological test starts i.e. by allowing a sufficiently long waiting time between closing the measuring gap and starting the test. During this time the structure of an e.g. thixotropic sample can recover from the partial destruction during the loading and closing procedure.

In some cases it is impossible to reach a stable equilibrium before starting the rheological test. Common examples are samples undergoing a chemical reaction like e.g. glues or coatings. When dealing with such samples, every step of the sample preparation has to be done following always the same sequence and the same timing to start all tests at the same state of the sample in order to get comparable data. In case of samples with a very long structural recovery like for example some thixotropic coatings, a defined pre-shear in the rheometer helps to start the test at least from the same degree of structural damage thus leading to comparable results. Newtonian fluids do not show any of the effects mentioned above. Here the focus "only" needs to be on correct thermal equilibrium and correct gap filling, which will be looked at in more detail below.

Especially when special accessories are used like for example a sample cover with solvent trap to minimize the evaporation of the solvent in the sample or a measuring geometry with a sand-blasted or serrated surface to avoid slipping, the same set up has to be used to yield comparable results.

The sample volume needed for the correct filling of a measuring geometry can be found in the HAAKE RheoWin software as part of the geometry's properties (Fig. 5) and in the appendix of the rheometer's manual.

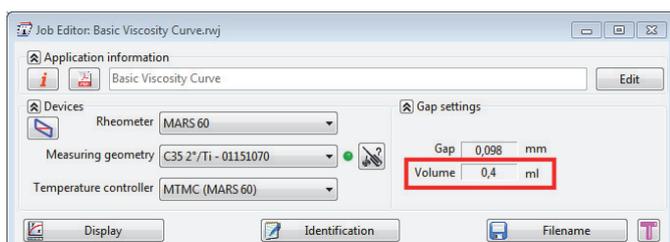


Fig. 5: HAAKE RheoWin software displaying the sample volume for correct gap filling. In this example of a cone C35/2° Ti L, all geometry parameters including the gap and the serial number have been read from the geometry after mounting it into the rheometer.

## Choosing a suitable measuring gap

One of the fundamental differences between PP- and CP-geometries is linked to the measuring gap. For every cone only one correct gap exists, equal to truncation of the cone's tip. In case a different gap is needed, a cone with a different cone angle has to be used. For the typical cone angles between 0.5 ° and 4 ° the gap is usually in the range between 25 µm and 140 µm.

In contrast, the measuring gap of a PP-geometry can be varied within a certain range, so the measuring conditions can be adapted to the sample's properties.

The correct measuring gap for any CP- or cylindrical geometry is part of its set of individual parameters, measured and calculated based on its dimensions. After production every part is measured precisely and its diameter, cone angle and truncation are printed into an individual certificate included in the geometry's box. For the classical measuring geometries, these parameters have to be entered manually into HAAKE RheoWin once and from then on are auto-matically available whenever the geometry is used for a test. With the Connect Assist geometries, all relevant parameters will automatically be transmitted to HAAKE RheoWin when the geometry is mounted into the rheometer.

For both PP- and CP-geometries the rule applies that the measuring gap has to be at least 5 times the diameter of the biggest particle in the sample to be able to measure the sample as whole. In the worst case some bigger particles could pile up under shear and block the gap leading to very noisy data or even damage the surface of the measuring geometry. For example, a suspension with particles up to 100 µm in diameter needs a gap of at least 500 µm. In this case only a PP-geometry can be used because CP-geometries with an angle bigger than 4 ° would not comply with the current standards and do therefore not exist. The factor 5 is just a rule of thumb. Depending on the particle's characteristics, it might become necessary to select an even bigger gap.

When doing tests on foams or emulsions the measuring gap has to be chosen based on the diameter of the biggest bubbles or droplets. Otherwise the sample's properties could already be changed simply because it is squeezed into the measuring gap.

When a sufficiently large measuring gap is used, like e.g. 1 mm with a PP-geometry, any kind of error in parallelism can be neglected due to the tolerance of manufacturing. For very small gaps these small imperfections can lead to an error of the zero gap determination and therefore the measuring gap itself. Either a bigger uncertainty has to be taken into account for test results collected with very small gaps or even greater care has to be invested when producing and adjusting the components for such a test.

## Sample loading, sample trimming, closing the gap- the optimum gap filling

Under ideal conditions, the sample fills the measuring gap completely and without any air bubbles. Around the edge of a PP- or CP-geometry the open sample surface should slightly bulge outwards.

Depending on the sample's consistency a suitable tool should be used to fill the sample into the measuring geometry. For low viscous samples a pipette can be used. For samples with a higher viscosity or stronger texture a spatula or spoon is the right tool. Samples with a delicate structure should be sheared as little as possible during the loading procedure to keep damages to the structure as small as possible. In general, the sample should be placed in the centre of the geometry.

The optimum amount of sample can be found amongst the parameters for each measuring geometry listed in HAAKE RheoWin (Fig. 5). It is recommended to slightly overfill the geometry first in order to avoid air remaining in the measuring gap after closing it. Underfilling of the measuring gap has to be avoided under all circumstances!

After closing the measuring geometry the sample has to be trimmed i.e. the excess of sample that was squeezed out of the gap has to be removed with a suitable tool. Since this procedure leads to a straight sample rim, it is recommended first to go to the trimming position above the measuring gap, trim the sample and then close the geometry thus forming a slightly bulged sample rim.

As rule of thumb, a gap 1 – 5% wider than the measuring position is used as trimming position. After loading the sample this position is set either manually or automatically during a running test method in the HAAKE RheoWin software. For sensitive samples the lift speed should be reduced to minimize the damage to the sample's structure during closing the gap.

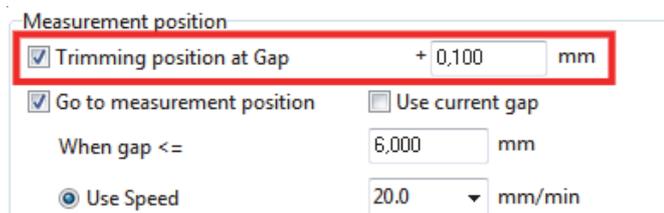


Fig. 6: Parallel plate geometry in measurement position without and with sample cover. The trimming position can be set in HAAKE RheoWin. Recommended are 1 - 5% above the measuring gap chosen for the test (in the example above 100  $\mu\text{m}$ ).

When the upper geometry approaches the trimming position using HAAKE RheoWin's lift function, the axis of the rheometer is locked to avoid any damage to the sample's structure by an accidental turning of the measuring geometry. The excess sample can be removed with a lab spatula or a special trimming tool [3]. The lower plate shown in Fig. 7 has been chosen to match the upper geometry's diameter, which makes the necessary trimming procedure much easier.

The tools selected for trimming should be made of a non-absorptive material to avoid any solvent being sucked out of the sample. Any kind of simple paper or wooden tool is therefore excluded. The tool should have a straight edge to form a clean straight sample surface.



Fig. 7: Lower measuring plate TMP with a diameter chosen to match the upper geometry.

For a properly trimmed sample the spatula is moved around the whole sample using the side of the lower plate as a guide (Fig. 8a). Afterwards, the rim is checked visually whether all excess has been removed. If necessary, this step has to be repeated.

Especially when trimming highly viscous samples, it is possible that a bit of the excess sample gets pushed onto the edge of the upper geometry. During the test procedure this material could flow down again, leading to disturbing edge effects thus having a bad influence on the data quality. Therefore it is recommended, especially for highly viscous samples and geometries with small diameters, to strip the edge of the upper geometry from any remaining material (Fig. 8b).

Finally the geometry will move to the measuring position and the sample will get a slightly bulged rim as indicated in Fig. 9.

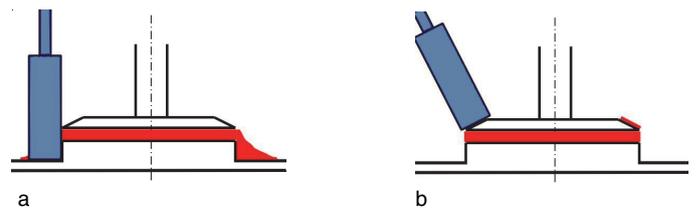


Fig. 8: Removing excess sample with a spatula in trimming position; 8b: Removing excess sample from the edge of the upper geometry.

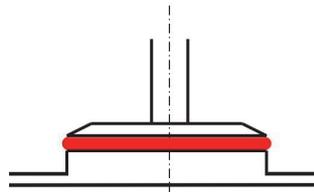


Fig. 9: Correct gap filling after closing the measuring geometry.

A perfect filling is the ideal basis for generating good data with a rheological test. Examples for such a test have been described in detail in [4] and [5] using the examples of testing a calibration oil and a viscoelastic PDMS standard respectively.

## Summary

For the determination of reliable rheological data the sample and the rheometer have to be prepared and handled care-fully. Apart from selecting the right measuring geometry and determining the correct zero point, there are some steps not directly linked to the rheometer itself, which are crucial for the data quality. The procedure how to prepare the sample into the rheometer and how carefully the sample is trimmed afterwards are at least equally important. Special care is needed when using small measuring geo-metries, small measuring gaps and high viscosities, since in these cases edge effects have a bigger influence on the data quality. In case of small measuring gaps an individual adjustment of all components involved can improve the data quality. Following the recommendations listed in this report, the accuracy and reproducibility of rheological results can be improved significantly. Especially when rheological results have to be compared with results from other departments or other companies, accurate results are an absolute must.

## References

- [1] Thermo Fisher Scientific Application note V285  
“Preparing the Rheometer for Highest Sensivity Tests“, Klaus Oldörp (in preparation)
- [2] Thermo Fisher Scientific Product information P029  
“Overview parallel plates and cone & plate geometries“, Cornelia Küchenmeister-Lehrheuer, Jint Nijman and Fabian Meyer
- [3] Thermo Fisher Scientific Product information P003  
“Trimming tool to remove overfilling in a plate/plate- and cone/plate-measuring geometry“, Küchenmeister-Lehrheuer and Klaus Oldörp
- [4] Thermo Fisher Scientific Application note V218  
“Test liquids“, Klaus Oldörp
- [5] Thermo Fisher Scientific Application note V264  
“Testing a Viscoelastic PDMS Standard in Oscillation“, Klaus Oldörp

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## APPLICATION NOTE

# HAAKE RheoWin software - features for quality control and routine measurements

**Author**

Fabian Meyer

Thermo Fisher Scientific, Karlsruhe, Germany

**Introduction**

Rheology is used in more and more industries for product development and quality control. A trend is to develop standard operation procedures like it is common for many other analytical methods. Standardized measuring procedures are necessary to optimize product properties and to determine possible qualitative fluctuations of a product.

By determining the relevant rheological parameters, relationships between structure, process behavior and final product properties can be established. Quality standards can be fulfilled and new products launched on the market faster. This applies to many industrial fields such as plastics and adhesives, paints and coatings, personal care and detergents, foodstuffs or even building materials.

Rheological measurements provide information about storage stability, processability or flow properties of liquid and semi-solid formulations, which are essential for quality control and further product development.

However, due to the increasing complexity of the materials and the high performance requirements, it is not always easy to develop the optimal testing method for a particular application. In this context, a versatile measurement and evaluation software can provide useful support to both, beginners and experts in the field of rheology, in order to establish and execute suitable procedures. The Thermo Scientific™ HAAKE™ RheoWin™ is the instrument control and data evaluation software for all Thermo Scientific™ HAAKE™ rheometers and is used to set up and run measurement procedures with subsequent automatic data evaluation and report generation.

The following article is intended to provide an overview of the possibilities offered by the HAAKE RheoWin software in order to be able to perform a comprehensive and meaningful rheological characterization in quality control.

**General structure of the HAAKE RheoWin software**

The HAAKE RheoWin software can be changed to 12 different languages with the touch of a button and consists of three different modules:

- The HAAKE RheoWin JobManager for creating and executing measurement and evaluation routines - so-called Jobs. The JobManager also allows for controlling all functionalities of the rheometer individually and outside of complete measurement and evaluation routines.
- The HAAKE RheoWin DataManager for displaying and further evaluating measured data. Different data sets can be overlaid and compared. Graphic and table layout can be formatted and data be transferred into various formats.
- The HAAKE RheoWin UserManager for creating user accounts of different levels and assigning specific and individual user privileges.

In addition, the following optional software modules are available for specific demands and applications:

- A CFR Part 11 tool to meet the requirements of US FDA 21 CFR Part 11
- Additional modules for polymer analysis: Time Temperature Superposition (TTS), generating relaxation spectra and the calculation of molecular weight distribution (MWD)
- Software module for interfacial rheology
- Software module for combination with FT-IR spectrometer

For creating Jobs with the HAAKE RheoWin JobManager, predefined graphical elements are used (Fig. 1). These elements cover all aspects of a complete standard operation procedure, including:

- pre- and post experimental instrument settings
- experimental settings
- data evaluation
- data handling, export
- report creation

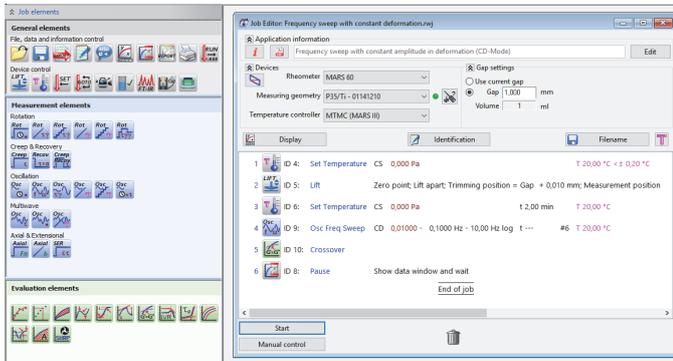


Fig. 1: Graphical elements for creating measurement and evaluation routines in the HAAKE RheoWin JobManager.

All elements can be selected quickly and comfortably via a drag & drop method. All measurements and evaluations can be carried out fully automatically in a single Job sequence. A manual operation mode can be used to perform rheological pre-tests or for gap setting and temperature control outside a measurement and evaluation routine.

The HAAKE RheoWin software allows for simultaneous sample testing and data evaluation or multiple measurements with different rheometers connected to the same PC. Measurement results can be exported and stored in various formats (ASCII, MS-Excel or PDF). The connection to a laboratory information management system (LIMS) is also possible.

### Selected measuring and evaluation elements for rheological characterization in quality control and product development

Important product properties for consumers and manufacturers are for instance storage stability, viscosity, yield stress, thixotropy or curing behavior. The determination of these rheological parameters allows for improving product performance as well as for an effective and reproducible evaluation during quality control.

How does a product react under stress or strain? How do different additives, such as fillers or pigments affect the properties of a material? Which thixotropic agent and how much of it has to be added to a product in order to maintain good flow properties or to prevent sagging effects? How should a yield stress be adjusted in order to ensure good shelf life and transportability of a product? How quickly should a micro structure rebuild, after a material was exposed to high shear?

These are just some of the many questions that product manufacturers have to deal with over and over again. The HAAKE RheoWin software provides evaluation routines with the possibility of defining QC criteria for many standard testing methods (Fig.2).

The following section presents selected options offered by the HAAKE RheoWin software to perform effective quality control test routines. The predefined measuring and evaluation elements only have to be adapted to the respective product and the corresponding quality criteria have to be defined accordingly.

### Reference curve with deviation tolerance

By using the reference curve element, new measuring results can be compared with previous measurement

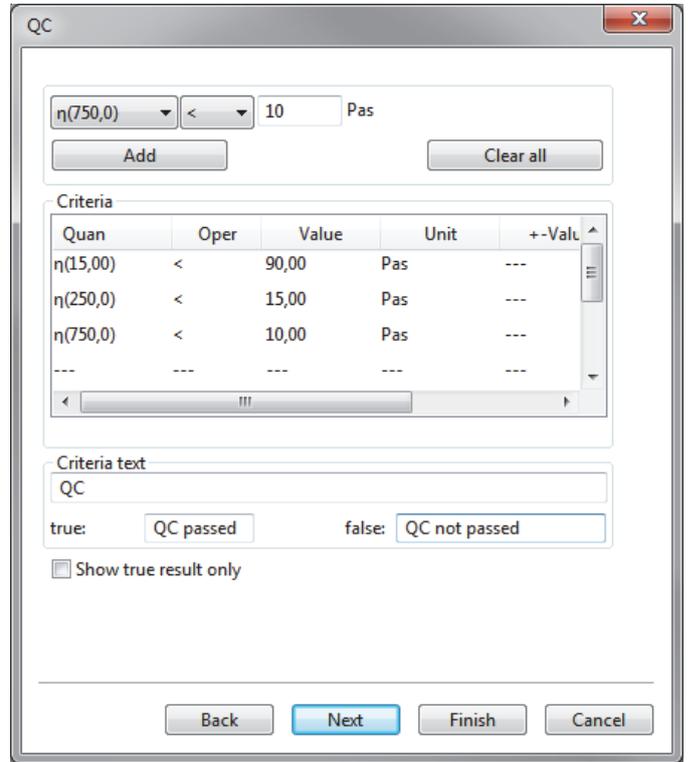


Fig. 2: Definition of Quality Control criteria in a measurement and evaluation routine.

data (Fig.3). A reference curve can be either a fixed data file or selected individually for every measurement by the operator.

The tolerance by which the measured values may deviate from the reference curve can be specified either as percentage or absolute values. Furthermore, the deviation tolerance can be set to either a linear or a logarithmic scale.

### Interpolation with deviation tolerance

Interpolation is the calculation of a data point between two measured values. An interpolation can be performed automatically after a measurement (Fig. 4). Various methods are available for this purpose. For the interpolated values, a deviation tolerance can be defined in the HAAKE RheoWin software. Interpolated values need to be inside the deviation tolerance in order for the sample to pass the quality assessment.

### Curve fitting

The HAAKE RheoWin software allows for performing curve fitting with various mathematical and rheological models (Fig. 5). Fitted curves can be extrapolated beyond the range of measured data. After a curve fitting was performed all calculated parameters are reported and stored along with the measured data.

### Determination of the linear-viscoelastic range

Within the linear-viscoelastic range rheological parameters are independent of the applied stress or strain value. The linear-viscoelastic range of a sample can be determined by performing an oscillation amplitude sweep at constant frequency. The HAAKE RheoWin software allows for the automatic determination of the linear-viscoelastic range from amplitude sweep data (Fig. 6). The end of the linear-viscoelastic range is reached at stress or strain values, where the rheological parameters will start to change from a constant behavior.

Which parameter is used for the evaluation ( $G'$ ,  $G''$ ,  $\ln^*I$ ,  $\delta$  or  $\tan \delta$ ) can be selected by the operator. The linear-viscoelastic range can be determined either as a stress or strain value. The HAAKE RheoWin software also allows for the determination of the linear-viscoelastic range according to the DIN 51810-2 standard procedure.

### Area under a measuring curve

The area under a measurement curve or a selected curve section can be calculated by the HAAKE RheoWin software (Fig.7). Upper and lower deviation tolerances can be defined as a quality control criterion.

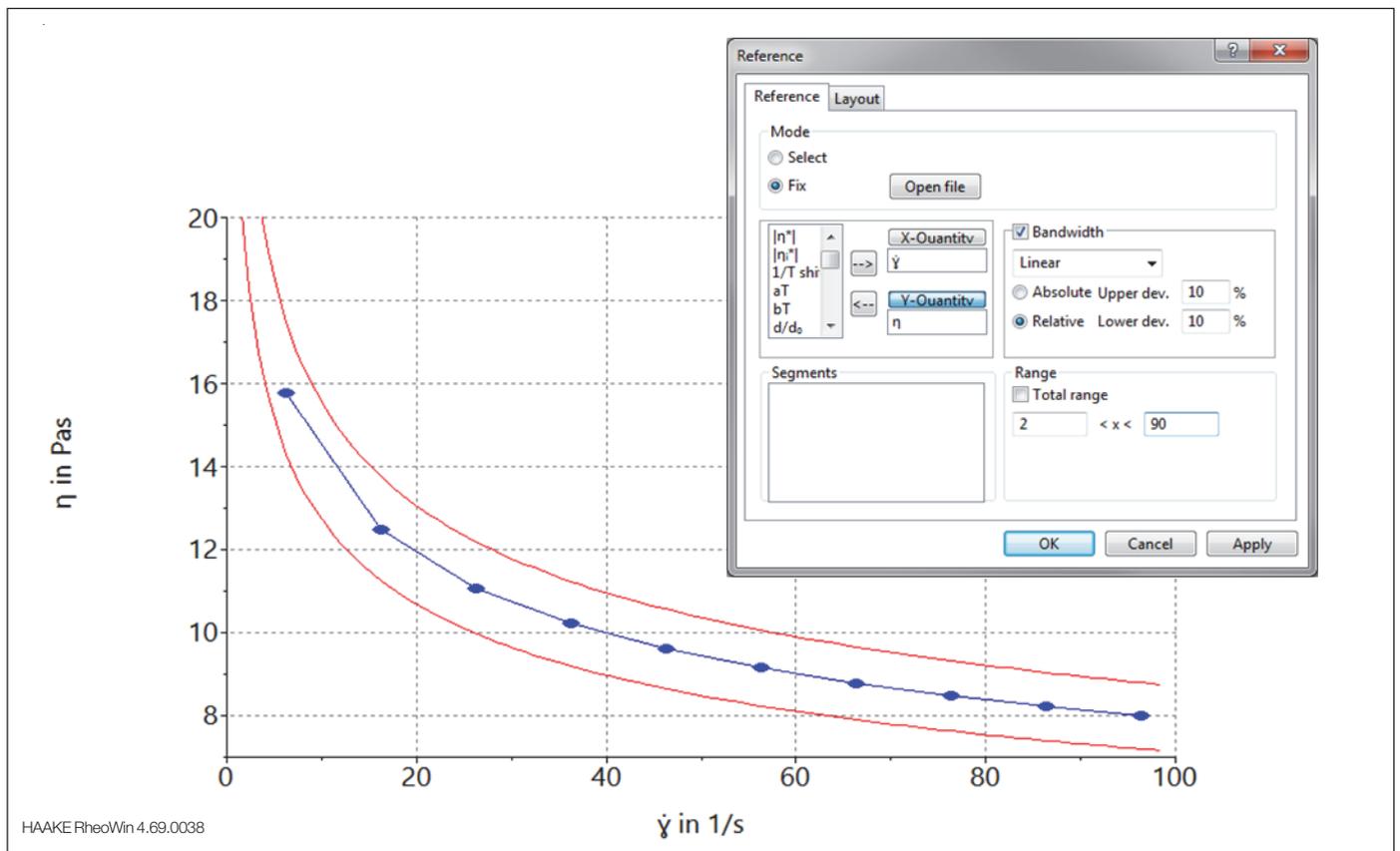


Fig. 3: Reference curve with deviation tolerance.

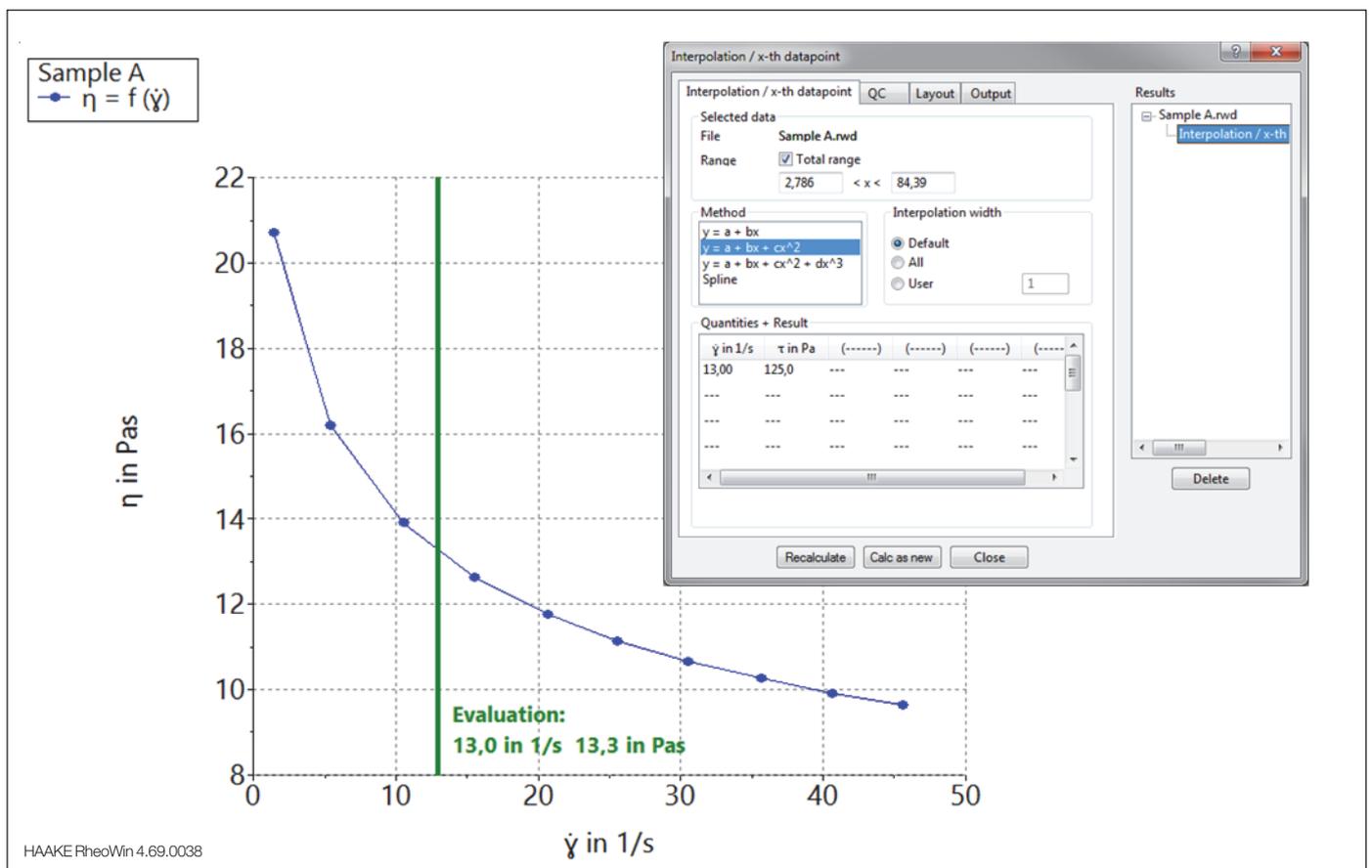


Fig. 4: Interpolation of a viscosity value at a defined shear rate.

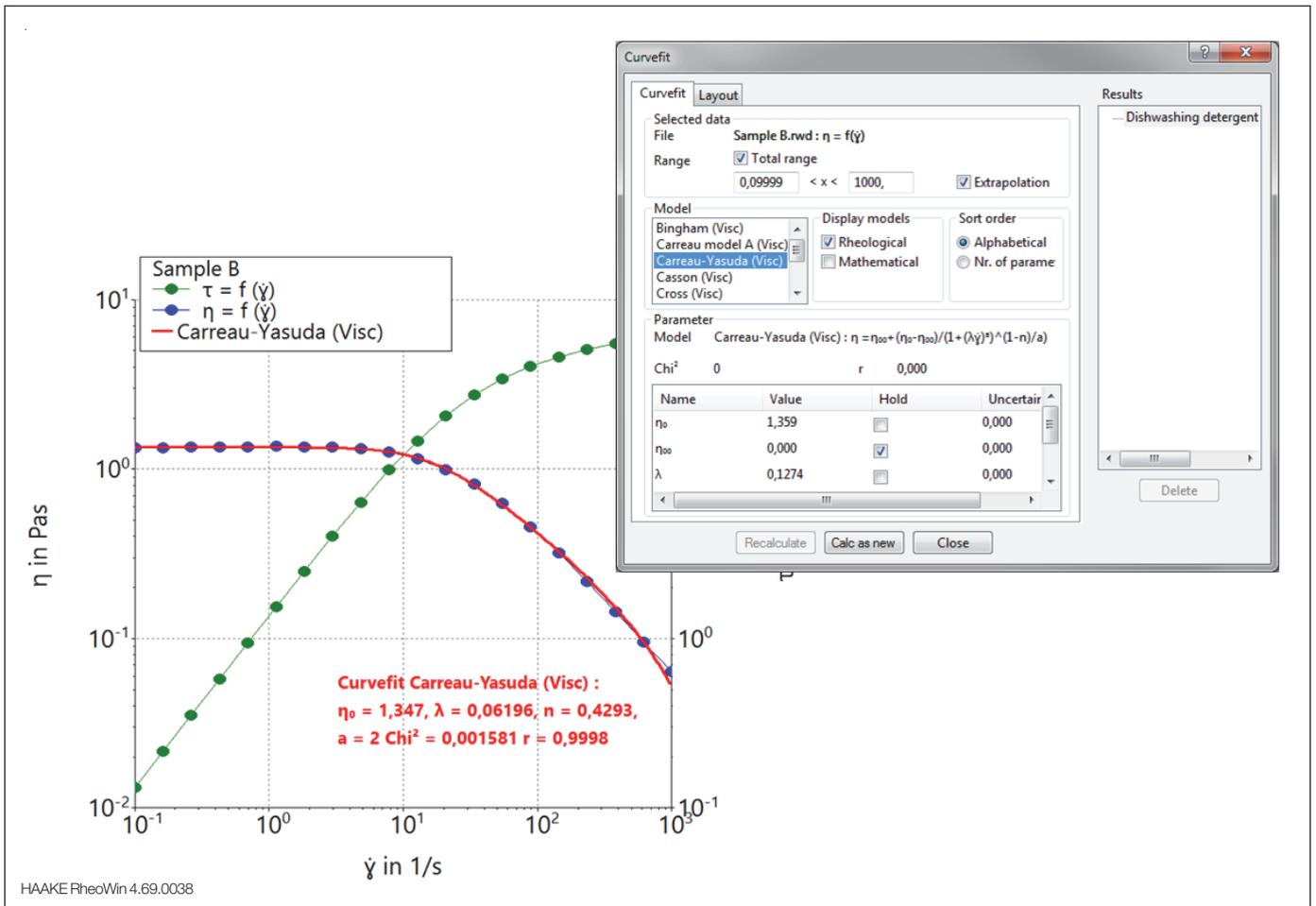


Fig. 5: Curve fitting of viscosity data with the Carreau-Yasuda model.

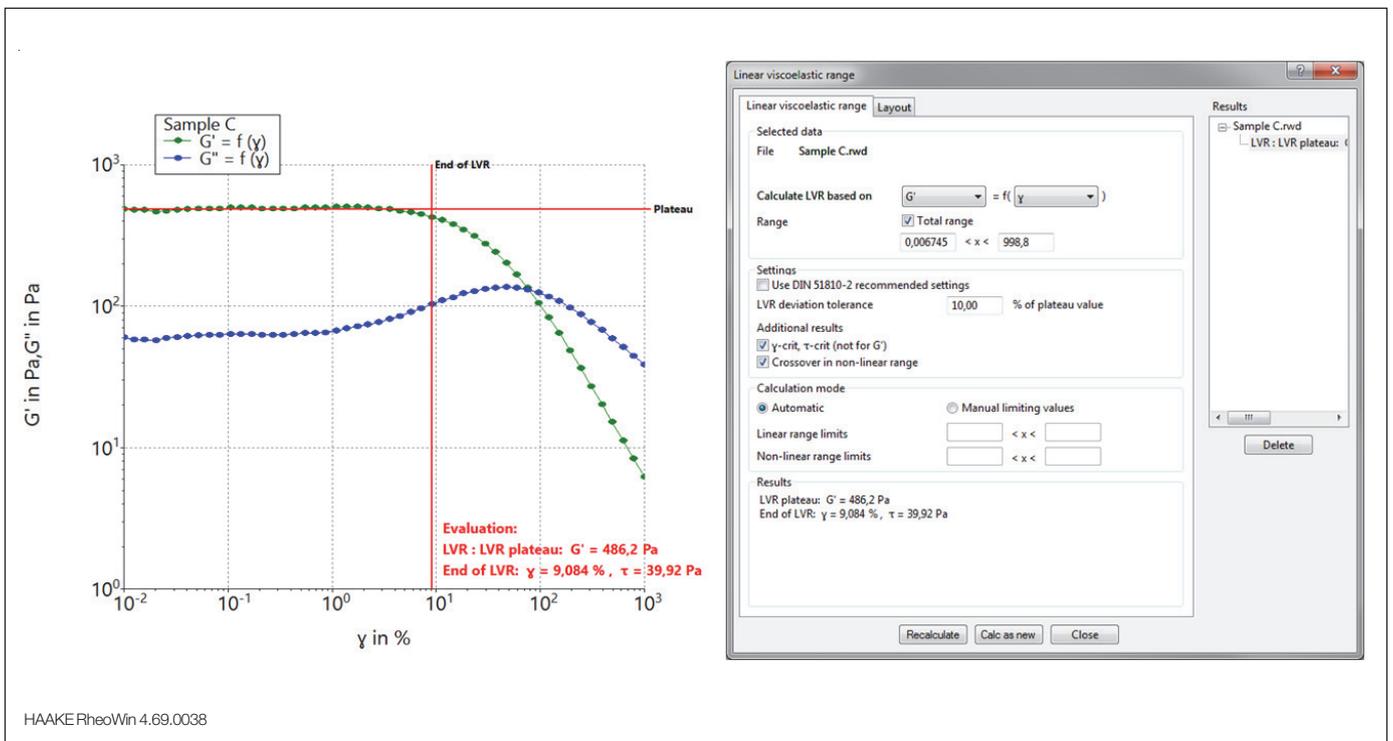


Fig. 6: Automatic determination of the linear-viscoelastic range from an amplitude sweep test.

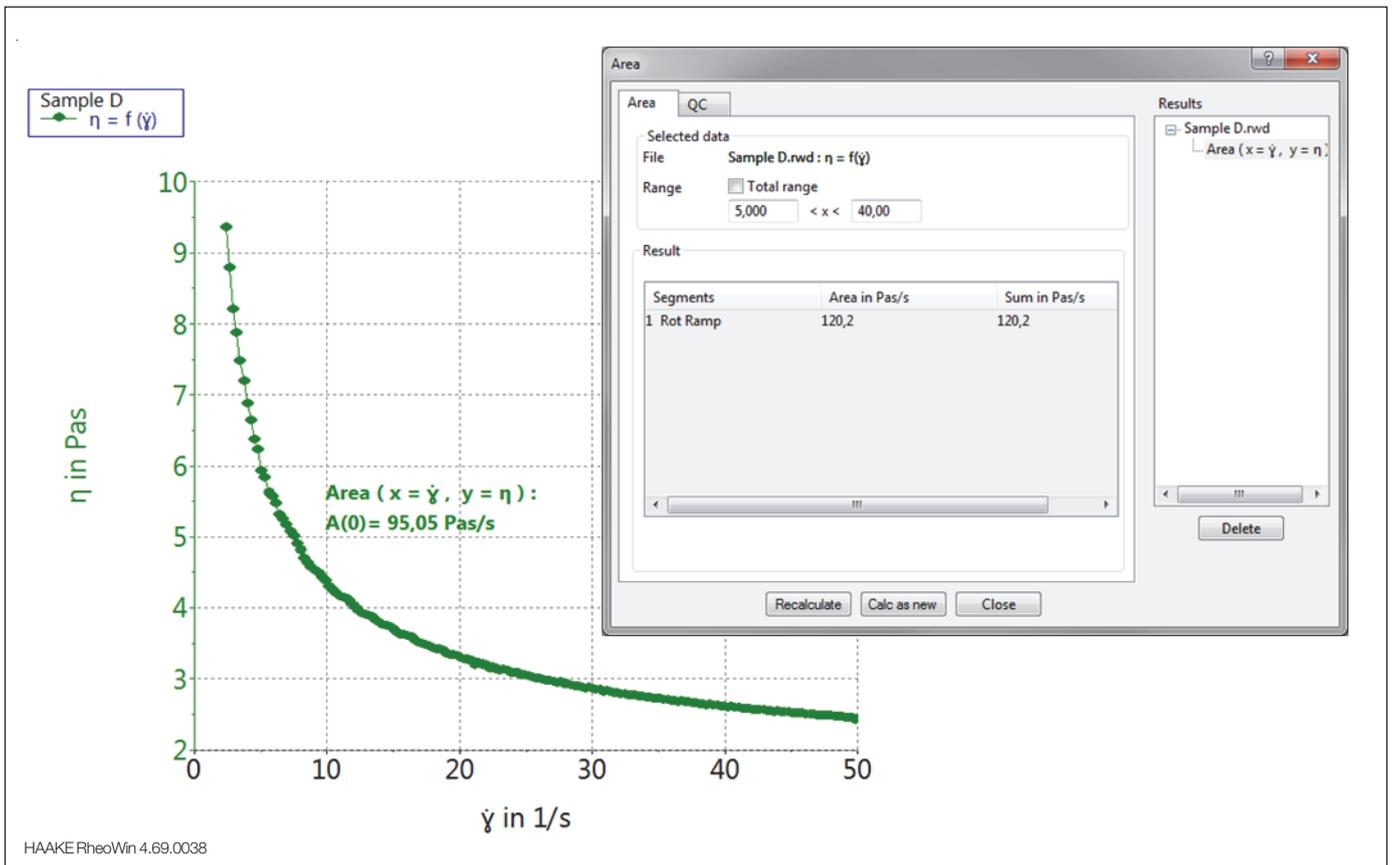


Fig. 7: Calculating the area under a viscosity curve.

### Thixotropic loop test

Thixotropy refers to a shear rate and shear time depending decrease in viscosity of structured fluids. In a thixotropic loop test, a sample is exposed to an increasing followed by a decreasing shear rate ramp. The apparent viscosity and the shear stress are recorded as a function of shear rate. The hysteresis area that

forms between the up and the down curve is a measure for the degree of thixotropy of the sample. When performing a thixotropic loop test, the HAAKE RheoWin software can determine the hysteresis area automatically for the viscosity or the shear stress data (Fig.8). Quality control criteria with deviation tolerance can be defined.

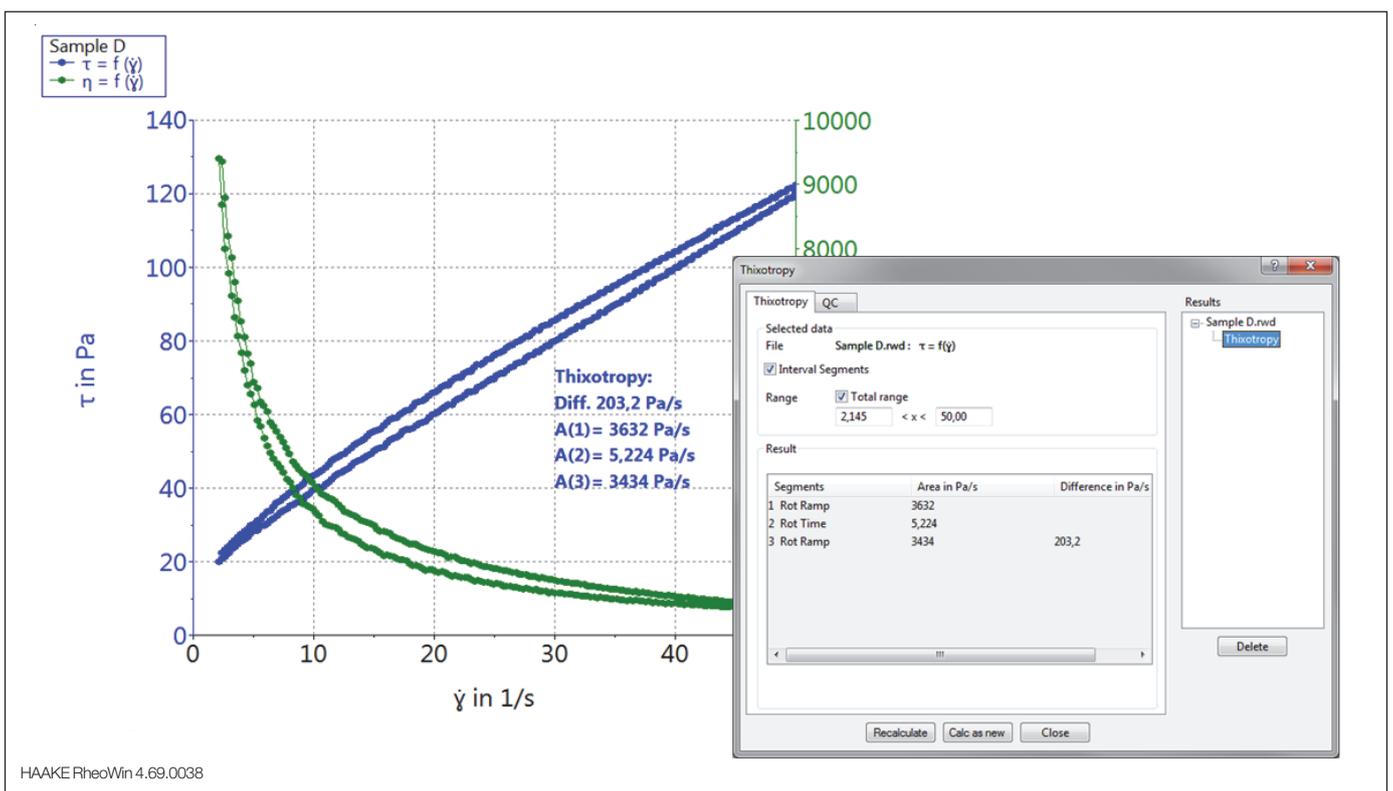


Fig. 8: Determination of the hysteresis area for shear stress data from a thixotropic loop test.

## Yield stress

The yield stress of a sample can be determined by performing a shear stress ramp experiment where the deformation is recorded as a function of the increasing stress in a double logarithmic plot. At shear stresses below the yield stress, the deformation will increase linearly (slope of around 1 in a double logarithmic plot) with increasing shear stress. When the shear stress is approaching the yield stress the slope will increase and the sample will start to flow. The yield stress evaluation element in the HAAKE RheoWin software determines the yield stress by means of two tangents that are applied to the measuring curve. The intersection of these tangents

is interpreted as the yield stress of the sample (Fig. 9). QC criteria with a deviation tolerance can be defined.

## Curve discussion

Two different elements for curve discussion are available in the HAAKE RheoWin software. With the regular curve discussion element minima, maxima, smallest, highest and mean values of a measurement curve can be determined (Fig. 10). With the advanced curve discussion element absolute and relative slopes, percentage of reference values as well as the intersections of tangents applied to the measured data can be calculated (Fig. 11). For both curve discussion elements quality control criteria can be defined.

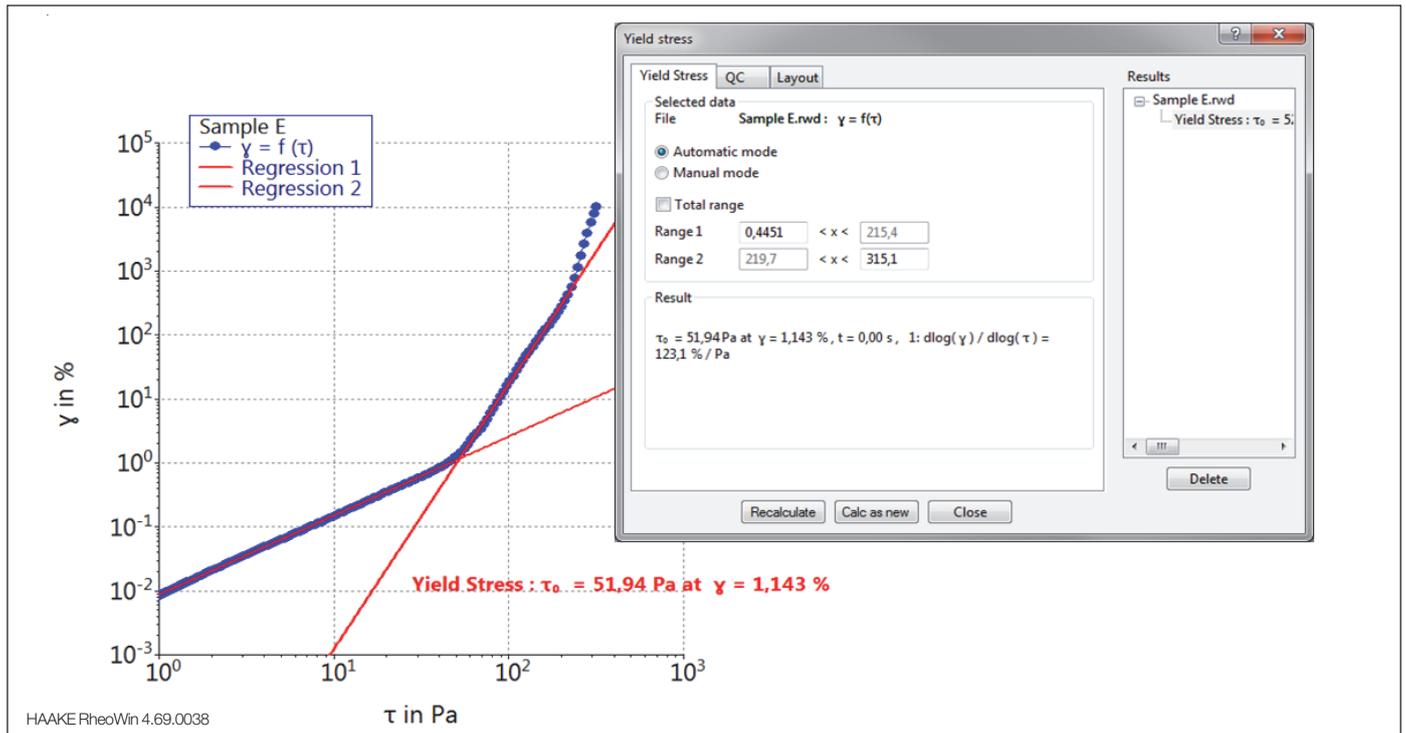


Fig. 9: Automatic determination of yield stress from shear stress ramp data with tangent intersection method.

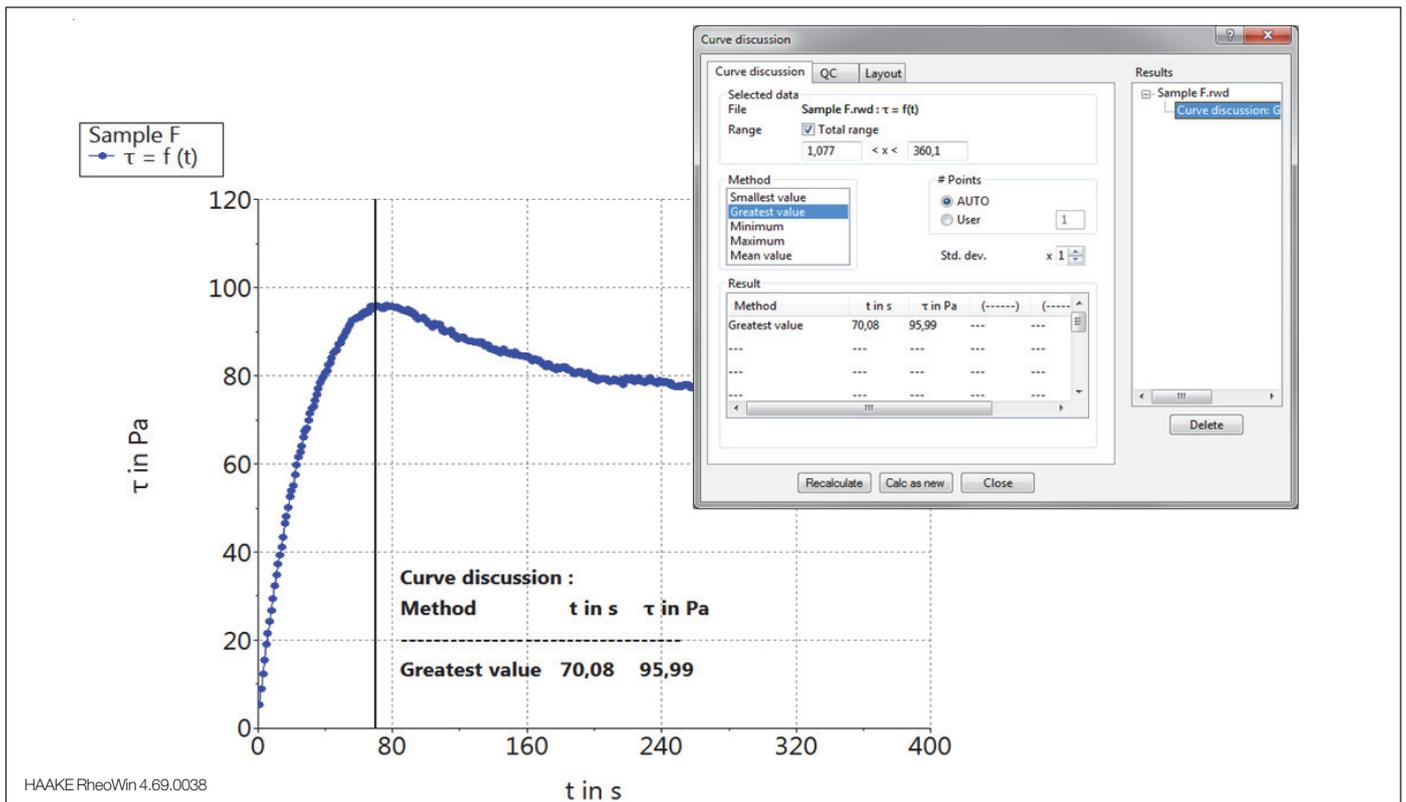


Fig. 10: Determination of the greatest value for the shear stress with the curve discussion evaluation element.

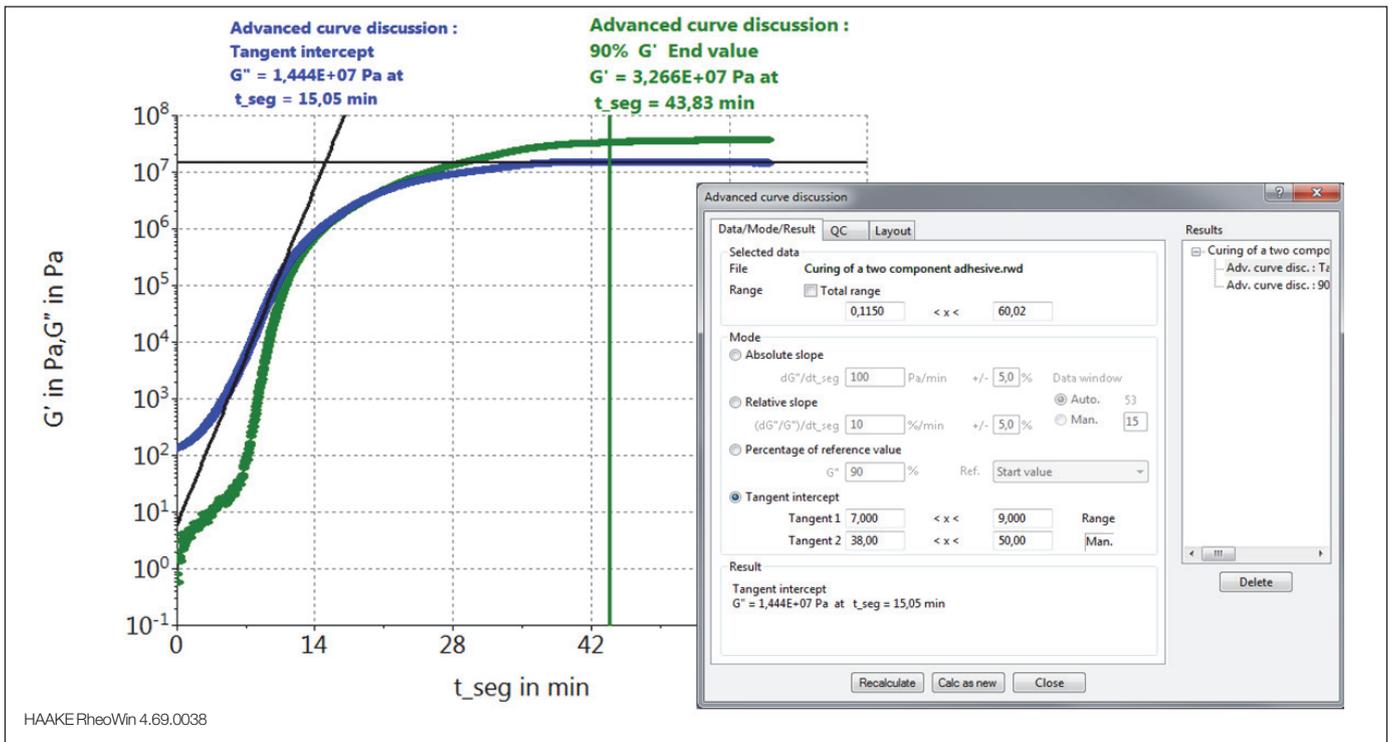


Fig. 11: Advanced curve discussion with  $G'$  and  $G''$  data from a curing experiment.

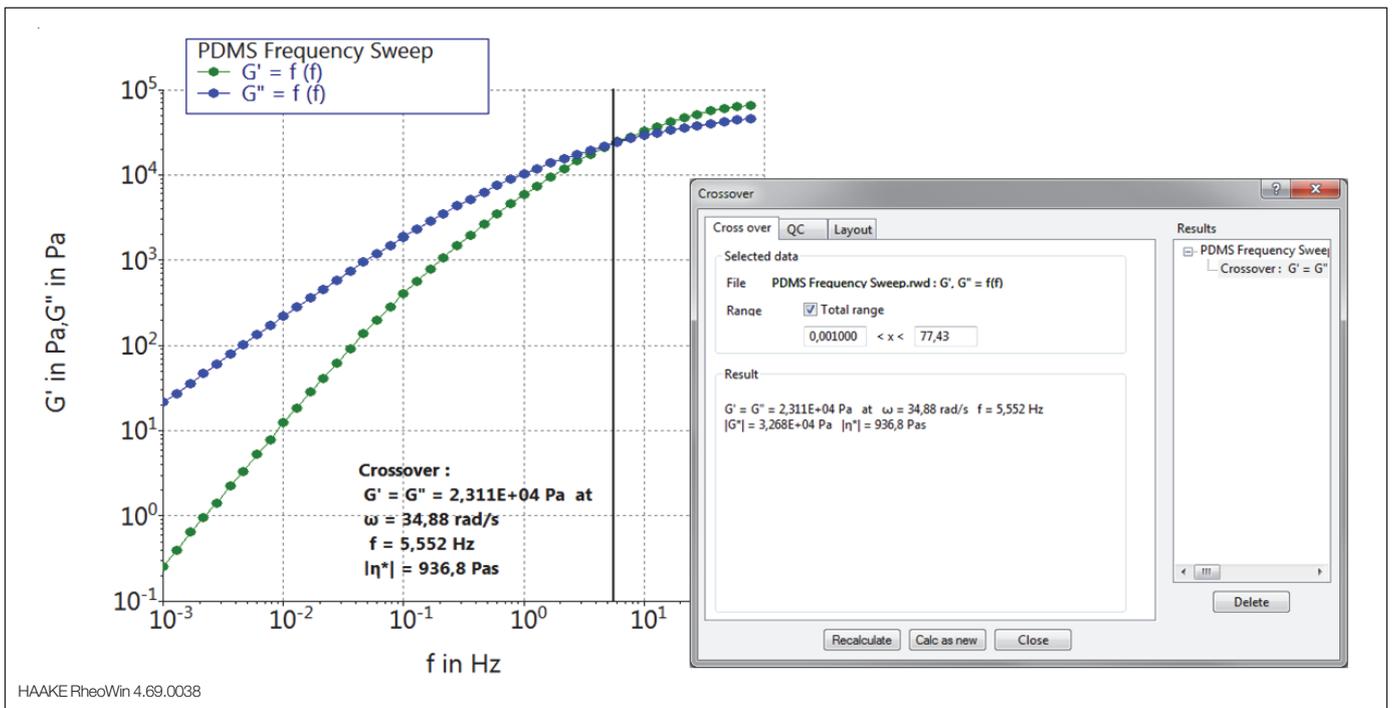


Fig. 12: Determination of the crossover of  $G'$  and  $G''$  in a frequency sweep test.

## Crossover

The crossover evaluation element determines the intersection point of the storage modulus  $G'$  and the loss modulus  $G''$  curve from an oscillatory shear measurement. These include amplitude, frequency, time and temperature sweep experiments (Fig. 12). Quality control criteria with deviation tolerance can be defined.

## Structure recovery

The structure recovery element provides information on how quickly and how well the structure of a sample recovers after it was exposed to a high shear rate. A structure recovery test consists of three steps. In an initial step the viscosity or complex viscosity of a material with an intact structure is measured as a reference. The second

step is a high shear rate period to break down the microstructure of the sample. In the third step the applied stress or strain signal is reduced to the initial value again and the recovery of the sample after a high shear impact is monitored. The structure recovery evaluation element of the HAAKE RheoWin software compares the data from the first and the third element to assess the recovery (Fig. 13). The evaluation options include the absolute change from the first to the end of the third step, relative recovery after a defined period of time and a relative recovery back to a defined percentage. Additionally, the time until the crossover of  $G'$  and  $G''$  occurs (sample becomes predominantly elastic again) in the recovery step can be detected automatically.

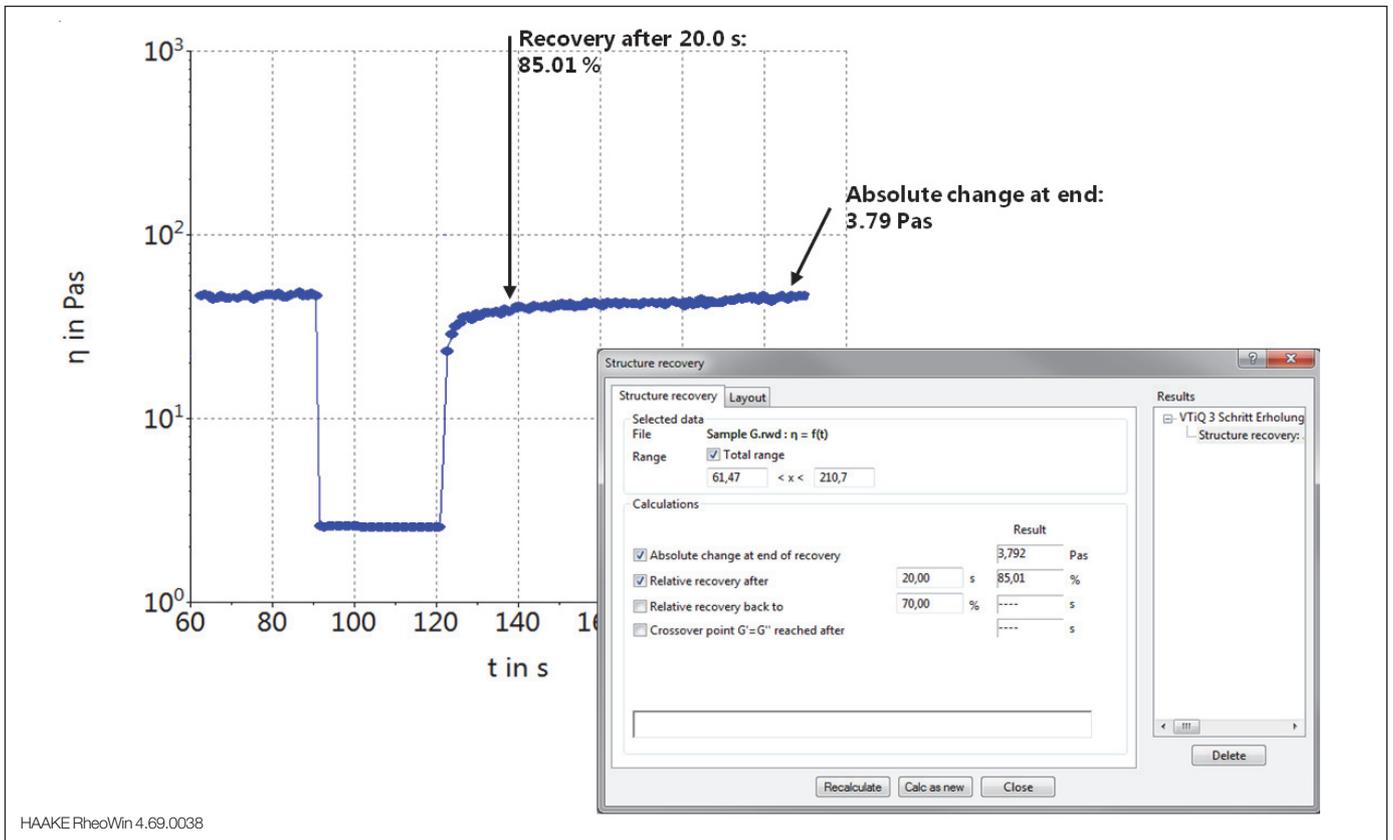


Fig. 13: Evaluation of the structure recovery after a sample was exposed to a high shear rate.

### Creep recovery

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. The creep and recovery evaluation element allows for an automatic and comprehensive creep analysis (see Fig. 14). Parameters like the zero shear viscosity, recoverable deformation or equilibrium compliance can be extracted from the creep and recovery curves. Quality control criteria with deviation tolerance can be defined for the different evaluation parameters.

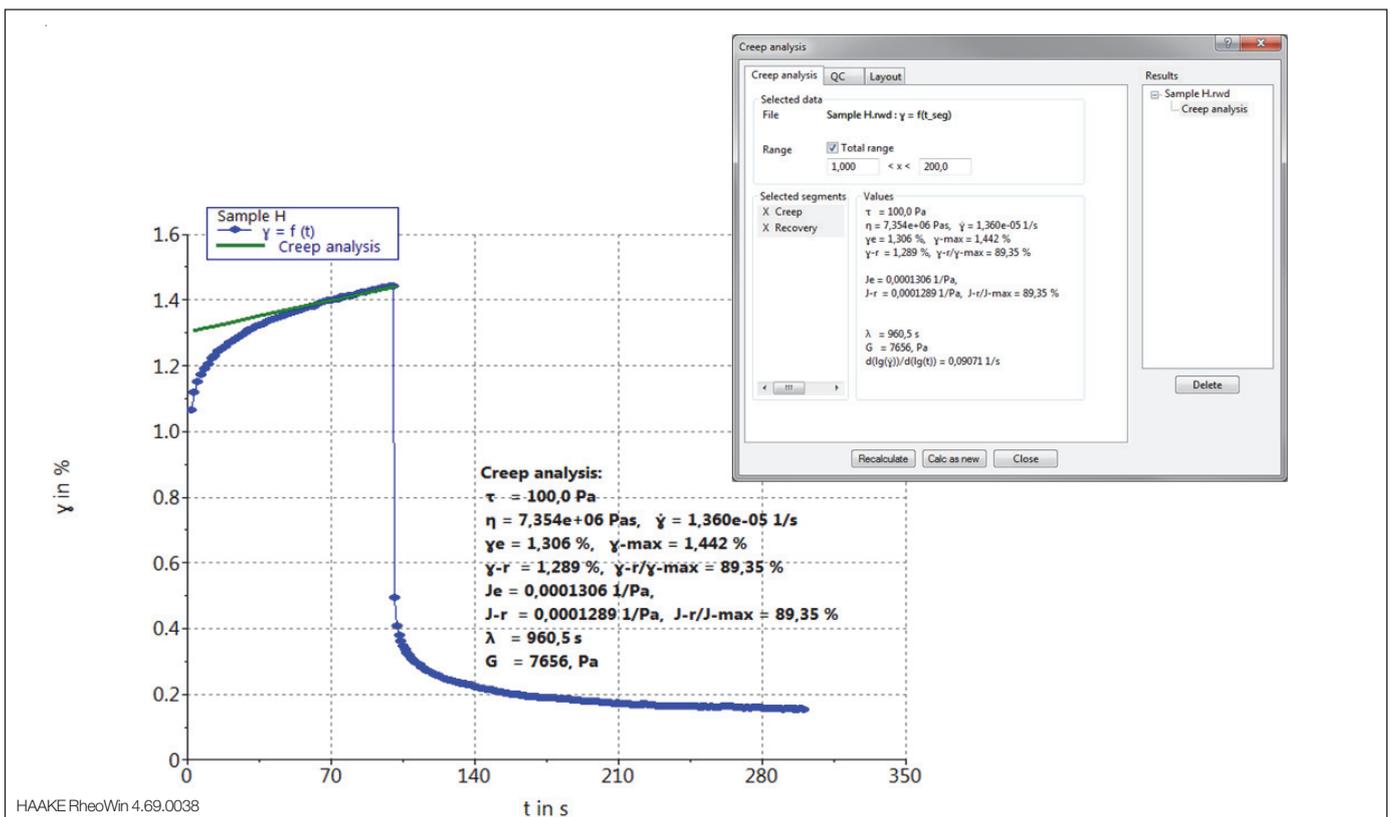


Fig. 14: Analysis of a creep and recovery test.

## Summary

The HAAKE RheoWin software enables a comprehensive rheological characterization of liquid, semi-solid and solid materials. Users can quickly and easily create suitable measurement procedures for various products and applications. A broad range of data evaluation routines allow for an automatic data analysis and the integrated QC criteria for a convenient operation in Quality Control.

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# Better rheological results: Create SOPs that drive sound rheological measurements

## Author

Cornelia Küchenmeister-Lehrheuer, Fabian Meyer  
Thermo Fisher Scientific, Karlsruhe, Germany

Rheological measurements play an important role in the quality control (QC) of many liquid and semi-solid materials. This includes final product evaluation as well as inspecting the properties of incoming raw materials or intermediates. To be fast and efficient, QC usually demands high sample throughput and a clear pass or fail assessment of the tested sample, regardless of the measurement technique used. To ensure smooth QC operation, the establishment of Standard Operating Procedures (SOPs) can be very helpful.

SOPs are written step-by-step instructions that provide guidance when performing routine operations. They ensure proper sample handling, correct instrument operation (even for untrained personnel) and sound data management and recording. A well-written SOP ensures fast sample assessment for quick product or batch release.

A comprehensive SOP for routine rheological measurements should encompass at least the following elements:

- Sample preparation and sample handling prior to loading samples into the rheometer
- Correct sample loading and sample treatment inside the rheometer prior to measurement
- Measurement procedure and data evaluation
- Report generation and data storage
- Preparation of the rheometer for the next measurement

A modern QC rheometer, together with its control software, provides useful tools and features that facilitate the establishment of a comprehensive SOP and failure-free instrument operation. These features, as well as the required elements listed above, are described in depth in the following paragraphs.

## Selecting the right measuring geometry

Selecting the correct measuring geometry plays an important role in rheological measurements and is the first step toward successful measurement. The choices are manifold, and the ideal measuring geometry depends on the measuring range of the rheometer, the sample

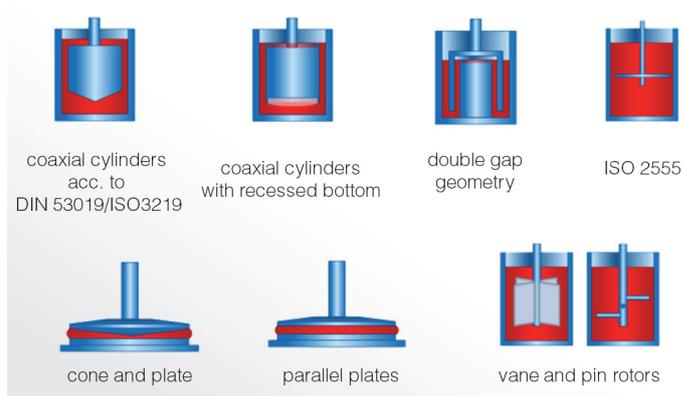


Fig. 1: Overview of standard measuring geometries.

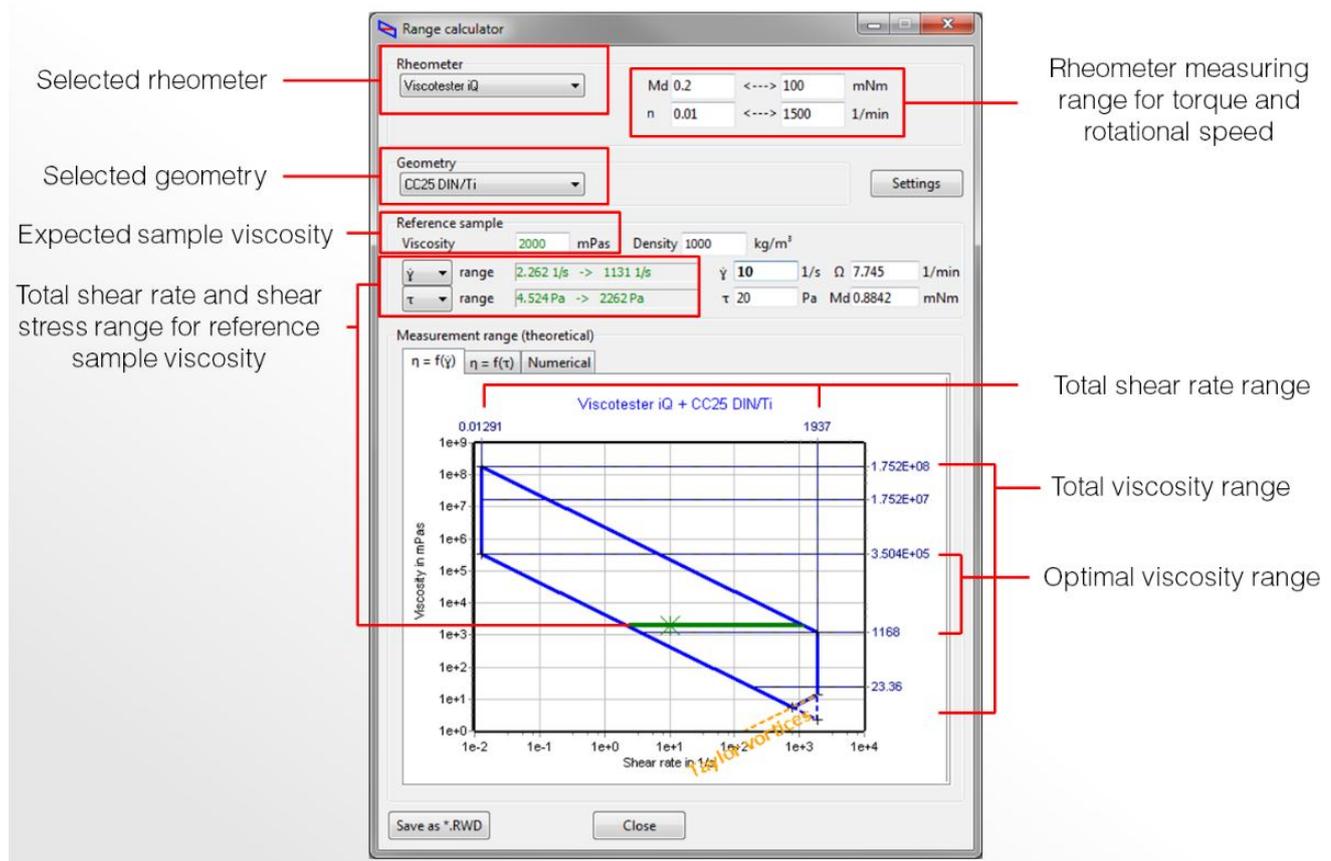
properties and the measurement parameters. A view of the different types of standard geometries is shown in Figure 1 while Table 1 provides information on what type of geometry can be used for different kinds of materials. More detailed information on how to select the right geometry can be found in our application note, "Well prepared – good results" [1].

Software tools such as the range calculator in Thermo Scientific™ HAAKE™ RheoWin™ software provide assistance for selecting the best measuring geometry for a specific rheological task (Figure 2). Depending on the viscosity of the tested material, this tool automatically calculates the optimal shear rate and shear stress range for any measuring geometry. If the operational range is too small, a different geometry should be selected.

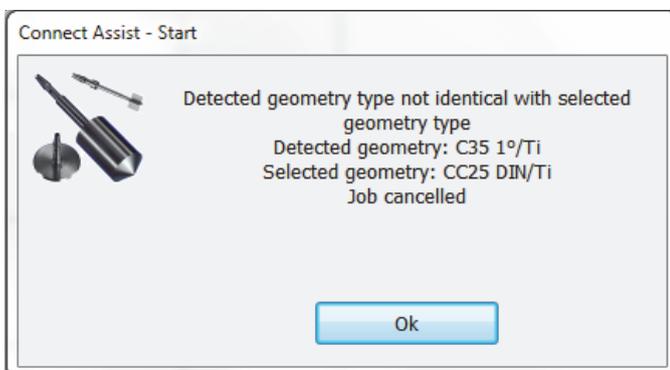
For reproducible QC measurements, the same type of measuring geometry should always be used for a specific sample test procedure. The rheometer should give a feedback message to the operator if the wrong measuring geometry is attached. Ideally, a measurement procedure cannot be performed unless the correct measuring geometry is attached (Figure 3).

	low viscous liquids	medium viscous liquids	high viscous liquids	weak semi-solids	gels	larger particles
cone and plate	✓	✓	✓	✓	✗	✗
parallel plates	✓	✓	✓	✓	✓	(✓)
coaxial cylinders	✓	✓	✗	✓	✗	(✓)
vane rotors	✗	✗	✗	✓	✗	✓

**Table 1:** Overview of measuring ranges for standard geometries.



**Fig. 2:** HAAKE RheoWin software range calculator tool.



**Fig. 3:** HAAKE RheoWin software Connect Assist message.

### Sample preparation and sample handling prior to loading samples into the rheometer

Before a sample can be tested with a rheometer certain pre-conditioning steps might be necessary to ensure reproducible and comparable results. For inhomogeneous

materials that show a tendency toward phase separation, this can include, for instance, pre-measurement stirring or mixing steps. Another possibility is the preheating of the sample in a heating cabinet prior to loading into the rheometer. These steps should be defined in the SOP as precisely as possible to ensure that every sample is prepared for the measurement in exactly the same way.

### Correct sample loading and treatment inside the rheometer

For highly thixotropic materials it is also important that all samples are loaded or filled into the measuring geometry in the same way and with the same tools. But correct sample loading also requires that the right amount of material is filled into the measuring geometry. Parallel plate and cone & plate geometries are usually overloaded first and then trimmed to the correct fill amount using a spatula or similar tool after the measurement gap is set.



Fig. 4: Level gauge for coaxial cylinder geometries.



Fig. 5: Fill Assist tool for HAAKE Viscotester iQ rheometer.

For coaxial cylinder geometries, accessories such as level gauges (Figure 4) or tools that measure the filling level by ultrasound (Figure 5) can be used to ensure that the correct sample volume is used. Underfilling as well as excessive overfilling should be avoided in any case. The rheometer software should provide feedback to the operator and guidance for correct sample loading. Figure 6 shows such a message that can be displayed during a rheological test procedure.

Once the sample is loaded into the rheometer geometry and the measuring gap is set correctly, the sample is

usually given a defined period of time to release all internal stresses that might have been introduced during sample loading as well as to adjust to the measurement temperature. The duration of these adjustment steps depends on the degree of thixotropy as well as the delta of sample temperature prior to sample loading and the actual test-ing temperature. For highly thixotropic materials the implementation of a pre-shear step followed by a defined resting period can improve the reproducibility of the tests and the comparability of the results.

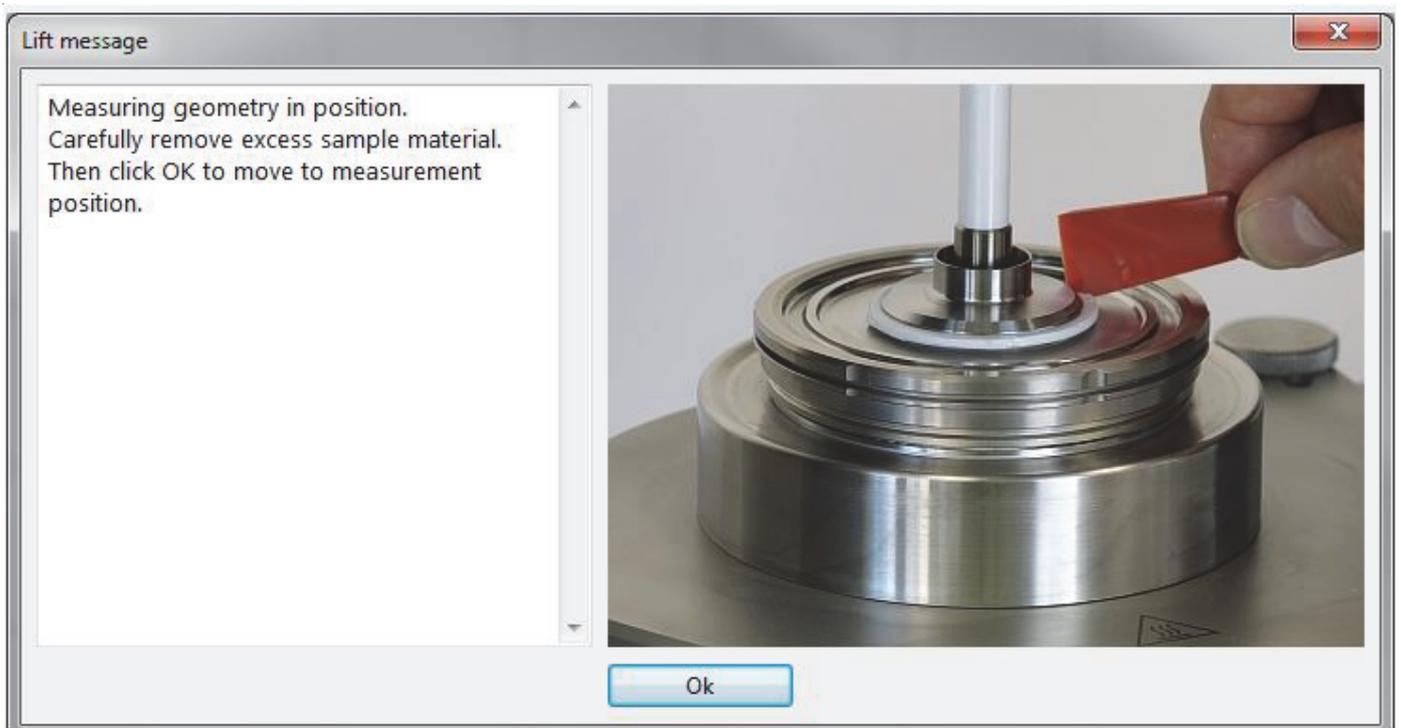


Fig. 6: HAAKE Rheowin software sample trimming message.

## Measurement and data evaluation

Once the sample is fully relaxed and in a temperature equilibrium, the actual measurement steps follow. After the last data point has been collected, further data evaluation can be performed to extract QC relevant information from the initial results. This can include simple mathematical operation such as mean value determination or interpolation as well as the application of rheological models. A complete overview of the data evaluation capabilities of HAAKE RheoWin software can be found in our application note, HAAKE RheoWin software – features for quality control and routine measurements [2].

## Report generation, data storage, preparation for next measurement

At the end of all data evaluation steps, the rheometer software should provide a clear assessment of the sample, ideally with a “pass or fail” classification as shown in Figure 7. The measurement procedure finishes with the generation of the automated measurement report and/or the data transfer into a laboratory information management system (LIMS) followed by instructions on how to prepare the rheometer for the next measurement. A complete measurement procedure that includes pre-measurement sample treatment, a thixotropic loop measurement procedure, automatic data evaluation and a report generation is shown in Figure 8.

Such a measurement procedure is usually established by the lab manager and executed by various operators.

The user management system in the rheometer software allows for setting up the system with different user levels and different privileges (Figure 9) [3]. This can prevent unwanted manipulation of the measurement procedure thereby ensuring trustworthy QC results.

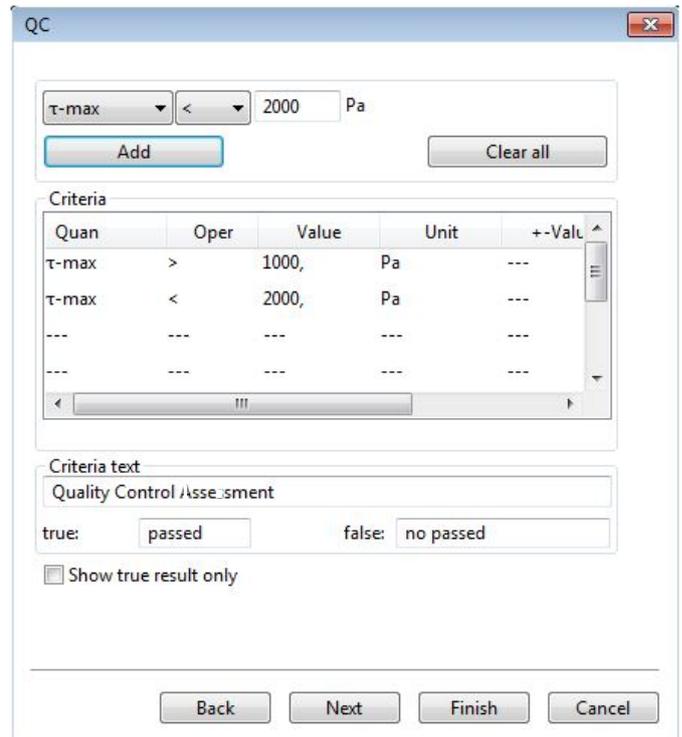


Fig. 7: Definition of QC criteria in HAAKE RheoWin software.

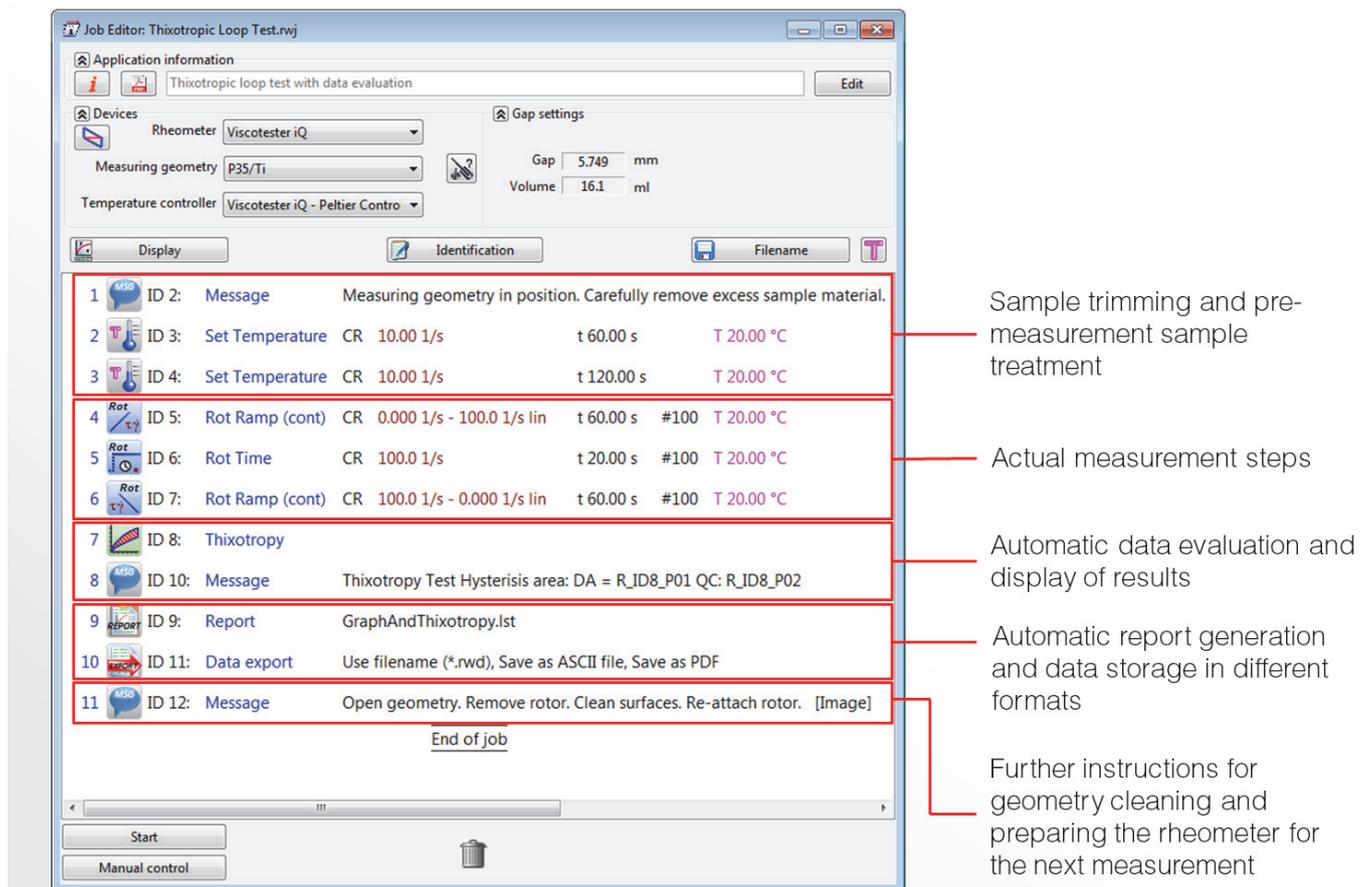


Fig. 8: Complete HAAKE RheoWin software test procedure.

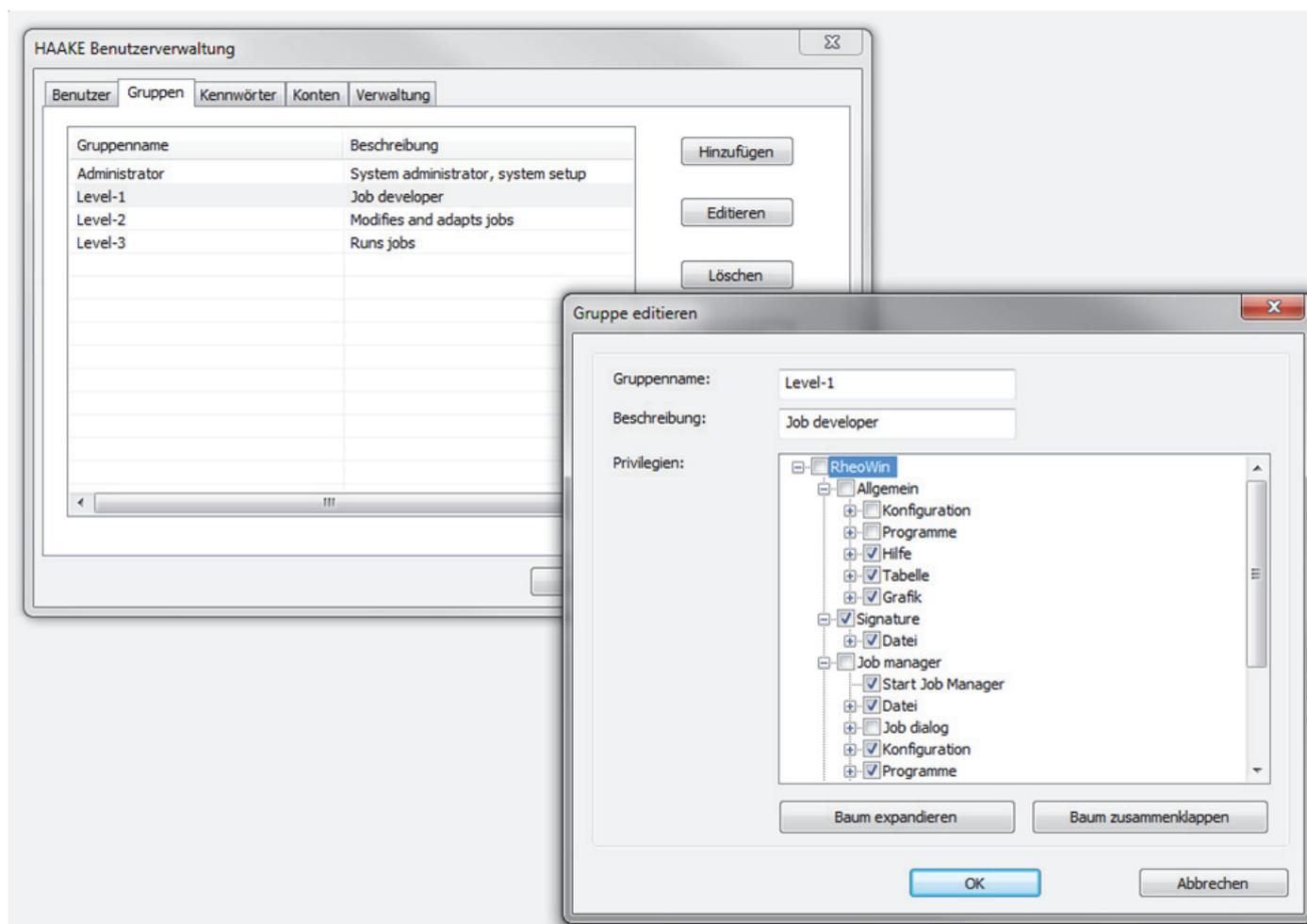


Fig. 9: HAAKE RheoWin software User Manager tool.

## Conclusion

Standard Operation Procedures guarantee a smooth and identical QC operation with reliable data and a clear “pass or fail” assessment of the sample even for untrained personnel.

Fast, efficient QC requires high sample throughput and a “pass or fail” assessment that’s clear for all users. SOPs help ensure smooth, consistent QC operation when written comprehensively to include key elements: sample preparation and handling, sample loading, measurement and evaluation, reports and data storage, and preparation for future measurements. From automatically recognized geometries to feedback functionalities of the control software, modern rheometers have many tools to support the development of a comprehensive, effective SOP.

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- [2] Thermo Fisher Scientific Application note V223 “HAAKE RheoWin software - features for quality control and routine measurements,” Fabian Meyer
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# The rheological behaviour of shampoos - What makes a product acceptable for a specific target customer?

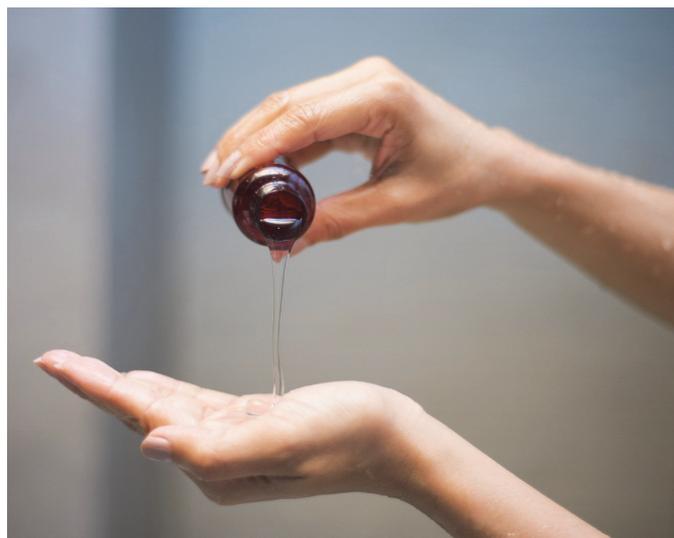
## Authors

Jan Philip Plog  
Thermo Fisher Scientific, Karlsruhe, Germany

## Introduction

Shampoos are based on complex systems of surfactants having the function to cleanse the hair. Because of their everyday use it is not surprising that the shampoo market comprises approx. 12% of the total personal-care industry [1]. These products are complex systems consisting of about 80 wt.% water, 10wt.% surfactants, 5wt.% viscosity modifiers, 2wt.% preservatives, fragrances and colorants and about 3wt.% of performance additives [2].

Few things are more important to customers than using a thick (rich) shampoo product correlating this directly with value and concentration. A shampoo is not only expected to be easy to use but to meet also sensory criteria that will appeal to the customer. One main rheological parameter that correlates with the thickness and flow properties of a shampoo is the viscosity. The viscosity affects both the cleansing efficiency and the user perception of a shampoo product. In addition to that it also influences the foaming properties, production filling, packaging, storage and long-term stability of the product. Viscosity is a quite important parameter! As was mentioned already, customer perception is one of the most important parameters, however who is the customer and what does he expect? The three different customer groups Female, Male and Children (Infants) have different views on the same product class because they usually put different amounts of energy into a shampoo when they i.e., squeeze it out of the bottle or distribute it on themselves. This is due to the fact that the different processes will happen at different stress levels (as the customer groups apply different forces) and thus result in different shear rates. As no customer wants to experience the viscosity the product has at rest (rich and creamy) when they actually use the product, a shampoo has to be a non-Newtonian or to be more precise shear-thinning fluid. To induce non-Newtonian flow and thus modify the flow behaviour towards the specific customer groups, water-soluble polymers are used as modifiers.



This contribution is to show how products for those different customer groups differ rheologically and how easy it is to absolutely determine the parameter viscosity with the help of the Thermo Scientific™ HAAKE™ Viscotester™ iQ rheometer.

## Methods and materials

Three different commercial shampoos have been tested on the Thermo Scientific HAAKE Viscotester iQ at room temperature with 35 mm plate/plate geometries (see Figure 1). One of them was a shampoo for men, one for women and one for children (infants).

After carefully filling the shampoo on the lower plate and manually adjusting the measuring head to a predetermined gap of 1 mm the testing procedure was conducted as can be seen in Figure 2.

With the described procedure the shampoo products have been tested in a shear rate range of 1 to 100 1/s, the results can be seen in Figure 3.

## Results and discussion

As can be seen in Figure 3 the rheological fingerprint for the three products is quite different. At low shear rates around 1 1/s the shampoo for men and the shampoo for children (infants) have about the same viscosity of about 12 Pas. The shampoo for women has a considerably lower viscosity of about 7.5 Pas. Male customers usually want to have an even richer (higher viscous) product than female customers that prefer slightly “creamier” (lower viscous) products. For child products more functional aspects have to be taken into account as a child usually does not choose a shampoo according to its viscosity. However, the parents that buy the product intuitively “know” that a high viscous product will stay longer in the child’s hand when using it in the bathtub.

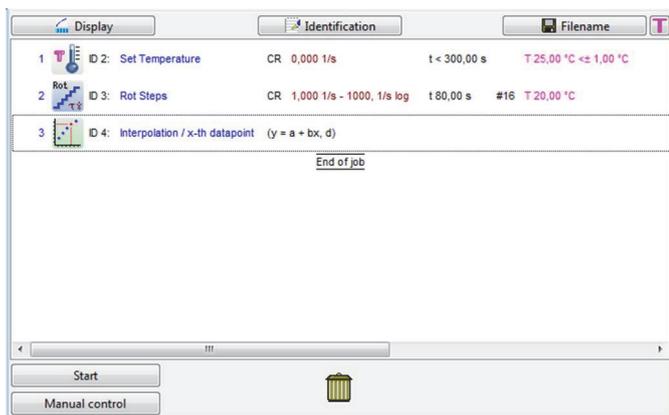


Fig. 2: HAAKE RheoWin Measuring Routine to determine the viscosity as a function of shear rate on the Thermo Scientific HAAKE Viscotester iQ.

When applying higher shear rates the behaviour differs between the products. Whereas the “male” product goes into non-Newtonian flow directly because of the higher molecular weight polymer additives that have been used in formulation to achieve a higher base viscosity, the “female” and “child” product show Newtonian plateaus. However whereas the “female” product leaves Newtonian flow at around 4 1/s to achieve lower viscosities when being used the “child” product maintains a constant viscosity for much longer (up until about 20 1/s) so that less product is lost before starting in the washing process.

Right now many users of viscometers, especially in an industrial QC/QA environment, are working with concentric cylinder measuring geometries (“cup and bob”). However, the use of plate/plate measuring systems is preferable because less sample volume is needed. This directly leads to two main advantages, namely that cleaning will be easier and temperature control will be faster. However do both measuring geometries yield the same result? To answer that question, Figure 4 shows the resulting viscosity for the “soft” shampoo measured at room temperature with the concentric cylinder system CC25Din in comparison to a 35 mm plate/plate geometry.

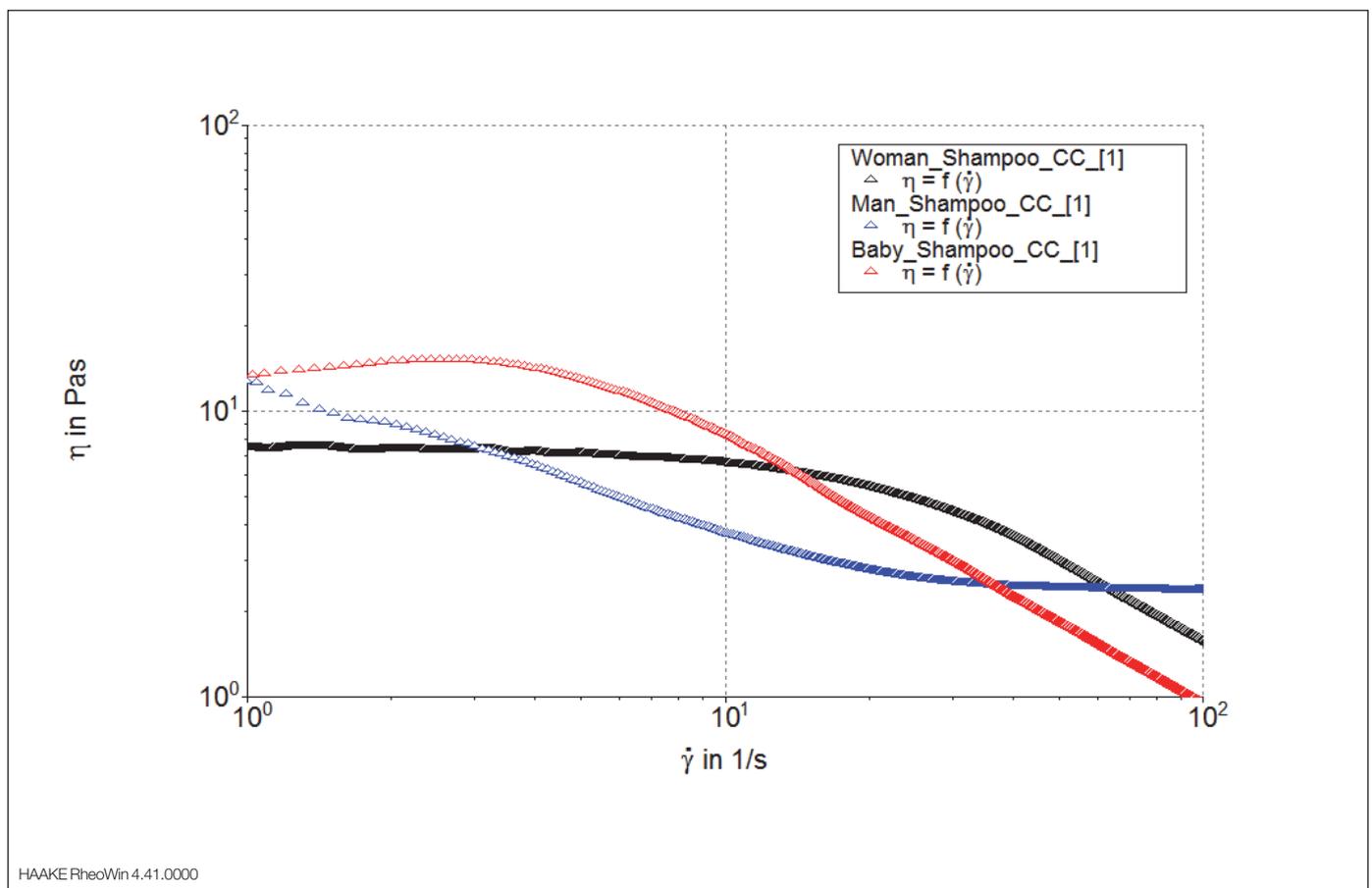
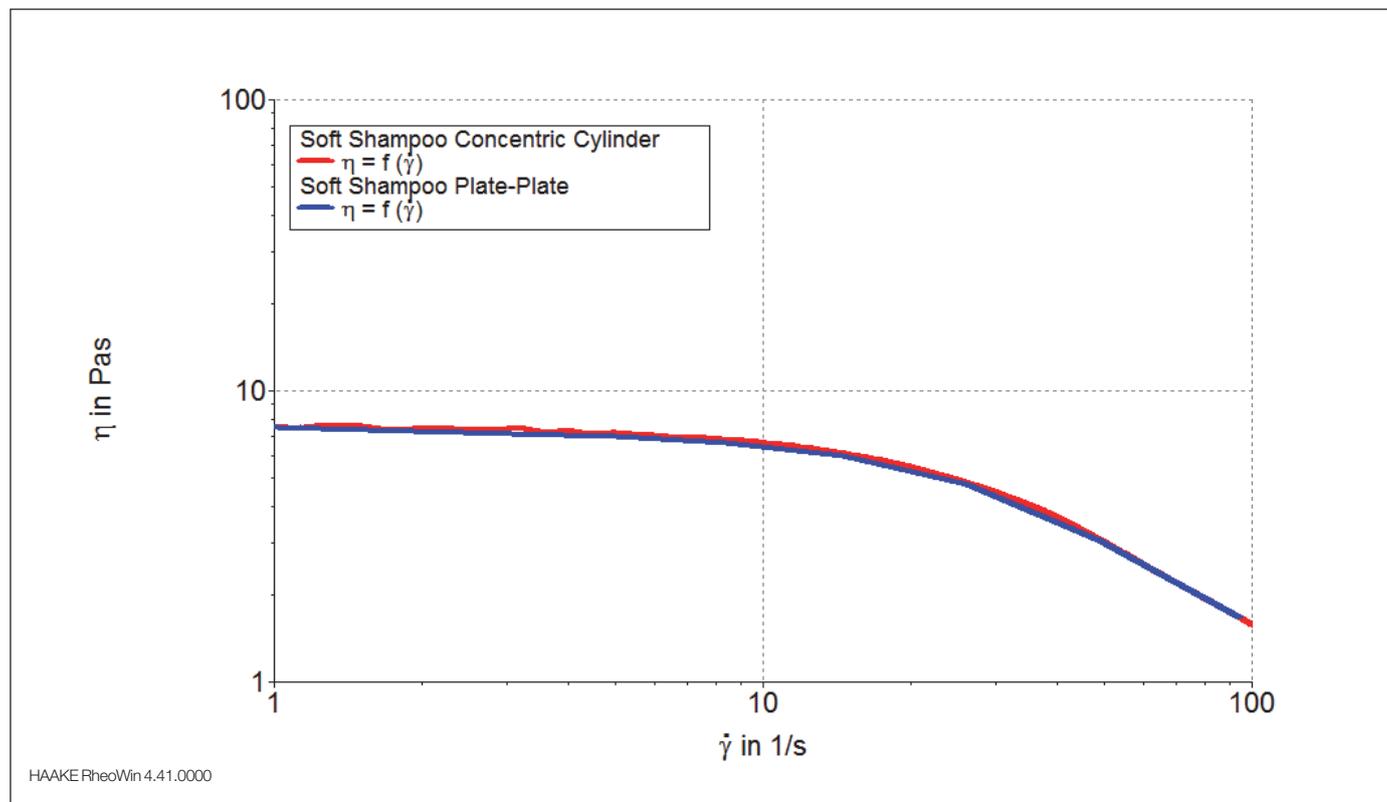


Fig. 3: Viscosity as a function of shear rate for three different shampoos at RT.

As can be seen in Figure 4, the measured viscosity is the same, independent of the measuring geometry.



## Conclusion

Determining the viscosity of a shampoo (or shower gel etc.) formulation is of utmost importance to understand if a product meets customer expectation. Additives have to be chosen wisely to formulate a product for a specific customer group. The Thermo Scientific HAAKE Viscotester iQ rheometer is a powerful tool to let you conduct those tests easy and reproducible, no matter if you test with concentric cylinders or plate/plate geometries.

## Literature

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# How much squeezing power is required to get the toothpaste out of the tube?

## Yield stress determination

### Authors

Cornelia Küchenmeister-Lehrheuer and Jan Philip Plog  
Thermo Fisher Scientific, Karlsruhe, Germany

### Key words

Crude oil, viscosity, temperature dependency, wax deposition

### Introduction

Toothpastes are viscoelastic products with a paste-like texture well known in everyday's life. They have a complex structure including many components influencing the rheological properties such as abrasives to support the mechanical cleaning effort of the toothbrush, moisture agents to prevent a drying out of the toothpaste as well as binding agents to prevent the phase separation between the liquid and the solid. Rheology plays an important role in the product development of toothpaste, the production, the filling and packaging processes as well as in fulfilling the expectation of a consumer target group [1].

This article will focus on the importance of the yield stress of different toothpastes. The yield stress characterizes the amount of force that it takes to break down the initial structure of the product and get the fluid moving. Squeezing is required to get the toothpaste out of the tube. There must be enough squeezing power to overcome the yield stress in the material. Two different toothpastes – one for adults and one for children – have been selected for this investigation. For the measurement and evaluation the preferred method described in [2] was applied.

### Methods and materials

For the measurements the Thermo Scientific™ HAAKE™ Viscotester™ iQ rheometer was used. This instrument equipped with an EC motor enables a variety of test methods in controlled rate (CR) and controlled stress (CS) mode in a broad measuring range. As temperature control unit a self-contained Peltier module was used, which enables a fast and reliable temperature control in the range between -5 °C and 160 °C. The tests were carried out by using a parallel plate measuring geometry with a diameter of 35 mm. To avoid slippage a measuring geometry with serrated surface has been selected. The lower measuring



plate matches the upper plate in diameter and appearance and therefore ensures ideal measuring conditions and an optimal sample filling [3]. Other advantages of this geometry are a small sample volume, shorter time for temperature equilibrium and reduced cleaning effort. In addition a sample cover was put over the filled measuring geometry to minimize the evaporation and the temperature gradient within the sample.

### Samples and preparation

One toothpaste for adults and one for children have been selected for the test described in the following report. At the beginning of the test a small amount of the sample was squeezed out of the tube and placed in the middle of the lower exchangeable plate. The upper plate was moved down to the measuring gap. The squeezing and gap filling procedure corresponds to a pre-shearing of the sample and a compromise has to be found for the waiting time which the sample needs to relax from the applied stress and other effects which influence the rheological behavior of the sample such as evaporation.

## HAAKE RheoWin software and alternative operation

There are different options to operate the HAAKE Viscotester iQ rheometer.

On one hand the fully software controlled operation using the Thermo Scientific™ HAAKE™ RheoWin™ software enables the maximum on flexibility regarding the definition of the measuring and evaluation routine. The following test procedure has been used for the investigation: after a waiting time of 5 minutes for temperature control at 20 °C a logarithmical CS ramp in a shear stress range between 20 Pa and 400 Pa was measured within 180 s and 180 data points were measured. A breakup criteria was included in the job to stop the measurement at a deformation higher than 20. The resulting deformation of the sample was plotted as a function of the applied stress in a double logarithmic plot. According to the tangent cross-over method, the yield stress is the point of intersection of two straight lines fitted to the two regimes with different slopes, namely the creep regime and the regime of flow.



**Fig. 2:** HAAKE Viscotester iQ used as a standalone unit with internal measuring procedures, HAAKE Viscotester iQ RheoApp for extended measuring capabilities.

Alternatively, the rheometer can be used as a standalone unit with internal measuring routines (Fig. 2) especially recommended for standardized measuring and evaluation routines.

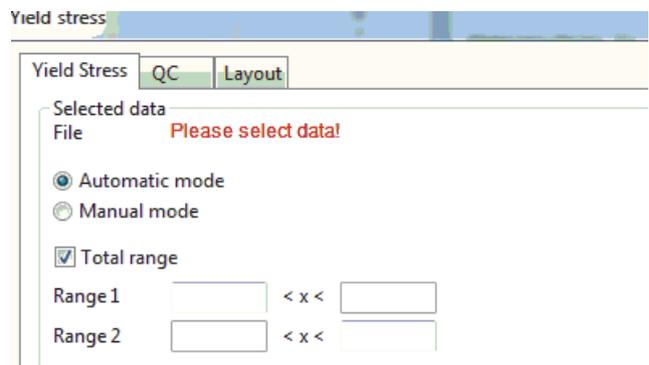
## Results and discussion

The measuring curves of the adult toothpaste and the children's product are shown in Fig. 3. Two curves for each sample are included to demonstrate the high level of reproducibility. The yield stress values are summarized in Tab. 1. As expected the yield stress of the children toothpaste is with a value of approximately 55 Pa much lower than the adult product with an average of 215 Pa.

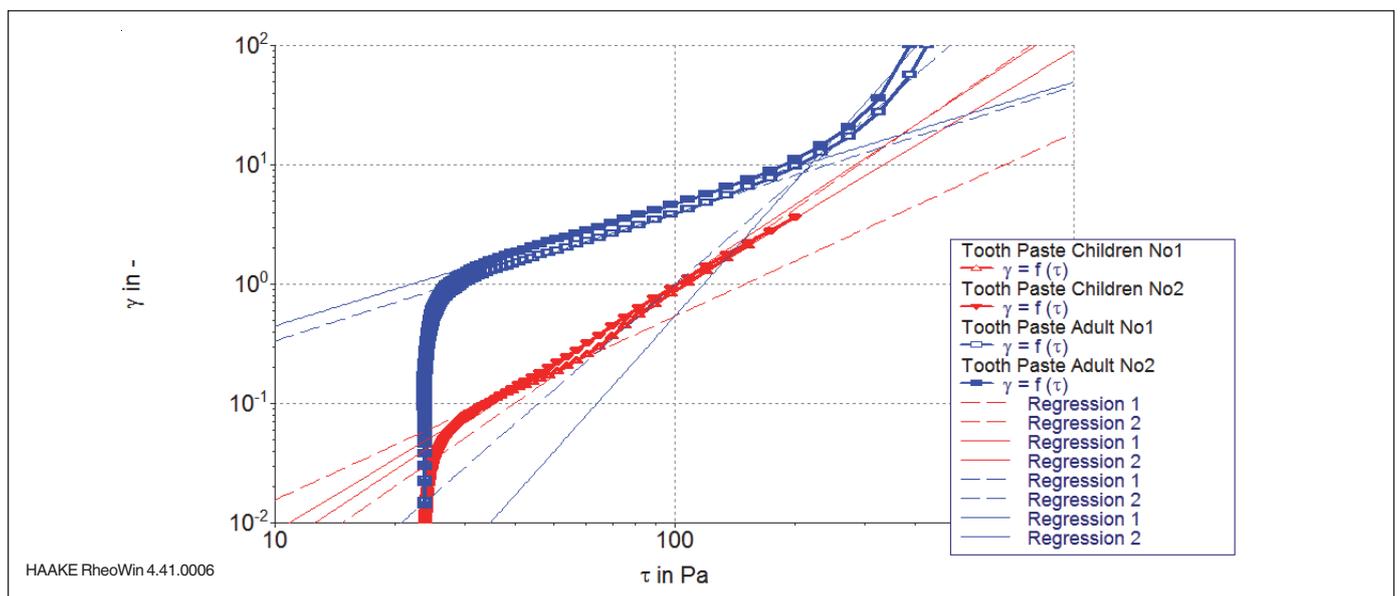
**Table 1: The yield stress values**

Toothpaste sample	Yield stress [Pa]	Deformation [-]
Children product meas. no 1	55.4	0.21
Children product meas. no 2	55.6	0.27
Adults product meas. no 1	210	8.64
Adults product meas. no 2	222	10.61

Two versions of yield stress evaluation are available in the HAAKE RheoWin software: the automatic routine and the manual mode (Fig 4.). Using the HAAKE Viscotester as a standalone unit only the automatic evaluation routine is available.



**Fig. 4:** HAAKE RheoWin software element for the yield stress determination in CS mode: automatic or manual mode.



**Fig. 3:** Deformation as a function of stress for two different toothpastes (20 °C, 35 mm parallel plate measuring geometry with serrated surface, 1 mm measuring gap). The yield stress is calculated as the point of interception of the two tangents fitted on the manually chosen ranges of the elastic deformation and the viscous flow.

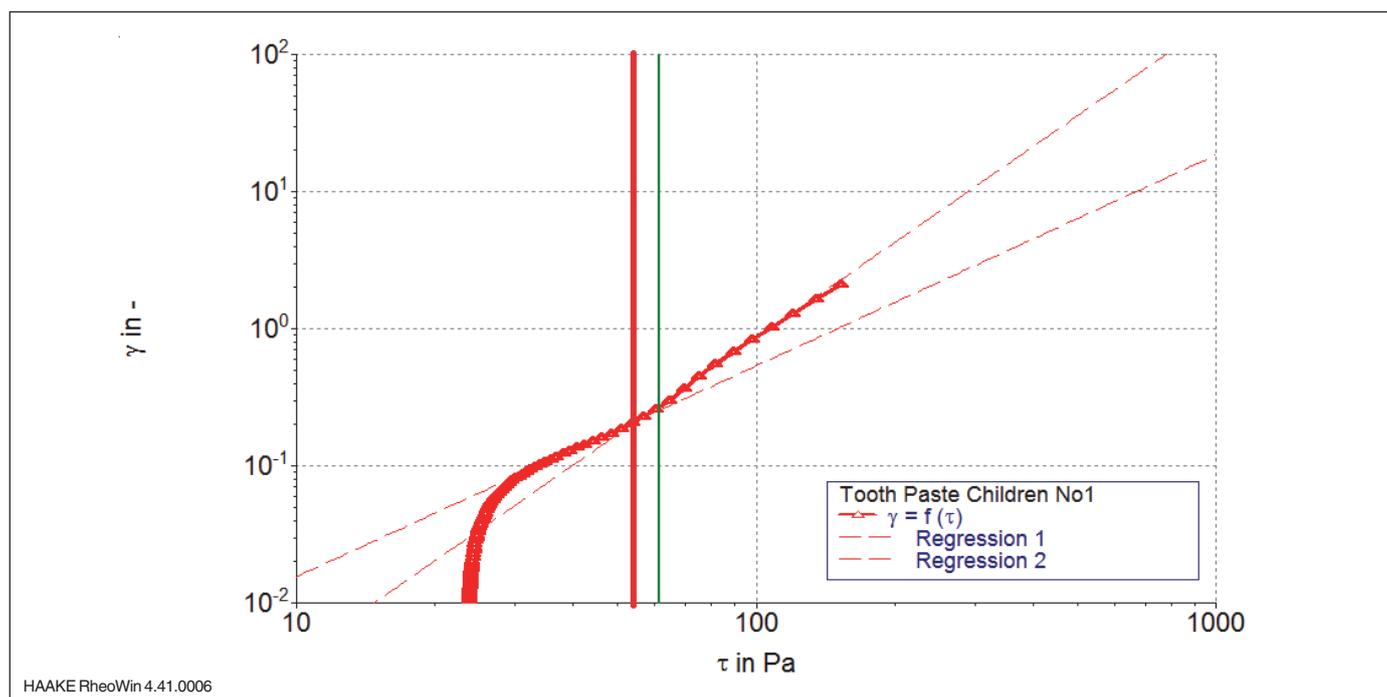


Fig. 5: Yield stress evaluation using the automatic mode (61.68 Pa, green line) and the manual mode (55.39 Pa, red line)

The manual routine gives more flexibility in finding the correct value for the yield stress. The range in which the yield stress is normally well visually detectable and the measuring ranges for the fit of the linear ranges can be selected. This mode has been used for the calculation of the yield stress values presented in Tab. 1. However, the yield stress strongly depends on sample preparation, the measuring routine itself but also on the evaluation procedure. Fig. 5 includes a comparison between both modes on a children toothpaste.

### Conclusion

The determination of the yield stress is an important rheological parameter to understand if a toothpaste meets the expectation of the customer target group. The yield stress strongly depends on the sample history and preparation, the measuring conditions and method as well as the evaluation routine.

The HAAKE Viscotester iQ is a compact rheometer focusing on modern QC demands. The modular design enables an adaptation to individual needs thanks to a broad range of accessories. Quick coupling and recognition of the temperature module as well as the measuring geometry in combination with an intuitive instrument concept with a smart lift function, guarantees smooth handling. The HAAKE Viscotester iQ is the instrument of choice as stand-alone unit for standard measuring and evaluation routines or as fully software controlled version with the HAAKE RheoWin software for highest measuring flexibility.

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# Performing quality control (QC) tests on cosmetic emulsions with the HAAKE Viscotester iQ rheometer

## Authors

Klaus Oldörp  
Thermo Fisher Scientific, Karlsruhe, Germany

## Introduction

The formulation of a cosmetic product can be quite complex and will vary depending on the active ingredients. Still, the customer expects a cream from a certain product range always to have the same texture, no matter the particular ingredients like for example aloe vera, lemon grass or milk and honey. Subsequently, one of the challenges when formulating a cosmetic product is to achieve the texture the customer expects or desires. Testing the rheological properties of a cosmetic emulsion therefore is an essential part of such a product's quality control (QC).

Typical rheological parameters tested for cosmetic emulsion are the shear viscosity  $\eta$ , the thixotropic behaviour and the yield stress  $\tau_0$ . The viscosity is related to various product properties depending on the shear rate range in question. For example, the feel of a cream when rubbing it into the skin is linked to the viscosity at higher shear rates, while the storage stability is related to its viscosity at low shear rates.

The yield stress of an emulsion is important for the storage stability and the look and feel of the product. A cream sold in a pot will have higher yield stress because the customer expects to be able to take a bit of cream out of the pot with his finger. A body lotion is filled in bottles and the customer expects a liquid-like behaviour. Thus this products needs to have a relatively low yield stress.

To be able to test these different rheological parameters, a QC viscometer needs to offer a variety of test methods and a broad measuring range. To make rheological tests in QC easier and more reliable, the Thermo Scientific™ HAAKE™ Viscotester™ iQ rheometer has been developed. This unique viscometer has some features especially designed for QC applications. For example, due to its improved sensitivity it is possible to use smaller cylindrical measuring geometries and even parallel plate geometries, thus reducing sample volume, time required for temperature equilibration and cleaning effort.



## Methods and materials

A soft cream and a body lotion have been selected for the test described in this report. To reduce the damage to the emulsion's structure during sample loading, the tests were carried out using a 35 mm parallel plate geometry with a 1 mm gap. Compared to a cylindrical measuring geometry this reduces the sample volume to about 1 ml and helps saving time by allowing much easier cleaning of the geometry after each test.

Before the tests a small amount of sample was placed onto the lower exchangeable plate sitting on the Peltier temperature control unit of the HAAKE Viscotester iQ. The upper plate was lowered carefully by hand down to the measuring gap in order to minimize the preshearing of the samples. Finally a sample cover was put over the closed measuring geometry to improve temperature control and to minimize evaporation.

## The HAAKE RheoWin Job

After lowering the upper plate, the HAAKE Viscotester iQ rheometer was operated using the Thermo Scientific™ HAAKE™ RheoWin™ software.

The first part of the HAAKE RheoWin job is the sample conditioning. For the emulsions tested here it simply consists of a waiting period to give the samples enough time to relax the mechanical stress from sample loading and to bring it to the test temperature. Even though it is “just” a waiting period, the sample conditioning should always be part of the test method itself to ensure that it is not forgotten and always performed in the same way, which improves the reproducibility of the results.

The next part of the HAAKE RheoWin job is the rheological test itself. The last part usually consists of the data evaluation, the generation of a report and its printout or export if required.

## Results and discussion

The viscosity is best tested by recording the steady-state viscosity curve i.e. the steady-state viscosity as a function

of shear rate. Compared to transient viscosity data from shear rate ramps, the steady-state viscosity is independent from time-dependent effect and the slope of the shear rate ramp. For comparison of viscosity data the steady-state viscosity is the best choice, because it is independent of the instrument used and can be correlated with the shear rate applied.

Within the almost four orders of magnitude in shear rate covered during the test, both viscosity curves displayed in Figure 2 show a pronounced shear thinning behaviour. As expected, the soft cream has the higher viscosity at low shear rates but it also shows the stronger shear thinning. Within the range of these measurements, the viscosity of the soft cream drops by a factor of almost 500, while the viscosity of the body lotion only drops by a factor of 120.

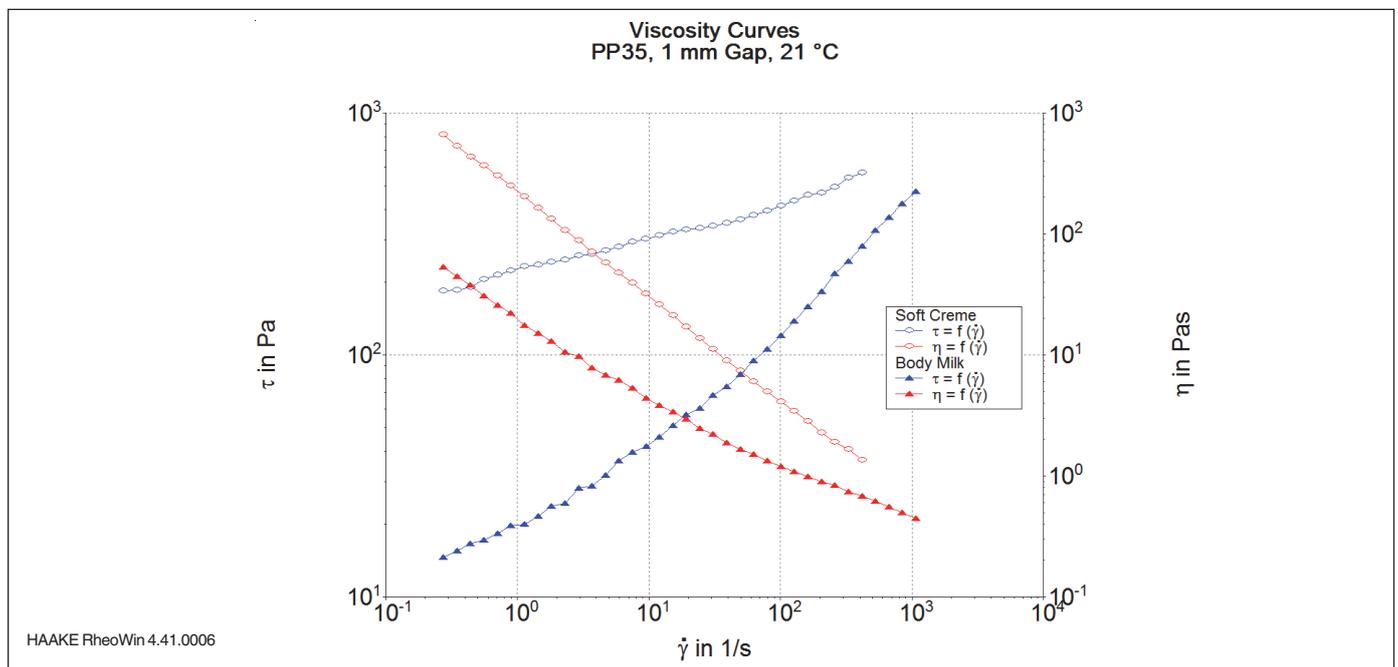


Fig. 2: Viscosity curves (red) and flow curves (blue) of a soft cream (open symbols) and a body lotion (filled symbols). The soft cream shows the higher viscosities and the stronger shear thinning.

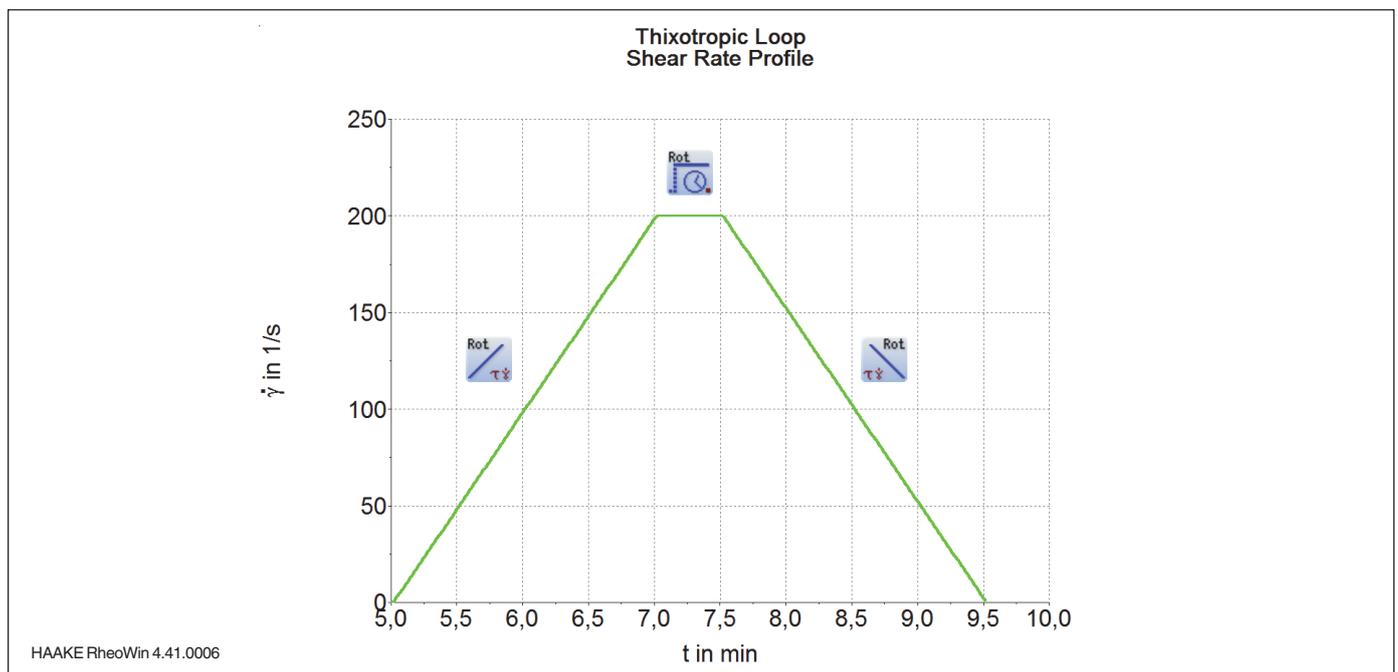


Fig. 3: Shear rate profile for the so-called “thixotropy loop“ consisting of an up ramp, a peak hold time at the maximum shear rate and a down ramp.

Extrapolating both viscosity curves to higher shear rates predicts that the viscosity of both products will be identical at approximately  $2000 \text{ s}^{-1}$ . This similarity is not accidental because rubbing a cream or lotion into the skin happens in that range of shear rate and the viscosity, which is felt as being pleasant on the skin, is of course the same for both products.

### Thixotropy

In QC, the thixotropic behaviour is usually tested with the so-called “thixotropy loop“. The advantage of this test method is the short time the test takes compared to other commonly used methods.

The test consists of 3 elements: A shear rate ramp from  $0 \text{ s}^{-1}$  up to the maximum shear rate (in this case  $200 \text{ s}^{-1}$ ), an element keeping the maximum shear rate constant over some time and a second shear rate ramp going back to  $0 \text{ s}^{-1}$  (Figure 3). Usually the durations of the up ramp and down ramp are identical. The time for the constant shear element should be long enough for the sample to reach a constant viscosity before starting the down ramp.

The results of these tests are evaluated by calculating the area between the flow curves from the up ramp and the down ramp. The bigger the area, the stronger the thixotropy of the sample.

One important fact to keep in mind: the result of this test depends on the test parameters, i.e. the maximum shear rate and the slope of the ramps. Only if the shear rate profile (like e.g. shown in Figure 3) is kept the same, results from different tests can be compared.

Running this test on both samples gave a significant difference in the results. While the soft cream clearly showed a thixotropic behaviour (Figure 4, open symbols), the body lotion showed no thixotropy at all.

### Yield stress

If a material has a yield stress, it behaves like an elastic solid when exposed to a shear stress below the yield stress and like a viscous liquid when the stress applied is higher than the yield stress. Therefore, the recommended method to test, whether a sample has a yield stress and at which stress value it appears, is a linear continuous increase of the applied stress [1].

For the evaluation of the test results, the deformation of the sample is plotted as a function of the stress applied. For the determination of the yield stress, only the first discontinuity in the deformation curve can be used. Similar points at higher stresses are related to other changes of structure in the sample. Straight lines are fitted to the linear parts (in the double logarithmic plot) of the deformation curve below and above the first discontinuity. The yield stress is calculated from the point of intersection of these two straight lines (Figure 5).

With this method, data below as well as above the yield stress is recorded. Thus, no extrapolation is needed, which increases the reproducibility and reliability of calculated value for the yield stress considerably.

While the body lotion showed no yield stress within the range of measurement, the soft cream showed a distinct yield stress of  $110 \text{ Pa}$  (Figure 5).

### Conclusion

The HAAKE Viscotester iQ rheometer is a compact instrument with the right combination of sensitivity and strength to successfully test a wide range of samples with different QC methods in controlled rate (CR) or controlled stress (CS) mode. The sensitivity of the instrument allows covering a wide range of shear rates with only one measuring geometry. For cosmetic emulsions, the parallel plate geometry proved

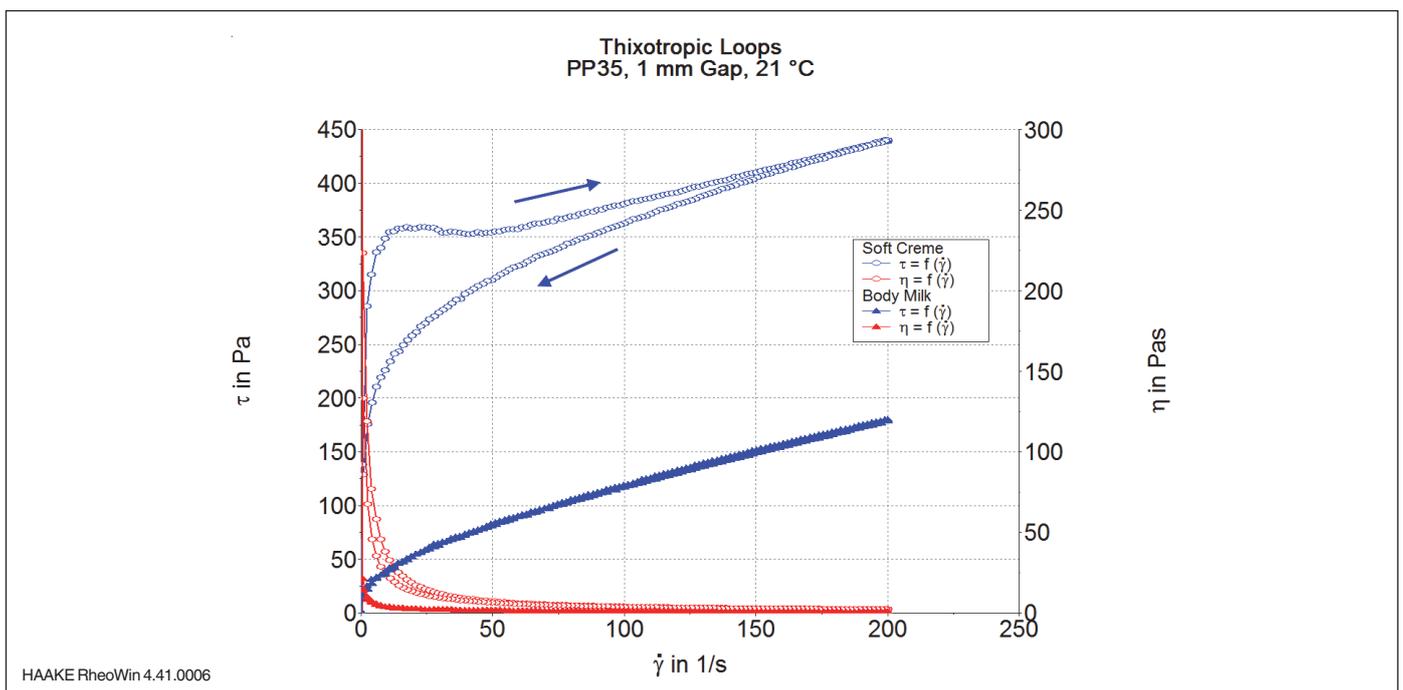


Fig. 4: Results of the thixotropy test for soft cream (open symbols) and body lotion (filled symbols). The soft cream shows a thixotropic behaviour, indicated by the clear difference between the up and down part of the flow curve. The up and down curve for the body lotion are identical, thus the sample is not thixotropic.

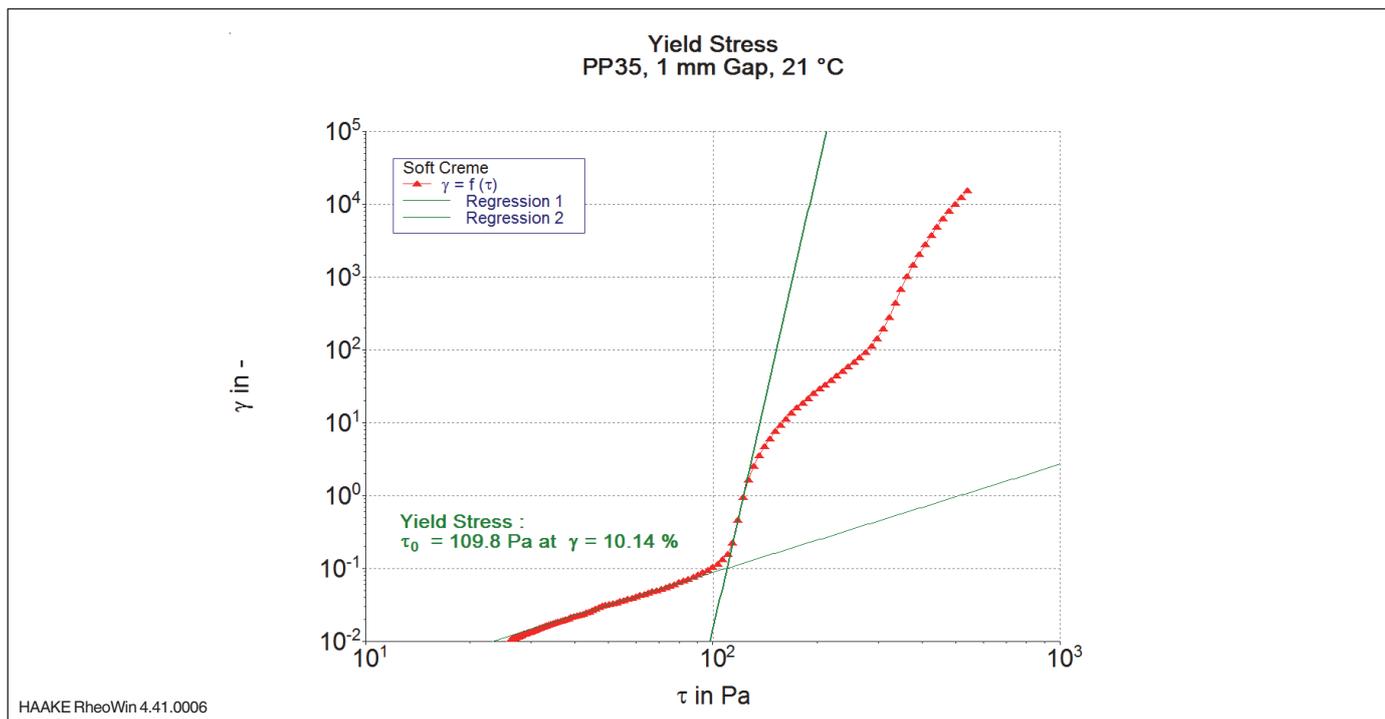


Fig. 5: Deformation as a function of stress for the soft cream sample. The yield stress is calculated as the point of interception of the two green tangents, marking the transition from elastic deformation to viscous flow.

to be particularly useful since its use reduces the stress on the sample during sample loading. In addition, it significantly reduces the time between tests due to a much simpler and therefore faster cleaning procedure.

The very good quality of the results shown in this report is an excellent base for a reliable data analysis with a variety of available methods and models.

### Reference

- [1] DIN Technical Report No. 143 of the NPF/NAB-AK 21.1 "Rheology" (Pigments and extenders)

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

## Author

Fabian Meyer  
Thermo Fisher Scientific, Karlsruhe, Germany

## Key words

Creep and recovery, viscoelasticity, yield stress, cosmetic emulsions, Viscotester iQ Air Rheometer

## 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 background

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.

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.



Once the stress is removed from the viscous sample the deformation signal will remain constant and no back-deformation 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 constant stress is applied.

In the recovery phase the deformation jumps back to zero (Figure 1b). The back-deformation is a result of the elasticity of the material. All energy is stored inside the material and released again once the 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 behavior. The degree of the two components depends on the characteristics of the sample as well as the magnitude of applied stress. The results of a creep and recovery test with an ideal viscoelastic sample are shown in Figure 2.

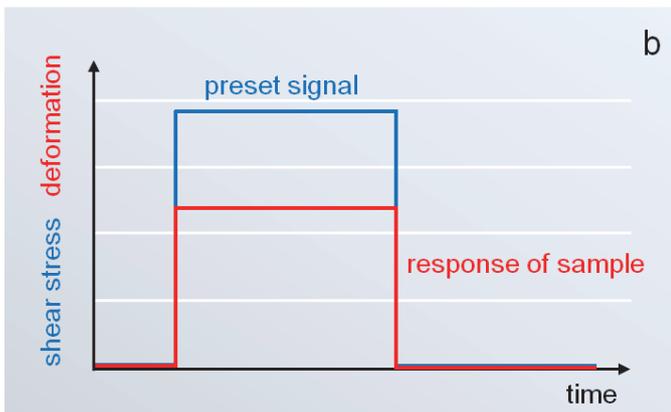
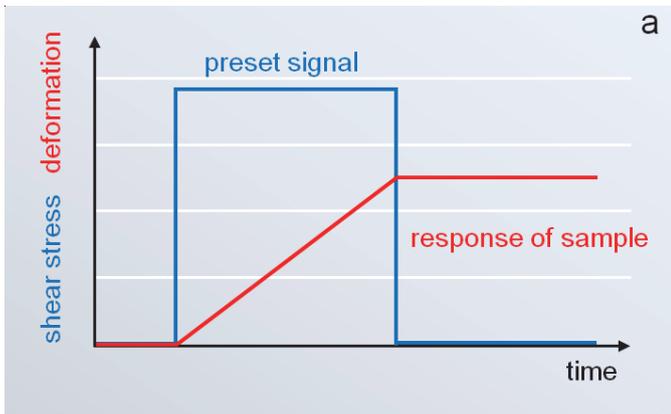


Figure 1: Behavior of a pure viscous (a) and a pure elastic (b) material in a creep and recovery test.

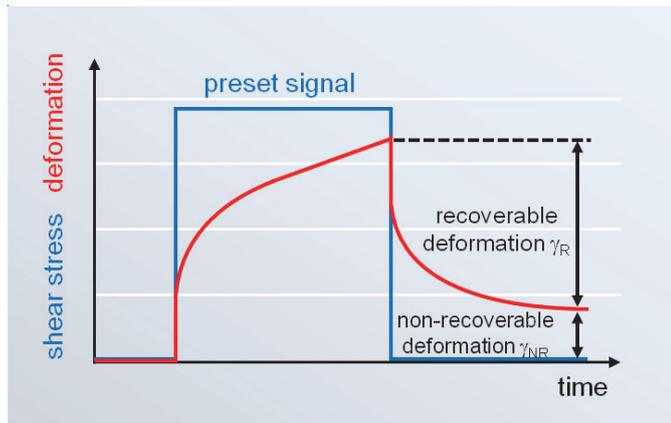


Figure 2: Behavior of an ideal viscoelastic material in a creep and recovery test.

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 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 back deformation, followed by a delayed viscoelastic 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  $\gamma_R$  and the non-recoverable defor-

mation  $\gamma_{NR}$ . 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:

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



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

### 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 is shown in Figure 4.

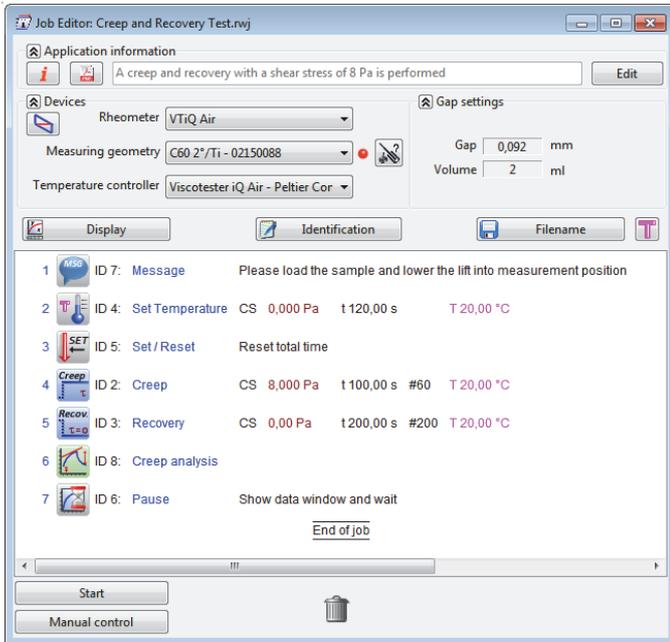


Figure 4: HAAKE RheoWin Software routine for a creep and recovery test including data evaluation.

## 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 back 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 of percentage of recoverable deformation as directly calculated by the RheoWin creep and recovery evaluation routine.

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

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. The compliance is defined as the ratio of the deformation,  $\gamma$  and the applied stress,  $\tau$ :

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

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  $\tau_0$  of the tested material. The yield stress is considered the minimum shear stress required to overcome 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.

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

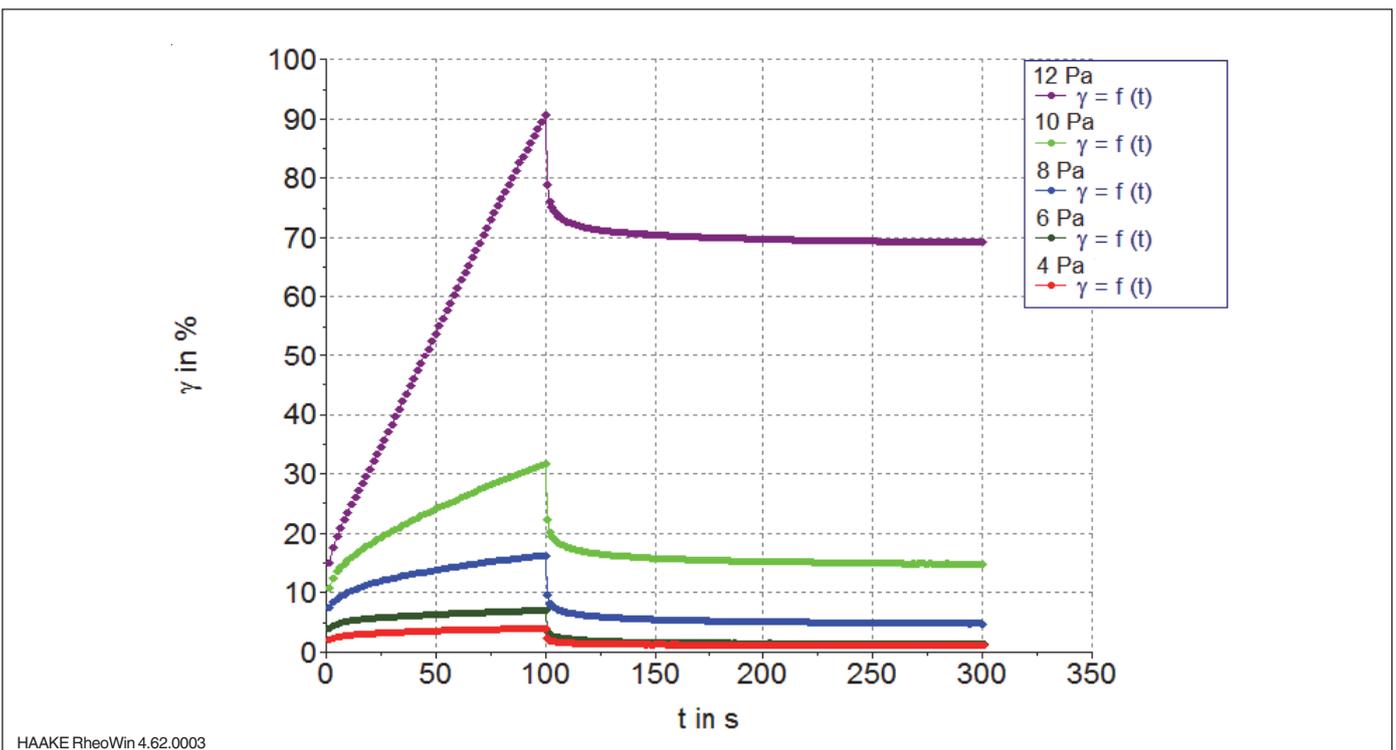


Figure 5: Creep and recovery test with cosmetic emulsion at different shear stress.

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 shear stresses of 6 and 8 Pa the values of the equilibrium compliance are smaller than at higher stresses. This is probably due to the fact that at the low shear

stresses 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 the stress ramp experiment with the same cosmetic emulsion used for the creep and recovery tests is shown in Figure 7.

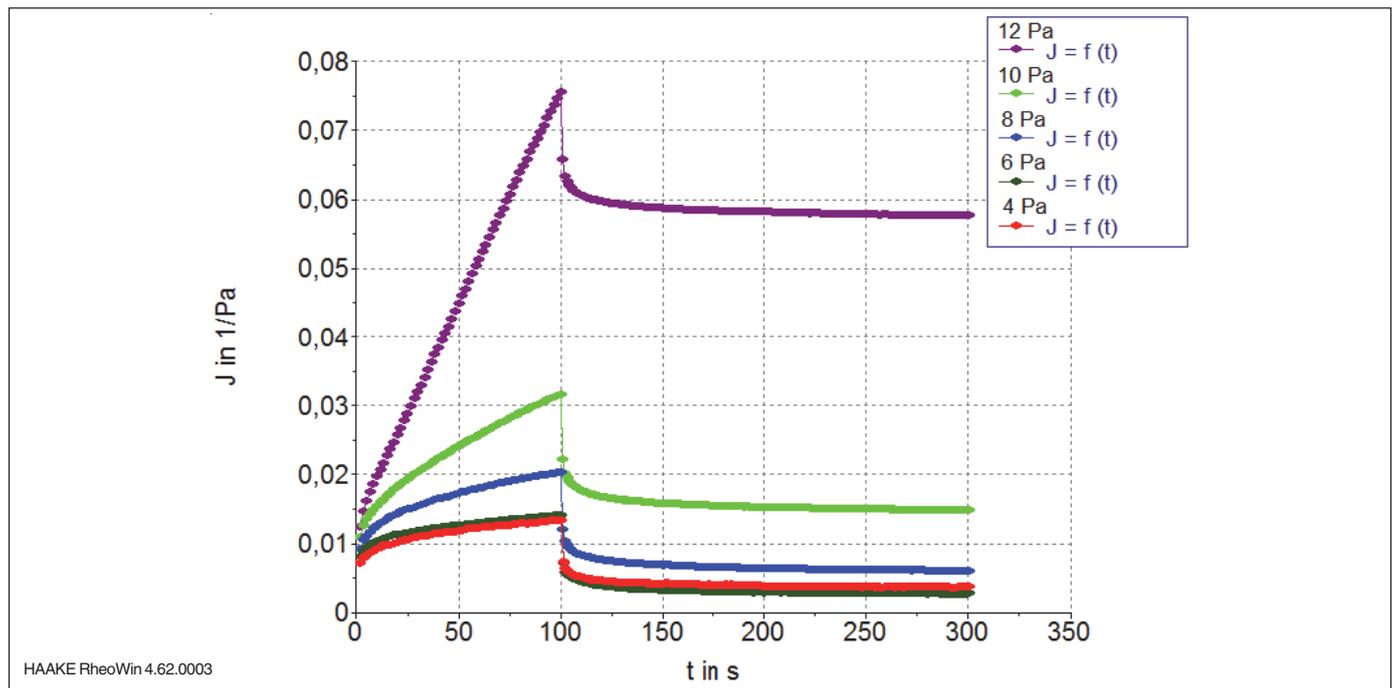


Figure 6: Creep and recovery test with cosmetic emulsion with different shear stress values during the creep phase.

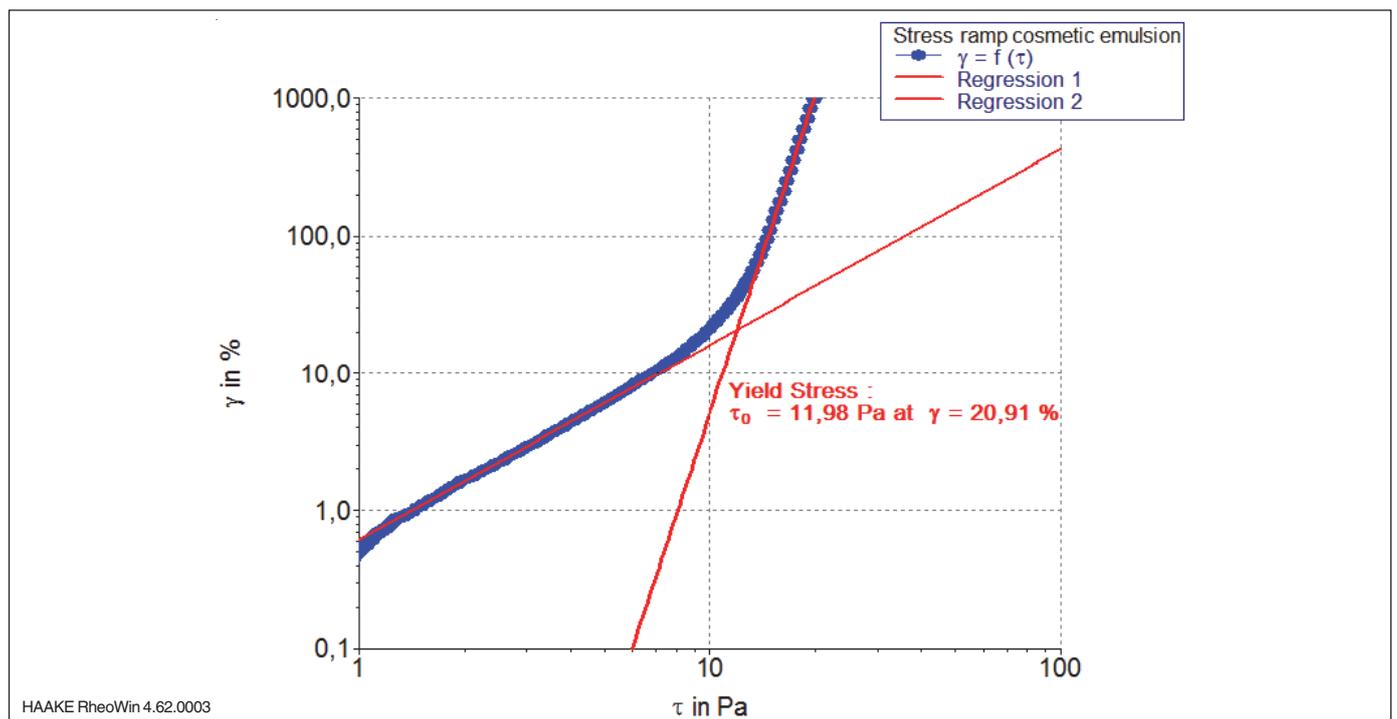


Figure 7: Stress ramp test with yield stress determination according to tangent method for cosmetic emulsion.

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.

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.

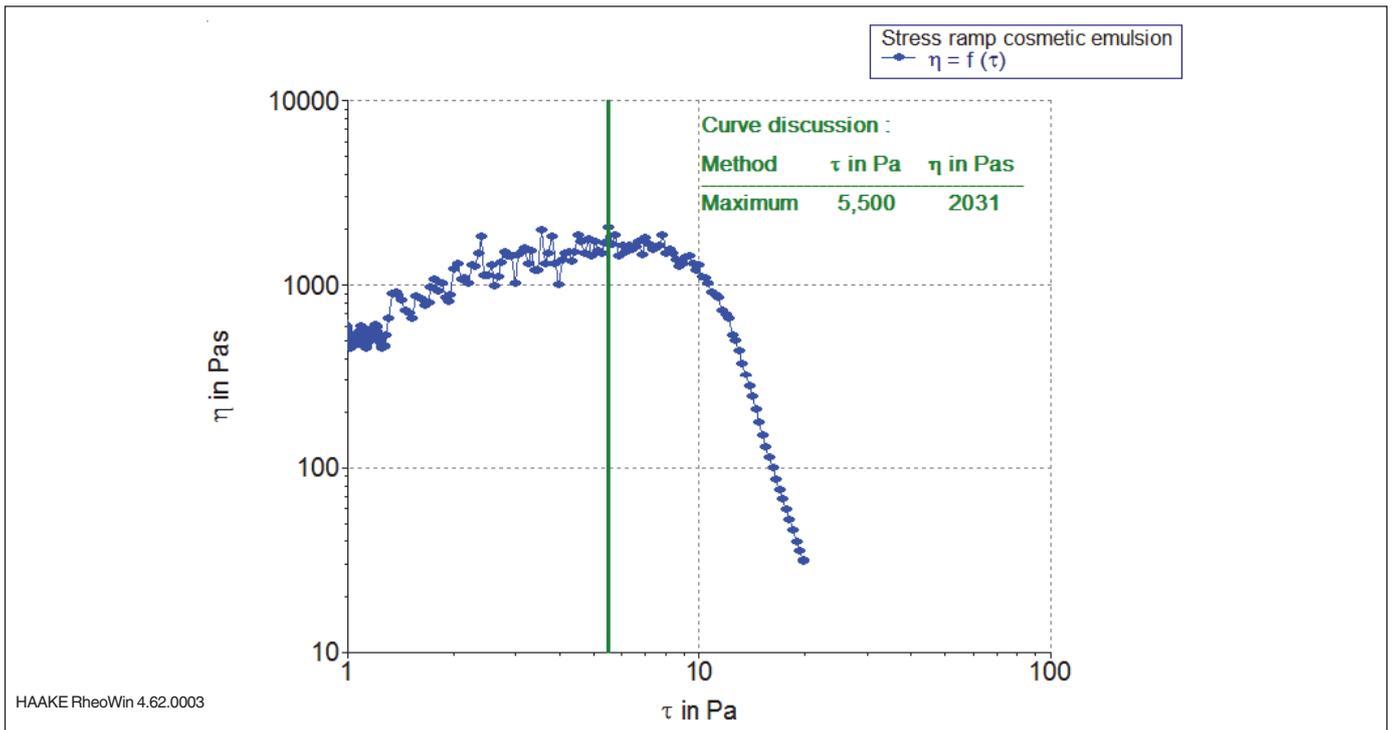


Figure 8: Viscosity as a function of shear stress for cosmetic emulsion with determination of maximum viscosity.

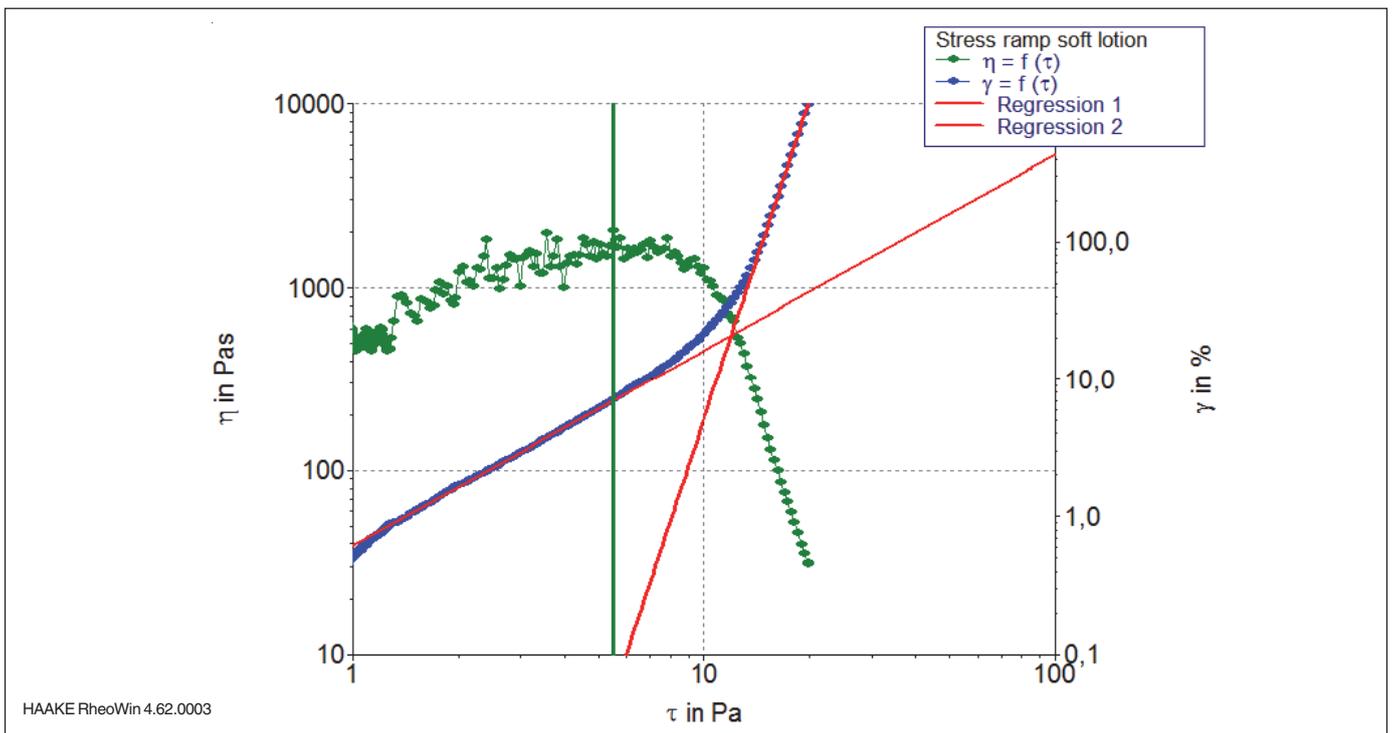


Figure 9: Viscosity as a function of shear stress for cosmetic emulsion with determination of maximum viscosity.

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.

## Conclusions

It was demonstrated that the HAAKE Viscotester iQ Air Rheometer 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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# Product stability and shelf-life - What rheology has to do with it

## Author

Klaus Oldörp  
Thermo Fisher Scientific, Karlsruhe, Germany

## Key words

Product stability, product shelf life, viscosity, yield stress

## 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.

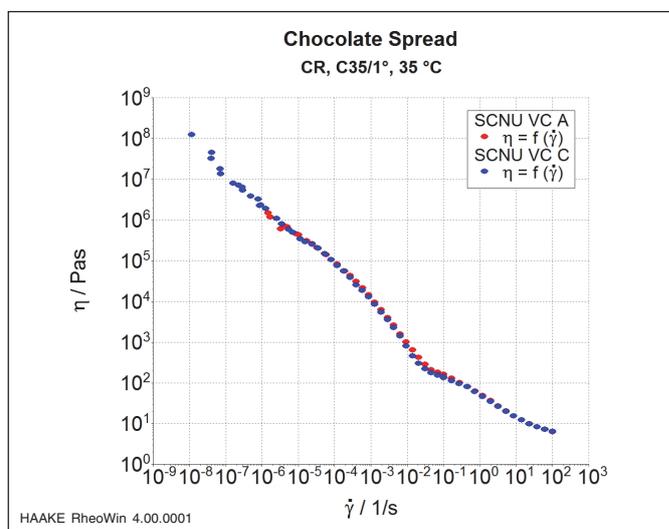
In order to avoid sedimentation of solid particles dispersed in a liquid phase, the viscosity at low shear rates has to be high to slow down the sedimentation process. To stop the phase separation completely a yield stress can be introduced into the product either by selecting suitable components or 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.

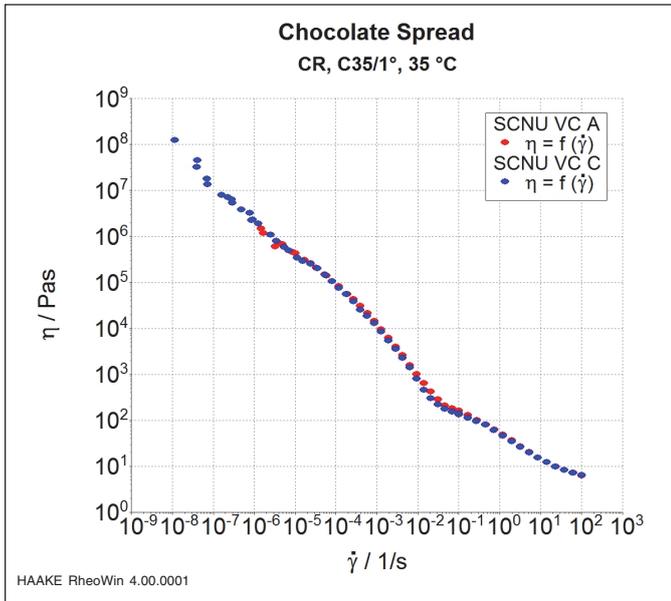
## Results and discussion

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



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

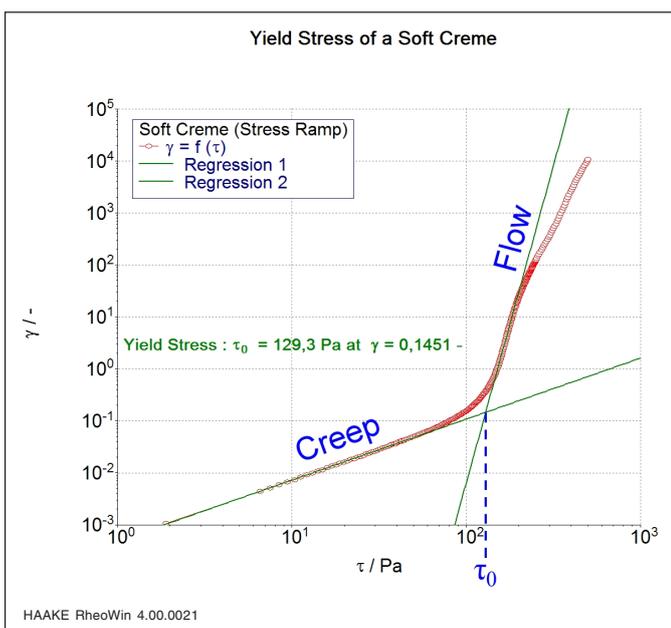
over a wide range of shear rates. Figure 2 shows an example for a viscosity curve starting from a shear rate of  $10^{-8}$   $s^{-1}$ . Despite the fact that the shear rate spans a range of 10 orders of magnitude, the curve has been recorded using a single measuring geometry within a single run.



**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.

The yield stress  $\tau_0$  is the stress level at which a material starts to cease to behave elastic and begins 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]. Its advantages are the continuous increase of stress on the sample, data is collected below and above the yield stress i.e. 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.



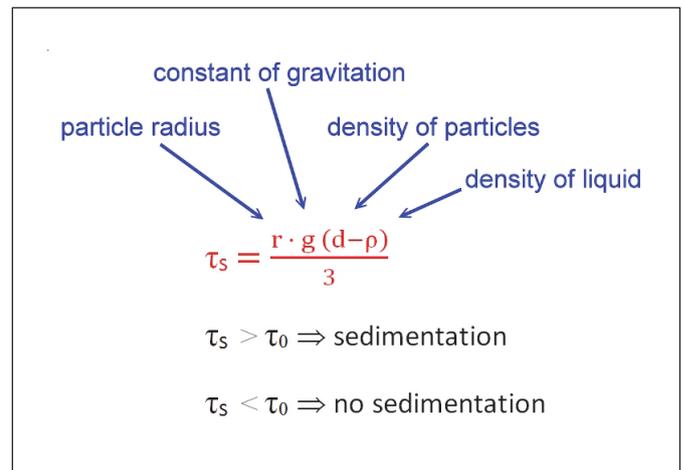
**Figure 3:** Deformation as a function of stress during a linear stress ramp for a soft crème. The intersect of the curve's slope in the creep regime and the curve's slope in the flow regime marks the yield stress  $\tau_0$ .

With increasing yield stress a substance is able to bear stronger forces like e.g. the weight force of suspended

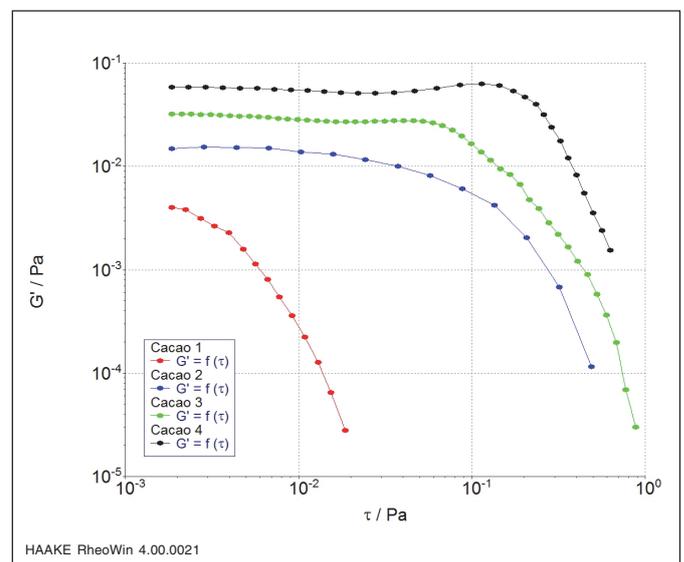
particles without yielding. Since with increasing yield stress a substance also becomes less flexible it is important to find the optimum value to have a good stability without losing the smoothness needed for the respective application like for a cosmetic emulsion, a lubricant or a specific food product. 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™ Software 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  $\tau_s$  that a particle puts on the fluid (Figure 4) to calculate whether sedimentation will occur or not [2].

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 4:** The sedimentation stress  $\tau_s$  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.



**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.

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- [2] P.B. Laxton and J.C. Berg, Gel trapping of dense colloids. J. Colloid Interface Sci. 285: 152-157 (2005)

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## APPLICATION NOTE

# Optimization of the filling process of shampoo sachets with the HAAKE CaBER 1 extensional rheometer

**Authors**

Kevin Barber<sup>1</sup>, Alexandra Ewers<sup>2</sup> and Jint Nijman<sup>2</sup>

<sup>1</sup>Thermo Fisher Scientific, United Kingdom

<sup>2</sup>Thermo Fisher Scientific, Karlsruhe, Germany

**Key words**

Shampoo, filling, elongational viscosity, stringiness, HAAKE CaBER

**Abstract**

With certain shampoo formulations, “strings” of shampoo are formed when filling sachets during production. This causes the product to spill across the sachet seam area. As a consequence, the sachet cannot be properly sealed. Using the Thermo Scientific™ HAAKE™ CaBER™ 1 extensional rheometer “string forming” shampoo formulations were easily and quickly distinguished from “well performing” samples. Rotational rheometers were not able to provide this information.

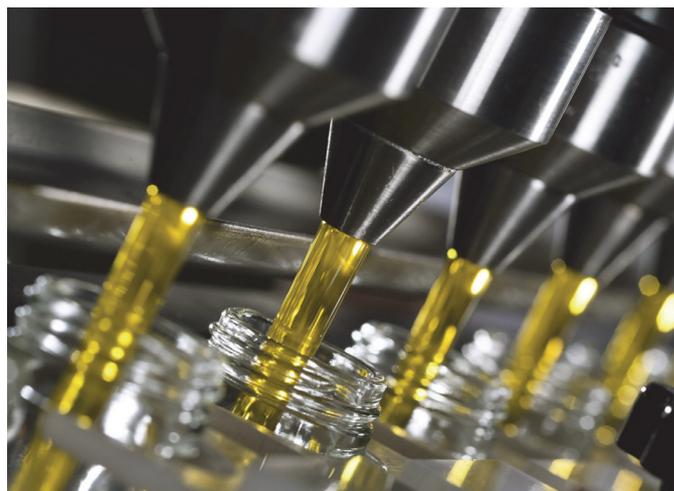
**Introduction**

While most commercial rheometers are capable of generating only shear flows, in many industrial processes and applications the flow is predominantly extensional in nature.

Typical examples of this type of flow are fiber spinning, paper coating, extrusion and filling food or toiletries in bottles. This paper describes the optimization of filling shampoo into sachets. With certain shampoo formulations, “strings” of shampoo are formed when filling the sachets, which causes the product to spill across the seam area. As a consequence, the sachet cannot be properly sealed. This failure is expensive as it will result in the disposal of many improperly sealed sachets.

Using classical rotational or oscillatory shear experiments, no discernible differences could be observed between the five shampoo formulations investigated. However, the use of the HAAKE CaBER 1 (Capillary Breakup Extensional Rheometer) allowed the characterization of the formulations' extensional properties in a quick and easy experiment, thus providing a solution to the problem.

Shampoos usually consist of 80 -90% water, more than 2% detergent, and foaming agents and about 1% of fragrances and preservatives [1]. Often shampoos contain



antistatic agents, thickeners and conditioners [2]. Current health and beauty trends make it important to stabilize special-effect particles in gels, body washes or shampoos. Thickening agents are used to prevent the sedimentation of these particulate phases [3]. However, a problem with thickeners is that they can be the cause of unwanted extensional properties, such as string formation.

These unwanted rheological properties can manifest themselves in an unpleasant and “slimy” feeling while using the product. They can also cause string formation during the high speed filling of a shampoo into sachets or bottles, resulting in improper sealing of the sachet or messy bottles. Slowing down the filling speed would solve the problem, but that has implications for the throughput capability of the production line. A far better solution would be to modify the formulation of the shampoo in such a way that the highest filling speed can be used.

**Methods and materials**

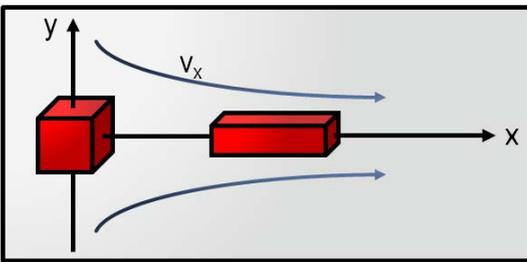
In this investigation five shampoos with different formulations were tested to find out which formulation could be filled into the sachets successfully at a high filling speed.

All formulations were previously tested on a high speed filling line with differing degrees of success. Some exhibited the string formation problem that resulted in failure of the sachet seams.

The measurements were carried out with the HAAKE CaBER 1 extensional rheometer. The CaBER experiment gives a quick insight into the material properties under an extensional deformation which occur, for example, during the sachet filling. It is impossible to determine the extensional properties of a fluid by using a traditional rotational rheometer.

In an extensional flow the stream-lines converge and the velocity increase (i.e. the acceleration) is in the direction of the flow (Figure 1a). This in contrast to the situation in a shear flow where the streamlines are parallel and the velocity increase is perpendicular to the direction of the flow (Figure 1b).

a)



b)

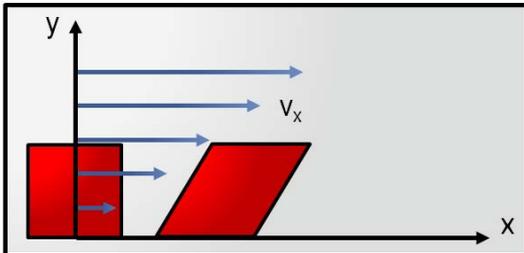


Fig. 1: Comparison between extensional flow (a) and shear flow (b).

The principle of the CaBER experiment is simple. A small quantity of sample (less than 0.2 ml) is placed between two parallel plates (diameter e.g. 6 mm). The fluid is then exposed to a rapid extensional step strain by moving the upper plate upwards, thereby forming a fluid filament (Figure 2). The filament evolution as a function of time is controlled by the balance of the surface tension and the viscous and elastic forces.

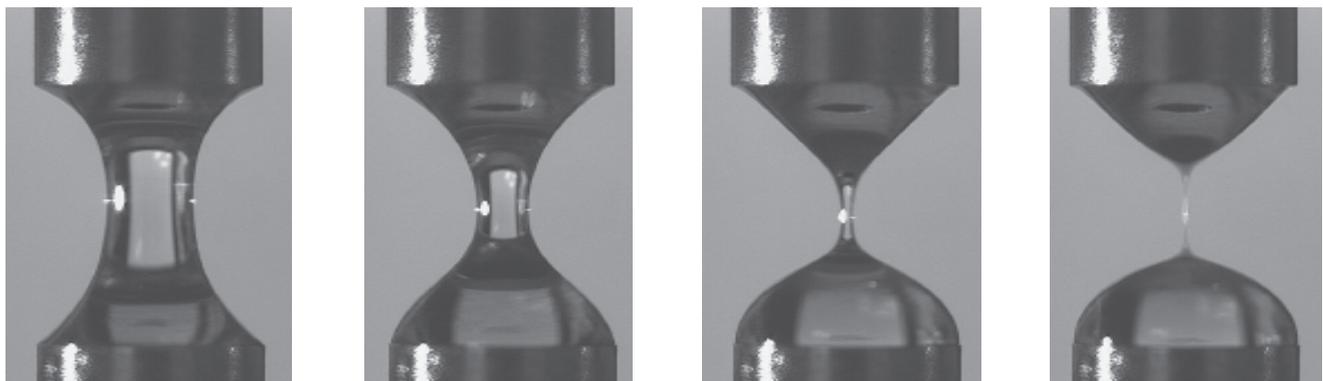


Fig. 2: Sequence of a CaBER measurement.



HAAKE CaBER 1 extensional rheometer.

The surface tension is trying to “pinch off” the filament while the extensional rheological properties of the fluid are trying to prevent that. A laser micrometer measures the midpoint diameter of the gradually thinning fluid filament after the upper plate has reached its final position (Figure 3).

From the measured data, which describes the evolution of the filament diameter as a function of time (Figures 2a, 2b and 2c), the filament break-up time (Figure 2d), the extensional deformation, deformation rate and the apparent extensional viscosity can be calculated.

## Results and discussions

Five different shampoo samples were tested. Two of the samples (samples 1 and 2), performed well in the sachet filling equipment; the three other samples (samples 3, 4 and 5) did not perform well.

When measured in a rotational rheometer, the five samples did not show any significant differences in the flow curves that would explain their different during the filling of the sachets (Figure 4).

In contrast, when exposed to an extensional flow fluid using the HAAKE CaBER 1 rheometer, the measured diameter versus time curves (see Figure 5) of the five samples nicely rank according to their filling behavior: the shorter the filament lifetime in the CaBER experiment, the better the filling properties.

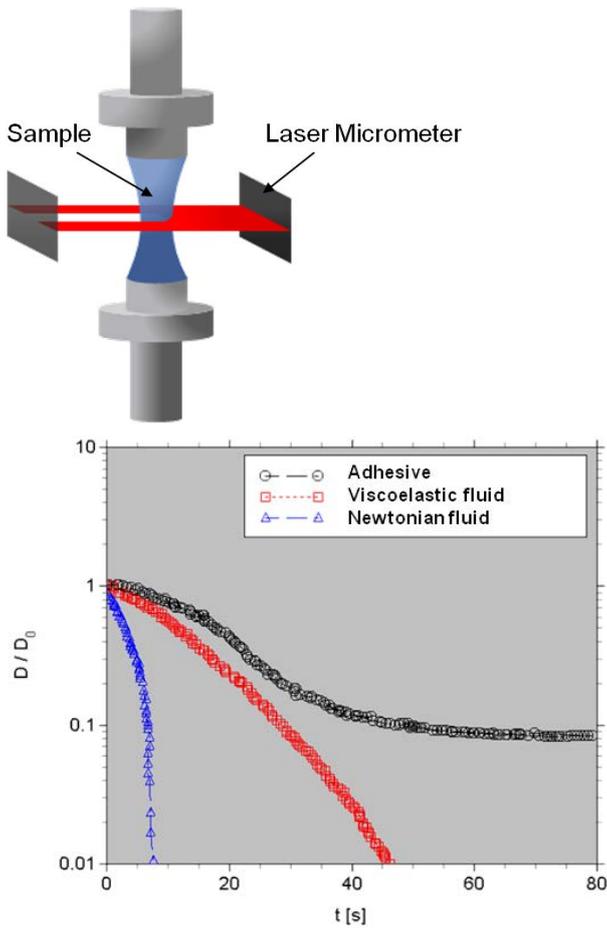


Fig. 3: Principle of the CaBER experiment.

The 5 samples clearly differentiated in their extensional flow properties. The filament lifetimes of the shampoos 1 and 2 are relatively short. These shampoos can be filled into sachets without any obvious problems. For the shampoos 3, 4 and 5, the filament lifetimes are significantly longer, which leads to problems in sachet filling. String formations prevented the sachets sealing, a problem which can only be resolved by slowing down the filling process.

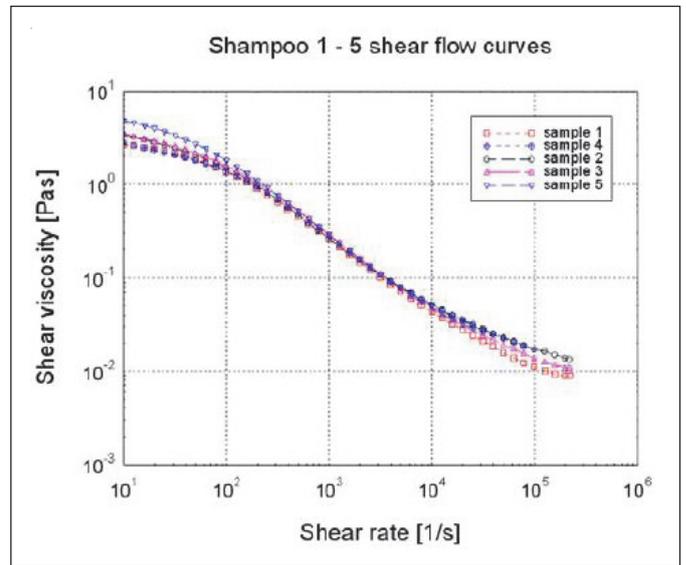


Fig. 4: Shear viscosity curves of shampoos 1-5.

The graph of the extensional flow curves (see Figure 6) shows that the extensional viscosities of samples 1 and 2 (which performed well in the high speed filling line) are clearly lower than those of samples 3 and 5 (which did not perform well in the high speed filling line). The lower extensional viscosity leads to a higher strain rate and shorter break-up time (filament life time) in the CaBER experiment and in the filling equipment.

### Conclusions

The HAAKE CaBER 1 extensional rheometer allows for an easy quick determination of the extensional flow properties of low to medium viscous fluids. In the presented case it was possible to distinguish between different shampoos and of predicting filament lifetimes for production and quality control. Shampoos 3 - 5 will need to be reformulated to solve the serious filling problems. In this way it is possible to optimize the quality of the shampoos and the production process.

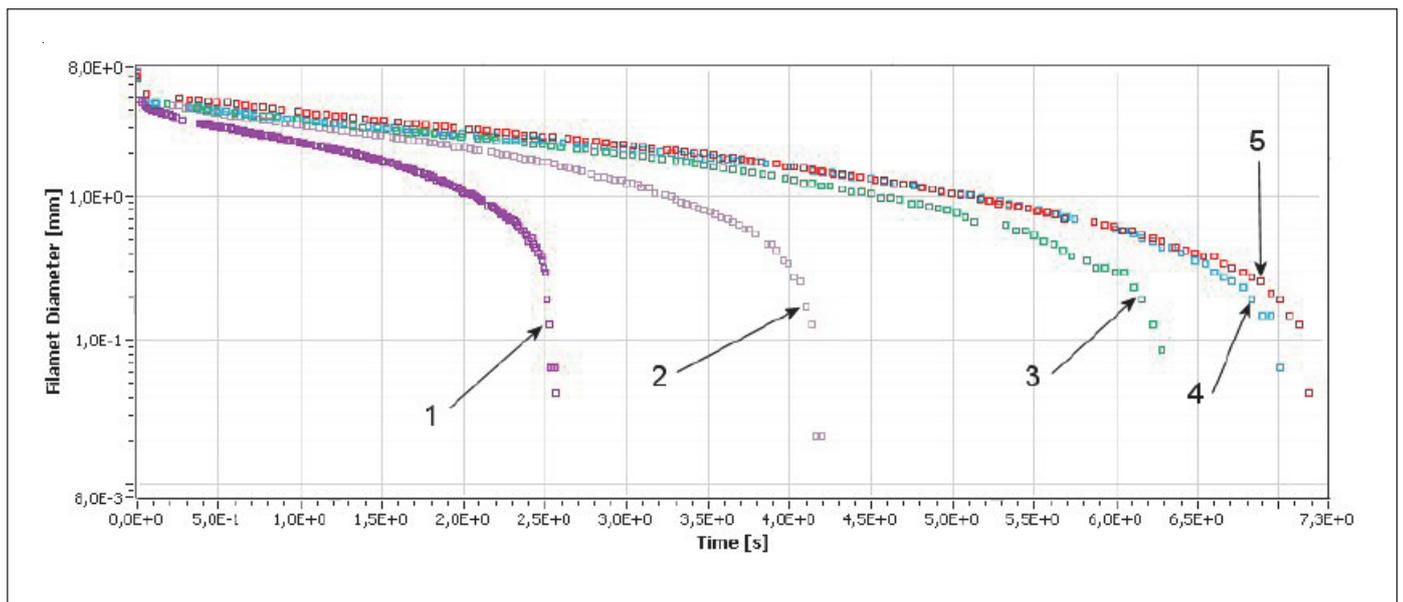


Fig. 5: Filament diameter decay of shampoos in the CaBER experiment.

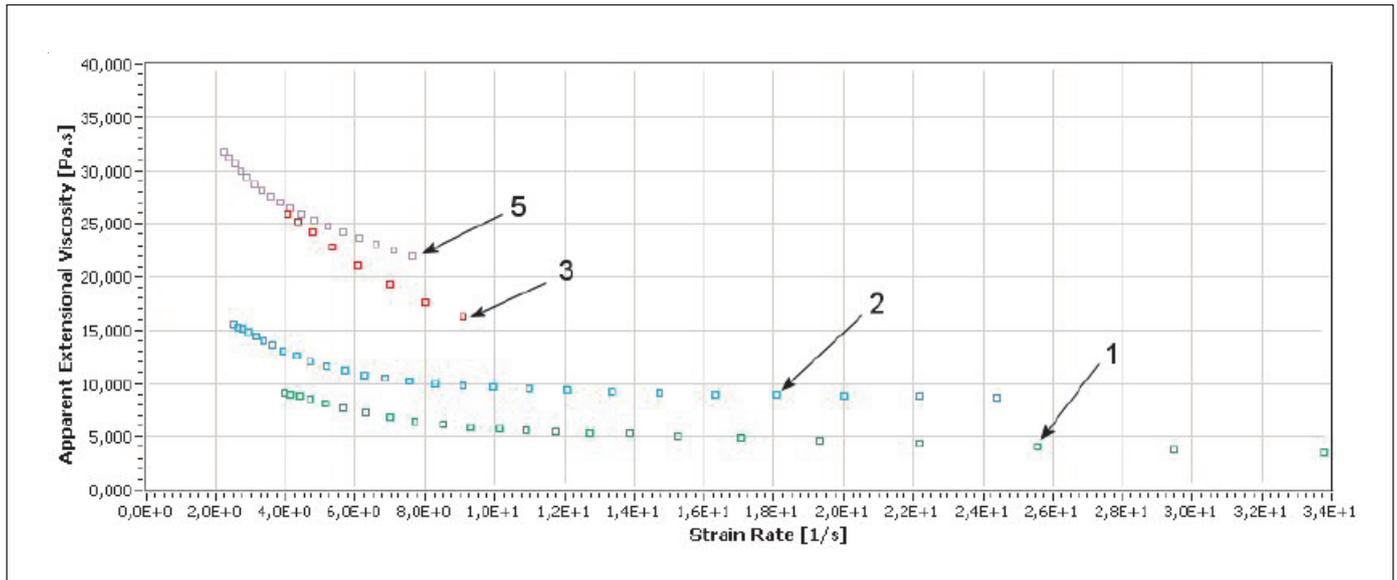


Fig. 6: Extensional flow curves of shampoos 1-5.

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# Monitoring emulsions morphology under shear via simultaneous rheometry and in-situ FT-IR spectroscopy

## Authors

Kiyoji Sugimoto<sup>1</sup>, Fritz Soergel<sup>2</sup>, and Manfred Feustel<sup>3</sup>

<sup>1</sup>Thermo Fisher Scientific, Yokohama, Japan

<sup>2</sup>Thermo Fisher Scientific, Karlsruhe, Germany

<sup>3</sup>Resultec analytic equipment, Illerkirchberg, Germany

## Key words

FT-IR spectroscopy, rheology, simultaneous analysis, emulsions, HAAKE MARS 40/60 Rheometer

## Introduction

Emulsions are of wide interest in the food, pharmaceutical, healthcare and cosmetic industries. They typically consist of at least two liquid phases, surfactant agents and stabilizers. Emulsions exhibit complex rheology, making it difficult to understand flow phenomena on a microscopic level.

A common technique utilized to analyze emulsions under shear deformation is light microscopy. However, emulsions showing droplet distributions with droplets on the submicron scale cannot be visualized using light microscopy because of given resolution constraints. Other limiting factors of light microscopy arise when the concentration of droplets with equal size is high or the refractive indices of the two phases are too similar.

In such cases, the Thermo Scientific™ HAAKE™ MARS™ Rheometer equipped with the Rheonaut module and a FT-IR spectrometer provides simultaneous rheometry and in-situ FT-IR spectroscopy under shear deformation and offers a versatile tool for efficient and comprehensive emulsion research and stability testing. Simultaneous rheometry and FT-IR spectroscopy proves to be a useful tool in understanding the microscopic state of droplets in concentrated emulsions.

In this contribution, we want to present some results on the dynamics of molecular organization of an emulsion under shear.

## Materials

For this study, as model substances, three commercially available hand cream emulsions with high volume fractions of oil in water containing submicron droplets were supplied by a manufacturer of cosmetics. The samples varied with respect to their hydrocarbon composition only. No further sample preparation was required.



## Methods

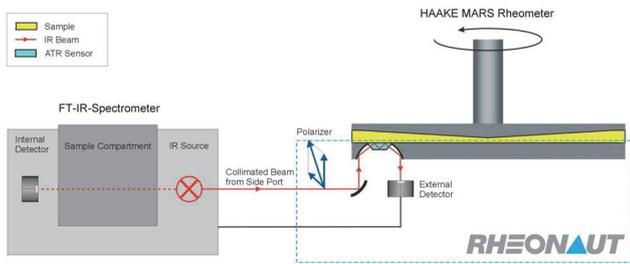
The patented\* Rheonaut module couples a standard FT-IR spectrometer with side port (here: Thermo Scientific™ Nicolet™ iS™ 10 FT-IR spectrometer) to the HAAKE MARS Rheometer.

The lower plate of the rheometer is temperature controlled (Peltier or electrical) and features a monolithic diamond element that serves as the ATR (attenuated total reflection) sensor, offering a single internal reflection. Compared to

\*Resultec Analytic Equipment: DE 10140711, EP 02762251, US 6988393, JP 4028484



**Figure 1:** The HAAKE MARS Rheometer with Rheonaut module and Nicolet iS 10 FT-IR spectrometer.



**Figure 1a:** Schematic diagram of coupling an FT-IR spectrometer to the HAAKE MARS Rheometer.

standard infrared transmission spectroscopy or specular reflection spectroscopy techniques, the sample thickness can thus be adjusted to the rheological needs and is independent from the infrared spectroscopy requirements.

The operation is managed by the Thermo Scientific™ HAAKE™ RheoWin™ Software providing full control over temperature settings, horizontal positioning of the lower plate, and the communication with the FT-IR spectrometer software for synchronous data acquisition.

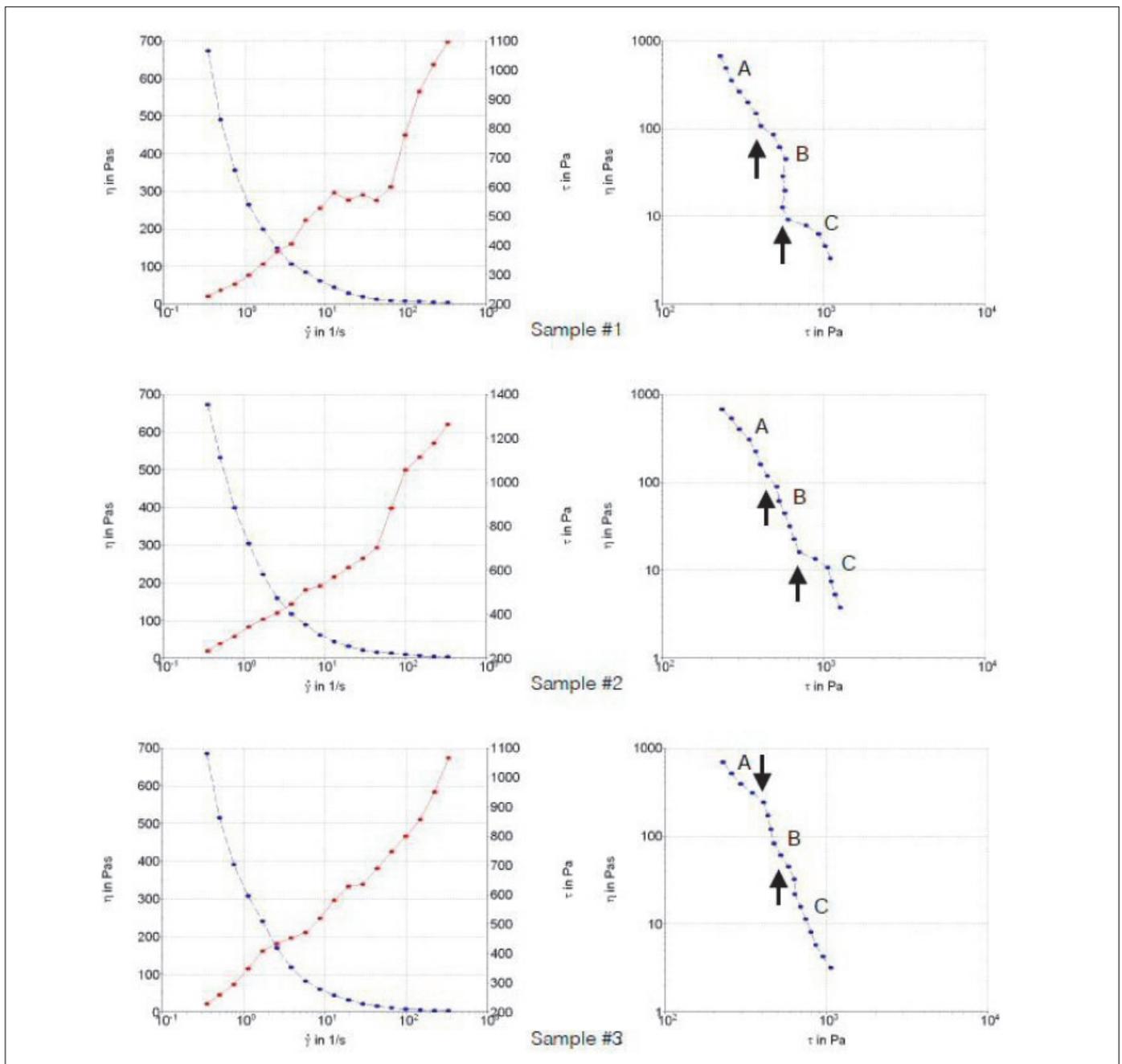
Steady shear flow experiments were carried out using a cone/plate measuring geometry with 20 mm diameter and a cone angle of 2°. Gap setting was 0.1 mm. All samples were tested in CR (controlled shear rate) mode from 0.5

up to 500 s<sup>-1</sup>. The temperature was set to 25.0 ± 0.1 °C. The infrared spectral range was 400 cm<sup>-1</sup> to 4000 cm<sup>-1</sup> with a spectral resolution of 4 cm<sup>-1</sup>. Each spectrum consists of 8 co-added scans.

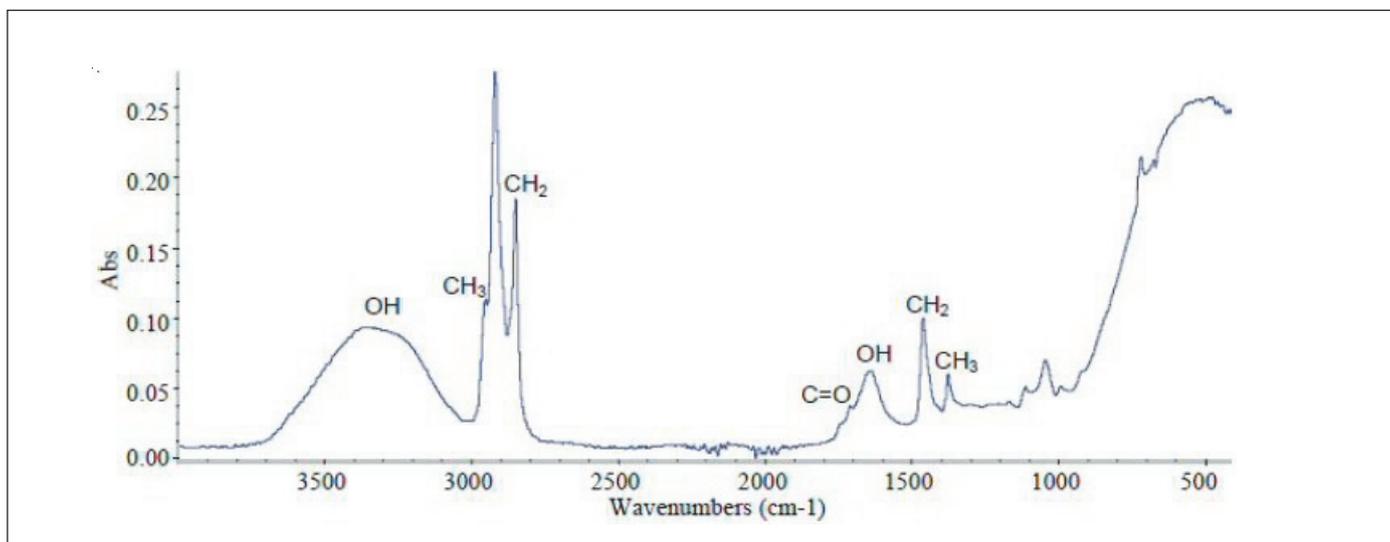
A complete data set was produced for each sample, consisting of 18 rheological data points and 18 related (simultaneously collected) FT-IR spectra.

## Results

Figure 3 displays the dynamic shear viscosity plotted against shear rate for the three samples #1, #2, and #3. As typical for highly concentrated emulsions, the materials show a decreasing viscosity with increasing shear rate (shear thinning or pseudoplastic).



**Figure 3:** Left column: Viscosity  $\eta$  (red graph) plotted against shear rate. Right column: Viscosity  $\eta$  (log scale) plotted against stress  $\tau$ .



**Figure 4:** A typical FT-IR absorbance spectrum with band assignments of the investigated samples.

A closer look, however, reveals a step-like shear thinning behavior as can be seen in the right graphs of figure 3 which display the viscosity plotted double-logarithmically against shear stress.

Such a viscosity behavior has been investigated amongst others by Saiki et al. [1]. Based on detailed rheological experiments, the proposed figurative model is a droplet distribution profile which changes with the applied stress. Whereas at very low shear the droplets are distributed homogeneously, ambiguous layers (or clusters) of droplets are formed at moderate shear causing slight segregation in droplet population and at higher shear discrete layers are formed. Another approach [2] proposes a figurative model showing a droplet deformation and stretching by the applied shear, leading to droplet rupturing and recombination through coalescence at higher shear stresses.

Simultaneously applied FT-IR spectroscopy enables a more sophisticated molecular insight and deeper understanding. Figure 4 displays a typical FT-IR sample spectrum. The broad absorption band at  $3354\text{ cm}^{-1}$  relates to the aqueous phase of the sample whereas the band at  $2922\text{ cm}^{-1}$  relates to the organic phase.

The sample changes with shear get easily traceable by calculating the absorption ratio ( $3354\text{ cm}^{-1}/2922\text{ cm}^{-1}$ ) from each spectrum and plotting the results against the experimental procedure (figure 5).

The change of the infrared absorption ratios in figure 5 reveals a concentration gradient within the samples. Close to the ATR sensor are sample layers at which the organic phase is enriched in relation to the aqueous phase.

As the experiment goes on, the enrichments dissolve again. Because the ATR sensor area dimensions are several orders of magnitude larger than the submicron droplets of the organic phase, neither droplet deformation and stretching nor coalescence is an object since they do not evoke a concentration gradient within a sample.

The shear thinning behavior of the investigated emulsion samples is initially controlled by perturbation and breakdown of complex droplet structures which lead to the formation of droplet layers causing flatter shear viscosity curve regions. With further increasing shear rates, however, a self-healing process is observed. The droplet structure is rearranged and hence the layers are dissolved, as the FT-IR spectra show.

## Conclusion

Rheometry and FT-IR spectroscopy have been applied simultaneously on model emulsions (3 commercially available hand creams) to study the structure development of emulsions under shear stress.

The results prove an ability of the investigated emulsions to repair the damage caused by mechanical impacts over time.

The Rheonaut offers a new approach to rheology by providing molecular insight and can thus reveal information about molecular organization and dynamics under deformational flow.

The exact knowledge of the interacting fundamental structuring mechanisms creates the basis for an optimized tuning of technical, process engineering, and material parameters with respect to a functionally optimized structuring of emulsion systems.

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Presented at the 6<sup>th</sup> International Symposium on Food Rheology and Structure, April 10-13, 2012, Zurich, Switzerland

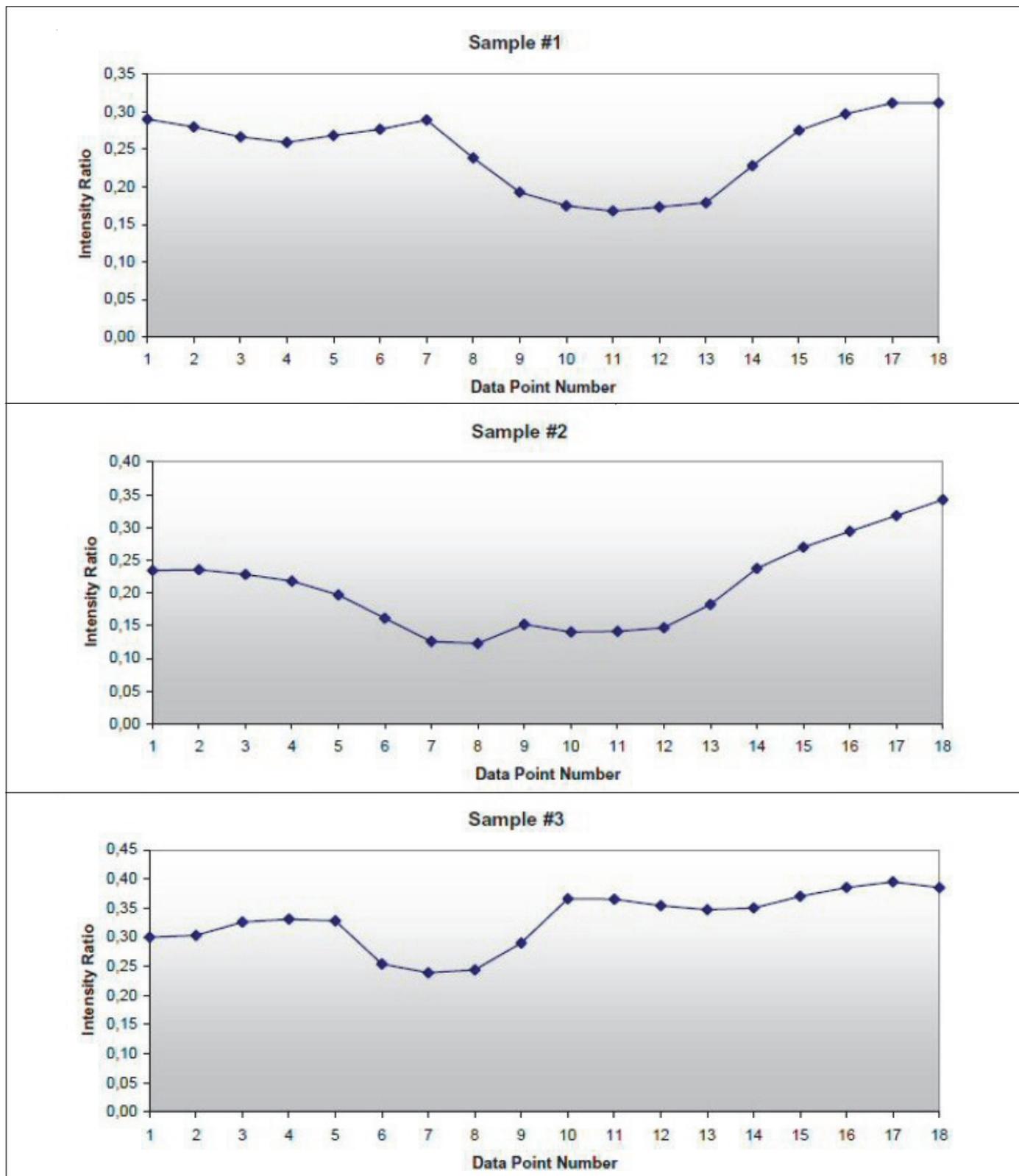


Figure 5: Absorption ratio ( $3354\text{ cm}^{-1}/2922\text{ cm}^{-1}$ ) from each FT-IR spectrum plotted against the data point number.

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# Rheology-Raman Spectroscopy: Tracking emulsion stability with the combination of a rheometer and Raman spectrometer

## Authors

Jan P. Plog<sup>1</sup> and Matthew Meyer<sup>2</sup>

<sup>1</sup>Thermo Fisher Scientific, Karlsruhe, Germany

<sup>2</sup>Thermo Fisher Scientific, Madison, USA

## Key words

Rheology, Raman spectroscopy, Emulsions, Shelf life, Combined methods

## Introduction

As the stress-strain response of complex fluids is closely linked to changes in physical or chemical structure within the material, rheology can be most useful when combined with simultaneous measurement of physical or chemical properties affecting flow.

Chemical information including molecular conformation, bond formation or scission, and chemical composition is also critically relevant to rheological measurements. Vibrational spectroscopic tools such as Raman spectroscopy have proven to be powerful noninvasive techniques to probe chemical information of interest in a variety of soft matter systems including emulsions [1].

The benefit of simultaneous measurements is clear: many soft materials are sensitive to temperature and flow history, so simultaneous measurements minimize experimental variation.



Figure 1: The Thermo Scientific HAAKE MARSxR RheoRaman System.



## Methods and Materials

In this application note, we present results obtained on a cosmetic emulsion in cooperation with NIST published previously [2].

The results shown can be obtained with the brand new combination of a Thermo Scientific™ HAAKE™ MARS™ Rheometer with a Thermo Scientific™ iXR Raman spectrometer (Thermo Scientific™ HAAKE MARSxR RheoRaman System) as shown in Figure 1.

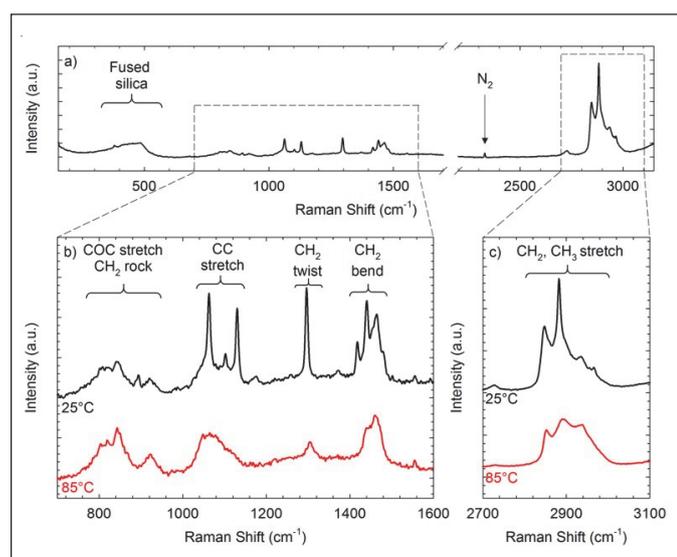
The experimental setup shown in Figure 1 represents a novel integration of commercial instrumentation: a Raman spectrometer (Thermo Scientific iXR Raman) and rotational rheometer (HAAKE MARS) are coupled through an optically transparent base modified from the Thermo Scientific™ RheoScope Module.

## Results and discussion

The cosmetic emulsion tested consists of oil droplets suspended in water and is stabilized by a mixture of surfactants. The Raman spectra of the emulsion over the spectral range at 25 °C is shown in Figure 2a. The broad peak in the range of 200 cm<sup>-1</sup> to 600 cm<sup>-1</sup> is attributed

to the fused silica window between the objective and the sample. Additionally, a small sharp band at  $2330\text{ cm}^{-1}$  is due to ambient nitrogen. A number of peaks are observed in the fingerprint region of  $650\text{ cm}^{-1}$  to  $1600\text{ cm}^{-1}$  and are magnified in Figure 2b. Although a complete chemical component analysis based on the measured spectra is outside the scope of this application note, the sharp peaks in the fingerprint region appear at positions attributed to the vibrational bonds of alkyl groups  $\text{C}_n\text{H}_{2n+1}$ : the C-C symmetric and asymmetric stretch peaks at  $1063\text{ cm}^{-1}$  and  $1130\text{ cm}^{-1}$  respectively, the  $\text{CH}_2$  twist mode at  $1296\text{ cm}^{-1}$ , and multiple modes associated with  $\text{CH}_2$  bending motion at  $1418\text{ cm}^{-1}$ ,  $1441\text{ cm}^{-1}$ , and  $1464\text{ cm}^{-1}$ .

These alkyl group modes are present due to the alkyl chains present on the stabilizers and fatty acids comprising the majority of the coconut and almond oils in the emulsion. The broad distribution of Raman bands in the range of  $750\text{ cm}^{-1}$  to  $950\text{ cm}^{-1}$  is common for C-O-C stretch modes expected for the polyethylene oxide groups present in polysorbate  $\text{CH}_2$  rocking modes for fatty acids and alcohols [3]. The presence of methyl  $\text{CH}_2$  groups is further evidenced by the presence of peaks in the  $2600\text{ cm}^{-1}$  to  $3000\text{ cm}^{-1}$  region (shown in greater detail in Figure 2c) attributed to  $\text{CH}_2$  and  $\text{CH}_3$  stretching modes.



**Figure 2:** (a) Raman spectra of the emulsion at room temperature over the instrument range. (b) Raman spectra of the emulsion in the range of  $(700\text{ to }1600)\text{ cm}^{-1}$  at temperatures indicated in the figure. (c) The same spectra collected in (b) in the  $(2700\text{ to }3100)\text{ cm}^{-1}$  region. Note that the intensity scaling varies from (b) to (c).

Upon heating, the sharp peaks due to the C-C stretch,  $\text{CH}_2$  twist, and  $\text{CH}_2$  bend modes decrease in intensity relative to broader peaks in the spectra as shown in Figure 2b. A similar loss of intensity of the sharp peak at  $2883\text{ cm}^{-1}$  in Figure 2c is evident at the higher temperature. The loss of intensity in these peaks corresponds to increasing conformational disorder along the alkyl chains present in the stabilizer, fatty acid, and fatty alcohol chains due to melting.

Quantitative measurement of alkyl chain measurement can be obtained by analysis of the peaks associated with the  $\text{CH}_2$  twisting modes [4]. Our analysis of the spectra in the

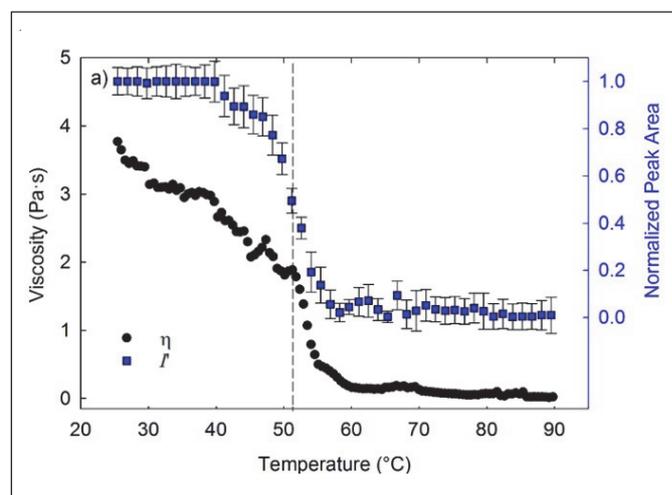
$\text{CH}_2$  twist region follows a similar protocol used to quantify *consecutive trans* and amorphous conformers in alkanes and polyethylenes [5]. The Raman spectra are fit using two Lorentzian peaks: a narrow peak of approximately  $2\text{ cm}^{-1}$  FWHM centered at  $1296\text{ cm}^{-1}$  and a broader peak of approximately  $13\text{ cm}^{-1}$  FWHM at  $1303\text{ cm}^{-1}$ . These fits are used to calculate the integrated area  $I$  of each peak. The total area under the curves in the  $\text{CH}_2$  twist region  $I_{1296} + I_{1303}$  is invariant with respect to chain disorder, which provides a method to normalize the spectra. The area of the peak at  $1296\text{ cm}^{-1}$  normalized by the total area

$$I' = \frac{I_{1296}}{I_{1296} + I_{1303}} \quad (1)$$

then quantifies the mass fraction of chains with more than four consecutive *trans* sequences along the chain. The value of  $I'$  quantifies the mass fraction of ordered chains.

Simultaneous Raman and viscosity measurements of the emulsion are shown in Figure 3 for the temperature ramp from  $25\text{ }^\circ\text{C}$  to  $90\text{ }^\circ\text{C}$  at a rate of  $1\text{ }^\circ\text{C}/\text{min}$ . The viscosity is measured at a steady shear rate of  $30\text{ s}^{-1}$  and a gap thickness of  $200\text{ }\mu\text{m}$ . Lower shear rates lead to shear localization in a thin fluid layer between the rotor and the droplet phase, which is confirmed via polarized optical imaging of immobile droplets in the bulk (however, this phenomenon is beyond the scope of this manuscript.) The viscosity decreases with increasing temperature until approximately  $50\text{ }^\circ\text{C}$ , at which point the viscosity sharply decreases.

The temperature range of  $45\text{ }^\circ\text{C}$  to  $55\text{ }^\circ\text{C}$  where viscosity and *consecutive trans* fraction exhibit a strong temperature dependence, correlates well with the melting temperatures of stabilizers in the emulsion including cetyl alcohol and stearylalkonium chloride. These simultaneous measurements allow for clear correlation of steady shear viscosity with conformational information.



**Figure 3:** Viscosity and normalized peak area  $I'$  as a function of temperature for the emulsion.

SummarySummarySummarySummarySummary  
With the Thermo Scientific HAAKE MARSxR RheoRaman System, simultaneous measurements of rheological properties and Raman-active molecular vibrations are possible. The emulsion example shown in this work, highlights the applicability of the MARSxR to characterize structural and conformational changes directly related to the rheological response of the material. Since all measurements are performed simultaneously, experimental conditions such as temperature and flow history are identical for Raman and rheology. In addition, the laser excitation and collection path can be equipped with optical elements for polarized Raman measurements. Based on the possibilities for direct correlation between chemical, structural, and mechanical properties, we expect the MARSxR to be critically relevant to both academic and industrial interests.

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