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Guide to skilled food rheology

Application compendium

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Rheology in the food industry

Welcome to the skilled guide on food rheology! Here you'll find a compendium of useful articles and application notes providing expertise on enhancing food properties via rheological measurements.

Foods can be structurally complex, incorporating emulsions and mixing solids, liquids and gels into a single product. The information in this compendium can help you better understand what to measure in your food development and processing workflows, and which tools are best to measure it.

Rheology involves the study of the mechanical properties of foods and how they flow or deform under different conditions – pouring, chewing, cold storage, over time, etc. Viscometers and rheometers measure viscosity, elasticity, yield stress, extensional flow, tack, and more to help ensure the final food product has ideal sensory perceptions when consumed.

Feel free to **contact us** if you have any questions or requests about food rheology.

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Food rheology

From production to consumption, rheological properties play an important role during the entire life cycle of liquid or semi-solid food formulations. Rheological measurements with different types of instruments are performed in the food 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 the research and development department

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 food production 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.

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. For simulating cooking processes, dedicated configurations with different pressure cells are available.

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. For simulating cooking processes, different pressure cells are available.

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
Available Food specific accessories					
Pressure cells			Yes	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 (juices, inks etc.)	Yes	Yes	iQ Air only	iQ Air only	Yes

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

**Rheo-DEA (dielectrical analysis, 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/us/en/home/global/forms/industrial/food-rheology-extrustion-contact-request.html.

Find more information how rheological measurement can support your QC and food formulation development in this food compendium and visit our food rheology homepage at www.thermofisher.com/foodrheology.

On-demand webinar

Handling food samples for reliable rheological results

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APPLICATION NOTE

Yield stress of jam, chocolate spread and peanut butter measured with HAAKE Viscotester iQ Rheometer and vane rotors

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Key words
Jam, chocolate spread, peanut butter, yield stress, vane rotor, automated QC evaluation and documentation

Abstract
A standard task in the Quality Control (QC) of typical food spreads – like jam, chocolate spread or peanut butter – is the determination of the yield stress in a container. For this purpose a vane rotor needs to be moved into the intact product structure in a perfectly vertical movement. Efficient and high-throughput QC measurements require a rheometer with an easy-to-operate lift function and a quickly adaptable universal container holder for different container designs as well as software routines for automated measurement, evaluation and QC documentation. An optionally available temperature sensor mounted parallel to the rotor allows to record the sample temperature.

The yield stress of a food product is a measure of important material characteristics such as stability, mouthfeel,

Figure 1: HAAKE Viscotester iQ Rheometer with mounted universal container holder and vane rotor FL26-2 blades (left); universal container holder with three vane rotors: 4-blade rotors FL16 and FL22 as well as FL26-2 blades (right).

pourability, spreadability and processability and is affected by the food ingredients and their formulation [1 - 3].

Introduction

In order to investigate the effect of particles and different formulations on the yield stress as well as to study the reproducibility of the method, three typical food spreads were tested.

An advantage of vane rotors is that they can be used for testing materials with larger particles. The size of the vane blades needs to be several times bigger than the maximum particle size (e.g. the seeds in a raspberry jam). From a rheological point of view, the solid particles act as passive filler (like glass beads) and therefore do not contribute to the elastic network caused by weak interaction of molecules or larger aggregates. Below the yield point, a sample is showing a linear response to an applied shear stress or deformation. Around the yield point, the applied stresses become large enough to alter the microstructure of the material and cause a non-linear viscoelastic response. Above its yield point, a material behaves like a liquid. The results obtained from yield stress determination strongly depend on the rheological method and experimental settings used [1 - 3].

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Chocolate spreads show differences in sugar, fat, cacao and protein content as well as the type of emulsifier. This may have a considerable effect on the yield stress. Two different commercially available chocolate spreads were selected for this investigation.

The yield stress of peanut butter is even higher than that of chocolate spread [4]. Therefore, creamy peanut butter was selected to check the reproducibility of the vane rotor measuring curves and yield stress evaluation.

Yield stress is by definition the minimum shear stress required to make a material flow. The yield stress is a measure for pourability, spreadability and spoonability and is also used to predict product stability [2 - 5]. The calculated yield stress values τ_0 depend on the one hand on the spread's ingredients and on the other hand on the rheological method and experimental parameters used for yield stress determination. Moreover, the pre-experimental sample handling plays an essential role and determines whether an intact or a disturbed structure is measured [2, 3, 5].

Regarding rheological measuring methods, the most accurate and recommended method to determine absolute yield stress values is the Controlled Stress (CS) ramp with plate/plate measuring geometry. This requires careful sample preparation, handling and loading in order to maintain the intact structure of the material [6]. Stirring or squeezing would lead from the static yield stress of the intact structure to the (lower) dynamic yield stress of a disturbed structure [1 - 3]. Loading a sample properly into a plate/plate, plate/cone (or concentric cylinder) measuring geometry with subsequent equilibration and CS ramp yield stress measurement takes about 10 (or 20) minutes.

For QC, this may be too time-consuming – therefore, relative vane rotor measurements with an intact sample structure in the original container are often preferred, since they can be conducted much faster and are related to the static yield stress [2, 3, 5]. The correct selection of the experimental parameters for vane rotor measurements is fundamental – this is discussed in more detail below and in [7]. In general, Controlled Rate (CR) mode with rotational speeds lower than 1 rpm is recommended [2].

Materials and methods

A Thermo Scientific™ HAAKE™ Viscotester™ iQ Rheometer equipped with a 4-blade vane rotor FL16 (vane diameter 16 mm, height 8.8 mm) or FL22 (vane diameter 22 mm, height 16 mm) and an universal container holder (Figure 1) was used for the yield stress determination in CR mode. In this investigation, the rotational speed was set to 0.05 rpm for all measurements.

Five commercially available food spreads were investigated with the same method using different vane sizes (see below). The sealed jar was opened and fixed in the universal container holder. Using the manual lift function of the HAAKE Viscotester iQ and the features of the Thermo Scientific™ HAAKE™ RheoWin™ Software (Figure 2), the vane rotor was prevented from rotating (element 1: CR mode $\dot{\gamma} = 0\ s^{-1}$) and lowered vertically into a well-reproducible position as well as penetration depth (according to the dimensions and shape of the container type; element 2).

Practical experience shows that stiffer products, which are filled into a container in a process line at higher speed, can show different material properties at different regions within the container. In such a case it is mandatory to make the vane measurement always in the same position in each particular container design in order to obtain comparable and reproducible results.

After a short equilibration and recovery time (element 3), the total time t was set to zero (element 4) right before the measurement was started. A low rotational speed (here: 0.05 rpm) was applied and a set number of data points was recorded within the set time (element 5). With an automated evaluation and QC element (element 6: curve discussion), the maximum in the shear stress τ vs. time t plot was automatically determined. The HAAKE RheoWin software provides the option to check, whether τ_0 is within (pass) or outside (fail) the given range [9]. Finally, a report was generated (element 7). It can either be saved in different file formats (e.g. in pdf, jpeg, tiff or emf format) or directly be sent to a printer.

For each sample class, the most suitable rotor type and rotational speed need to be determined in a preliminary test. Smaller vane rotors are used for samples with stronger texture and higher yield stress, like peanut butter, while larger vane rotors are more suitable for samples with lower viscosity and lower yield stress, like chocolate spread, jam or mayonnaise [7].

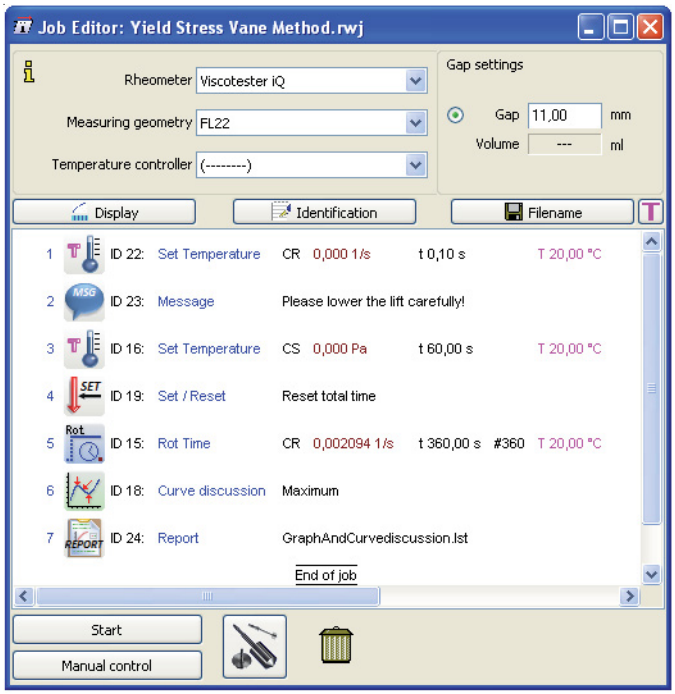

Figure 2: HAAKE RheoWin Software measuring job for measurement and automated evaluation and documentation.

In order to determine one rotational speed, which fits all samples of a class, different rotational speeds need to be tested. A too high rotational speed leads to a sharp peak which cannot be evaluated (red triangles in Figure 3). A too low rotational speed delivers an asymptotic curve with no maximum (green circles). The goal is to select a rotational

speed, which generates a curve with evaluable maximum (blue rectangles). The speed corresponding to the highest evaluable maximum is the best choice for this particular sample [7]. For this investigation, a rotational speed of 0.05 rpm turned out to be a suitable set value.

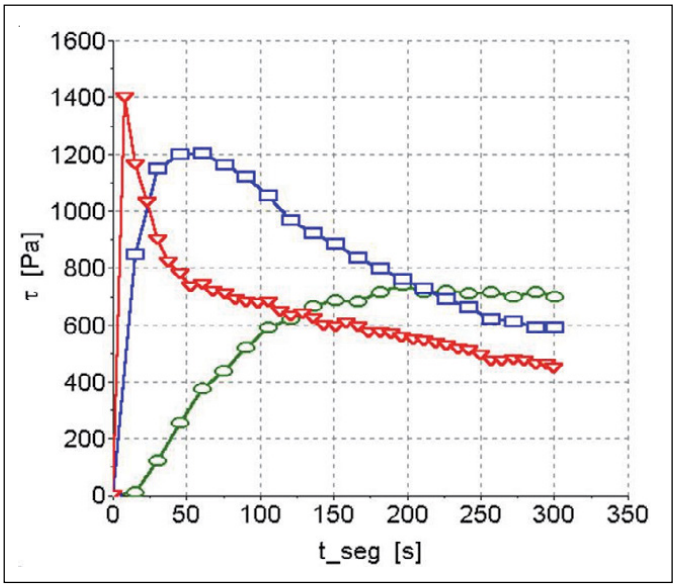

Figure 3: Schematic comparison of vane rotor yield stress measurements with higher (red triangles), medium (blue rectangles) and lower rotational speed (green circles).

Results and discussion

The effect of the composition on the yield stress was subject of several investigations in the past. Different behaviors were observed according to the nature and number of ingredients of the formulation used for the studies [1 - 3].

The rheological characteristics of jams depend strongly on fruit type and jam formulation [8]. Figure 4 shows the vane rotor yield stress measuring curves for two raspberry jams – one with seeds, the other sieved. As expected, the yield stress of the sieved jam is much higher than the yield stress of the jam with seeds, because the seeds behave like hard spheres and do not contribute to the stress bearing elastic structure. On the other hand, the time values for both jams are similar (Tab. 1).

As an example, the reproducibility of the measuring results was checked with the sieved jam – see last line in Table 1. Compared to the average value, the yield stress values differ only by ± 0.5% and the time value is identical.

After a 4-blade rotor has turned by 85° to 90°, no more intact sample can be sensed by the vane rotor. Therefore, the measuring curves exhibited a little decrease at around 300 s.

Table 1: Comparison of FL 22 vane rotor yield stress measurements with 0.05 rpm for a sieved raspberry jam and one with seeds.

Rasberry jam	τ_0 in Pa	t in s
With seeds	590	100
Sieved	967	104
Sieved (measurement 2)	977	104

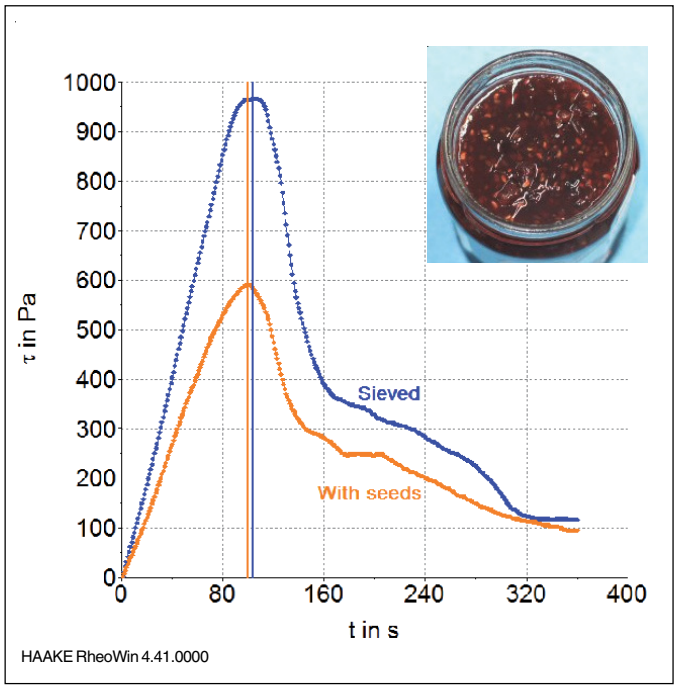

Figure 4: Comparison of FL 22 vane rotor yield stress measurements with 0.05 rpm for a sieved raspberry jam (blue curve) and raspberry jam with seeds (orange curve, inserted image).

Figure 5 and Table 2 show the results of the yield stress measurements for the tested chocolate spread products A and B. Product A contains more cacao, more protein (7%) and more sugar (56%) than product B (6% protein; 50% sugar). On the other hand, the fat content of product A (32%) is lower than in product B (35%). Furthermore, different emulsifiers were used – from soya (A) or sunflower (B). The yield stress value of product B is more than twice as high as of product A.

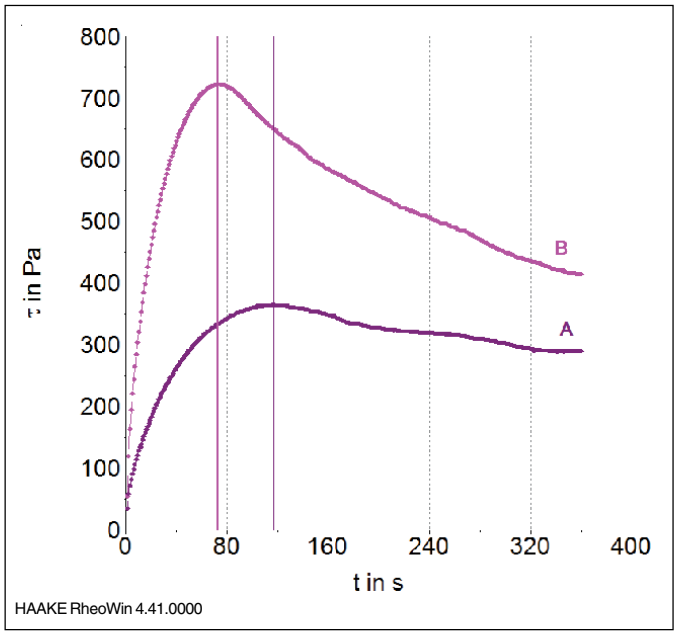

Figure 5: CFL 22 vane rotor yield stress measurements with 0.05 rpm for chocolate hazelnut spread products A and B.

Table 2: Comparison of FL 22 vane rotor yield stress measurements with 0.05 rpm for chocolate hazelnut spread products.

Chocolate spread	τ_0 in Pa	t in s
A	364	117
B	722	73

The reproducibility of CR vane rotor yield stress determination was tested with creamy peanut butter. Three independently conducted measurements with a FL16 rotor in CR mode with 0.05 rpm show excellent correlation – see Fiure 6 and Table 3. Compared to the average value, the yield stress values differ by less than ± 1.5 % and the time values are nearly identical.

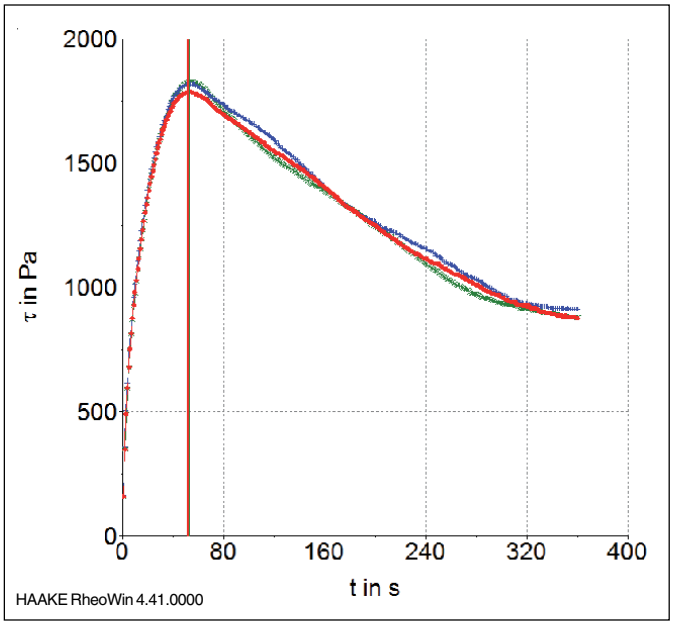

Figure 6: Three independently conducted vane rotor (FL16) yield stress measurements in CR mode with 0.05 rpm for creamy peanut butter.

Table 3: Three independently conducted vane rotor (FL16) yield stress measurements in CR mode with 0.05 rpm for creamy peanut butter.

Peanut butter	τ_0 in Pa	t in s
Measurement1 (blue)	1818	52.1
Measurement2 (red)	1785	52.1
Measurement3 (green)	1829	53.2

Conclusions

The HAAKE Viscotester iQ Rheometer equipped with the universal container holder and a vane rotor allows efficient, high-throughput measuring routines for spread QC testing, using samples in their original containers with intact sample structure.

The instrument's smart lift function ensures convenient and fast handling. In combination with the easy-to-adjust universal container holder, it allows for a very well-controlled and perfectly vertical placement of the vane rotor in a reproducible position in the particular container type – a key to reproducible results.

The HAAKE Viscotester iQ Rheometer can be operated either as a standalone unit with pre-defined or customized measurement and evaluation routines or, even more powerful, with the HAAKE RheoWin measurement and evaluation software. Its evaluation elements offer (as a standard feature) fully automated QC routines including pass/fail evaluation and documentation [9]. With all three types of spread, the maximum in the shear stress vs. time curve could be evaluated automatically.

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APPLICATION NOTE

Investigation the effect of fat content on the yield stress of mayonnaise measured with HAAKE Viscotester iQ Rheometer and vane rotor

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Key words

Rheology, mayonnaise, yield stress, vane rotor, automated QC evaluation and documentation

Abstract

In the Quality Control (QC) of mayonnaise, one of the standard tasks is to determine the yield stress in the original container using a vane rotor, which needs to be moved into the intact product structure in a perfectly vertical movement. Efficient and high-throughput QC measurements require a viscometer with an easy-to-operate lift function as well as an easy-to-adapt universal container holder for different container designs as well as software routines for automated measurement, eva-luation and QC documentation. An optionally available temperature sensor mounted parallel to the rotor allows for recording of the sample temperature.

The yield stress in food corresponds with important material characteristics as stability, mouth feeling and

Figure 1: HAAKE Viscotester iQ Rheometer with mounted universal container holder and vane rotor FL26-2 blades (left); universal container holder with three vane rotors: 4-blade rotors FL16 and FL22 as well as FL26-2 blades (right).

processability and is affected by the ingredients and their formulation – particularly the fat content [1 - 4].

Introduction

Mayonnaise is a semi-solid oil-in-water emulsion consisting basically of an oil and an acidic water phase plus emulsifier. Formulations differ widely in composition, texture and flavor. Conventional full-fat mayonnaise has an oil (i.e. fat) content of up to 80 %. Lowest-fat or no-fat mayonnaise, on the other end, is not even an emulsion in the classical sense. As soon as the fat content is reduced, it is necessary to adjust the formulation and to add further ingredients in order to obtain a texture, which will be well accepted by consumers [1 - 4].

Home-made mayonnaise usually consists of vegetable oil, egg yolk, vinegar and/or lemon juice and flavoring ingredients like pepper, salt, mustard and maybe sugar. Industrial mayonnaise products may also contain modified starch and thickeners like carob bean gum or guar gum and colorants (e.g. beta-carotene) as well as additional flavors. Fat-reduced and light mayonnaise products may require a higher content of water and the addition of fat-reduced yoghurt or other milk products, other thickeners (e.g. xanthan gum) as well as artificial sweeteners. More-over, fiber-rich ingredients like pectin can be used for fat replacement and for texturing [1].

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Yield stress is by definition the minimum shear stress required to make a material flow. The yield stress is a measure for pourability, spreadability and spoonability and is used to predict the product stability [1 - 5, 8 - 10]. The calculated yield stress values τ_0 of mayonnaise can range from about 20 Pa (pourable) to about 300 Pa (spoonable), depending on the particular formulation as well as on the method used for yield stress determina-tion and the pre-experimental sample handling [1 - 11].

As far as the composition is concerned, the yield stress strongly depends on the fat content.

Regarding rheological measuring methods, the most accurate and recommended method to determine absolute yield stress values is the Controlled Stress (CS) ramp with plate/plate measuring geometry, which requires careful sample preparation, handling and loading to maintain the intact structure [7].

Sample stirring or squeezing would lead from the static yield stress of the intact structure to the (lower) dynamic yield stress of a disturbed structure [9 - 10]. Loading a sample into a plate/plate, plate/cone or concentric cylinder measuring geometry with subsequent equilibration and CS ramp yield stress measurement takes about 10 to 20 minutes per sample.

For QC, this may be too time-consuming – therefore, relative vane rotor measurements with an intact sample structure in the original container are often preferred, since they can be conducted much faster and are related to the static yield stress [8 - 10]. The correct selection of the experimental parameters for vane rotor measurements is fundamental – this will be discussed in more detail below. In general, Controlled Rate (CR) mode with rotational speeds lower than 1 rpm is recommended [9].

Materials and methods

A Thermo Scientific™ HAAKE™ Viscotester™ iQ Rheometer equipped with a 4-blade vane rotor FL22 (vane diameter 22 mm, height 16 mm) and an universal container holder (Figure 1) was used for the yield stress determination in CR mode. Three industrial mayonnaise products from the same manufacturer with different fat content levels were investigated (Table 1). A sealed glass container was opened and fixed in the easy-to-adjust universal container holder. Using the manual lift function of the HAAKE Viscotester iQ Rheometer and the features of the Thermo Scientific™ HAAKE™ RheoWin™ Software (Figure 2), the vane rotor was kept from rotating (element 1: CR mode $\dot{\gamma} = 0\ s^{-1}$) and lowered vertically into a well-reproducible position as well as penetration depth (according to the dimensions and shape of the container type).

Products, which are filling into a container with considerable speed in a filled plant, often show slightly different material properties when comparing sample-taking from the bottom center area, top center area or close to the container wall. In such a case it is mandatory to make the vane measurement always in the same position (in each particular container type) in order to obtain comparable and reproducible results.

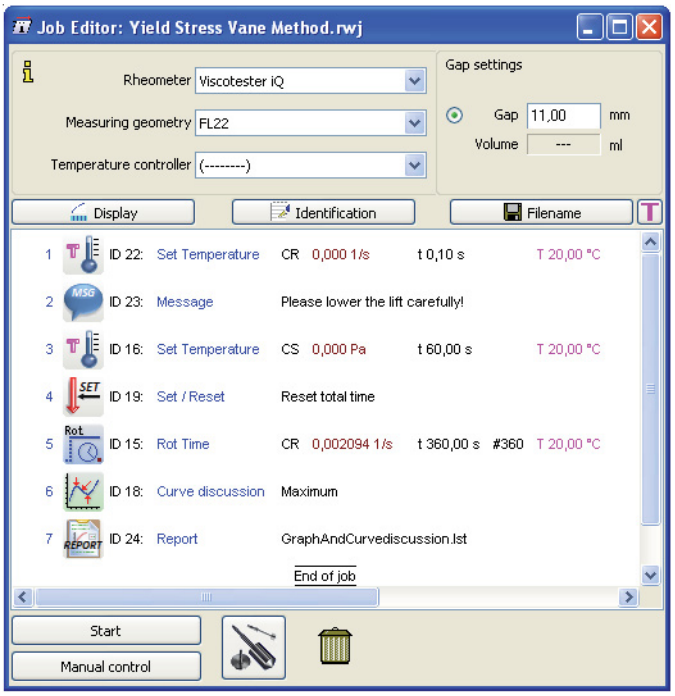

Figure 2: HAAKE RheoWin Software measuring job for measurement and automated evaluation and documentation.

After a short equilibration and recovery time (element 3), the total time t was set to zero (element 4) right before the measurement was started. A low rotational speed was applied and a set number of data points were recorded within the set time (element 5). With an automated evaluation and QC element (element 6: curve discussion), the maximum in the shear stress τ vs. time t plot was automatically evaluated and checked whether whether τ_0 is within the given range (pass) or outside (fail). Finally a report was generated (element 7), which can be either saved as a file (e.g. in pdf, jpeg, or tiff format) or can be directly printed out.

For each sample class, the most suitable rotor type and rotational speed need to be determined in a preliminary test. Smaller vane rotors are used for samples with stronger texture and higher yield stress, like peanut butter [5, 6], while larger vane rotors are more suitable for samples with lower viscosity and lower yield stress [8 - 10].

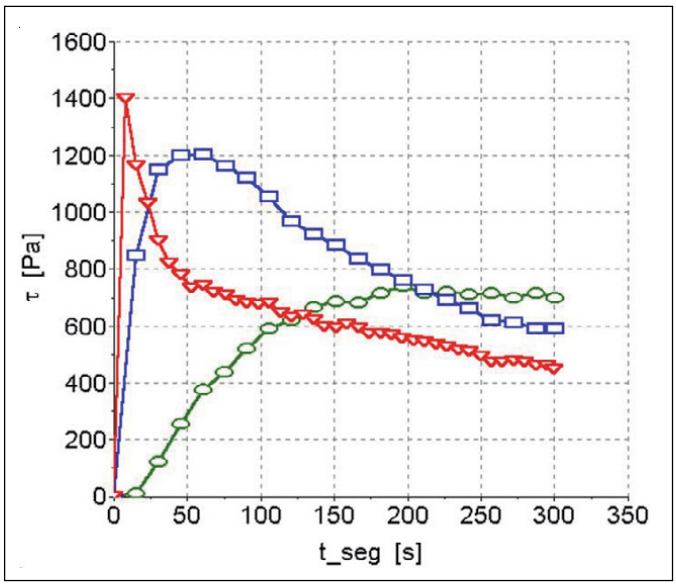

Figure 3: Schematic comparison of vane rotor yield stress measurements with higher (red triangles), medium (blue rectangles) and lower rotational speed (green circles).

In order to determine one rotational speed, which fits all samples of a class, different rotational speeds need to be tested (Figure 3). A too high rotational speed leads to a sharp peak which cannot be evaluated (red triangles). A rotational speed too low delivers an asymptotic curve with no maximum (green circles). The goal is to select a rotational speed, which generates a curve with evaluable maximum (blue rectangles). The speed corresponding to the highest evaluable maximum is the best choice for this particular sample.

Results and discussion

The effect of the composition on the yield stress has been subject of different investigations in the past. Different behaviors have been observed according to the nature and number of ingredients of the formulation used for the studies [1 - 4].

Among the three tested mayonnaise samples, the highest fat content (22.5 %) product was most critical with regard to obtaining an evaluable maximum in the measuring curve. Therefore the preliminary test described above was run with different rotational speeds. Suitable settings were 0.02 rpm and 0.05 rpm, which delivered comparable yield stress results (95 Pa and 96 Pa) – see Figure 4 and Table 1. With these both rotational speeds all sample were measured (Figures. 5, 6 and Table 1).

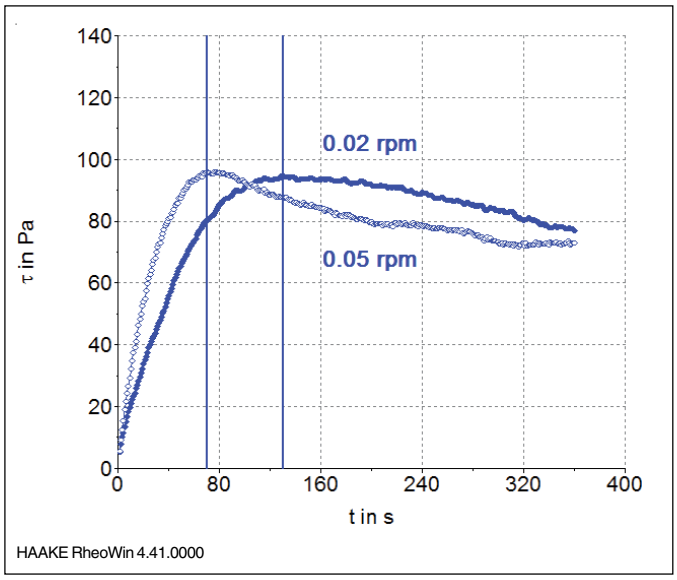

Figure 4: Comparison of vane rotor yield stress measurements with 0.05 rpm (open circles) and 0.02 rpm (filled circles) with the mayonnaise with 22.5 % fat content.

After a 4-blade rotor has turned by 85° to 90°, no intact sample can be sensed by the vane rotor anymore. Therefore, the measuring curves recorded with 0.05 rpm exhibited a little decrease at around 300 s (Figures 4 - 6).

Figure 5 and Table 1 show the results of the yield stress measurements for the tested three commercial mayonnaises at 0.05 rpm. All shear stress curves clearly exhibit a maximum. It can be seen that the product containing the lowest fat content (5.2 %) correlates with the highest yield stress (127 Pa). On the opposite, the sample containing the highest amount of fat (22.5 %) presents the lowest yield stress (96 Pa).

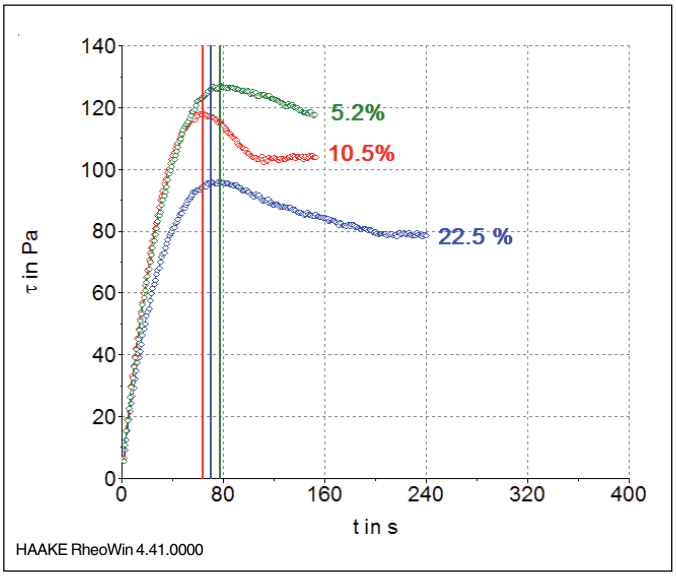

Figure 5: Vane rotor yield stress measurements with 0.05 rpm for mayonnaises with three different fat contents.

The rheological data collected at 0.02 rpm (Figure 6) confirm the trend observed in the measurements carried out at 0.05 rpm. As expected, with the lower rotational speed each maximum in the stress curve appears at a later time and the measurement takes longer. The evaluated yield stress data for 10.5 % and 5.2 % fat content are higher at 0.02 rpm than at 0.05 rpm. Therefore, for the QC yield stress testing of these three samples, 0.02 rpm is the recommended rotational speed.

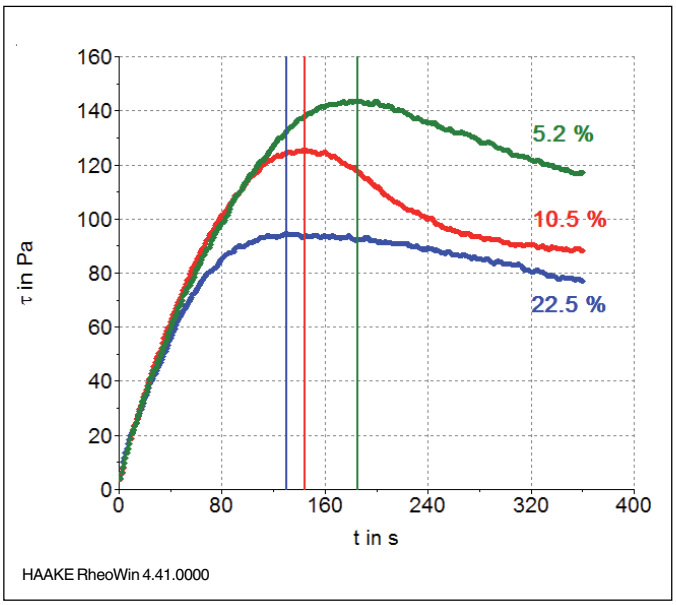

Figure 6: Vane rotor yield stress measurements with 0.02 rpm for mayonnaises with three different fat contents.

Table 1 lists the yield stress values which were calculated automatically by the HAAKE RheoWin Software for both rotational speeds. For the formulation with the highest fat content the values are very close to each other, being 95 Pa and 96 Pa at 0.02 rpm and 0.05 rpm, respectively. As the fat content decreases, the difference between the two values becomes more significant. This clearly indicates how the set parameters can affect the results of the rheological measurements in a vane rotor measurement.

Table 1: Yield stress results determined with two rotational speeds for mayonnaises with three different fat contents.

Fat content in %	τ_0 in Pa at 0.02 rpm	τ_0 in Pa at 0.05 rpm
22.5	95	96
10.5	126	118
5.2	144	127

Conclusions

The HAAKE Viscotester iQ rheometer equipped with the universal container holder and a vane rotor allows efficient, high-throughput measuring routines for mayonnaise QC testing, using samples in their original containers with intact sample structure.

The instrument's smart lift function ensures convenient and fast handling. In combination with the easy-to-adjust universal container holder, it allows for a very well-controlled and perfectly vertical placement of the vane rotor in a reproducible position in the particular container type – a key to reproducible results.

Operation of the HAAKE Viscotester iQ rheometer can be done either as a standalone unit with pre-defined or customized measurement and evaluation routines or, even more powerful, with the HAAKE RheoWin measurement and evaluation software, which even offers (as a standard feature) fully automated QC routines including pass/fail evaluation and documentation [11].

The maximum in the shear stress vs. time curve can be easily evaluated automatically and depends significantly on the fat content of the mayonnaise samples.

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APPLICATION NOTE

No. V-269

Flow behaviour of chocolate melts-working according to ICA standards

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Key words
Chocolate, QC, ICA standards, viscosity, yield stress

Introduction

The flow behaviour of molten chocolate is a crucial parameter for many reasons. During production the transport, filling, dipping, coating or dosing steps depend on a well defined viscosity and yield stress. Likewise, the properties of the final chocolate like the look of it surface or its mouth feeling are directly related to the chocolate's viscous behaviour.

Testing the viscosity is therefore one of the standard quality control (QC) test methods for any company producing chocolate or using chocolate for their own production of e.g., chocolate-coated cookies.

To make viscosity testing in QC easier and more reliable, the Thermo Scientific™ HAAKE™ Viscotester™ iQ Rheometer (Figure 1) has been developed. This viscometer includes features especially designed for QC applications. For example, due to its improved sensitivity it is possible to use smaller measuring geometries, which reduces sample volume, time

Figure 1: The HAAKE Viscotester iQ Rheometer.

for temperature equilibration and cleaning effort. Also, with improved sensitivity smaller shear rates are accessible, which improves the reliability of yield stress calculations [1] with extrapolation methods like the Casson model.

Preparations

Two chocolate samples, a milk chocolate and a dark chocolate, have been prepared according to ICA method 46 [2] by putting chocolate pieces into glass containers, sealing the containers and leaving them in an oven at 52 °C for between 45 and 60 minutes. Meanwhile the cup and bob of the measuring geometry are preheated to 40 °C the HAAKE Viscotester iQ Rheometer in the Peltier temperature control unit.

The HAAKE RheoWin Software job

For the tests done for this report, the CC25 DIN Ti measuring geometry has been selected. This small cylindrical system with only 16.1 ml sample volume fits into the Peltier cylinder temperature control and is easy to disassemble and clean.

The test method itself has been taken from ICA method 46 and has been translated into a Thermo Scientific™ HAAKE™ RheoWin™ Software job. The shear rate profile is shown in Figure 2.

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The HAAKE RheoWin Software job (Figure 3) consists of three parts: Sample conditioning, testing and evaluation. 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. This improves the reproducibility of the results. During the conditioning part (job element 1-4) the sample is kept at rest with the cylindrical upper part of the measuring geometry already in measuring position. During this time any mechanical stress caused by sample loading and closing the geometry should relax completely while at the same time, the whole sample should reach the temperature, the test is going to be performed at.

In the final part (job element 11-13), the data evaluation is performed automatically by HAAKE RheoWin Software. To calculate the yield stress of a chocolate melt, the traditional Casson model and the modern Windhab model [3] can be selected from a long list of fit models. In a more simple approach Servais [4] suggested to use the shear stress value at 5 s^{-1} as the yield stress. If this method is preferred, a simple interpolation calculation in HAAKE RheoWin Software will do the job.

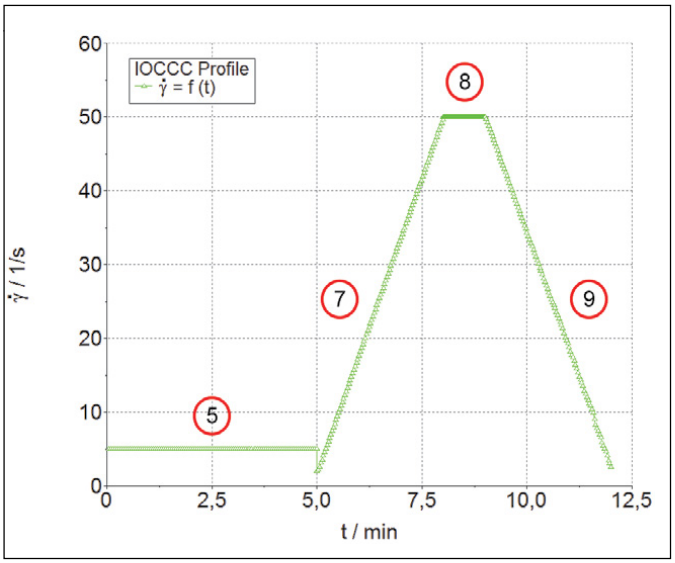

Figure 2: Shear rate profile applied according to ICA method 46. The numbers 5 to 9 represent the job element number of the HAAKE RheoWin Software job shown in Figure 3.

In addition a steady-state viscosity curve at 40 °C has been recorded for both samples. 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 directly correlated with the shear rate applied.

The results

A typical representation of the results from a test according to ICA method 46 is shown in Figure 4. The red curves depict the viscosity and the blue curves the shear stress. It clearly shows that the milk chocolate has the higher viscosity by a factor of two or more.

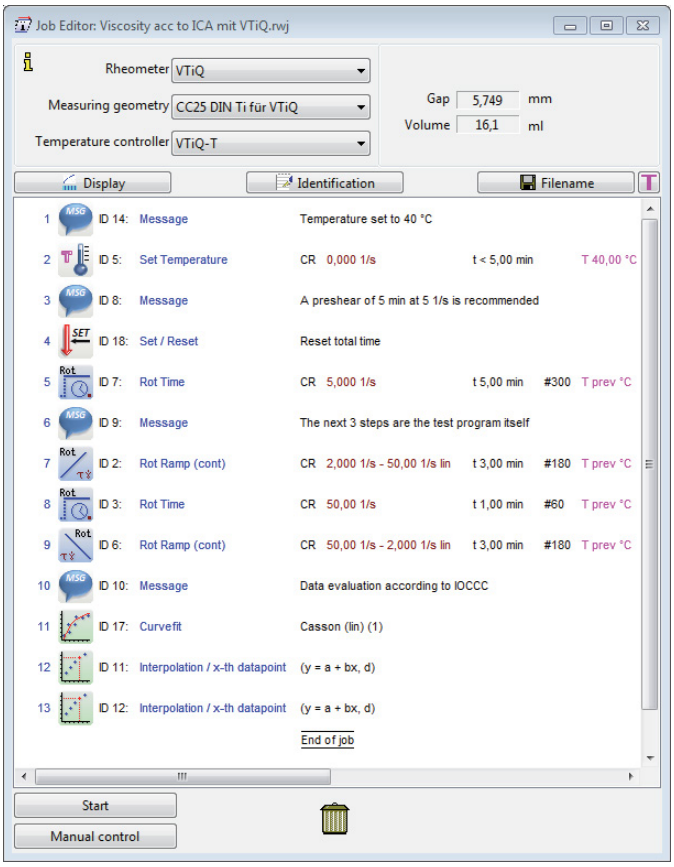

Figure 3: The HAAKE RheoWin Software job composed to run the test according to ICA method 46. The test consists of sample conditioning (elements 1-4), the rheological test (elements 5-9) and data evaluation (elements 10-13).

The viscosity curves for the increasing shear rate ramp and the decreasing shear rate ramp are almost identical for the dark chocolate. In contrast, the milk chocolate shows a pronounced thixotropic behaviour with significant differences between the two viscosity curves.

The green parabolic curves extrapolating the flow curves to a shear rate of 0 s^{-1} represent the Casson fit. The vertical green lines indicate where the interpolation according to Servais has been calculated. The results of the different methods to determine the yield stress of the two chocolate melts have been summarized in Table 1.

Table 1: Determination of yield stress based on the data from Figure 4 using different models.

	Milk Chocolate	Dark Chocolate
τ_0 Casson/Pa	8.9	2.1
τ_0 Windhab/Pa	14.7	4.0
τ_0 Servais et al./Pa	30.0	10.4

The first and probably most important result from Table 1 is the insight that even from the same data, different models give different results. Therefore, only yield stress values calculate with the same mathematical model can be compared.

Independent of the model chosen, the milk chocolate in this example shows the higher yield stress, the higher viscosity and the stronger thixotropy.

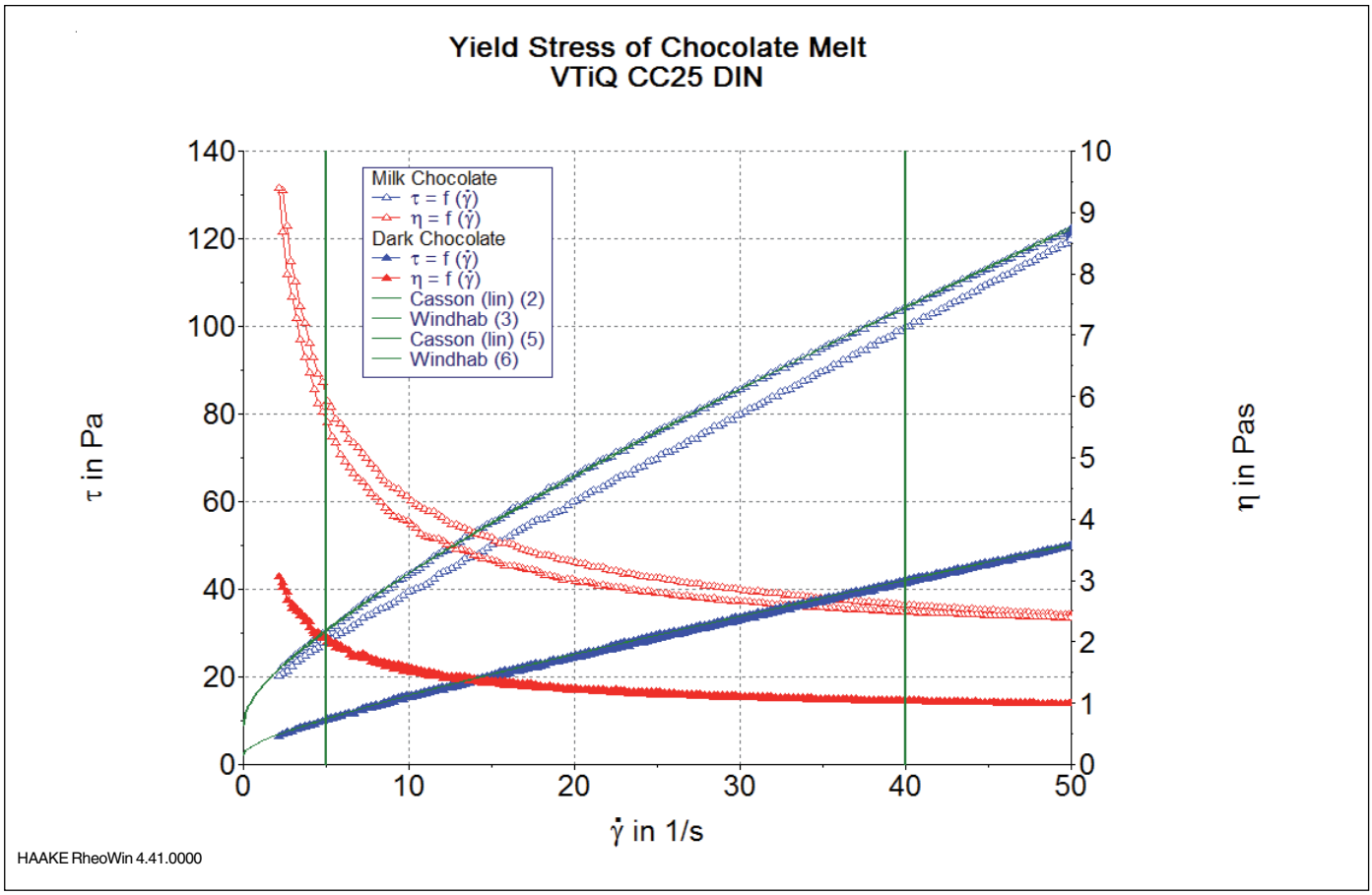

Figure 4: Test results for a milk chocolate (open symbols) and a dark chocolate (filled symbols). The milk chocolate shows the higher viscosity values (red curves), stronger thixotropy and a higher yield stress. The extrapolation of the flow curves (blue curves) to 0 s^{-1} has been calculated according to Casson. The green vertical line at 5 s^{-1} represents the yield stress according to Servais.

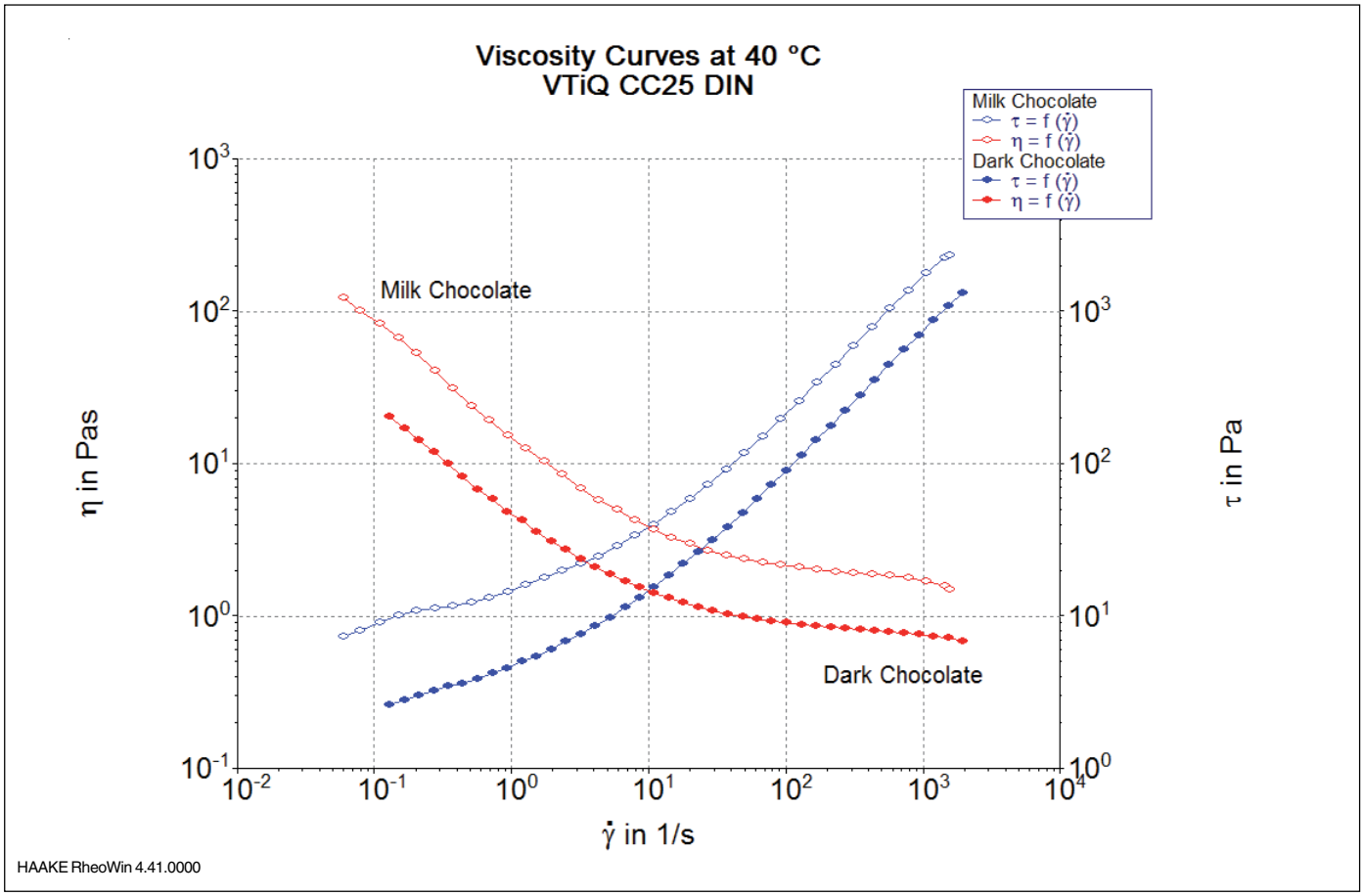

Figure 5: Viscosity curves of milk chocolate and dark chocolate at 40 °C. The milk chocolate shows a significantly higher viscosity.

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Summary

In QC the rheological characterization of chocolate focuses mainly on its viscosity and yield stress. The HAAKE Viscotester iQ Rheometer is a compact instrument with the right combination of sensitivity and strength to successfully test chocolate melts over a wide range of shear rates.

The commonly accepted test method according to ICA method 46 can easily be performed using only a small sample. The same is true for steady-state viscosity curves. 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.

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APPLICATION NOTE

Rheological and textural properties of various food formulations analyzed with a modular rheometer setup

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Key words
Rheology, food, viscosity, yield stress, texture analysis, tribology

Introduction

Since foodstuff comes in such a vast variety of structures and textures, the range of rheological methods used to characterize its mechanical properties is even wider.

Rheological and texture properties play an important role during the entire life cycle of liquid or solid food formulations. Starting with simple single point viscosity measurements in the original containers for batch release in production, over the determination of classical rheological parameters like shear viscosity or yield point for quality control purposes, the mechanical testing of foods reaches a certain level of complexity with comprehensive rheological investigations for the development of new formulations in the research and development department.

Figure 1: HAAKE MARS iQ Rheometer with Peltier plate temperature control for use with parallel-plate and cone-and-plate geometries.

While some methods rely on classic rheometer geometries like parallel plates, cone & plate or coaxial cylinders, some other methods try to emulate a certain application by utilizing special rotors and/or measuring fixtures. One such application is studying the texture of food products, which has to match the consumer's expectations. With specially designed probes a rotational rheometer can test various important food properties such as softness, stickiness or spreadability, and can even be utilized for performing tribological tests.

In this application selected rheometer accessories and physical measurements of various food products will be reviewed using a modular rheometer designed for product development and quality control purposes. This includes measuring "classic" rheological properties such as viscosity and yield stress, as well as customized setups for a comprehensive mechanical investigation of food formulations.

Materials and methods

Different commercially available food products were examined using the Thermo Scientific™ HAAKE™ MARS™ iQ Rheometer with a mechanical bearing (Figure 1). The tests to be performed included viscosity and yield stress measurements, axial bending, breaking and squeezing tests as

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well as tribological measurements. Shear rate-dependent viscosity was determined by steady-state shear-rate step tests in a range from 0.1 to 100 s-1. Yield stresses were determined by shear stress ramp tests. Different evaluation methods were used to determine distinct values for the yield stress. All viscosity and yield stress tests were performed with a 60 mm parallel plate geometry. In order to avoid sample slippage during the measurement, parallel plates with a serrated (crosshatched) surface profile were used. For the investigation of the tribological profile of different food products, friction coefficients were measured as a function of the circumferential velocity (sliding speed) in a range from 0.001 to 1000 mm/s. The tribological measuring fixture used was based on the ball-on-3-plates principle (Figure 2). Both, the ball as well as the three plates were made of hardened stainless steel. A detailed description about this setup can be found in the corresponding product report [1]. Bending and breaking tests were performed using a 3-point bending tool as shown in Figure 3. With this setup axial ramp tests at a defined set value for the lift speed were performed. The resulting normal forces were recorded and analyzed. Axial squeeze tests were performed with a 35 mm diameter parallel plate setup.

Fig. 2: Tribology setup for HAAKE MARS iQ Rheometer based on the ball-on3-plates principle.

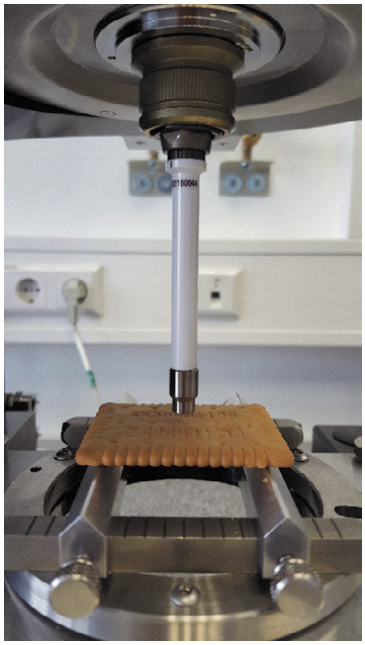

Fig. 3: 3-point-bending-tool for performing bending and breaking tests with the HAAKE MARS iQ Rheometer with 8 mm plate rotor.

Results and discussion

Viscosity and yield stress measurements

Liquid and semi-solid food formulations are exposed to a wide range of shear conditions during their entire life-cycle. During storage for instance, when only gravitational forces are present, very low shear rates are applied. During production (mixing, pumping or stirring) and consumption (oral processing) medium-to-high shear rates are observed. Thus, when performing only single point viscosity measurements at one rotational speed, an incomplete picture of the viscous properties is obtained that does not reflect the true nature of the tested material. Only a complete flow curve over a wide shear rate range provides the information required to estimate how a specific food product will behave under different shear conditions. Figure 4 shows the results of steady- state shear rate step tests of three commercially available mayonnaise products.

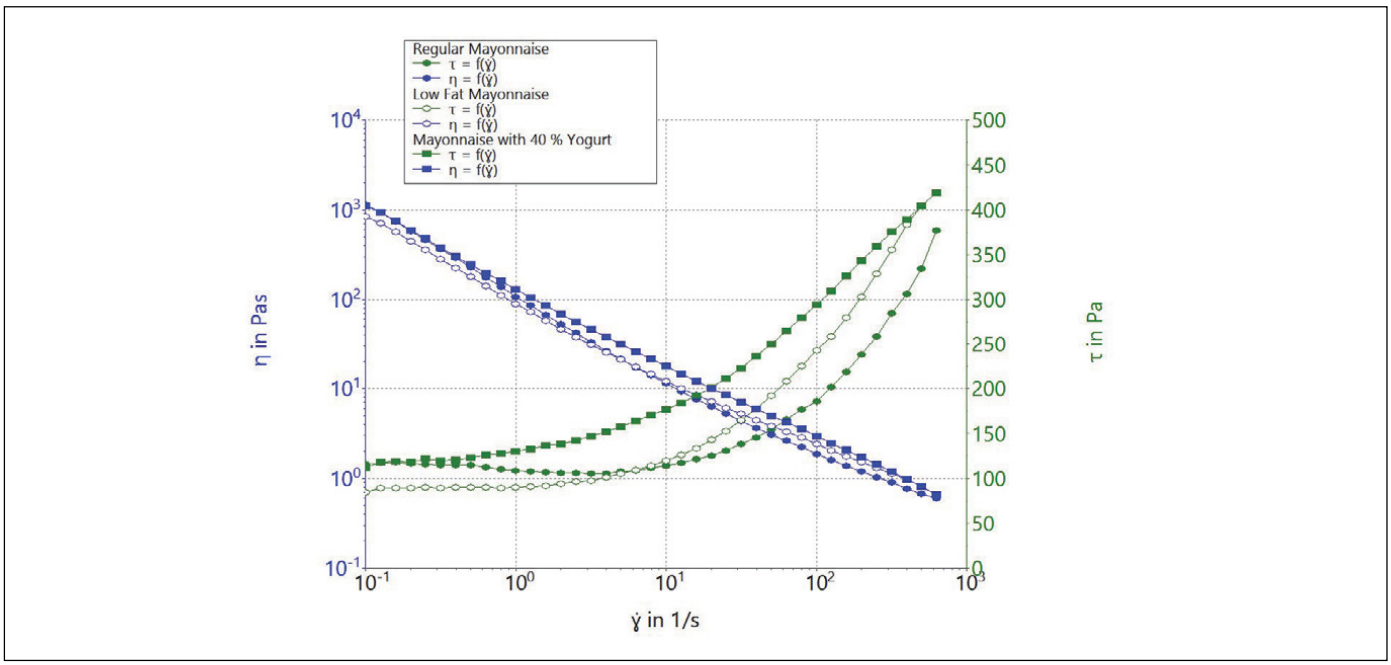

Fig. 4: Steady-state-viscosity η (blues symbols) and shear stress τ (green symbols) as a function of shear rate $\dot{\gamma}$ for three different mayonnaise products.

As expected for emulsion-based food products, all mayonnaises exhibited significant shear thinning behavior in the investigated shear rate range. Starting at a viscosity of around 1000 Pas at 0.1 s^{-1} all three samples drop to values below 1 Pas at around 800 s^{-1}. At shear rates higher than 800 s^{-1} sample was ejected out of the geometry leading to a dramatic drop in viscosity as well as in shear stress. That faulty data was removed in Figure 4. Exhibiting such a shear thinning profile is a desired behavior for many semi-solid food products. A high viscosity at low shear rates prevents phase separation of multi component foods and contributes to the overall stability of a product. However, too high of a viscosity at higher shear rates is, in general, less desired. Since it has disadvantages for the application (spreadability, spoonability) and consumption (chewing, swallowing).

Figure 4 also shows that a steady behavior of the shear stress signal at low shear was present for all samples, indicating a yielding behavior. For the regular mayonnaise and the version that contains yogurt, the plateau was occurring almost at identical shear stress values of 120 Pa. The low fat version yielded at a lower shear stress of 90 Pa. Yield stresses are considered an important parameter in research as well as in quality control to describe the 'flow' behavior of many structured fluids and semi-solids. A yield stress can improve the stability of dispersed systems by preventing sedimentation or as an example simply keeping a ketchup from sinking in too much into French fries instead of forming a nice thick layer on top of the fries. Furthermore, yield stresses are connected to certain food properties that are deemed important during oral consumption such as initial firmness [2].

However, the measured value of a yield stress is strongly dependent on sample handling, the chosen rheological measuring method, the data evaluation and even the measuring geometry selected for testing. A common way to investigate the yielding behavior of a sample very precisely is to perform a shear stress ramp test where a linearly increasing shear stress is applied and the deformation or the viscosity is monitored. The results of stress ramp experiments performed with the same mayonnaise samples used for the steady-state shear tests are shown in Figure 5.

The deformation stress curves shown in Figure 5 exhibit three distinct regions. In the first region (at low stresses below the yield stress threshold) the samples underwent an elastic deformation. Here the slope of the deformation stress curve is not much larger than 1 in the double logarithmic plot. As the stress increased and approached the yield stress value of the sample, the deformation started to change more rapidly and the slope increased. At higher shear stresses a second linear region with a significantly higher slope was observed. In this region steady flow occurred and the microstructure was altered by these higher shear forces. A common way to calculate the yield stress out of a deformation curve is to apply tangents to the two linear regions. The yield stress then corresponds to the stress value at the intersection of the tangents. In Figure 5 this method was used to determine the yield stress of the regular mayonnaise sample (black lines). The corresponding yield stress value was at 82 Pa. The tangent method provides a yield stress that is located more in the middle of a transition range between elastic deformation and steady flow. An alternative way to determine the yield stress from a shear stress ramp test is to use the maximum in viscosity as a measure. This method was also applied and is also shown in Figure 5 (red line). The corresponding yield stress value was at 45 Pa and clearly lower than the value derived from the tangents method. It can be seen in Figure 5 that the maximum in viscosity occurred more at the beginning of the transition and deformation just left the region of almost pure elastic deformation behavior.

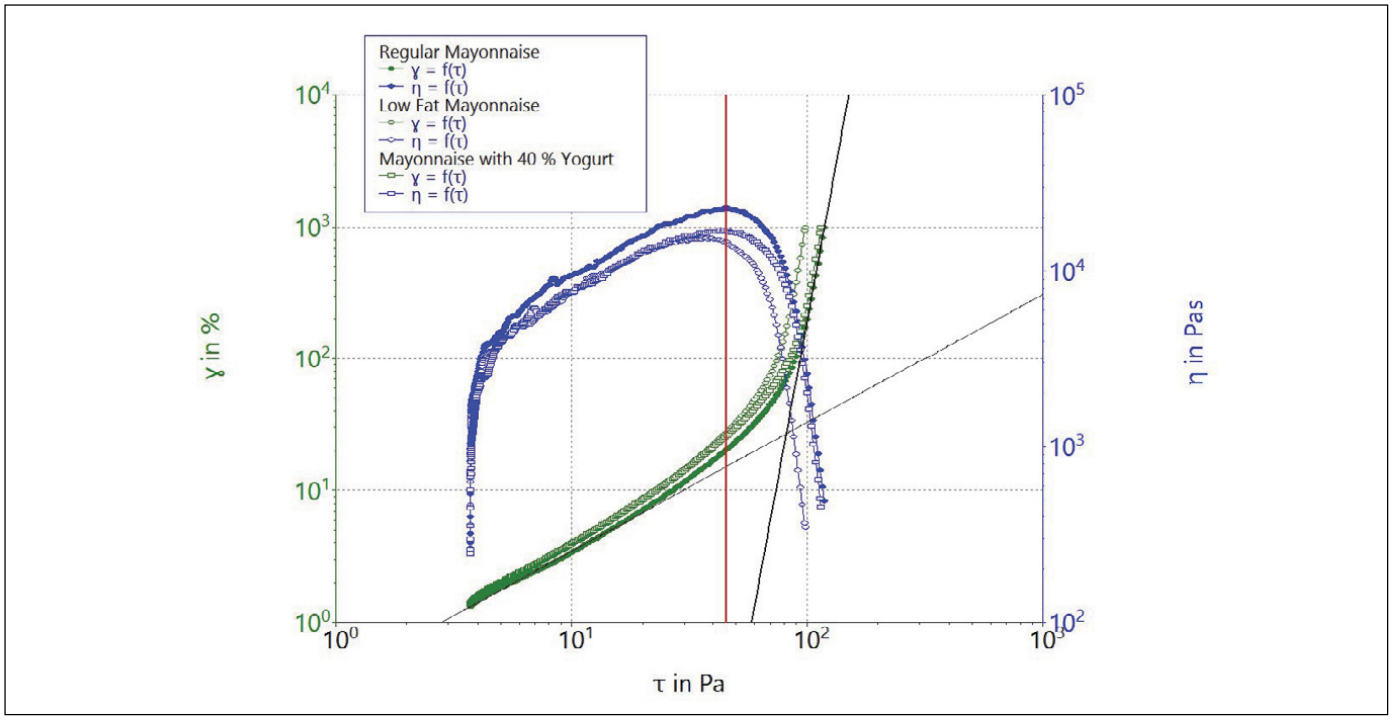

Fig. 5: Deformation γ (green symbols) and viscosity η (blue symbols) as a function of shear stress τ for three different mayonnaise products. The red line indicates the yield stress according to the maximum in viscosity for the regular mayonnaise. The black lines are the tangents applied to the different regions of deformation (elastic deformation and steady flow). The intersection of both tangents represents an alternative method for the yield stress determination.

Table 1: Yield stresses of different mayonnaise obtained from different rheological tests and evaluation methods.

	Test / evaluation method		
Mayonnaise type	**Stress ramp maxumum viscosity**	**Stress ramp tangent intersection**	**Steady-state step-test stress plateau**
Regular	45 Pa	82 Pa	116 Pa
Low fat	37 Pa	70 Pa	89 Pa
40% yogurt	45 Pa	83 Pa	119 Pa

Table 1 gives an overview of the yield stress values derived from the different evaluation methods. It also includes the shear stress plateau values from the steady-state shear-rate step tests. It can be seen that this value provided the largest value for the apparent yield stress, which corresponds to the fact that the data has been collected at the beginning of a rotational test and therefore the sample is already at the end of its transition between elastic and viscous behavior.

In general it can be said that yield stresses of different materials can be compared when the experimental setup and the evaluation method are identical.

Texture analysis

Apart from the classic rheological test methods described above, food formulations are often also characterised regarding their textural properties. A texture analyzer tries to simulate a real-world -treatment of a food such as scooping, chewing, spreading or breaking. This is accomplished by moving a measuring geometry onto or into a food formulation with either a defined speed while recording the force necessary to do so or with a defined force recording the resulting deformation. Precise lift movement and sensitive axial force control are inherent capabilities of a modern rheometer. Consequently, it is rather easy to use a rheometer for texture analysis. In cases, where the normal measuring geometries like cones, plates or cylinders are not suitable for such a texture test, almost any kind of special measuring geometry can be adapted using a universal adapter fixture.

Marshmallows are a typical example for sweets, where the desired mouthfeel during chewing is an important part of their success. To simulate the chewing behaviour, marshmallows were placed onto the lower plate of the rheometer's measuring geometry and a 35 mm plate was used to squeeze them down to 8 mm height with a speed of 5 mm/s. Then the top plate went up again with the same speed and afterwards the squeezing step was repeated several times to simulate chewing. The results of this testing are shown in Figure 6.

The maximum force at each compression step went down from cycle to cycle indicating that the marshmallow became softer simply due to repeated compression without any influence of liquid (saliva).

The breaking behaviour is another important property for certain types of food like biscuits or chocolate. In the latter case it needs again to fulfil the consumer's expectation. For example a milk chocolate is expected to be softer whereas a dark chocolate is expected to be harder, maybe even brittle. Regarding the texture of biscuits, it gets a bit

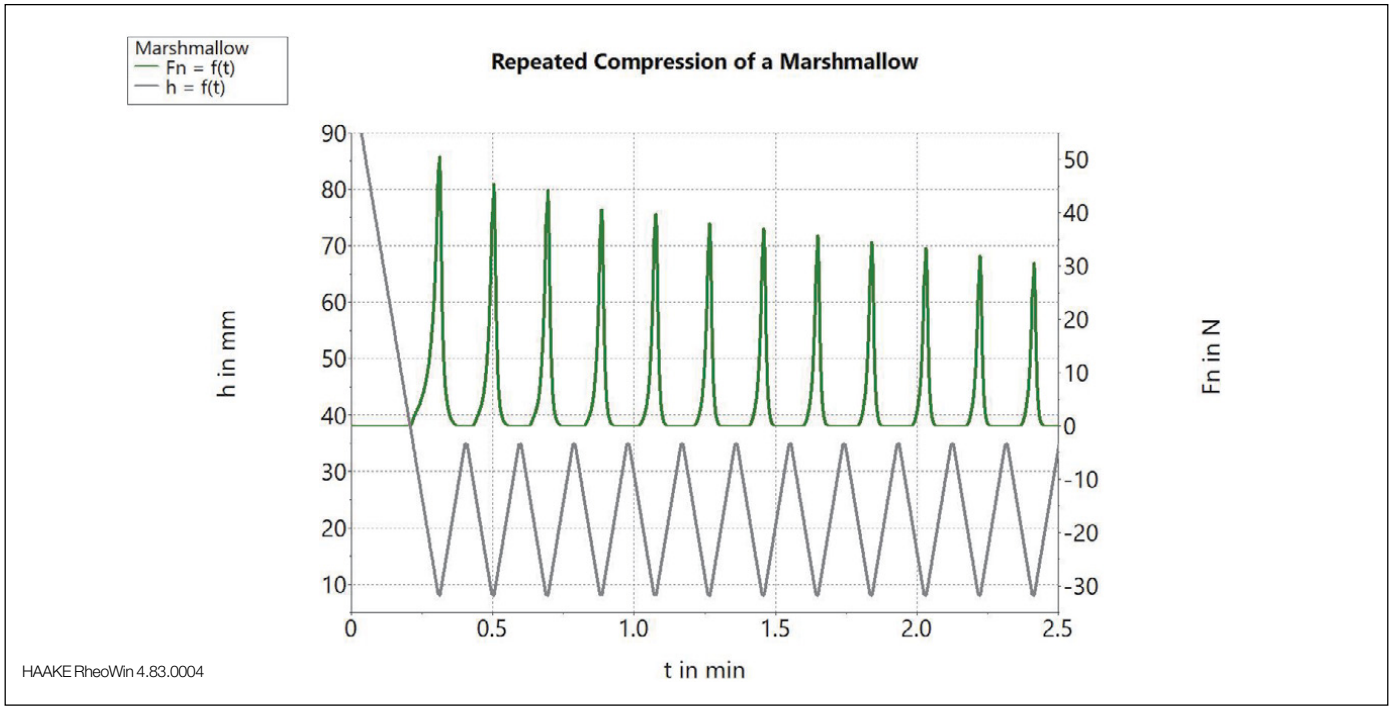

Fig. 6: 12 cycles of compression and relaxation of a marshmallow. The black Curve shows the down and up movement of the upper geometry. The green curve shows the corresponding changes in the force needed to compress the sample.

more complex since starch-based products usually change their texture over time due to the influence of air humidity. So, apart from their initial properties the aging of biscuits is also a topic for investigation where usually the force needed to break the biscuit, and the amount of bending before the biscuit breaks, were evaluated.

To test the breaking behaviour, biscuits were placed onto the 3-point-bending-tool (Figure 3). A plate rotor with a diameter of 8 mm was selected as the upper part of the measuring geometry. The starting position of the upper geometry was chosen sufficiently high enough to allow the convenient positioning of the biscuits. The upper geometry moved downwards with 0.1 mm/min to detect the surface of the biscuit with a sensing force of 0.1 N. From that point on, the upper geometry continued downwards with 1 mm/min, bending and breaking the biscuit.

Afterwards, using the loop function in the Thermo Scientific™ HAAKE™ RheoWin™ Software, the measuring geometry was lifted up again to make way for positioning the next biscuit. The results of multiple tests on fresh biscuits, tested immediately after opening the package, showed some scattering in maximum bending and breaking force as expected when testing samples based on natural raw materials (Figure 7).

The same tests were repeated 14 days after the biscuit package was opened (Figure 8). The maximum of the force curves became broader and the amount of bending slightly increased compared to the fresh biscuits, indicating that slight aging had occurred over this time period.

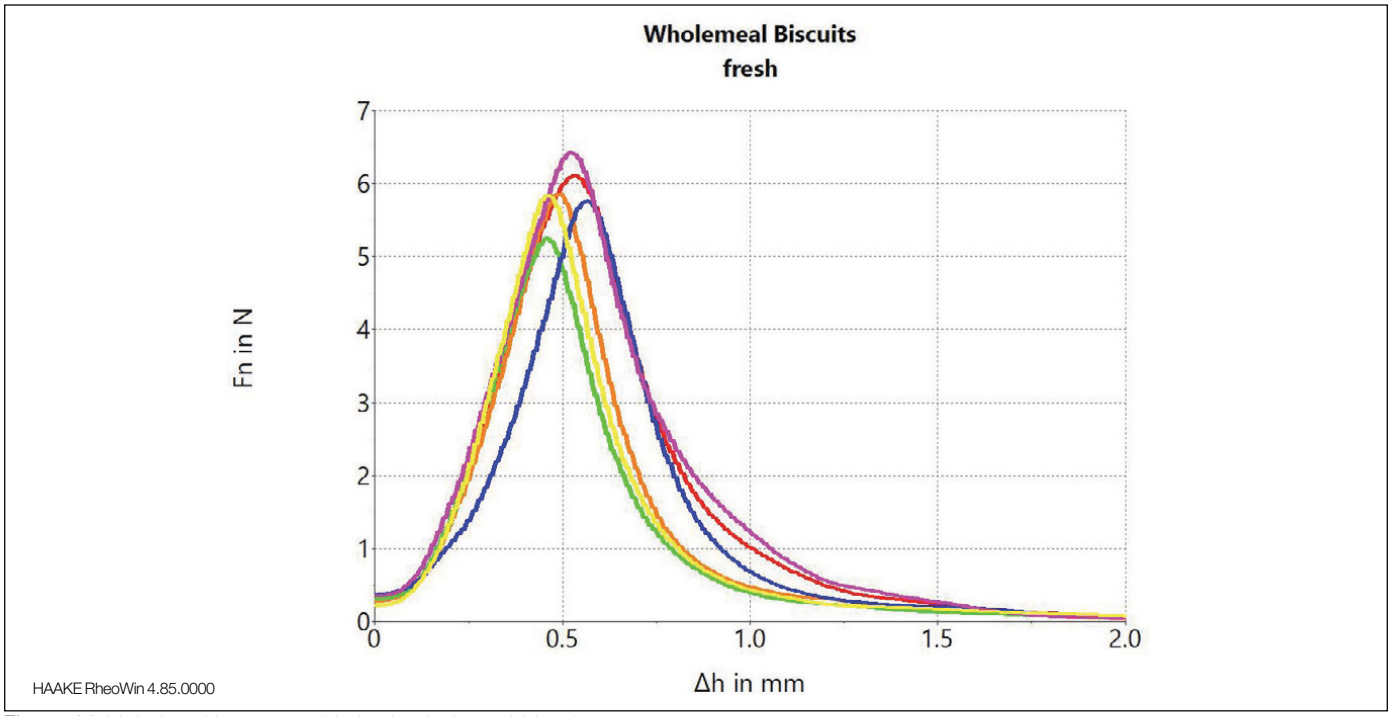

Fig. 7: Multiple breaking tests with fresh wholemeal biscuits.

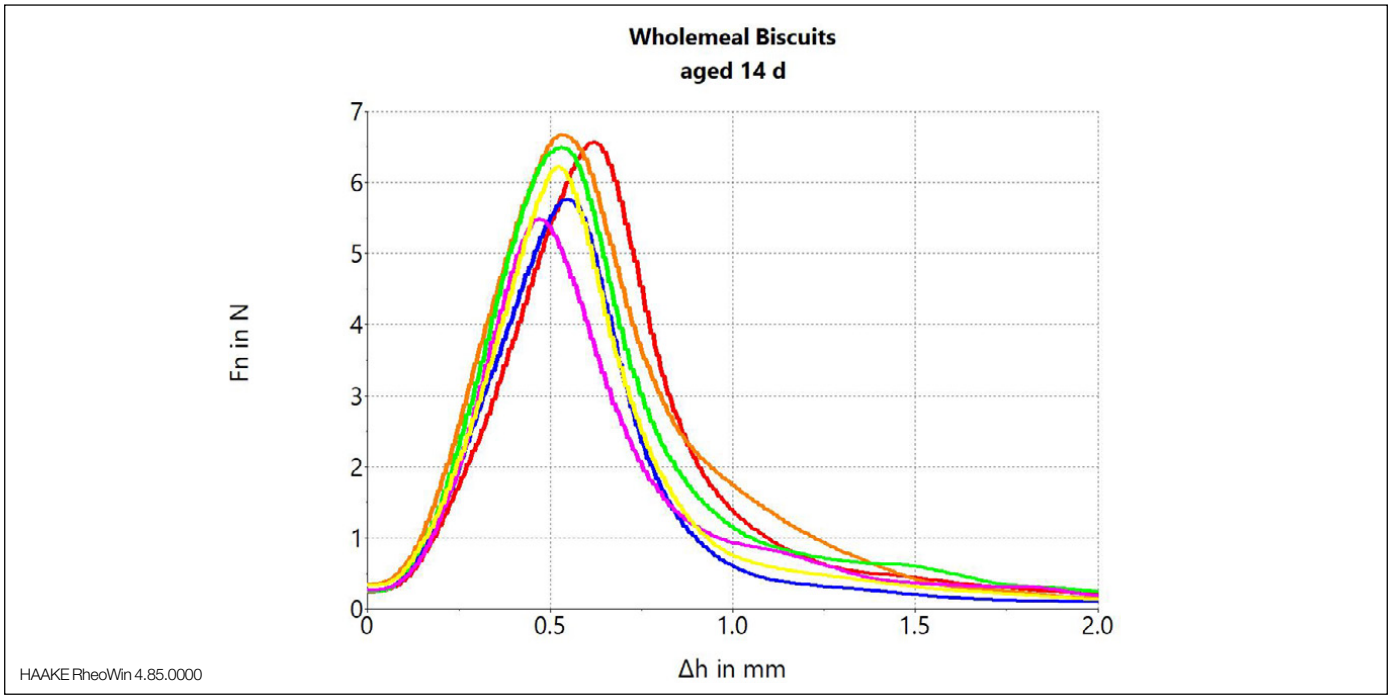

Fig. 8: Multiple breaking tests with aged wholemeal biscuits.

Tribological tests

Tribology is a field of materials science and mechanical engineering that deals with the properties of interacting surfaces in relative motion. It includes the study and application of the principles of friction, lubrication and wear. Tribological measurements have raised interest in the field of food science as an additional technique to describe the complex concept of texture and mouthfeel.

Surfaces of different materials and roughness have been used to simulate the complex interaction of tongue, food (saliva) and palate during oral processing [Ref 2]. The ultimate goal is to correlate tribological parameters, such as the friction coefficient, with textural mouthfeel properties (e.g. creaminess or fattiness) usually derived from sensory panels.

Tribological data is commonly presented in the form of a Stribeck curve where the friction coefficient is displayed as a function of the sliding speed. The general form of a Stribeck curve is presented in Figure 9 and can be divided in three regions. At low sliding speeds where no lubricating film is present, the behavior is dominated by direct solid/solid contact. This part is commonly referred to as the boundary lubrication range and the resulting coefficients of friction are high. At medium sliding speeds the increasing hydrodynamic pressure of the lubricating sample is causing the development of a lubricating film between the two surfaces and the coefficient of friction will start to drop. At high sliding speeds the lubricating film has separated the two surfaces completely and no solid/solid interactions are present anymore. In this hydrodynamic lubrication range the coefficient of friction will start to increase again. In general one can say that the lower the coefficient of friction, the better the lubricating properties of a liquid/semi-solid surface system. Figure 10 shows the comparison of Stribeck curves obtained from tribological tests with two different chocolate spread products and an olive oil on a ball-on-3-plates setup.

The graph reveals the different lubrication properties of the olive oil compared to the two chocolate spreads. Due to their higher viscosity and more paste-like structure, the chocolate spreads formed a more stable lubricating film at lower speeds. At higher sliding speeds, the lower viscosity of the olive oil had a clear advantage, and it showed the best lubrication properties with the lowest friction coefficients in that range. In addition, the Stribeck curves revealed differences between the two spreads. While at higher sliding speeds the friction coefficients were almost identical, chocolate spread 2 showed better lubrication properties at low and medium sliding speeds.

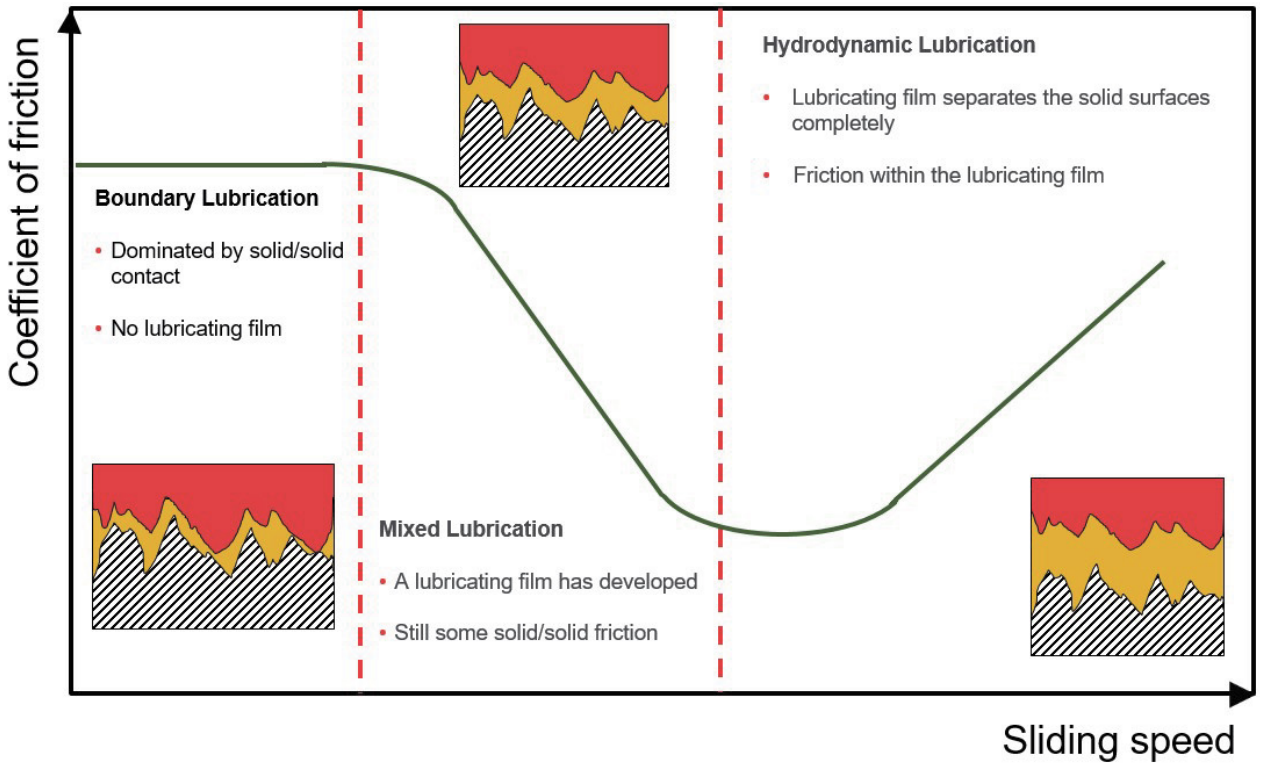

Fig. 9: General shape and regions of a Stribeck curve for tribology measurements.

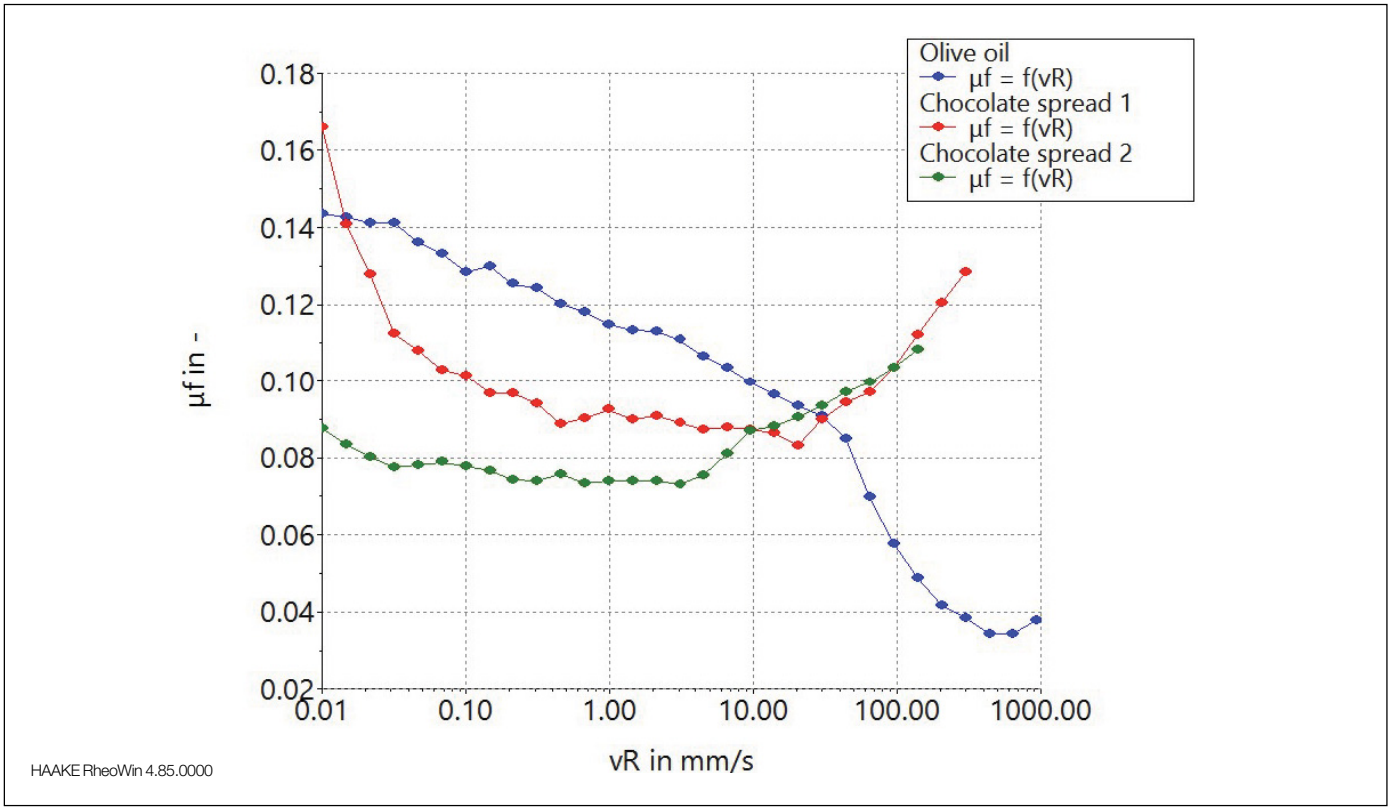

Figure 10: Stribeck curves (friction coefficient μf as function of sliding speed vR) of two different chocolate spreads and an olive oil.

Conclusions

The HAAKE MARS iQ Rheometer with mechanical bearing is a versatile and modular instrument ideal for investigating the mechanical properties of liquid and semi-solid food formulations. Due to a large number of measuring geometries and other accessories, it is capable of performing standard rheological tests to measure shear-rate-dependent viscosity over a wide shear range and yield stresses in stress-controlled measuring mode as well as more comprehensive texture analysis and tribological tests. While viscosity and yield stress are important parameters for predicting the behavior of food products during processing, transport and storage, texture and tribological properties allow for a more comprehensive study of oral processing and the general concept of mouthfeeling. The HAAKE MARS iQ Rheometer allows food scientists in R&D to characterize all stages of a product's life cycle from its raw materials to its consumption. Rheological tests developed by R&D can then be easily transferred over to quality control departments using the same HAAKE MARS iQ Rheometer for batch release testing.

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APPLICATION NOTE

No. V-238

Applied food rheology
Using fast speed control and axial measurements

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Key words
Food, viscosity, yield stress, texture, spreadability

Abstract
The characterization of food requires more information than just the usual viscoelastic properties accessible with any standard rheometer. This article shows some classical rheological data and some results, which can now be collected with the new capabilities of a modern rheometer.

Introduction

Food comes in a huge number of varieties and the number of rheological methods used to characterize it is even bigger. For example it can be a simple test to check the viscosity of an oil or a molten chocolate or it can become quite difficult when quantifying the texture of a peanut butter.

Some tests rely on classical rheological terms like viscosity or yield stress. Others try to emulate an application by using a special measuring geometry or try to save time by measuring directly in the original container coming from the production.

Figure 1: The HAAKE MARS Rheometer with individual container holder.

In this article some special capabilities of the Thermo Scientific™ HAAKE™ MARS™ Rheometer are shown. For example, very small and extremely fast controlled deformations have been used to test a food's undamaged structure. The normal force sensor has been used in combination with the lift to expand the range of information accessible with a rheometer.

Small deformations

Bread spreads are interesting materials regarding their rheological behaviour. How a bread spread looks like when a fresh container is opened, how easily it can be spread and whether it looks appetizing on a slice of bread is related to its solid-like behaviour at rest and the force necessary to overcome it. Thus the yield stress is an important parameter to characterize the "look and feel" of a bread spread.

When a sample is put into a rheometer the weak part of its structure can already be destroyed by handling or squeezing it. Thus some authors distinguish between the static yield stress, measured on the "undamaged" sample, and the dynamic yield stress, measured after the loss of the weak structure [1].

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Therefore and to save time it is often preferred to measure the static yield stress in the original container. Equipped with a special flexible container holder (Figure 1) and e.g. a star-shaped vane rotor, the HAAKE MARS Rheometer can measure in a variety of containers [2]. Due to its unique spacious design it allows measurements in containers up to 10 l buckets. When measuring with a vane rotor in the original container, the yield stress is measured by applying a constant shear rate to the sample and by determining the initial maximum of the shear stress. To get a yield stress independent of the shear rate applied, the shear rate has to be as low as possible [3]. At the same time, the shear rate has to be constant before the weak structure breaks to get reliable and reproducible results. To combine these two requirements is a very demanding task for a rheometer since it takes the longer to get a constant shear rate the lower the shear rate is.

A peanut butter and a chocolate spread were tested with such a low shear rate of 0.001 1/s. Even against the high resistance of the bread spreads the control loop managed to stabilize the shear rate in less than 1 s leading to the perfect reproducibility shown in Figure 2.

The combination of the wide dynamic range of the HAAKE MARS Rheometer and its CR control loop offer the possibilities for fast and reliable measurements.

Axial measurement

The texture of a food determines whether the consumer likes for example its touch or its mouth feeling. For a solid food like chocolate even the force needed to break it and the sound when it breaks add to the impression of good quality, provided they are in the right range.

Apart from test panels where food is tested with the human senses, so-called texture analyzers are used to measure impartial texture-related parameters. These instruments mainly consist of a lift, which drives a probe onto or into the food's surface and a force transducer, which measures the force required for bending, breaking, or penetration. A modern rheometer like the HAAKE MARS Rheometer is equipped with a precise lift and an extremely sensitive normal force transducer, a configuration suggesting itself for texture analysis. The owner of the rheometer gains the capability to measure data comparable with the data used by e.g. suppliers or customers using only a texture analyzer.

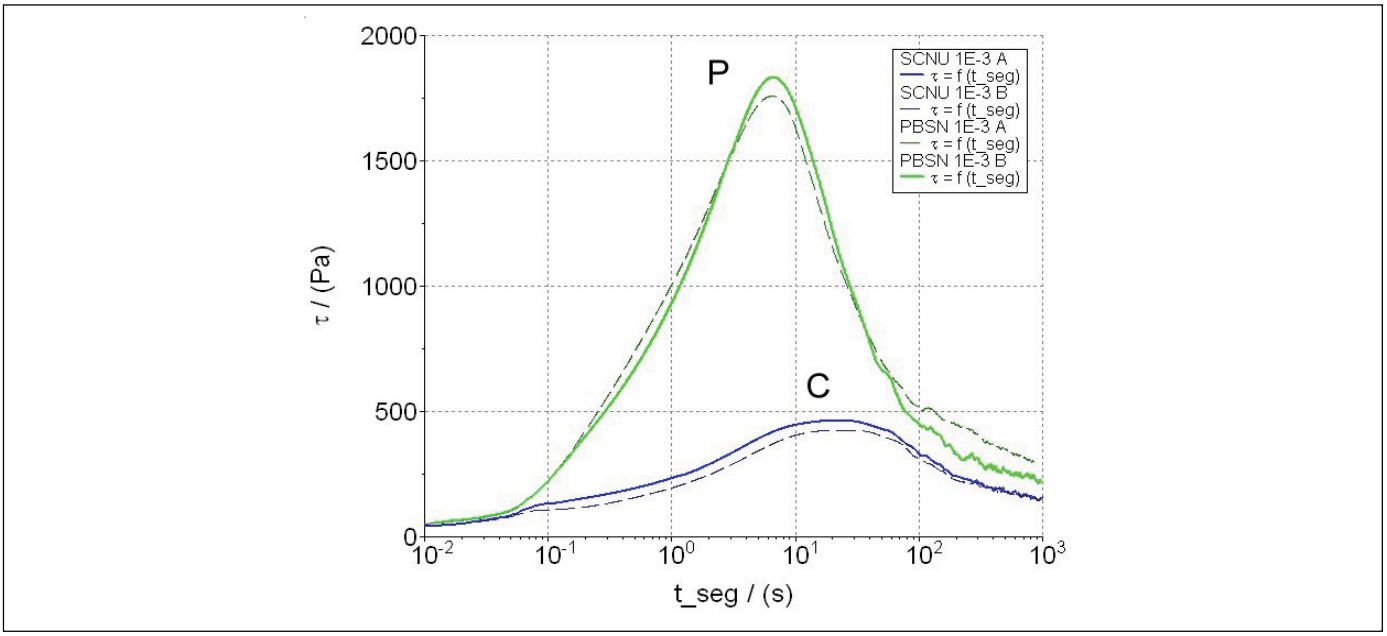

Figure 2: Yield Stress of a peanut butter (P) and a chocolate spread (C) measured with a vane rotor in their original glasses using a shear rate of 0.001 1/s.

Fast speed control

The shear viscosity is probably still the most commonly know rheological property of food products. Its importance can be seen from the huge variety of different thickeners available to stabilize food or to make it appeal to the customer's expectations.

To completely describe a food's behaviour during e.g. storage, pumping or chewing, its viscosity has to be measured over a wide range of shear rate. In the industry especially the lower shear rates are often ignored simply due to the long time it can take to get stable viscosity data.

Following the industries demands, a control loop has been developed to significantly shorten the time to get stable data in CR mode. Figure 3 shows the viscosity curve of a chocolate spread measured with a cone plate geometry at 35 °C in one run. In less than 20 min the viscosity has been measured over 10 decades in shear rate.

Bending and Breaking

For bending and breaking tests, a special sample holder is available based on the design of a three-point-bending fixture [4]. The chocolate sample is placed onto 2 blades with adjustable distance. A round piston is mounted to the measuring head using an adapter (Figure 4). During the test the piston drives downwards with a constant speed until the chocolate breaks.

The evaluation of the data makes it possible to quantify the breaking behaviour by the maximum force needed and the slope of the curve when the force returns to zero. As an example, the breaking curves for dark chocolate and milk chocolate are shown in Figure 5. Piston speed was 1.3 mm/min.

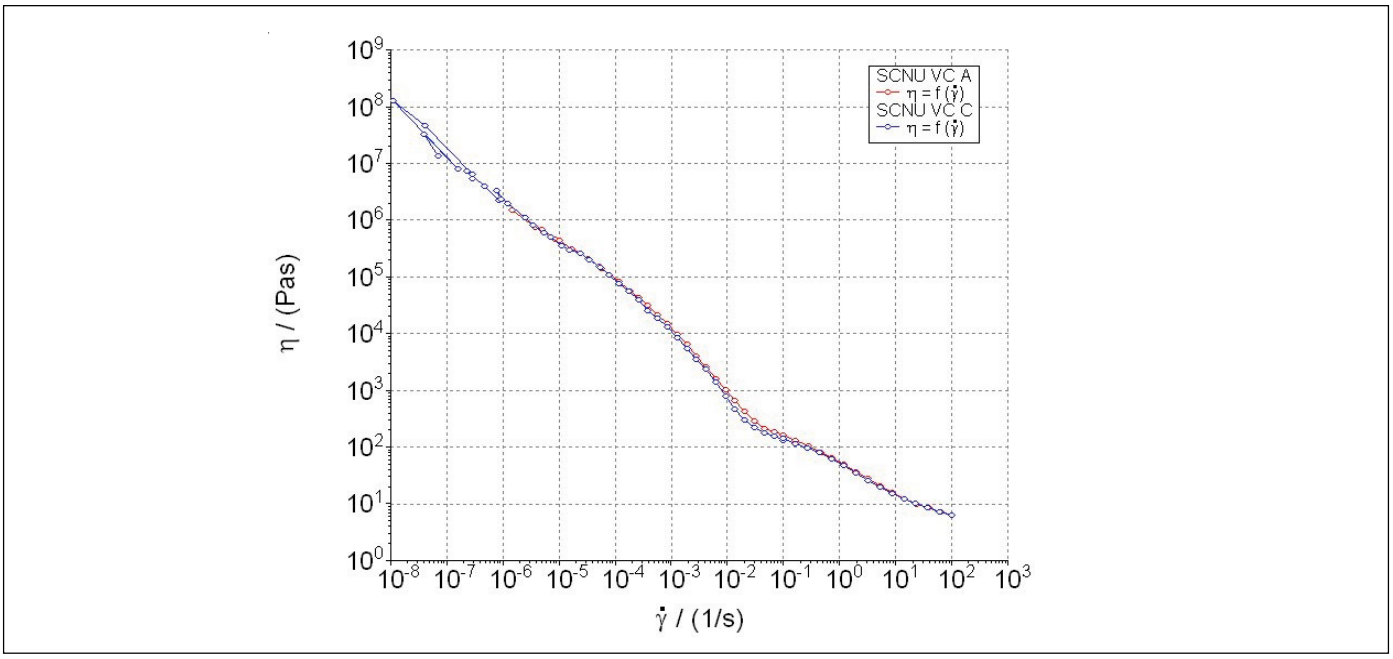

Figure 3: Viscosity curve of a chocolate spread. 2 measurements in one run over 10 decades of shear rate in CR mode with a cone 35 mm/1 ° at 35 °C.

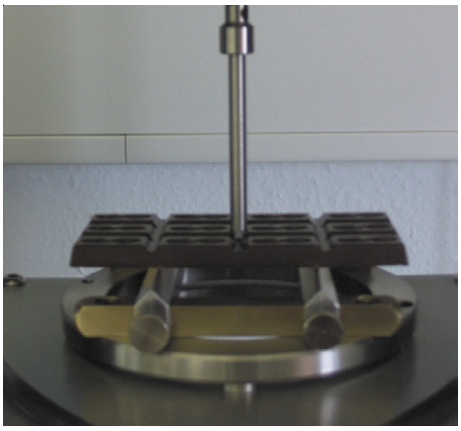

Figure 4: Measuring the breaking resistance of chocholate with the HAAKE MARS Rheometer using a two-blade-fixture and a 6 mm piston.

Here the dark chocolate breaks sharply when the necessary force has been reached, while the milk chocolate slowly breaks in 2 steps. The typical hard texture of the dark chocolate and the soft creamy texture of a milk chocolate can easily be identified with the test performed.

Penetration

Another common method to determine the spreadability of a bread spread is the determination of its firmness with a penetration test. Different methods and different probes are used.

For tests on margarine the 6 mm piston has been used again. The margarine has been stored in the fridge until just before the measurement and is then placed onto the universal container holder. First the rheometer lowers the probe until the sensitive normal force sensors detects the contact with the margarine's surface. Then the piston is driven some millimetres into the sample with a constant speed. This final position is then held and the relaxation, i.e. the decaying normal force, is measured.

The test has been repeated several times on different spots of the same block of margarine. After every second measurement the sample was put in the fridge again for 5 min.

The curves presented in Figure 6 are the results of 8 measurements done on the same block of margarine and show the good repeatability of this method. For data evaluation the maximum force at the end of the movement and the residual force at the end of the relaxation can be used.

Summary

With its extremely fast CR control loop, the HAAKE MARS Rheometer is able to stabilize the shear rate extremely fast. This capability enables the user to measure the strength of weak structures with such a rheometer in a reproducible way before they are destroyed by the rotation.

The same capability satisfies the need of QC for fast measurements covering the wide shear rate range from storage to application within an acceptable timeframe.

A modern high-end rheometer with a very sensitive normal force sensor and a precise lift control can be used like a texture analyzer or a penetro-meter, which are commonly used in the food industry. It therefore expands the variety of information accessible using only one instrument.

Aknowledgement

Special thanks to Ulrich Schulz and Philippe Sierro for their support during the measurements.

References

[1] Steffe, J.F. (1996), "Rheological Methods in Food Process Engineering", Freeman Press, pp. 200-208

[2] Thermo Fisher Scientific Product information P048 "Universal holder for measurements in original containers" Cornelia Küchenmeister-Lehrheuer, Klaus Oldörp and Jint Nijman

[3] Thermo Fisher Scientific Application note V228 "What Happens when Rheological Properties Change?" Klaus Oldörp

[4] Thermo Fisher Scientific Product information P014 "Sample fixturefor bending and breaking tests for Thermo Scientific rheometer" Cornelia Küchenmeister-Lehrheuer and Klaus Oldörp

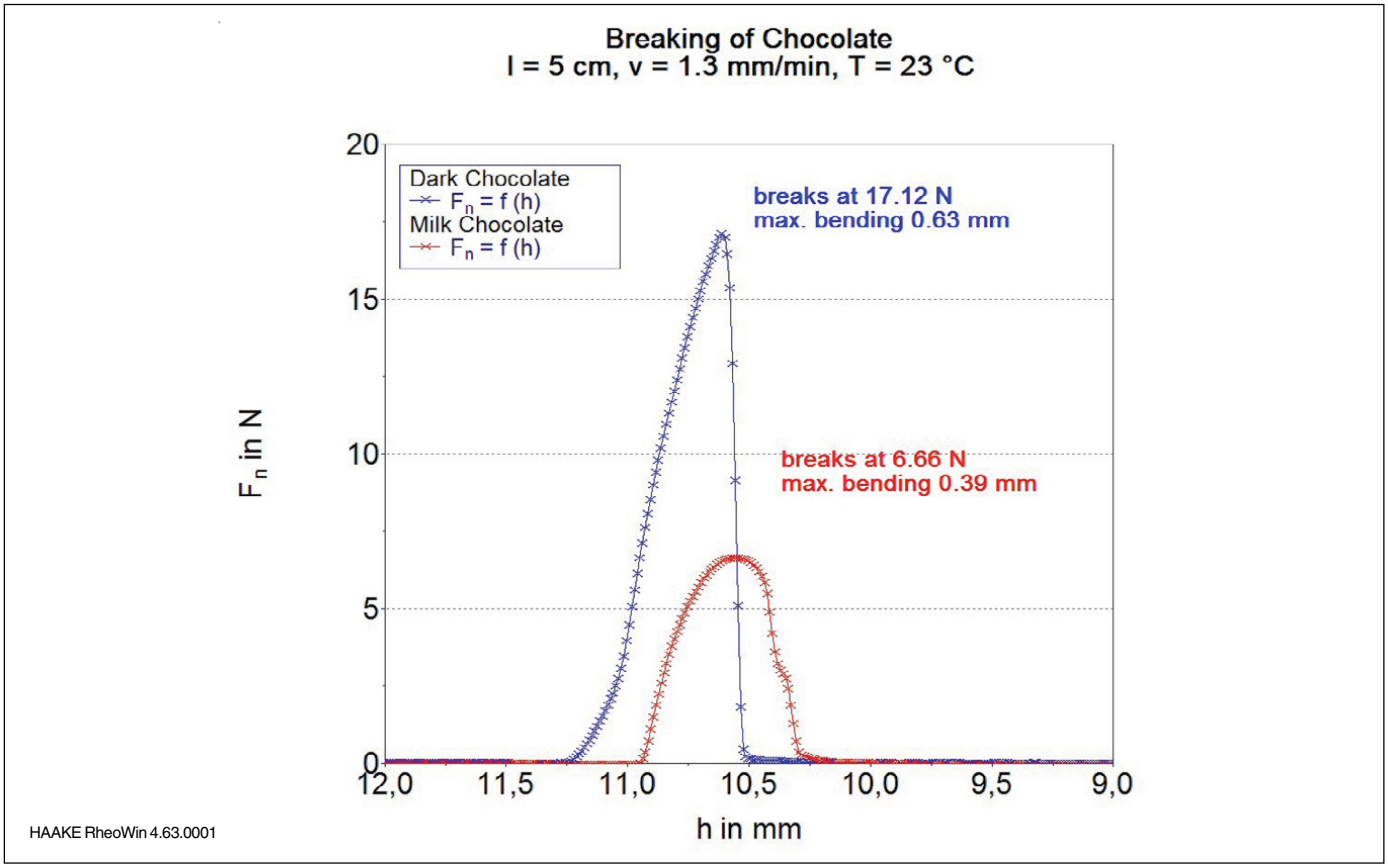

Figure 5: Axial force as a function of piston position for dark chocolate (higher peak) and milk chocolate (smaller peak).

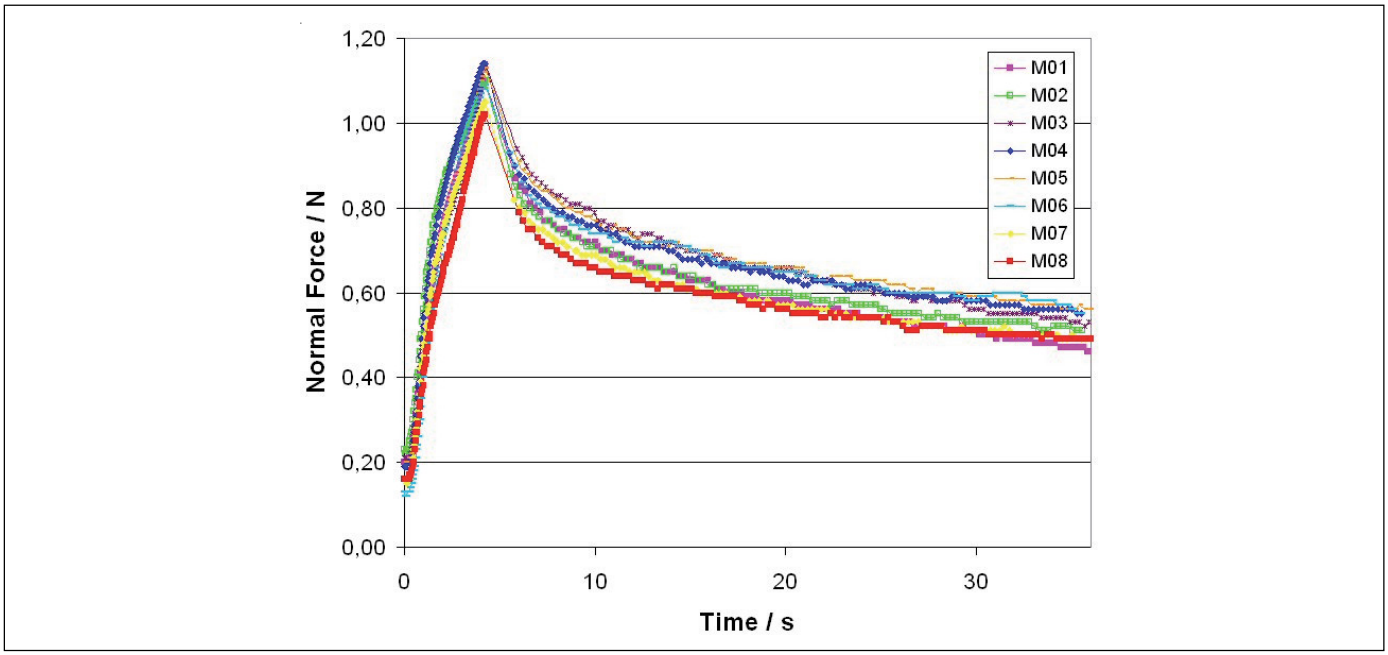

Figure 6: Penetration test on margarine repeated 8 times. First the probe moves into the sample, then the relaxation of the normal force is measured.

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APPLICATION NOTE

No. V-228

What happens when rheological properties change? Looking into rheological properties with simultaneous collection of microscopic images

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Key words
Food, viscosity, yield stress, texture, spreadability

Abstract
To gain information about the reasons for certain changes in rheological properties, a special module for the Thermo Scientific™ HAAKE™ MARS™ Rheometer has been developed. It combines a temperature control unit for cone/plate- and plate/plate-geometries with a state-of-the-art microscope. The RheoScope module is presented and example data from different applications is shown.

Introduction

Rheology is a “macroscopic“ method, which tells us how a material behaves under given conditions but never tells us why. For an understanding about the reasons why a certain behaviour occurs, we need to combine rheology with a “microscopic method“ able to look into the structure of the material.

Figure 1: The HAAKE MARS Rheometer with RheoScope and upper electrical temperature module TM-EL-H.

Examples for such techniques complementing rheological measurements are GPC, thermal analysis, (FT) IR, Raman or microscopy. Running two independent measurements on different instruments, however, doubles instrument time and measuring time and often leaves a bit of a doubt whether the sample and its treatment before measuring have been exactly the same.
The double effort of time and resources can be avoided by running two different methods on the same sample simultaneously, testing its macroscopic and its microscopic properties. The two resulting data sets can easily be correlated since they have been collected at the same time on the same sample.

The RheoScope module

The RheoScope is designed as a compact module (Figure 2). This RheoScope module can be mounted into the HAAKE MARS Rheometer like any other temperature control unit.

To guarantee an even temperature distribution and to make temperature ramps between -5 and 120 °C (optional 300 °C) possible, the whole bottom plate rests on the heat exchanger.

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Only a small window has been left open for “watching“ the sample during measurement. Below this window the lens can move along the radius of the bottom plate to select the best spot for monitoring (see Figure 3).

On top of being part of a modular rheometer system the RheoScope module is modular itself. Lens, camera, light source, lower glass plate and sensor (polished Titanium, up to 60 mm diameter) can be adapted to the individual application.

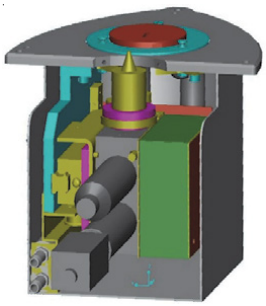

Figure 2: Inside the RheoScope module optical and mechanical components are arranged to give a high quality, fully software controlled microscope in addition to the temperature control unit.

Apart from the data collection and data evaluation (Figure 3) the control of the RheoScope module is fully integrated into the Thermo Scientific™ HAAKE™ RheoWin™ Software. All settings like position, focus, integration time, contrast and using the polarizing filter can be saved and thus be recalled e.g. for later routine measurements. For advanced image analysis for e.g. a particle size distribution specialized software is available.

Applications

Cooking of Starch in Water

Huge amounts of starch extracted from different kind of plant species are used for a large variety of applications. Native starch usually has a grain-like structure where all “grains“ are small crystalline particles. To break up this crystalline structures starch is cooked in water to get a starch solution. Depending on the natural source of the starch and its pre-treatment, the viscosity and texture of the final solution or paste as well as its storage stability can differ significantly.

During the cooking process the viscosity of the starch/water mixture reaches a maximum due to the swelling of the starch crystals. When the crystalline domains break up, the viscosity drops again. During cooling the amylose content can recrystallize the so called retrogradation. With the RheoScope module we looked at starch “grains“ during the cooking process, correlated the changes to the viscosity and looked at the structure of the final starch solution.

5% starch in water was filled into the rheometer at 40 °C, heated up to 90 °C in 25 min, kept at 90 °C for 15 min, cooled down to 20 °C in 35 °C min and kept at that temperature for additional 15 min. The viscosity was measured with a constant shear rate of 5 s^{-1}. The pictures were taken with crossed polarisers.

Figure 5 shows the cooking process of native potato starch in water at 90 °C. The pictures taken with the RheoScope module show the initial starch crystals, the swollen crystals when the viscosity reaches inhomogeneous solution after cooling down to 20 °C.

Running the same cooking program with hydroxypropylated potato starch shows the viscosity maximum shifted to a lower temperature indicating a better water solubility (Figure 6). This is confirmed by the pictures showing a high degree of swelling at viscosity maximum and a homogeneous solution after cooling down to 20 °C (photo #3 in Figure 6).

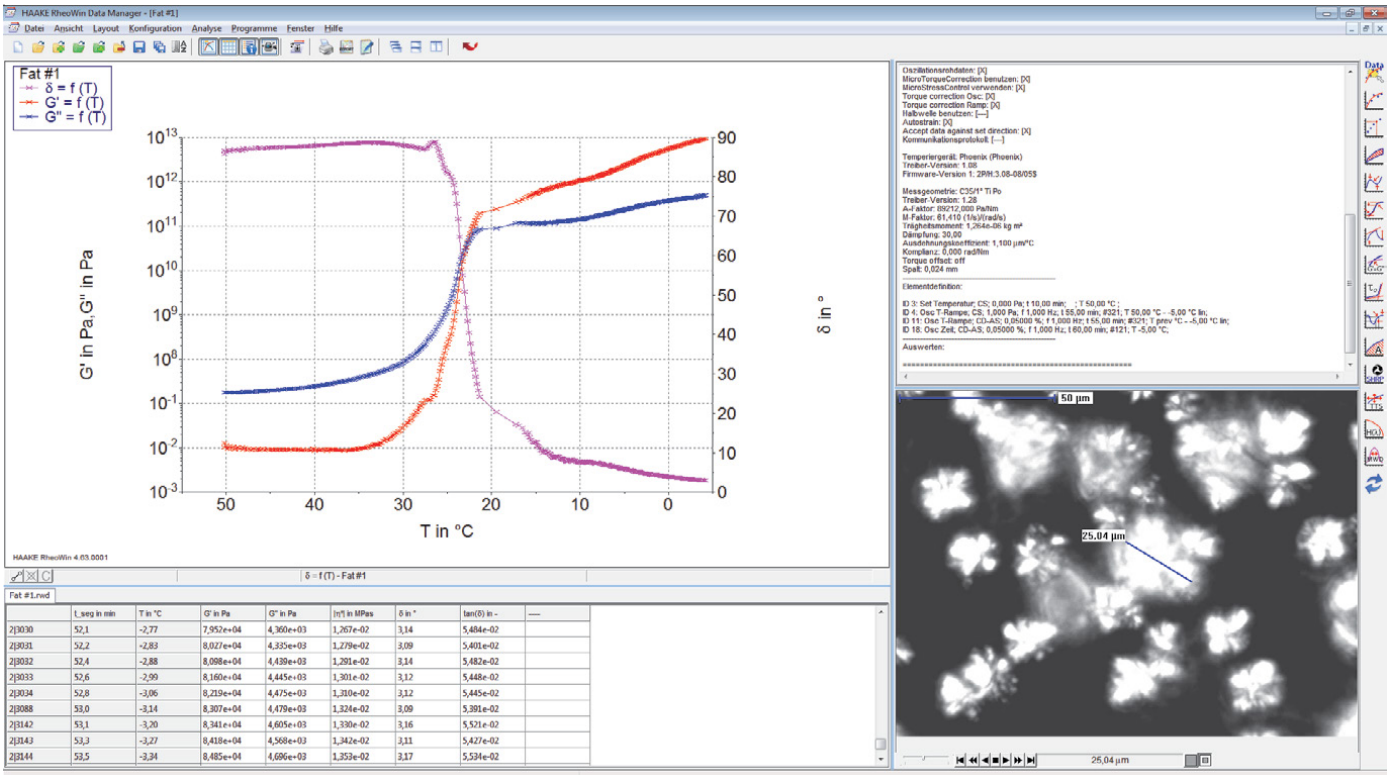

Figure 3: Rheological data and pictures are handled by the HAAKE RheoWin Software and are linked to each other, i.e. for every data point the picture, which has been taken simultaneously can be displayed. Simple evaluation of the pictures can be directly done in HAAKE RheoWin Software.

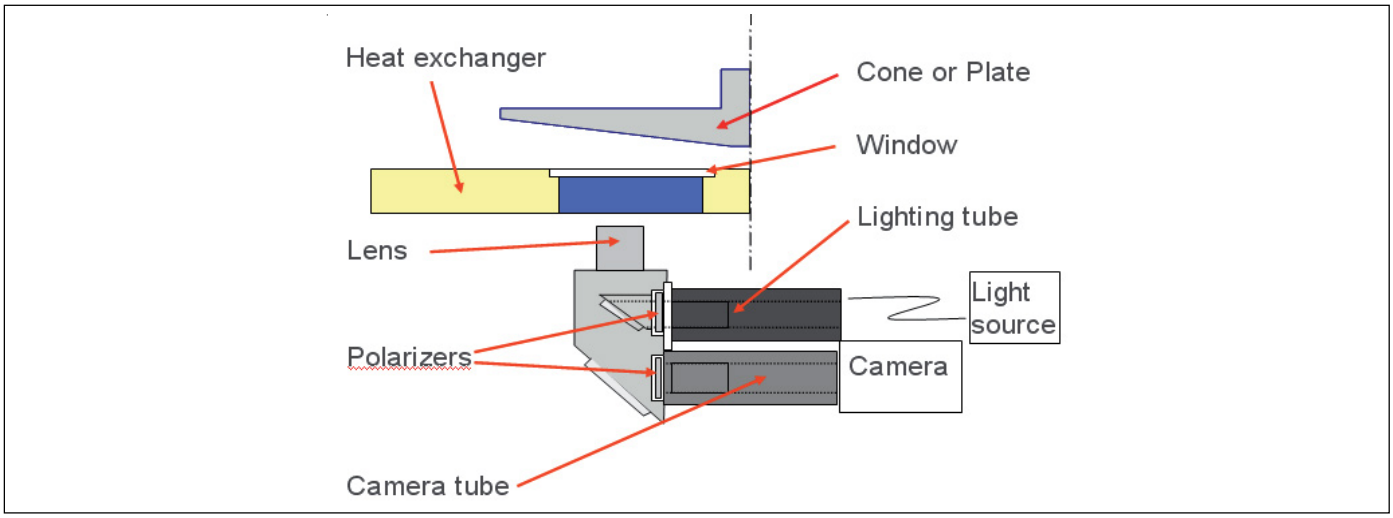

Figure 4: Pictures are taken through a small window in the heat exchanger guaranteeing good temperature distribution.

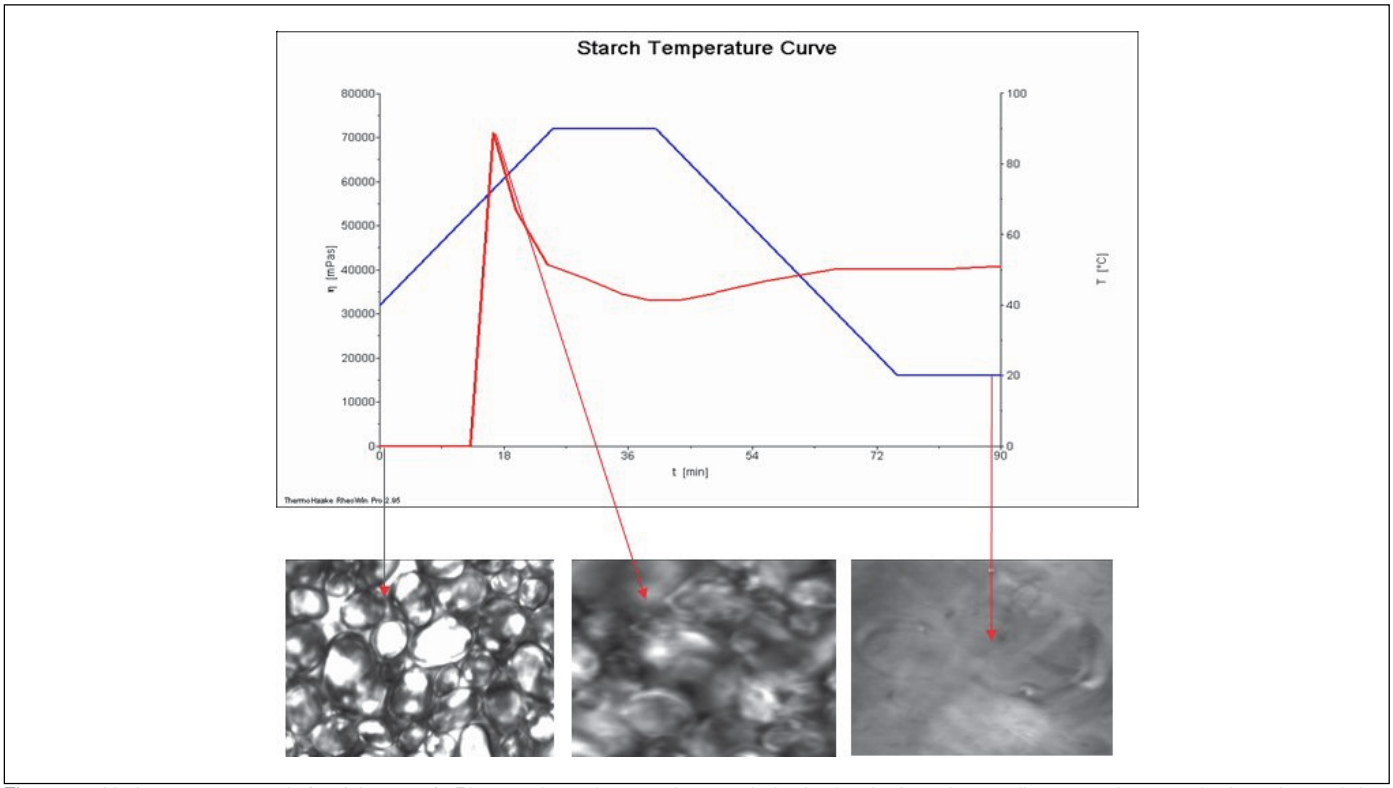

Figure 5: Native potato starch (5 % in water): Photos show the starch crystals in the beginning, the swollen crystals at peak viscosity and the inhomogeneous solution after cooling down.

Wheat starch in water shows a completely different behaviour. The viscosity shows a second local maximum before 90 °C are reached (Figure 7). The microscopic pictures show that already the starch particles at the beginning of the test look totally different (photo #1 in Figure 7). Photo #2 proves that the first maximum corresponds with the maximum found when testing potato starch since here we also can see the fully swollen starch "grains". Photo #3 shows an almost homogeneous solution. Why this structure corresponds with another maximum in the viscosity will be found by further work on this topic. When cooling down to 20 °C, the wheat starch solution becomes very inhomogeneous as can be seen in the 4th photo in Figure 7.

Using the HAAKE MARS Rheometer with the RheoScope module, we could follow the changing viscosity during the cooking process of starch in water. The photos simultaneously taken showed what happened with the starch during cooking and can be used to optimize the whole process.

Crystallization of Fats

One of the factors, which decide about the success of a food product, is the mouth feeling. When talking about solid or at least semi-solid food containing fat like e.g. chocolate, ice cream or butter, it is most likely that the crystallization of the fats is one of the more important factors to look at.

Melting or crystallisation temperatures can easily be determined with a modern rheometer or DSC. Fats often show a more complex behaviour where several crystal phases have crystallization temperatures close to each other. In a DSC the sample is usually clean and undisturbed while cooling down, which can lead to an undercooled melt. When crystallization from an undercooled melt is triggered all crystalline phases form in one instant and their crystallisation cannot be regarded separately.

The mechanical oscillation put onto a sample in a dynamic mechanical method like a rheological oscillation measurement

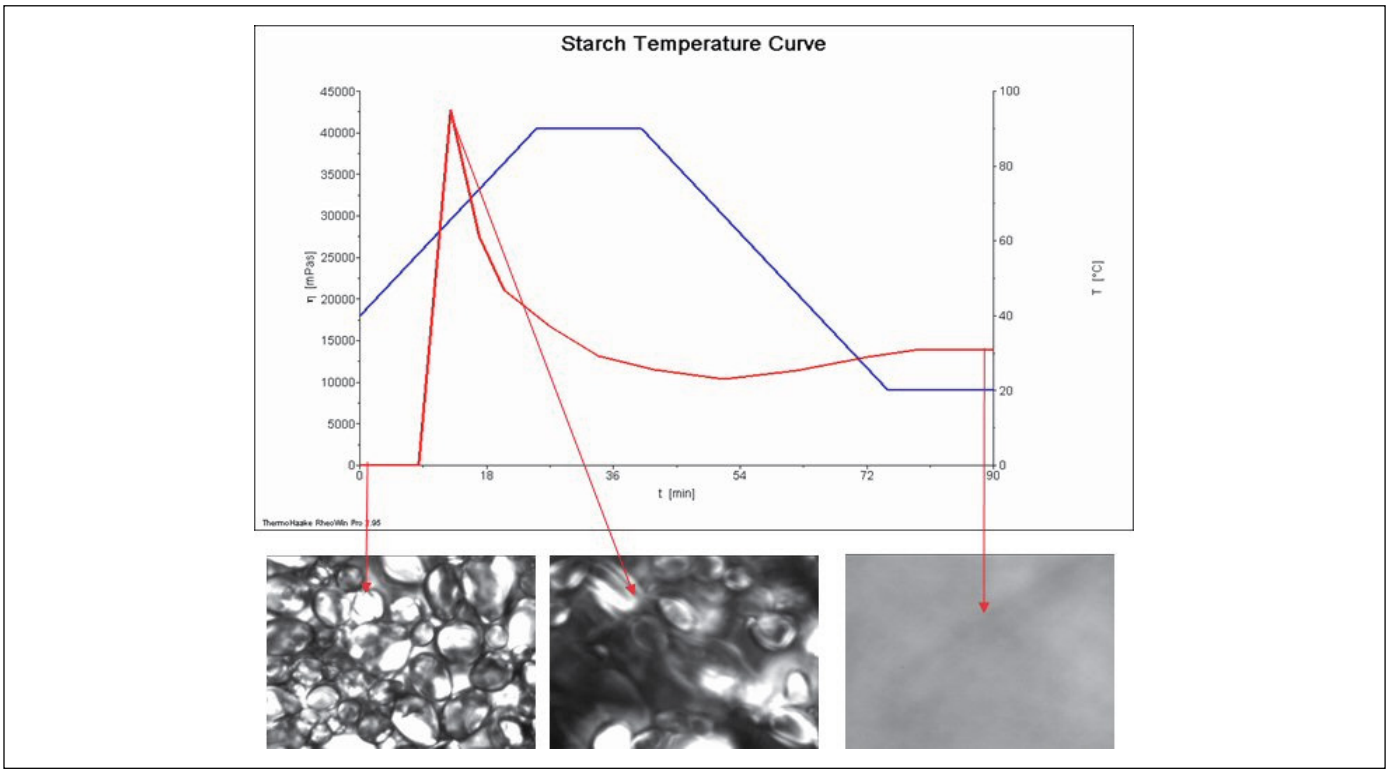

Figure 6: Native potato starch (5 % in water): Photos show the starch crystals in the beginning, the swollen crystals at peak viscosity and the inhomogeneous solution after cooling down.

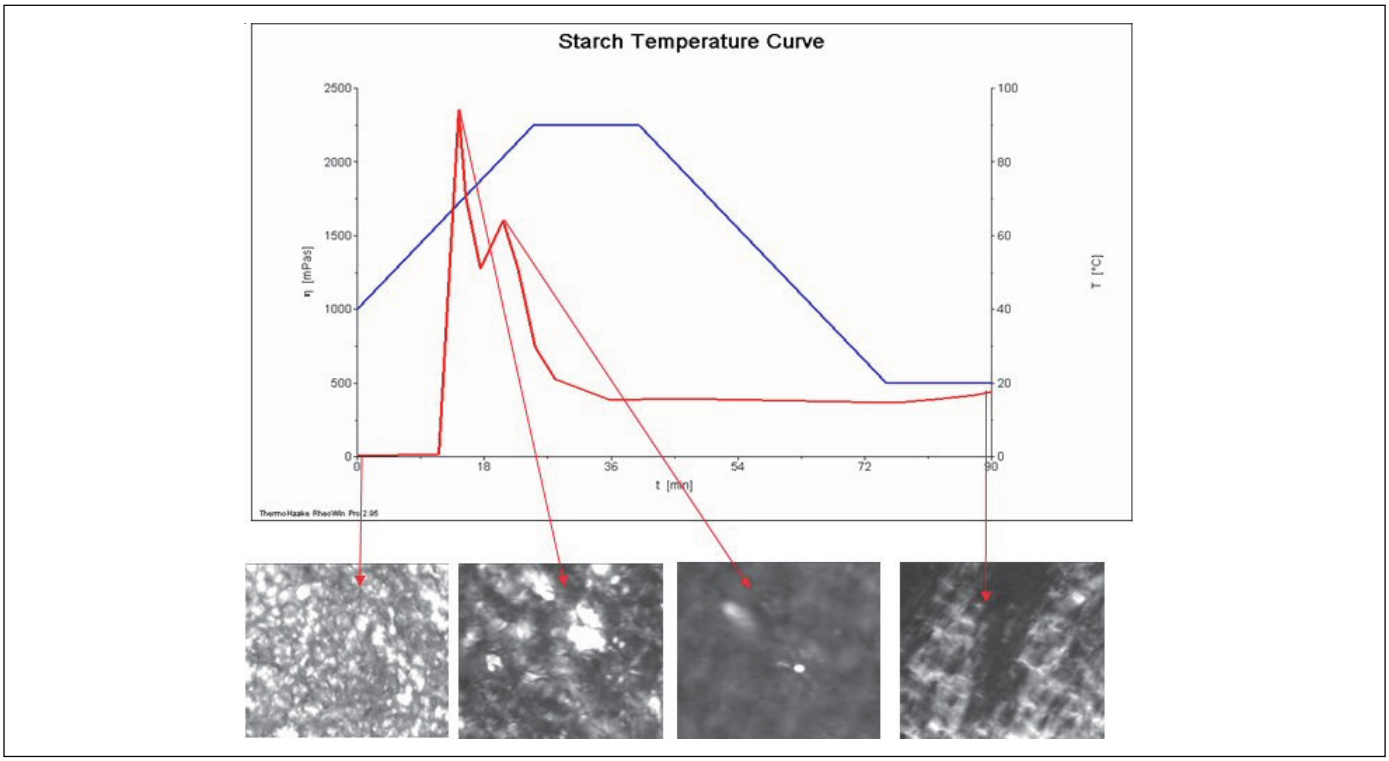

Figure 7: Wheat starch (5% in water): Photos show the starch crystals in the beginning, the swollen crystals at peak viscosity, an almost homogenous solution at the second local maximum and the inhomogeneous solution after cooling down.

is a permanent trigger, avoiding the undercooled melt and leads to the separate crystallization of different crystal structures.

Different vegetable fat samples have been measured with a HAAKE MARS Rheometer equipped with the RheoScope module. After melting the fat in the cone-plate-geometry of the rheometer, a temperature ramp going down from +50 °C to -5 °C with 1 K/min was run while recording the changing rheological properties of the fat with a constant oscillation with small deformation and the optical properties with the RheoScope module simultaneously.

The results show the crystallization of the fat samples by a more or less pronounced increase of the moduli G' and G" or decrease of the loss angle d. At the same time the growth of different crystals can be observed.

Fat #1 e.g. shows a very steep drop in d between 27 °C and 21 °C plus another weaker drop between 21 °C and 13 °C (see Figure 8). At the end of the temperature program, fat #1 consists of round crystalline domains embedded in an isotropic matrix (Figure 9, right photo).

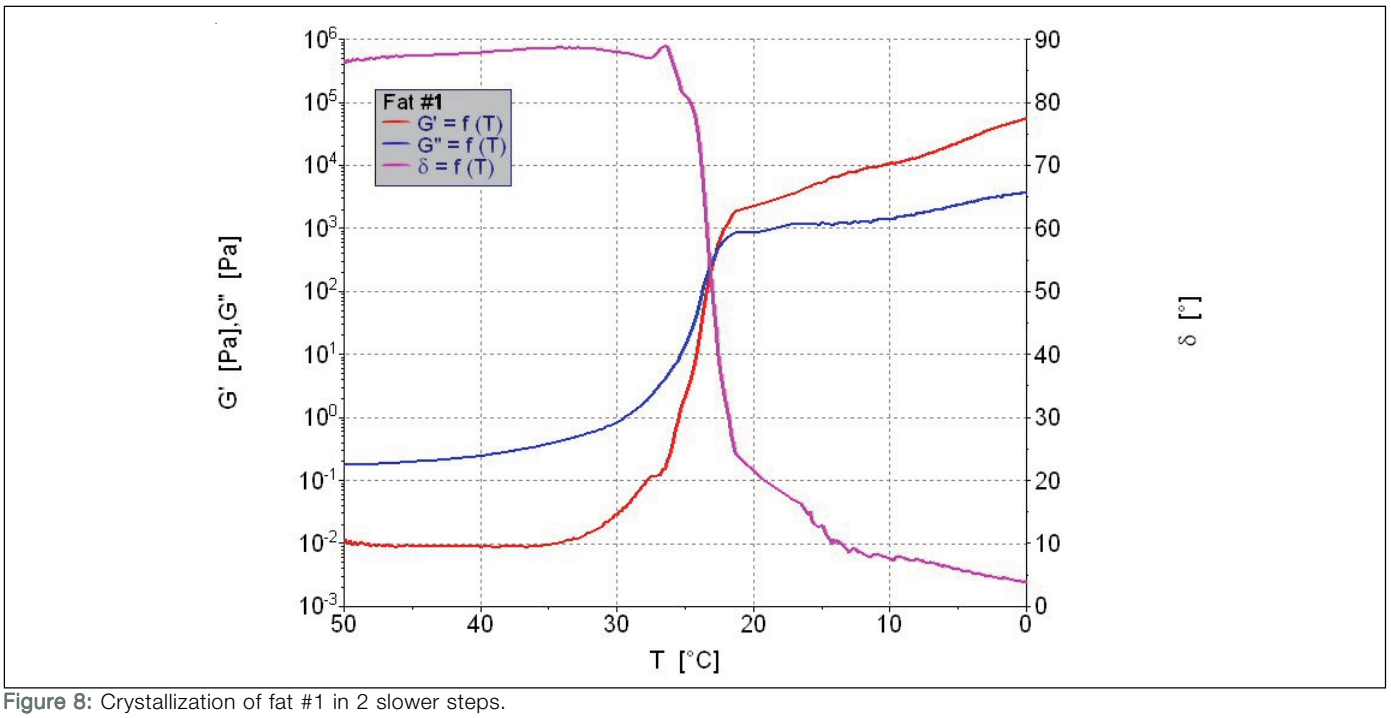

Figure 8: Crystallization of fat #1 in 2 slower steps.

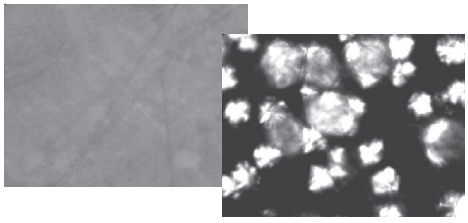

Figure 9: Microscopic pictures of the homogeneous molten fat #1 (left) and the same are after crystallization has begun (right).

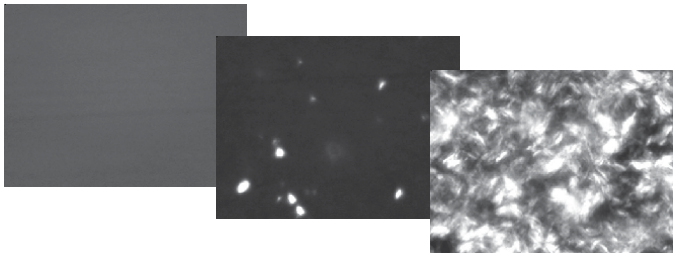

Figure 10: Microscopic pictures of the homogeneous melt of fat #2 (left), a first crystal phase formed below 32 °C (middle) and a second crystal phase formed below 20 °C (right).

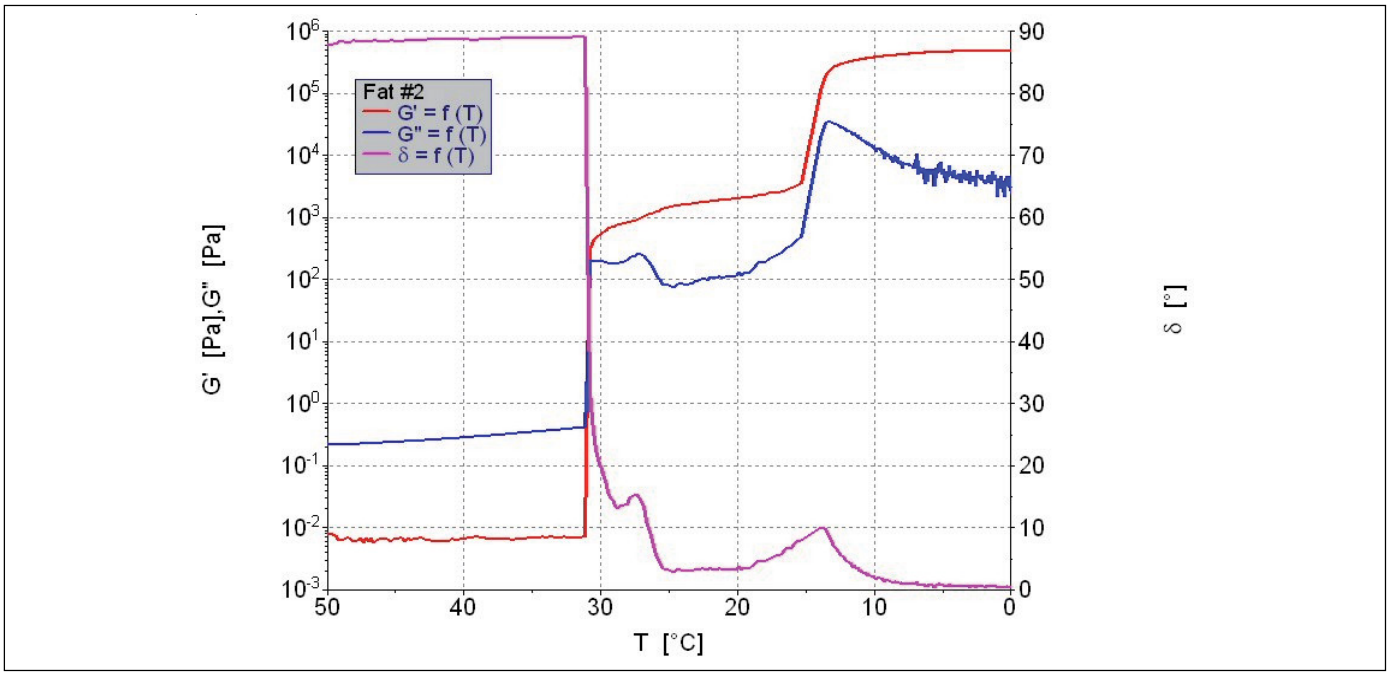

Figure 11: Crystallization of fat #2 in 2 fast steps.

Fat #2 also crystallizes in 2 steps but compared to fat #1 the crystallization happens very fast (Figure 11). First we have a homogeneous melt down to approx. 32 °C. Then we see a sudden appearance of small crystals together with a sharp decrease of δ.

In a second step beginning around 20 °C we see another smaller drop in δ and now bigger, needle-shaped crystals are formed (Figure 10, right photo). These needles grow until they fill the whole sample volume. In total we can distinguish samples by the shape, size and speed of growth of the crystals or crystalline domains and we can correlate this data with their rheological behaviour.

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Conclusion

The RheoScope module combines all characteristics of a compact temperature control unit and a fully software controlled, state of the art microscope. It can simply be added to a HAAKE MARS Rheometer without needing any prior modifications or affecting the function of the rheometer. The performance of the temperature control is not affected by combining it with a microscope. It is no problem to achieve stable constant temperatures as well as running heating or cooling ramps to investigate temperature induced changes in the sample.

With the examples of the cooking of starches and the crystallization of fats it was demonstrated how the microscopic information delivered by the RheoScope module can be correlated with the macroscopic behaviour of the sample and thus explain it.

The HAAKE MARS Rheometer with the Rheo Scope module enables the user to generate structure-property-relationships with measurements on the same sample and on one instrument only, saving time and money.

Acknowledgment

We thank the University of Wageningen for their friendly contribution of the starch measurements.

Special thanks to Dr. Massimo Bettin, EN.CO. Srl for carrying out the measurements on crystallization behaviour.

Find out more at thermofisher.com/mars

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APPLICATION NOTE AN53002

Investigating cocoa butter crystallization using simultaneous rheology and Raman spectroscopy (RheoRaman)

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Keywords
Cocoa butter, crystallization, Raman spectroscopy, rheology, RheoRaman, *in situ*, storage modulus G', loss modulus G"

Thermo Fisher Scientific solutions

- HAAKE MARS 60 rheometer
- iXR Raman Spectrometer
- HAAKE RheoRaman module
- OMNIC for Dispersive Raman software

Watch the video on measuring setup (RheoRaman)

Application benefits

Simultaneous rheology and Raman spectroscopy measurements were used to examine the isothermal crystallization of cocoa butter (CB). The results indicate that CB crystallized by first hardening into an amorphous solid. The amorphous solid then underwent a morphological transition to form a crystalline solid. Without coupling these two separate analytical techniques, the observed amorphous-solid to crystalline-solid transformation would have been left undetected. Alone, each technique suggests a single-stage process, however, only when the two techniques are coupled is the multi-phase crystallization process revealed, further exemplifying the unique analytical capability unleashed by hyphenating rheology with *in situ* Raman spectroscopy.

Introduction

Cocoa butter (CB) is an edible vegetable fat extracted from the cocoa bean. CB is commonly used in home and personal care products (such as ointments and lotions) and CB is a vital ingredient in chocolate. CB forms the continuous phase within chocolate confections and is responsible for the chocolate's texture, snap, gloss, melting behavior, and resistance to fat bloom. These physical characteristics are a direct result of CB's triacylglycerol (TAG) composition and overall crystalline structure.

In general, TAG molecules assume a tuning fork configuration and the TAG "forks" assemble to form crystal lattice structures. During crystallization, the TAG molecules slow down as the CB oil cools and the TAGs come to rest in contact with one another, forming what are known as "sub crystalline cells."[1] Once the sub-cells are formed, they are thermodynamically driven to aggregate into larger and more stable crystalline structures.[2] The self-assembly of sub-cell structures and their further aggregation is governed by a balance of intra- and inter-molecular interactions. Depending on the molecular level packing and orientation of the TAGs, CB can form different types of crystal lattice structures (or polymorphs), where some crystal structures are more desirable than others. Overall, CB crystallization is a highly complex, multistage process. Understanding the isothermal crystallization behavior of CB is vital for improving chocolate manufacturing processes and maintaining product quality.

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In this note, rheology coupled with *in situ* Raman spectroscopy was used to examine the isothermal crystallization of cocoa butter. Raman spectroscopy is a highly sensitive, relatively fast, and nondestructive technique that can probe the molecular structure and conformation in both liquid and solid TAG assemblies, as well as intra- and inter-TAG interactions. With simultaneous Raman spectra and rheological data, molecular-level interactions and conformational shifts during the isothermal crystallization of CB were directly correlated with the changes in bulk viscoelastic properties, providing unique insight into the multifaceted crystallization behavior of cocoa butter.

Materials and methods

Materials

Commercially available, organic cocoa butter (*Theobroma cacao*) was acquired from Inesscents™ (Ashland, OR, USA).

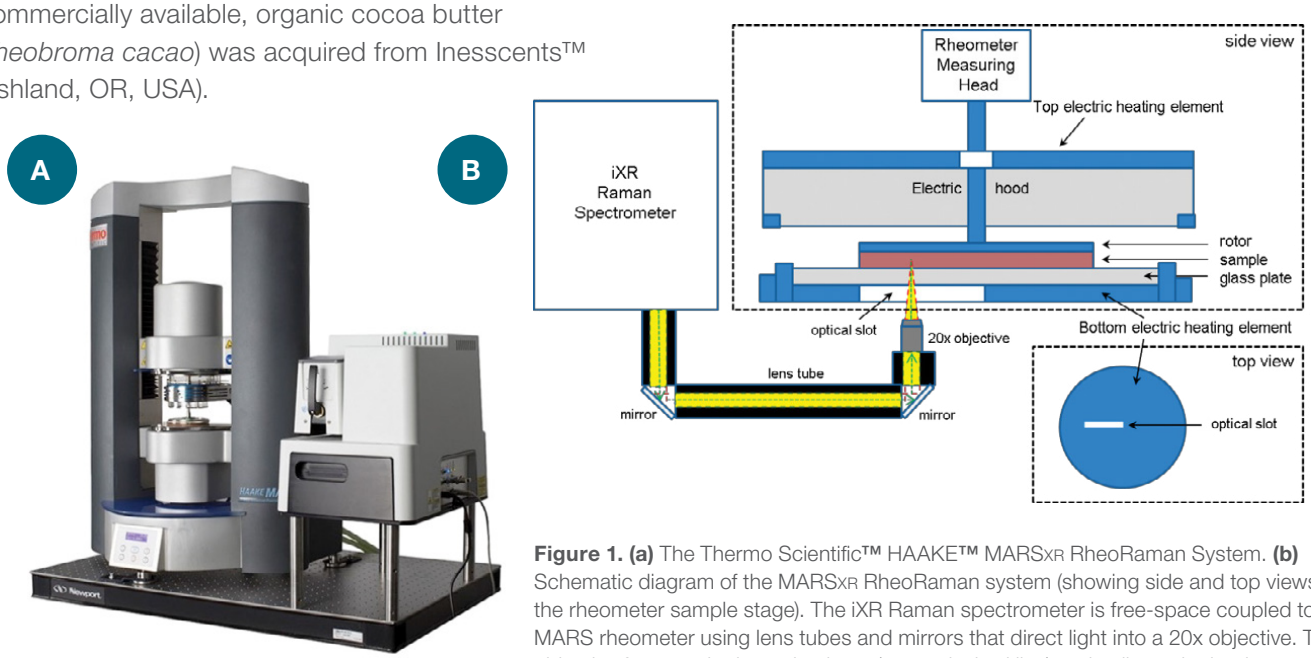

Figure 1. (a) The Thermo Scientific™ HAAKE™ MARSXR RheoRaman System. **(b)** Schematic diagram of the MARSXR RheoRaman system (showing side and top views of the rheometer sample stage). The iXR Raman spectrometer is free-space coupled to the MARS rheometer using lens tubes and mirrors that direct light into a 20x objective. The objective focuses the incoming laser (green dashed line) and collects the back-scattered Raman light (yellow) coming out of the sample sitting atop the rheometer stage.

Raman spectroscopy

Raman spectroscopy measurements were performed using a Thermo Scientific™ iXR™ Raman Spectrometer. A 532 nm laser was used with 10 mW laser power at the sample. The spectral range was 50-3500 cm^{-1}. The spectra were collected using a 2-second exposure time and 4 sample exposures. Data acquisition and processing were controlled by the Thermo Scientific™ OMNIC™ Software for Dispersive Raman. For the data presented here, Sequential Raman spectra (in parallel with the Rheological measurements) were collected over a predetermined time window using the time series collection function of the SERIES software within the OMNIC for Dispersive Raman software package.

Rheology

Rheological measurements were performed using a Thermo Scientific™ HAAKE™ MARS™ 60 Rheometer equipped with a serrated 35 mm diameter plate rotor at a gap height of 1 mm. The serrated plate was used to prevent slip at the sample-rotor interface. All measurements were conducted in the oscillatory mode, with a frequency of 1 Hz and a constant strain of 0.1%. CB samples were loaded onto the rheometer at 60 °C and allowed to equilibrate for 10 min to erase any crystal structures and/or shear history from sample loading. After the equilibrium step, the temperature was rapidly decreased from 60 °C to 22 °C at a rate of 10 °C/min. The temperature was then held constant at 22 °C for 120 min, collecting data every 10 s.

RheoRaman coupling

The Thermo Scientific™ HAAKE™ MARSXR RheoRaman System consists of the iXR Raman spectrometer and the HAAKE MARS 60 rheometer coupled together using the HAAKE RheoRaman module (Figure 1a). The iXR Raman spectrometer was free-space coupled to the rheometer with an optical train which used a series of mirrors to direct the incident laser into the RheoRaman module (Figure 1b). Within the module, a mirror directed the laser beam into a 20x objective, where the laser light was focused into the sample (perpendicularly to the flow or vorticity plane). Backscattered Raman light was collected using the same 20x objective and guided back to the spectrometer using the same optical train as the incident laser (eventually to the spectrograph inside the spectrometer; Figure 1b).

The sample was positioned between a sandblasted glass bottom plate and the serrated 35 mm plate rotor (the textured plates were used to avoid slip at the sample-plate interfaces). An electrical heating element within the RheoRaman module provided temperature control from below the sample, while an active electrical hood was used to provide temperature control from above (eliminating the potential for a temperature gradient within the sample). Cooling of the sample was supplied from a temperature-controlled water bath circulator.

Results and discussion

Raman spectroscopy: Cocoa butter crystallization

Raman spectra for the liquid phase CB melt and the crystalline solid CB in the 500-3100 cm^{-1} range are shown in Figure 2. Prominent Raman features were observed in both the C–H stretching region (2700-3050 cm^{-1}) and the fingerprint region (1000-1800 cm^{-1}). More specifically, the lower Raman shift features include: the carbonyl (C=O) stretching region (1700-1800 cm^{-1}), the olefinic (C=C) band at ~1655 cm^{-1}, the CH_3 and CH_2 deformations (~1460 and 1440 cm^{-1}, respectively), the CH_2 twisting region (1250-1300 cm^{-1}), and the C–C stretching region (1000-1200 cm^{-1}).

The C-H stretching regions for the melted and solidified CB specimens are highlighted in Figure 3. Two strong peaks were observed at ~2850 cm^{-1} and 2882 cm^{-1}, which are attributed to symmetric and asymmetric CH_2 stretching, respectively.[2] The symmetric vibrational modes at 2850 cm^{-1} were dominant in the liquid (melt) phase, while the asymmetric vibrations at 2882 cm^{-1} were dominant in the solid phase. Thus, the 2850 cm^{-1} and 2882 cm^{-1} bands are strong indicators of amorphous and crystalline content, respectively.[3] Subsequently, the I_{2882}/I_{2850} peak intensity ratio was used to dynamically track crystal formation during the *in situ* RheoRaman measurements.

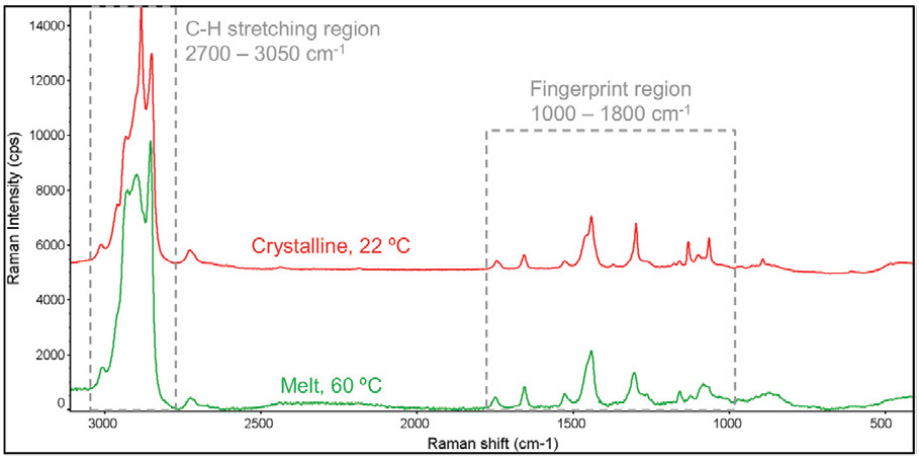

Figure 2. The full Raman spectra of melted and crystalline cocoa butter.

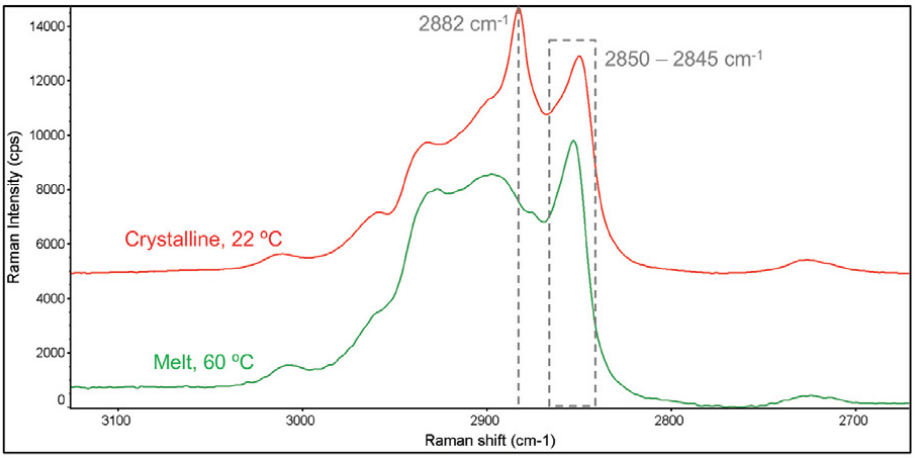

Figure 3. Raman spectra of the C-H stretching region (2700-3050 cm^{-1}) for melted and crystalline cocoa butter.

Although less intense than the C-H stretching region, approximately eight unique spectral features were identified in the fingerprint region (1000-1800 cm^{-1}; Figure 4). When comparing the CB melt state to the crystalline phase, the most significant changes were observed in the C–C stretching region (1000-1200 cm^{-1}). Two well-defined features emerged at 1130 cm^{-1} and 1063 cm^{-1} during the solidification process, which originate from the symmetric and asymmetric C-C stretching, respectively.[4,5] In the melt phase, all C-C stretching bands were relatively weak and broad due to the disordering effects of methyl gauche conformations.

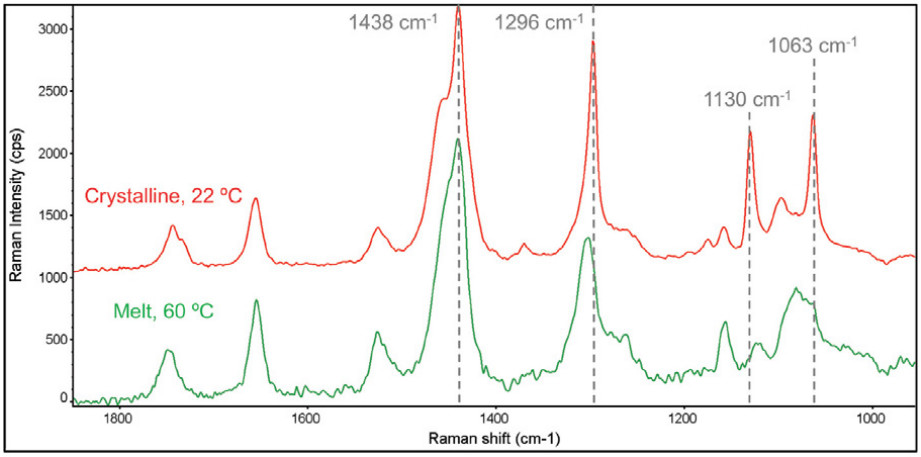

Figure 4. The 1000–1800 cm^{-1} Raman spectral range for melted and crystalline cocoa butter.

However, as the CB solidified, the backbone methyl groups were ordered into the trans-conformation, signified by the emergence of the peak at 1130 cm^{-1}. Therefore, in addition to the I_{2882}/I_{2850} peak intensity ratio, the I_{1130}/I_{2850} spectral marker was also used to track the crystalline-phase transition within CB via *in situ* rheoRaman measurements.

Simultaneous rheology and Raman spectroscopy (RheoRaman)

The melt-to-solid phase transition of cocoa butter was probed rheologically using small amplitude oscillatory shear measurements (Figure 5a), where the storage modulus G' and loss modulus G" were measured as a function of time at the isothermal temperature of 22 °C. G' and G" are measures of a material's elastic and viscous behavior, respectively. A liquid-like material will be more viscous than elastic (i.e., viscously dominated), and as a result, G" will be greater than G'. Conversely, a solid-like material will display more elastic than viscous behavior (i.e., elastically dominated), where G' will be greater than G". The overall magnitudes of G' and G", as well as their relative difference in magnitude, often reported as the ratio of G"/G', determines the general viscoelasticity and overall resistance to deformation for a given material.

The ratio of G"/G' (plotted on the right y-axis of Figure 5a) is commonly used to track viscoelasticity of a material:

$$\frac{G''}{G'} = \tan(\delta),$$

where δ is the phase angle defined as the shift or lag between the input strain and resultant stress sine waves (or vice versa) during an oscillatory shear measurement. The term "tan(δ)" is often referred to as the loss or damping factor. Values of tan(δ) less than unity indicate elastically dominant (solid-like) behavior, while values greater than unity indicate viscously dominant (liquid-like) behavior.

Unlike the individual moduli, tan(δ) can be used to quantify overall brittleness of a material and is commonly used to assess glass transition behavior. In general, as tan(δ) becomes smaller, the more G' deviates from G", and the more brittle (or glass-like) the material becomes.

During the initial portion of the isothermal hold at 22 °C from 0 to 5 min (immediately following the rapid decrease in temperature from 60 °C to 22 °C), both G' and G" increased as the CB transformed from a melted liquid to a soft semi-solid (Figure 5a). This initial increase in modulus is most likely due to a delay between the set temperature and the internal temperature of the loaded sample. Once the sample had reached thermal equilibrium and was at the isothermal set point of 22 °C, the moduli were relatively stable from 10 to 25 min. From 25 to 50 min, however, both G' and G" begin to gradually increase and then from 50 to 80 min, the moduli rapidly increased, where G' and G" increased by approximately 5 and 4 orders of magnitude, respectively. The exponential increase in the moduli indicates a solidification process, where the CB transformed from a pliable semi-solid to a more robust, hardened solid. At 80 min and beyond, growth in the elastic modulus slowed and eventually plateaued, showing no further significant change past 100 min. The viscous modulus, however, reached a slight plateau from 80 to 100 min and then proceeded to gradually decrease from 100 min and beyond.

During the increase in G' and G", a rapid decrease in the loss factor tan(δ) was observed from ~65 min and beyond (Figure 5a, right y-axis). The decrease in the loss factor indicates a deviation in overall magnitude between G' and G". As the CB hardened, the increase in G' exceeded the increase in G", triggering the decrease in tan(δ). At the end of the 120 min isothermal study, G' was more than a full order of magnitude greater than G" and the loss factor was approaching 0.01, indicating the CB had transitioned into a brittle glass-like solid.

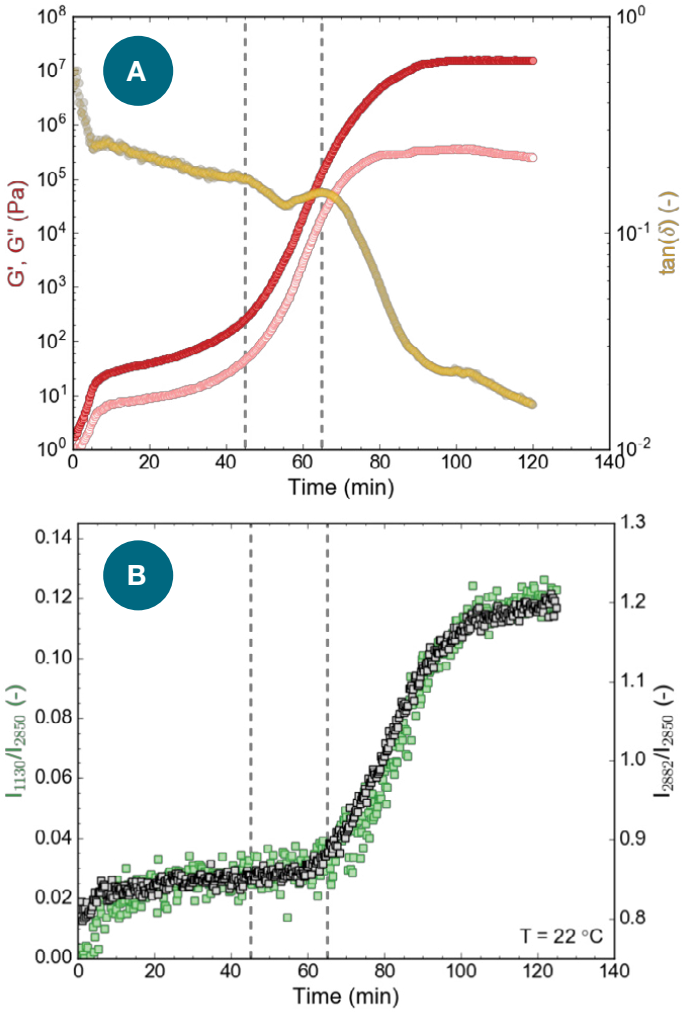

Figure 5. (a) Rheology: G' and G" (filled and open circles, respectively; plotted on the left y-axis) and tan(δ) (plotted on the right y-axis) and **(b)** Raman: the I_{1130}/I_{2850} (left y-axis, green) and I_{2882}/I_{2850} (right y-axis, black) peak intensity ratios for CB during isothermal crystallization at 22 °C. The vertical dashed line at 45 min indicates the increase of G' and G", while the dashed line at 65 min indicates the decrease in tan(δ) and increase in the Raman ratios.

The observed rheological behavior was further confirmed using simultaneous Raman spectroscopy (Figure 5b). Initially, both the I_{1130}/I_{2850} and I_{2882}/I_{2850} peak intensity ratios remained unchanged during the first ~65 min of the isothermal study. Then a sharp increase of the I_{1130}/I_{2850} and I_{2882}/I_{2850} ratios began at ~65 min, indicating the formation of crystal structures within the CB. As the CB further crystallized, both spectral markers continued to increase from 65 to 100 min. Beyond 100 min, the growth in both Raman features had subsided and the peak intensity ratios began to stabilize.

Overall, the rate of increase in the 1130 and 2882 cm^{-1} spectral ratios were similar to the rate of change for both G' and G" (i.e., they increased with similar slopes). However, there was a noticeable 15-20 min lag between the observed increase in G' and G" and the rise of the Raman intensity ratios. The sharp upturn in G' and G" indicates an increased resistance to deformation (i.e., a bulk hardening of the CB), signaling the start of the solidification process. The Raman spectral markers, on the other hand, are indicators of crystal formation. Thus, the time delay between the rheology and Raman profiles suggests that CB first hardens into an amorphous solid, followed by a transformation from an amorphous to a crystalline solid. This morphological transformation was signified by the subsequent increase in the Raman band intensities associated with crystal CB structures (the 1130 and 2882 cm^{-1} peaks). The temporal separation of the rheological and Raman spectral profiles indicates a clear distinction between bulk hardening of the CB and the formation of crystalline domains.

Interestingly, the increase in the Raman spectral features (I_{1130}/I_{2850} and I_{2882}/I_{2850}) directly correlated with the observed reduction in tan(δ) (Figure 5a and b). The loss factor is an indication of material brittleness and crystalline structures are commonly known to be brittle. Thus, it is reasonable that the formation of crystal domains at the molecular level (as indicated by Raman) coincides with the overall brittleness of the CB. As a result, the loss factor may be a more revealing indicator of bulk CB crystallization than G' and G" alone.

Conclusions

Simultaneous rheology and Raman spectroscopy measurements were used to examine the isothermal crystallization of cocoa butter. This multimodal analytical technique allowed the bulk mechanical properties of cocoa butter (G', G", and tan(δ)) to be directly correlated with conformational changes at the molecular level ($\nu_{as}(CH_2)$ mode at 2882 cm^{-1} and the ν_s(C-C) mode at 1130 cm^{-1}) in real-time. After rapid cooling (10 °C /min) and at an isothermal temperature of 22 °C, there was a noticeable time lag between the rheological response (G' and G") and the Raman spectral profiles. The observed time delay indicates that CB crystallized by first hardening into an amorphous solid, manifested by a sharp increase in G' and G" while the Raman features remained unchanged. The amorphous solid then underwent a morphological transition to form a crystalline solid, signified by the increase in Raman features associated with crystal CB structures (1130 and 2882 cm^{-1}). Without coupling these two separate analytical techniques, the observed amorphous-solid to crystalline-solid transformation would have been left undetected. Alone, each technique suggests a single-stage process, however, only when the two techniques are coupled is the multi-phase crystallization process revealed, further exemplifying the unique analytical capability unleashed by hyphenating rheology with *in situ* Raman spectroscopy. While this work focusses on the isothermal crystallization of CB, the underlying principles applied here should be applicable for a wide range of material processes including gelation, polymerization, curing behavior, as well as other shear-induced phenomena.

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References

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