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Guide to Skilled Food Rheology & Extrusion

Application Compendium

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Rheology & extrusion in the food industry

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

Food extrusion is an established and highly versatile technique for producing food, feed, nutritional additives and flavors. Extruders with varying dies are used to design and shape foods with high starch content such as pasta, cereals, snacks, analogue meat products, and pet food, and to determine their final texture. In addition, extrusion enables a cost-effective, continuous means of production with precise control for maintaining high product quality.

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

Read our blog post:
Food Rheology – You Just Can't Cook Without It!
September 22, 2016

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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.

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

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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:

	Hand held viscometer	Bench top spindle viscometer	Entry level rheometer	Research grade rheometer
	Thermo Scientific™ HAAKE™ Viscotester™ 1 plus and 2 plus	Thermo Scientific™ HAAKE™ Viscotester™ C, D and E	Thermo Scientific™ HAAKE™ Viscotester™ iQ series	Thermo Scientific™ HAAKE™ MARS™ rheometers
Hand held operation/ battery operation	✓			
Single speed viscosity measurements	✓	✓		
Test according to ISO 2555		✓		
Standalone instrument	✓	✓	✓	
Portable instrument	✓	✓	✓	
Software control		(✓)*	✓	✓
Absolute viscosity measurements			✓	✓
Tixotropic behavior			✓	✓
Yield stress determination			✓	✓
Viscoelastic properties			✓	✓
Integrated temperature control			✓	✓
Low torque, low rotational speed performance				✓
Axial ramps for tack and squeeze testing				✓
Application related measuring cells			(✓)**	✓
Combined analytical methods				✓

*Thermo Scientific™ HAAKE™ RheoWin™ Data evaluation software available for HAAKE Viscotester D, HAAKE RheoWin measuring and evaluation software available for HAAKE Viscotester E.

**Dedicated HAAKE Viscotester iQ configurations for pressure cells and for building material cell.

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.

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

Francesca De Vito, Fabian Meyer and Fritz Soergel, Thermo Fisher Scientific, Material Characterization, Karlsruhe, Germany

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, 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].
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.

Fig. 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)

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].

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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].

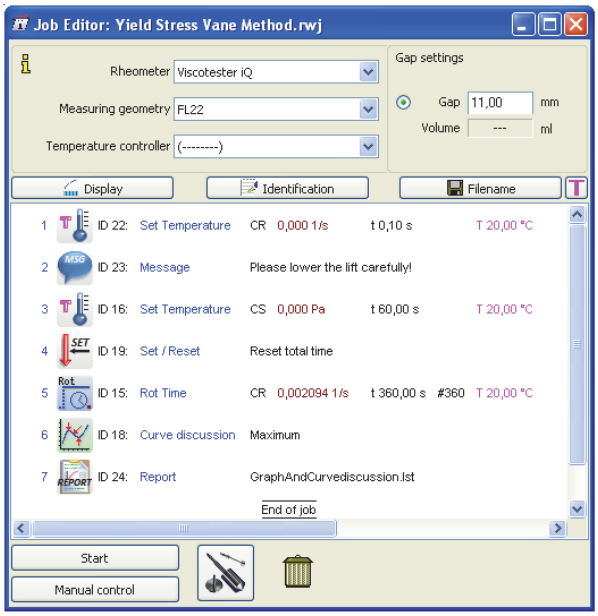

Fig. 2: HAAKE RheoWin measuring job for measurement and automated evaluation and documentation

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 (Fig. 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 (Fig. 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].

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 Fig. 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.

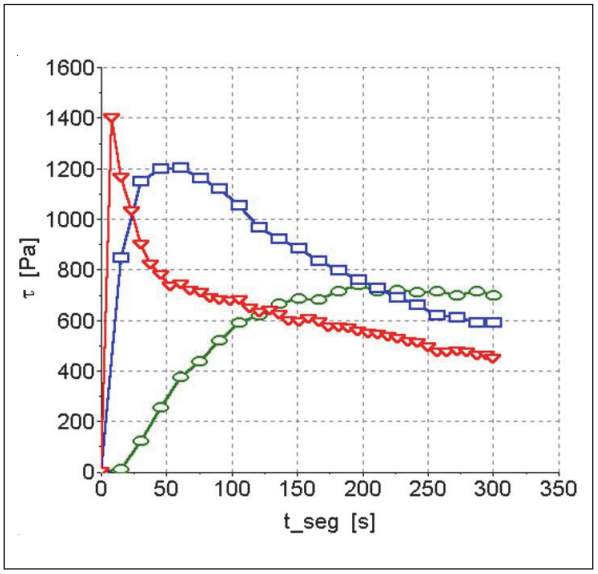

Fig. 3: Schematic comparison of vane rotor yield stress measurements with higher (red triangles), medium (blue rectangles) and lower rotational speed (green circles)

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]. Fig. 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 Tab. 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.

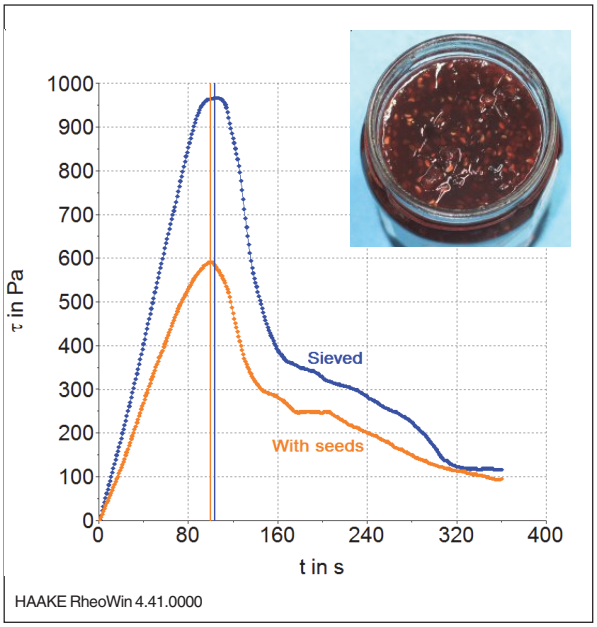

Fig. 4: Comparison of FL 22 vane rotor yield stress measurements with 0.05 rpm for a sieved raspberry jam (blue curve) and raspberry jam with seeds (orange curve, inserted image)

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

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

Fig. 5 and Tab. 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.

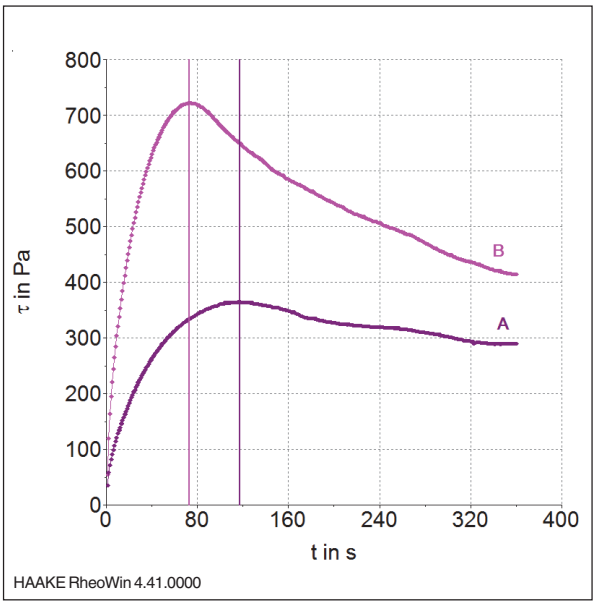

Fig. 5: FL 22 vane rotor yield stress measurements with 0.05 rpm for chocolate hazelnut spread products A and B

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

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

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 Fig. 6 and Tab. 3. Compared to the average value, the yield stress values differ by less than ± 1.5 % and the time values are nearly identical.

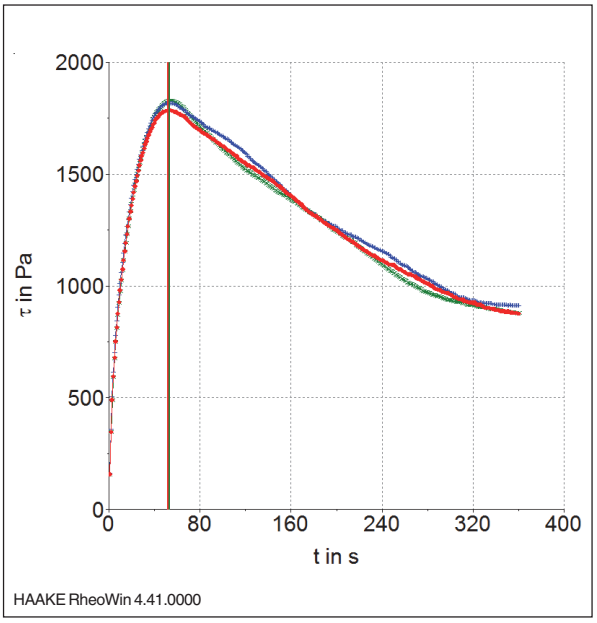

Fig. 6: Three independently conducted vane rotor (FL16) yield stress measurements in CR mode with 0.05 rpm for creamy peanut butter

Peanut butter	τ_0 in Pa	t in s
Measurement 1 (blue)	1818	52.1
Measurement 2 (red)	1785	52.1
Measurement 3 (green)	1829	53.2

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

Conclusion

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

Francesca De Vito, Fabian Meyer and Fritz Soergel, Thermo Fisher Scientific, Material Characterization, Karlsruhe, Germany

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, evaluation 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 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. Moreover, fiber-rich ingredients like pectin can be used for fat replacement and for texturing [1].
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 determination 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].

Fig. 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)

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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 (Fig. 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 (Fig. 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).

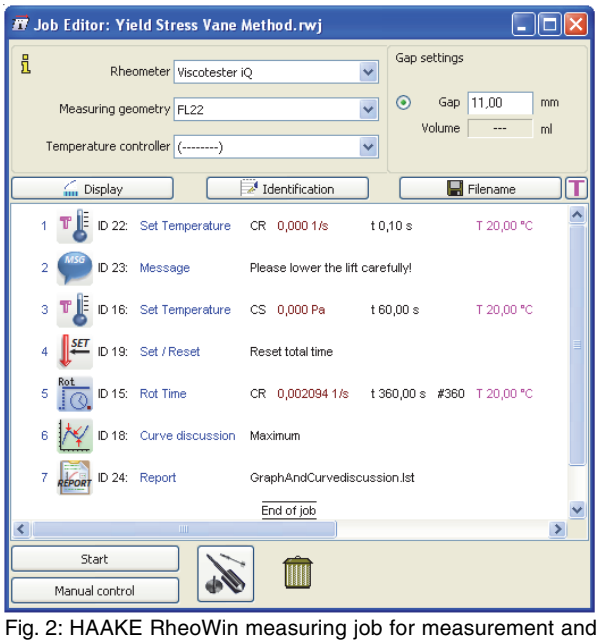

Fig. 2: HAAKE RheoWin measuring job for measurement and automated evaluation and documentation

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.

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].
In order to determine one rotational speed, which fits all samples of a class, different rotational speeds need to be tested (Fig. 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.

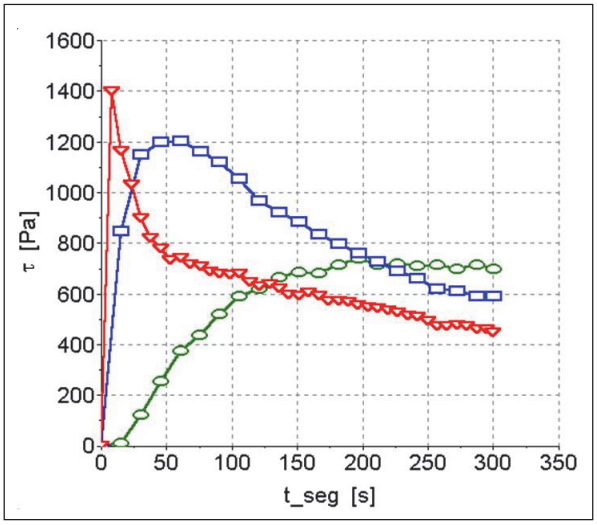

Fig. 3: Schematic comparison of vane rotor yield stress measurements with higher (red triangles), medium (blue rectangles) and lower rotational speed (green circles)

Results and discussion

The effect of the composition on the yield stress 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 Fig. 4 and Table 1. With these both rotational speeds all sample were measured (Figs. 5, 6 and Table 1).

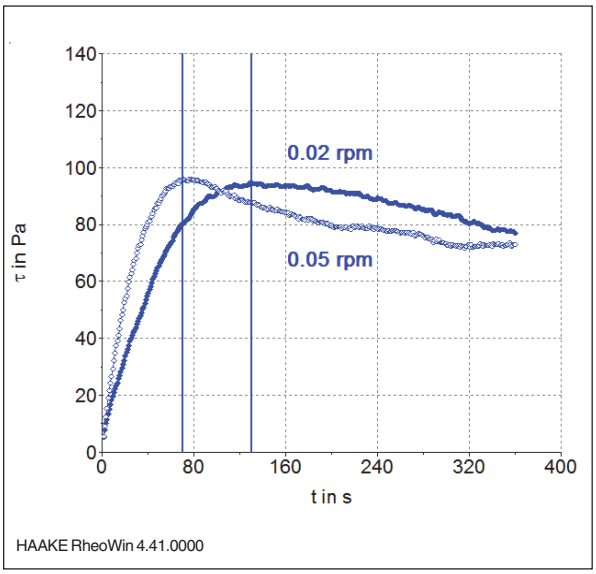

Fig. 4: Comparison of vane rotor yield stress measurements with 0.05 rpm (open circles) and 0.02 rpm (filled circles) with the mayonnaise with 22.5 % fat content

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 (Figs. 4 - 6).
Fig. 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).

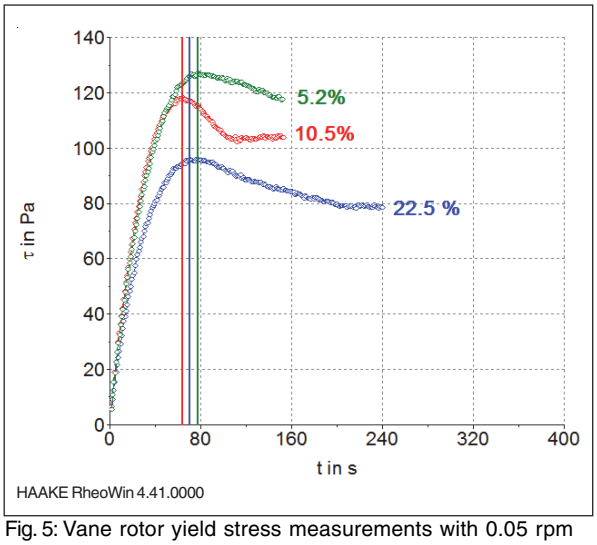

Fig. 5: Vane rotor yield stress measurements with 0.05 rpm for mayonnaises with three different fat contents

The rheological data collected at 0.02 rpm (Fig. 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.

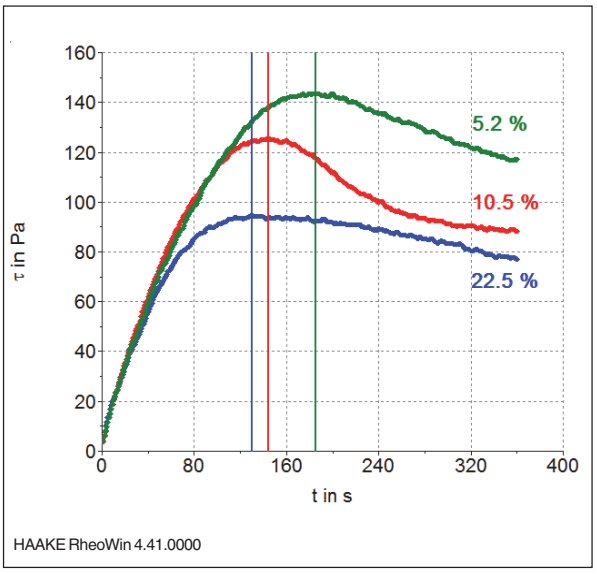

Fig. 6: Vane rotor yield stress measurements with 0.02 rpm for mayonnaises with three different fat contents

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.

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

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

Conclusion

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 mea-surement 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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Spreadability of Cream Cheese - Influence of Temperature and Fat Content

Jan Philip Plog, Thermo Fisher Scientific, Material Characterization, Karlsruhe, Germany

Key words
Rheology, Yield Stress, Dairy Products, Cream Cheese

Introduction

Soft, spreadable foods such as cream cheese are viscoplastic materials. Consumer acceptance of these foods depends on their textural characteristics such as spreadability – a measure of how easily and uniformly they can be deformed and spread at end-use temperatures. It also determines if a given substrate like soft white bread will be able to withstand the spreading force.

The rheological properties correlating with spreadability of food products have been studied by a variety of methods. Breidinger and Steffe [1] for instance used yield stress and yield strain data from vane measurements to construct texture maps of spreadable foods. As semi-liquid and soft foods like spreadable foods are often difficult to work with when using conventional plate/plate or concentric cylinder geometries on rotational rheometers because of the possible wall slip and excessive sample disruption during loading into narrow gaps vane geometries are recommended here.

When the vane rotor is fully immersed in the sample, the yield stress itself can then be calculated according to Boger [2]:

$$\sigma = \frac{T}{K} \qquad [a]$$

With T being the Torque and K the vane parameter that depends on the height (H) and the diameter (D) of the paddle according to:

$$K = \frac{\pi \cdot D^3}{2}\left[\frac{H}{D} + \frac{1}{3}\right] \qquad [b]$$

Experimental Results and Discussion

As described earlier it is recommendable to test dairy products with vane rotors. Figure 1 shows the new Thermo Scientific™ HAAKE™ Viscotester™ iQ rheometer with vane configuration.

Two cream cheese products with varying fat content (10% versus 50%) have been studied at room temperature (25 °C) as well as at refrigerator temperature (8 °C). After the vane rotor has been fully immersed into the sample we apply a constant rotational speed Ω = 0.05 rpm. We then monitor the shear stress as a func-tion of measuring time. After an initial purely elastic res-ponse in the sample the structure collapses, the shear stress again

Fig. 1: HAAKE Viscotester iQ rheometer

decreases. The maximum value in shear stress then corresponds with the yield stress. Figure 2 shows the results for both products at RT.

As can be seen in Figure 2 the yield stress for the high fat content product is 1000 Pa versus 200 Pa for the low fat product. In comparison, Figure 3 shows the test results for the same products at 8 °C, simulating that the cream cheese was just taken out of the refrigerator.

As can be seen in Figure 3 the yield stresses for the cream cheese products rise considerably at 8 °C to 1500 Pa for the high fat product and 370 Pa respectively for the low fat product. Let us now consider that we want to spread these products on soft white bread. Specific soft white breads can have a shear Modulus G of as low as 1200 Pa.

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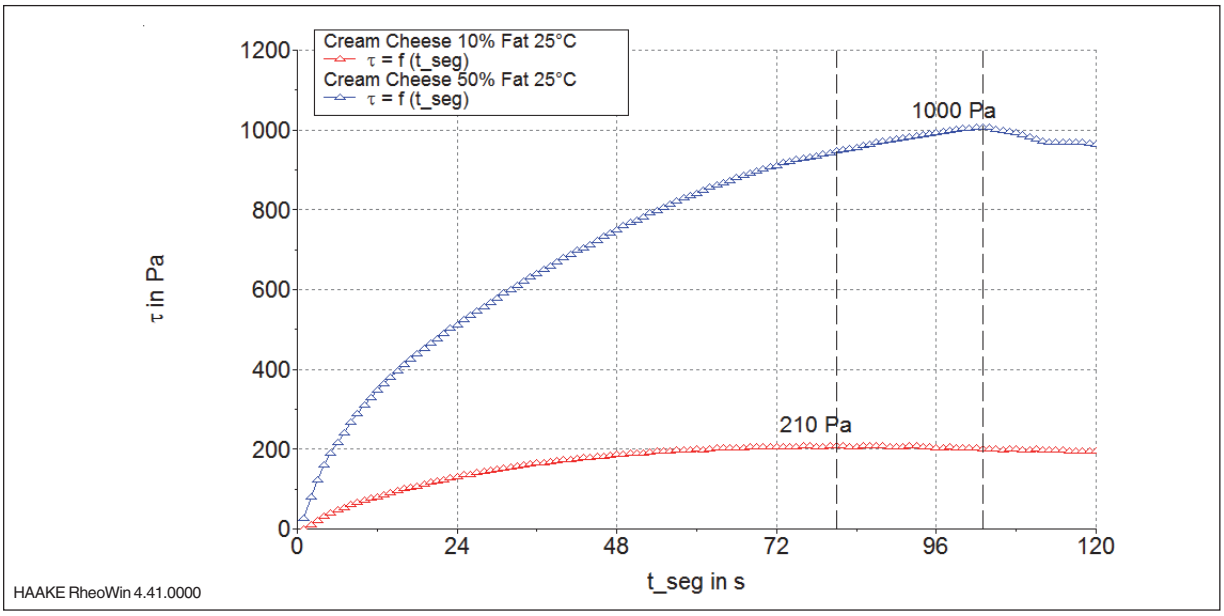

Fig. 2: Shear Stress versus Time for the two different cream cheese products at 25 °C

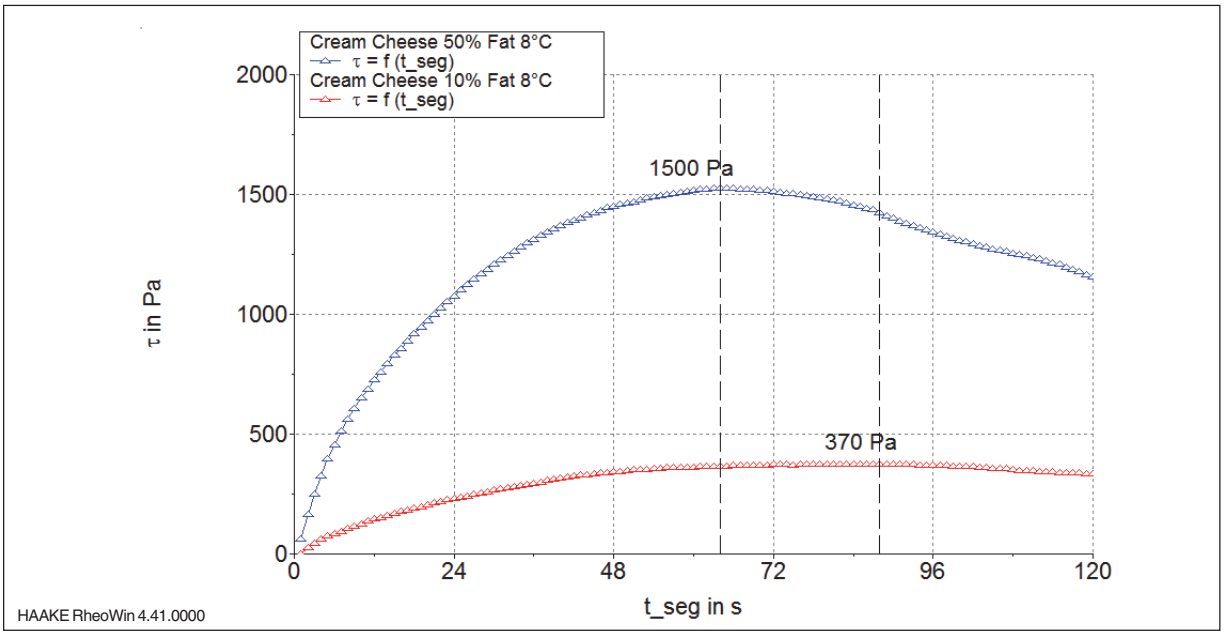

Fig. 3: Shear Stress versus Time for the two different cream cheese products at 8 °C

From the results above we can thus see that problems will arise when trying to spread the refrigerated high fat content product on soft white bread as yield stress of cream cheese > Shear Modulus of bread.

Conclusion

The vane method on the Thermo Scientific HAAKE Viscotester iQ rheometer is a quick, simple and accurate approach to understand spreadability and customer acceptance of spreadable foods like cream cheese.

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Flow Behaviour of Chocolate Melts- Working according to ICA Standards

Klaus Oldörp, Thermo Fisher Scientific, Material Characterization, Karlsruhe, Germany

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 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 Viscotester iQ in the Peltier temperature control unit.

The HAAKE RheoWin 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™ job. The shear rate profile is shown in Figure 2.

The HAAKE RheoWin 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.

Fig. 1: The HAAKE Viscotester iQ rheometer

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 inter-polation calculation in HAAKE RheoWin software will do the job.

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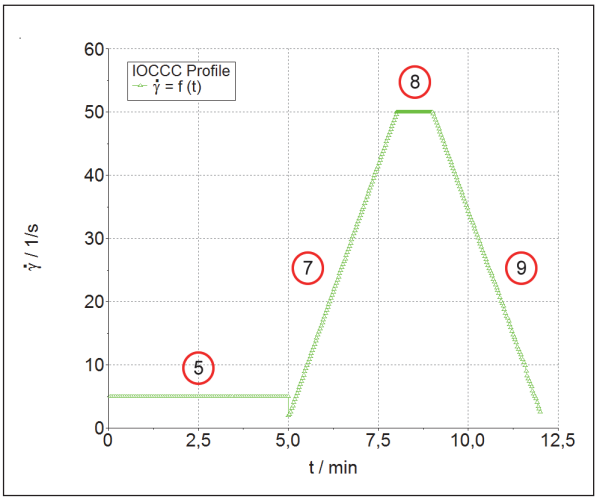

Fig. 2: Shear rate profile applied according to ICA method 46. The numbers 5 to 9 represent the job element number of the HAAKE RheoWin job shown in Figure 3.

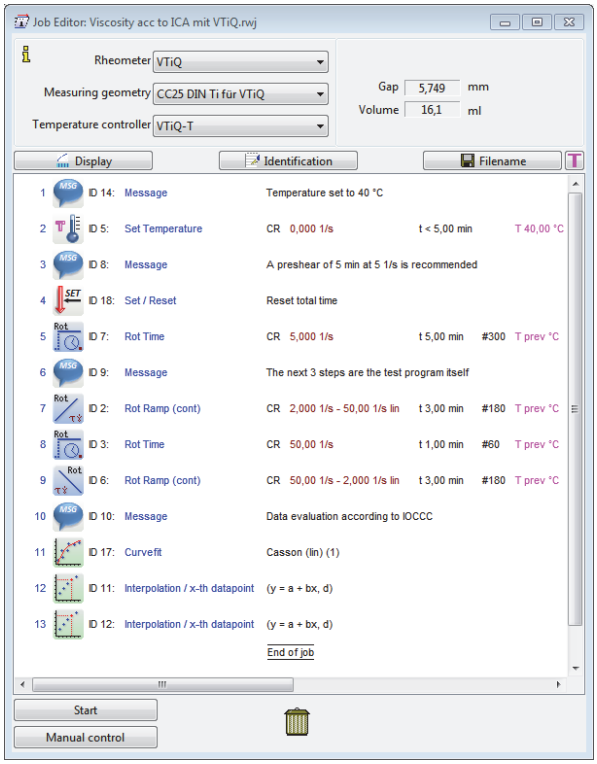

Fig. 3: The HAAKE RheoWin Job composed to run the test according to ICA method 46. The test consists of sample conditioning (elements 1-4), the rheological test (elements 5-9) and data evaluation (elements 10-13).

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.

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.

	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

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

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.

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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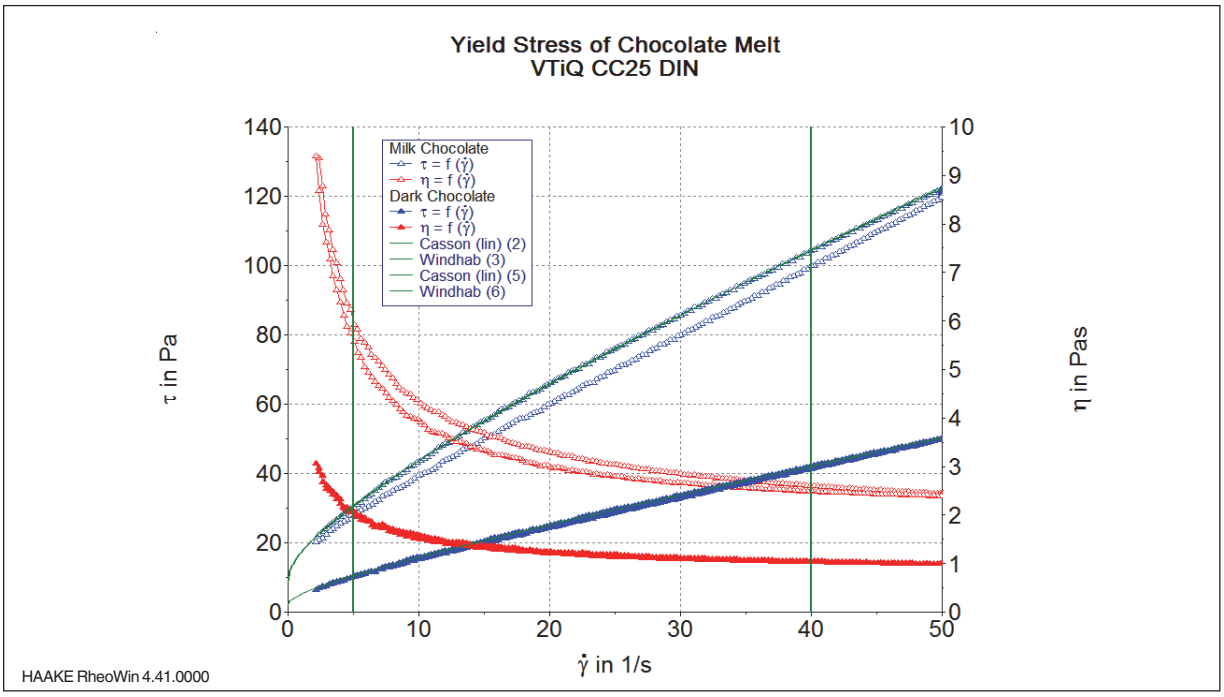

Fig. 4: Test results for a milk chocolate (open symbols) and a dark chocolate (filled symbols). The milk chocolate shows the higher viscosity values (red curves), stronger thixotropy and a higher yield stress. The extrapolation of the flow curves (blue curves) to 0 s^{-1} has been calculated according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

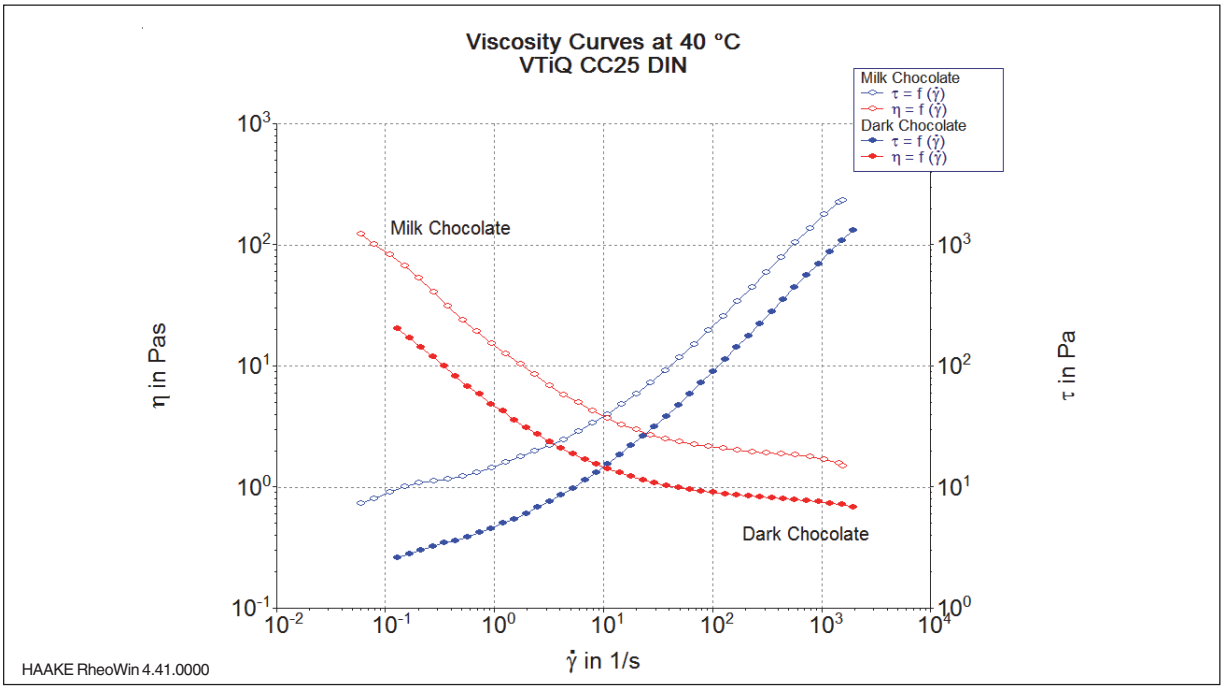

Fig. 5: Viscosity curves of milk chocolate and dark chocolate at 40 °C. The milk chocolate shows a significantly higher viscosity.

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Applied Food Rheology
Using Fast Speed Control and Axial Measurements

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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.

In this article some special capabilities of the Thermo Scientific™ HAAKE™ MARS™ 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 deformation

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].

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 (Fig. 1) and e.g. a star-shaped vane rotor, the HAAKE MARS can measure in a variety of containers [2]. Due to its unique spacious design it allows measurements in containers up to 10 l buckets.

Fig. 1: The HAAKE MARS rheometer with individual container holder.

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 Fig. 2.

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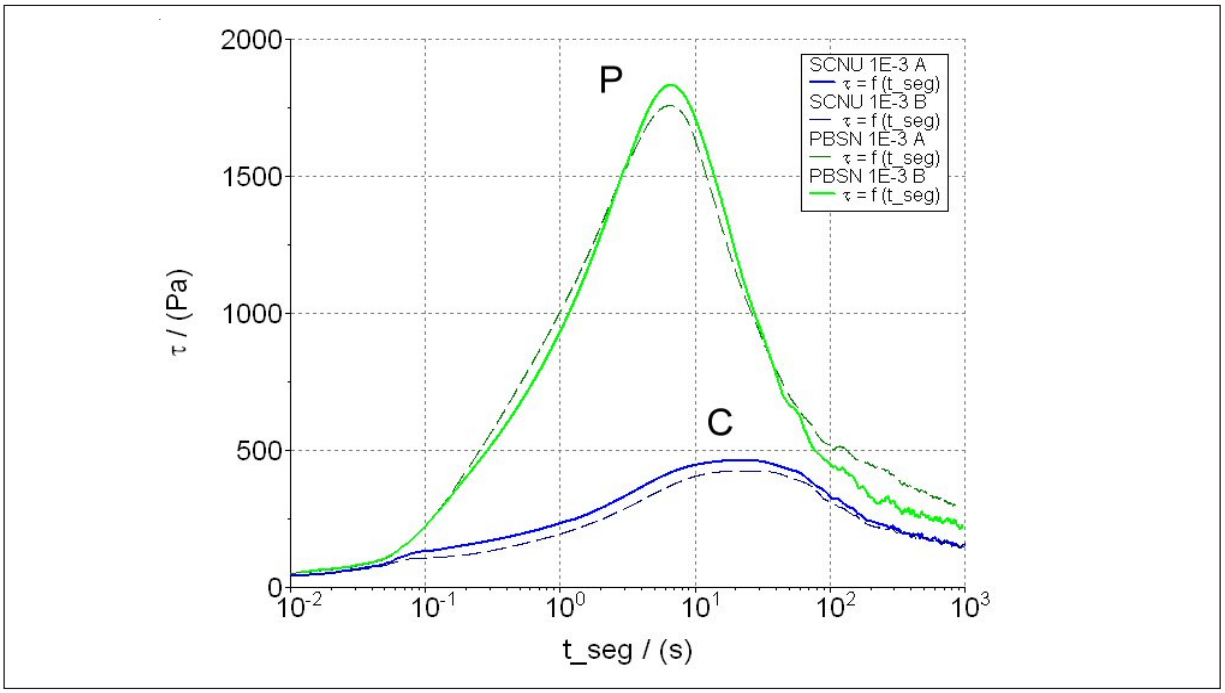

Fig. 2: Yield Stress of a peanut butter (P) and a chocolate spread (C) measured with a vane rotor in their original glasses using a shear rate of 0.001 1/s.

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. Fig. 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.

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

Axial measurements

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 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.

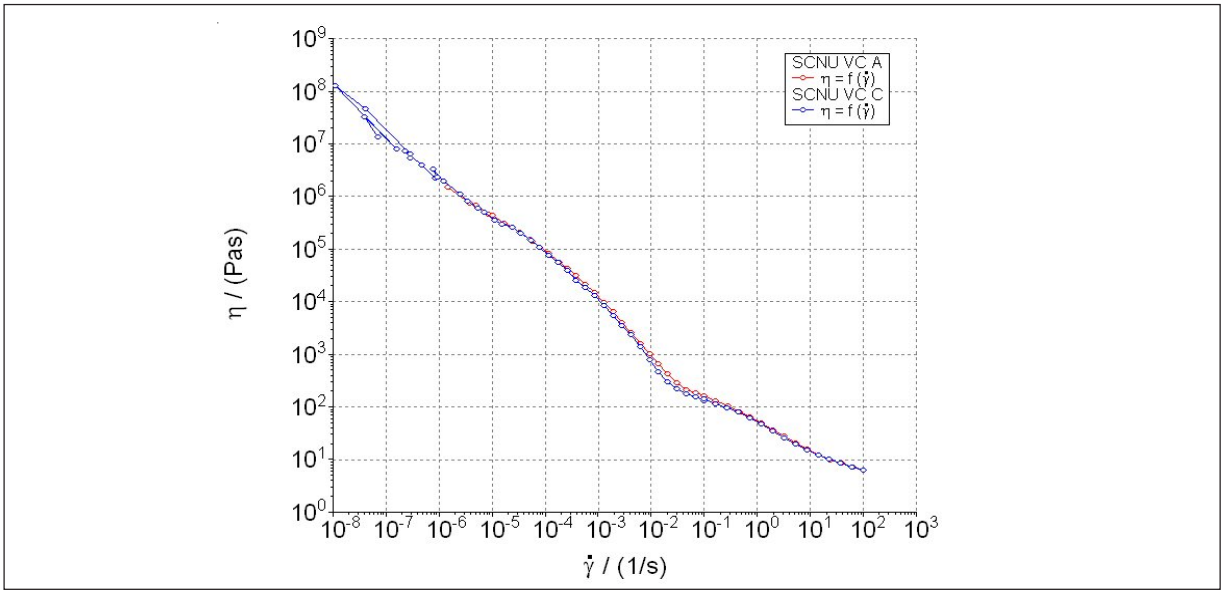

Fig. 3: Viscosity curve of a chocolate spread. 2 measurements in one run over 10 decades of shear rate in CR mode with a cone 35 mm/1 ° at 35 °C.

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 (Fig. 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 Fig. 5. Piston speed was 1.3 mm/min.

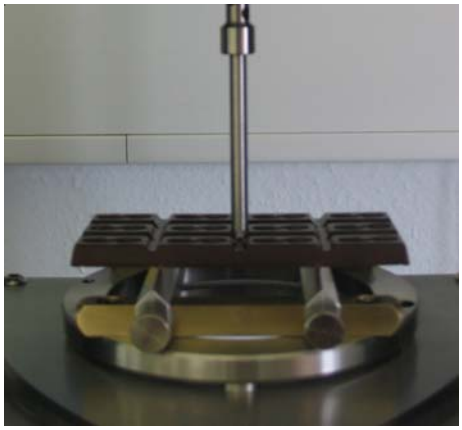

Fig. 4: Measuring the breaking resistance of chocholate with the HAAKE MARS using a two-blade-fixture and a 6 mm piston.

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 Fig. 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 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.

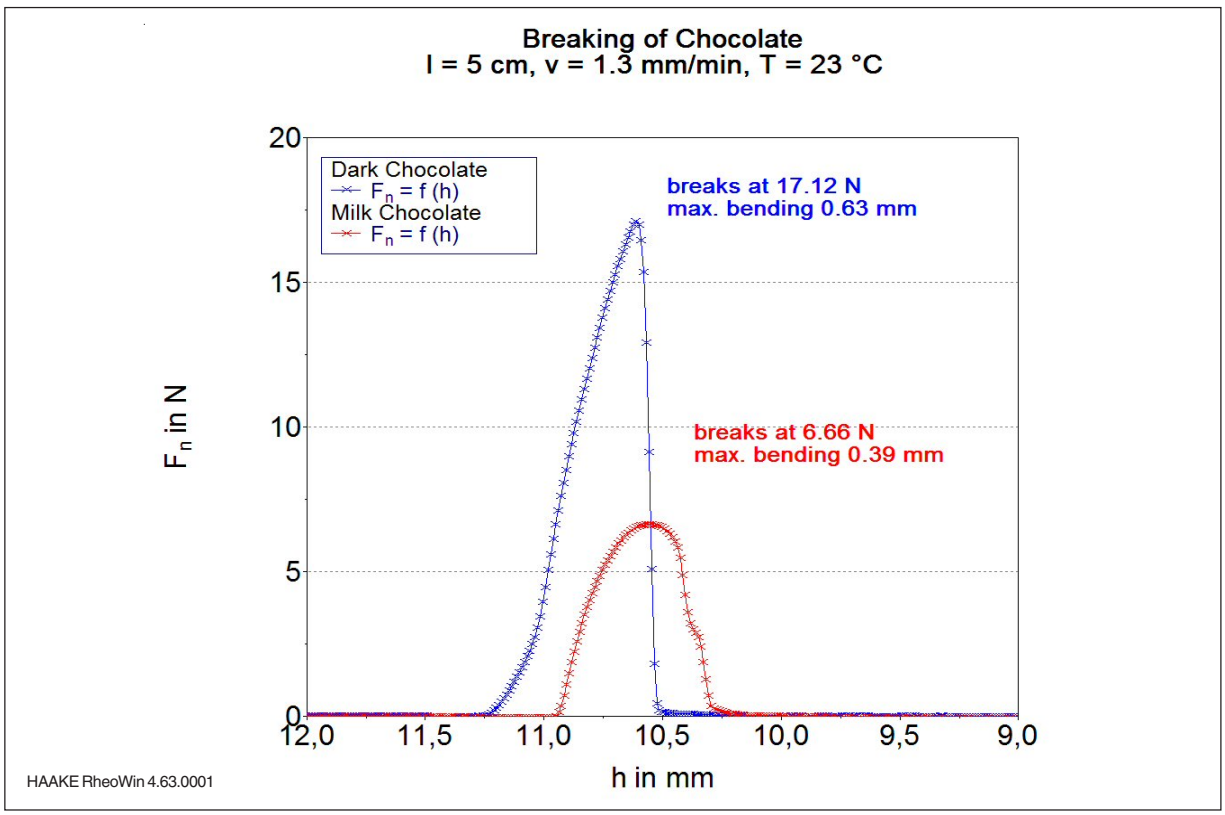

Fig. 5: Axial force as a function of piston position for dark chocolate (higher peak) and milk chocolate (smaller peak).

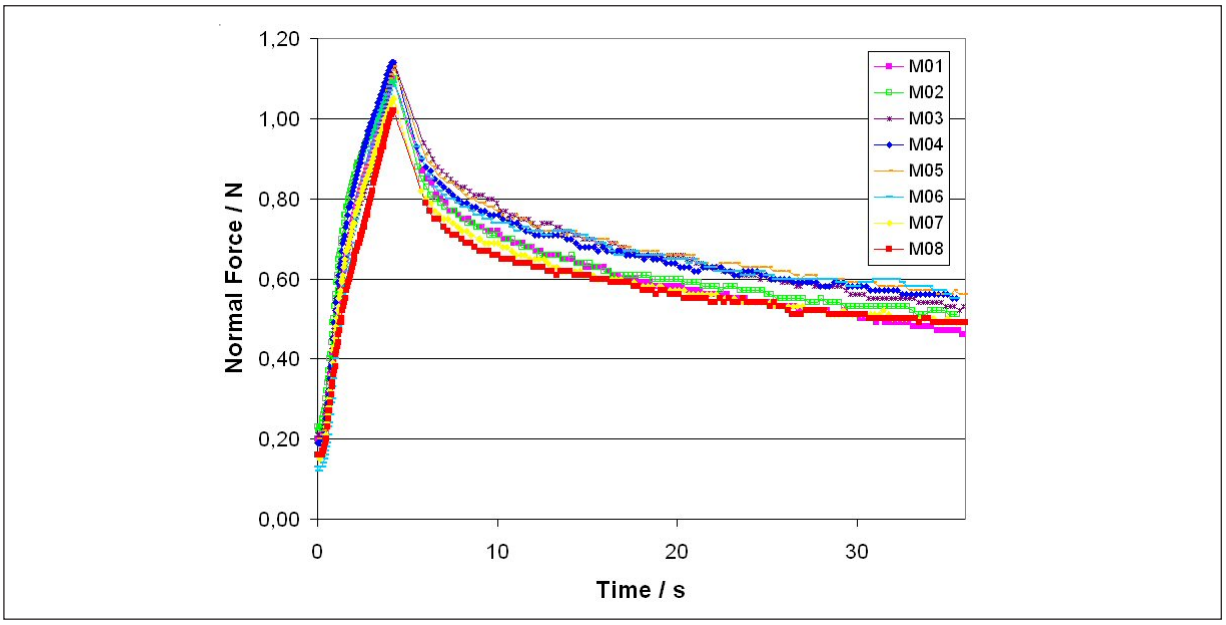

Fig. 6: Penetration test on margarine repeated 8 times. First the probe moves into the sample, then the relaxation of the normal force is measured.

Acknowledgment

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

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A Rheometer with Bite – Marshmallows in the Rheometer

Klaus Oldörp, Thermo Fisher Scientific, Material Characterization, Karlsruhe, Germany

Introduction

We use many of our senses to experience our food. For a food product to be popular and therefore successful, it must meet many requirements: it has to look appealing, smell good, have a pleasant texture in the mouth - or "mouth feel" - and of course taste good. As soon as a food product is perceived as being "unpleasant" during even one of these subjective "tests," it can quickly lead to consumer rejection.

When regarding natural products like bread, meat or cheese, certain fluctuating or individual "bad" qualities are sometimes accepted, such as the smell of certain cheeses. However for industrially-produced foodstuffs, and particularly when dealing with treats such as sweets, all of the above criteria have to be met to gain consumer acceptance. No matter how good something looks or tastes, the "mouth feeling," i.e. the texture in the mouth, has to be right, otherwise the pudding will remain on the shelf in the refrigerated section and the cookies will never be purchased.

Marshmallows are another example of food where not only the flavour and sweetness, but also the "bite", is critical for enjoyment. Using a rheometer or a testing machine such as a texture analyzer, this consistency or texture can be described using objective parameters and thus making quality control or targeted improvement possible. A modern rheometer allows various options for characterising marshmallows and similar products. It also allows the viscosities of the starting materials to be measured, and the finished product can be characterized in an oscillatory test.

By combining a sensitive normal force sensor with a high-precision lift drive, the Thermo Scientific™ HAAKE™ MARS™ provides the additional option of stressing samples axially, i.e. by exerting a vertical force on them from above at a maximum of 50 N (which corresponds to a weight of 5 kg) by either pressing on or pulling the marshmallow sample. In this type of situation, the Thermo Scientific HAAKE MARS measures the axial force and position of the measurement geometry precisely while the sample is being squeezed, or the penetration of a probe into the sample is tracked.

Fig. 1: Samples M (left) and S (right) before measurement.

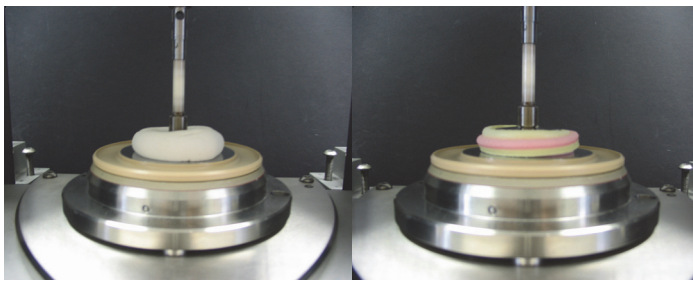

Fig. 2: Samples M (left) and S (right) during measurement.

Measurements and Results

Two products were compared during the experiment. Marshmallows (M) of about 30 mm in height and a sugar foam product (S) of about 10 mm in height. In order to compare the absolute values discs were cut from product S matching the diameter of the marshmallows and were stacked three high (Fig. 1). A 35 mm-diameter plate as used for rotational and oscillation measurements was run down to a height of 7 mm (Fig. 2) at a speed of 1 mm, and then run back up to 30 mm at 1 mm/s. This process was repeated on the samples five times in a row to simulate chewing in the mouth.

When compressing first sample M, the force increased to about 45 N before dropping again. During the following cycles the force only reached about 40 N but remained nearly constant through each cycle. A force of 50 N is required to compress sample S; the sample is thus felt to be somewhat harder. The maximum applied force decreases throughout subsequent cycles, dropping from 44 N during the second cycle to 40 N during the fifth cycle.

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The change in sample height shows clear differences between the two products. After the first compression, sample M relaxes to about 80% of its original height, while sample S only recovered to 59%. The two samples behave comparably when considering the rest of the measurement. Sample M's height is reduced by another 1.4 percentage points; that of sample S by a further 1.8 percentage points.

Interestingly, the slightly softer sample M is also more elastic and maintains nearly constant properties after the first compression. This marshmallow has a softer mouth feel and keeps its volume longer when chewed, so it probably feels like "more" in the mouth. Sample S is slightly harder and springs back much less after the first compression. In addition, sample S remained stuck on the upper geometry, which is reflected in the negative axial forces during the expansion. Sample S is thus the tackier sample, which may be one reason for the greater loss in height. Compared with the marshmallow, the sugar foam product has "more bite", that is, a little more force is required to eat it. Afterward, the product is stickier and its volume decreases faster during chewing.

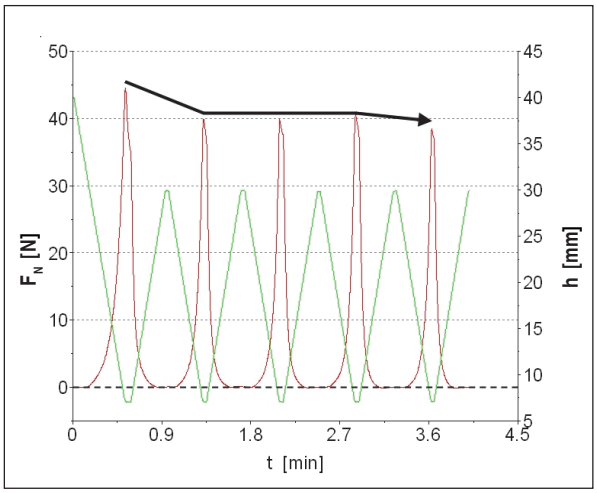

Fig. 3: History of axial force exerted on sample M when exposed to multiple compression to 7 mm. On the initial loading the force rises to approximately 45 N. After that, the maximum force remains more or less constant at about 40 N. When the sample is allowed to decompress, the axial force returns to 0 N.

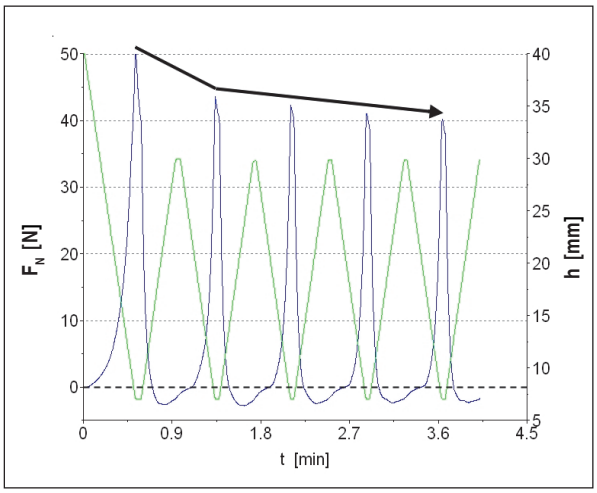

Fig. 4: History of axial force on sample S at multiple compressing to 7 mm. On the initial loading the force rises to approximately 50 N. After that, the maximum force of 44 N decreases in stages to 40 N. After the sample relaxed the axial force returns to negative values, i.e. the outer side of the sample becomes sticky under pressure.

Summary

In addition to the classical measuring modes rotation and oscillation, modern rheometers with a lift drive with precise position control and a sensitive normal force sensor such as the Thermo Scientific HAAKE MARS rheometer offer the option of squeezing and pulling samples in the axial direction. Tests were carried out on marshmallow samples which allow conclusions to be drawn about the texture of these sweets during chewing. Both the force for compressing the sample and its elastic recovery were determined.
With this application, range of measurement capabilities which can be used on the HAAKE MARS has been expanded, providing users with a cost-effective solution for characterizing its samples with an additional method. How soft or elastic the perfect marshmallow should be and whether a certain stickiness is part of its enjoyment when eating it is up to the consumer to decide. Using a modern rheometer and a simple method can always ensure that the desired quality is always consistently produced.

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Breaking Strength of Chocolate

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Hans-Michael Petri,Thermo Fisher Scientific, Material Characterization, S. Paulo, Brazil

Chocolate appeals to all of our senses. We see the colour and the glossy surface of the bar, we smell the elusive flavours, we weigh it in our hands and feel how it melts, we hear it break and sense its resistance, and savour the taste. With so much "sensuality", it is easy to forget how quickly the pleasure can be destroyed, if even just one of these properties is not as we expect it or are accustomed to.

Even unconsciously, the breaking behaviour of chocolate plays an important role in influencing the consumer's impression. Chocolate experts can even evaluate the quality of a sample by breaking off a piece.

Rheology plays an important role in several steps of chocolate production. The liquid chocolate formulation and the fats used can be characterized by their viscosities, yield stresses and solidification behaviours. These parameters are important for quality control and processing, and can be determined using rotational or oscillation measurements.

Sensory properties as experienced during the melting process, or "mouth feeling", can be described with the viscosity curves and the yield stress. However, these rheological parameters contain no information about the breaking strength of the final chocolate bar – and therefore a new method and new equipment are necessary to assess the resistance to break.

The Thermo Scientific™ HAAKE™ MARS™ rheometer, manufactured by Thermo Fisher, features a highly sensitive normal force sensor and a very precise lift motor which allows the customer to apply controlled axial forces to the sample, pushing or pulling it, and to analyze its axial deformation.

For example, with a new measuring geometry (Fig.3), chocolate bars can be positioned on the rheometer and submitted to an increasing axial force until they break. This measuring geometry [1] consists of two parallel support bars which can be mounted onto a base plate in a variable distance from 1 to 7 cm. The sample lies on these bars and a user-defined piston can be lowered onto the sample, making possible bending, breaking and penetration tests.

Fig. 1: HAAKE MARS Rheometer.

The bending geometry was used to investigate the breaking behaviour of small bars of milk and dark chocolate. The distance of the support bars was fixed at 5 cm. The piston was cylindrical with a diameter of 6 mm. The piston was lowered at a rate of 1.3 mm/min.

The comparison of the results in Fig. 2 shows a much greater deformation prior to breakage for the dark chocolate – it is more elastic than the milk chocolate. The normal force increases quickly and then falls to zero almost immediately (blue curve). This behaviour is typical for hard and brittle samples.

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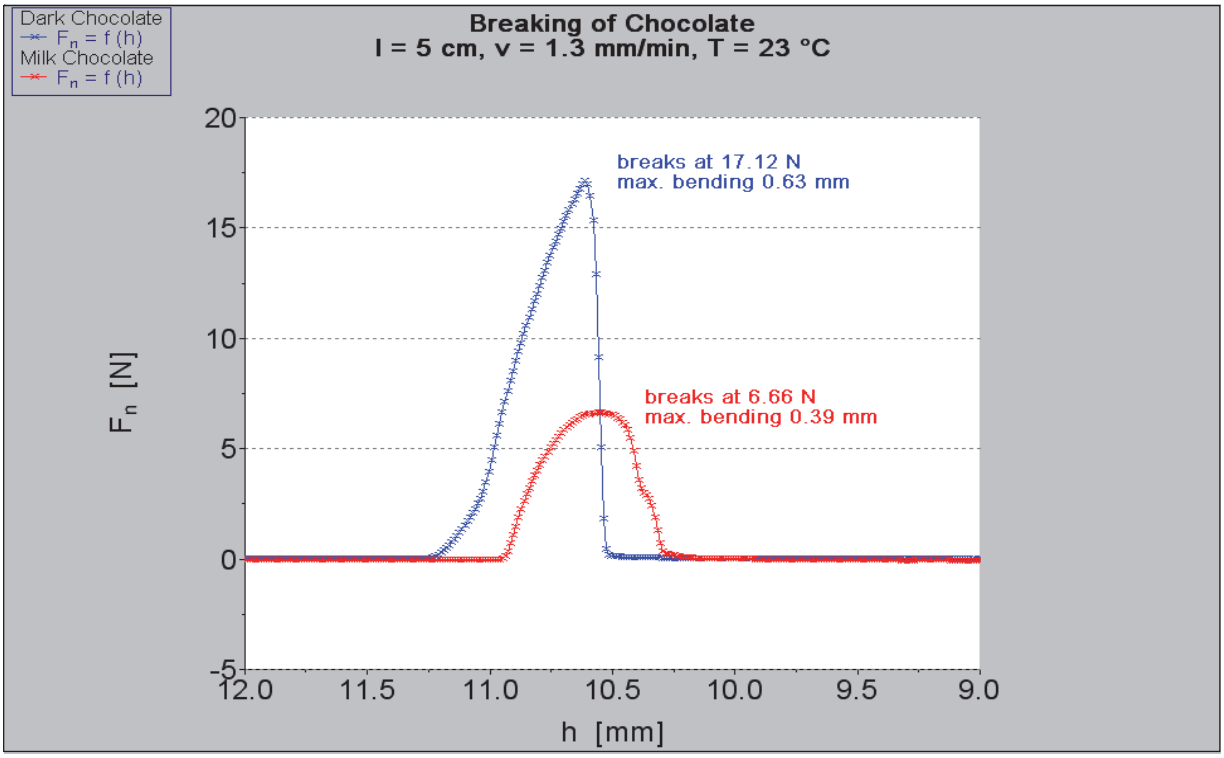

Fig. 2: Breakage curves of half bitter (blue) and a milk (red) chocolate bars.

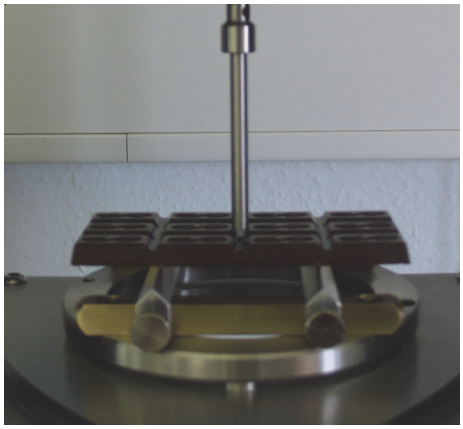

Fig. 3: Breaking test on a chocolate bar on the HAAKE MARS using the new bending geometry.

The milk chocolate is much "softer", which can be seen in the moderate increase in the normal force (red curve). Only a third of the normal force required for the dark chocolate is needed to break the milk chocolate bar. The bar breaks in two steps: first it cracks to about the middle of its thickness before breaking completely.

Using the bending geometry for the HAAKE MARS rheometer, it was possible to characterize two types of chocolate with respect to their breaking behaviour. The axial deformation, the necessary normal force for breakage and the shape of the force/deformation curves can be used as evaluation parameters. With the same method, different formulations of a certain chocolate type may be analyzed for an efficient product development, or the quality of different production lots can be controlled.
Unlike subjective sensory tests which depend on the test person, the described method provides objective and reproducible results, independent of the analyst.
This accessory significantly broadens the application range of the HAAKE MARS rheometer. The determination of additional relevant product properties can be performed on the same instrument used for the analysis of flow and viscoelastic behaviour of the samples - which is much more cost efficient than the purchase of a second specific instrument. The geometry for bending and breaking tests is just one example of the wide range of application-specific accessories available for the HAAKE MARS.

Reference

[1] Thermo Scientific Product Information P014 "Sample fixturefor banding and breaking tests for Thermo Scientific rheometer" Cornelia Küchenmeister and Klaus Oldörp

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What Happens When Rheological Properties Change? Looking into Rheological Properties with Simultaneous Collection of Microscopic Images

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Abstract

To gain information about the reasons for certain changes in rheological properties, a special module for the Thermo Scientific™ HAAKE™ MARS™ 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.

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 (Fig. 2). This RheoScope module can be mounted into the HAAKE MARS like any other temperature control unit.

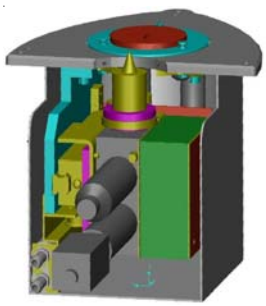

Fig. 2: Inside the RheoScope module optical and mechanical components are arranged to give a high quality, fully software controlled microscope in addition to the temperature control unit.

Fig. 1: HAAKE MARS rheometer with RheoScope module and upper electrical temperature module TM-EL-H.

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. 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 Fig. 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.

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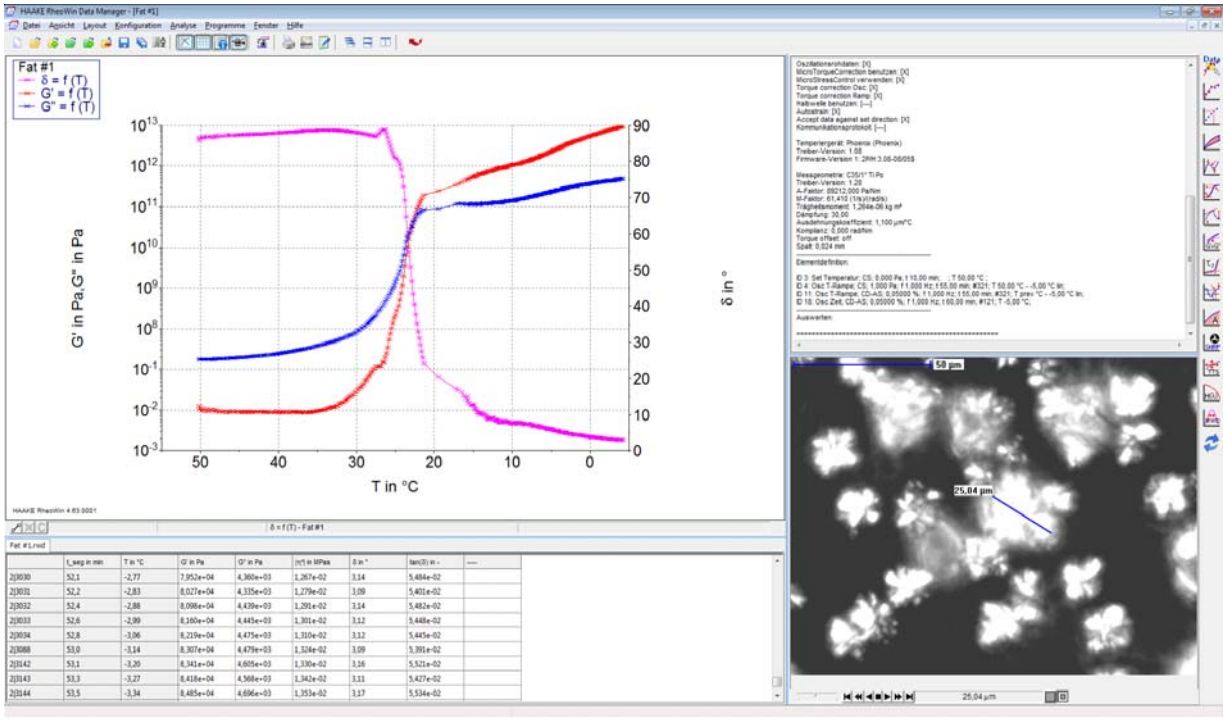

Fig. 3: Rheological data and pictures are handled by the HAAKE RheoWin software and are linked to each other, i.e. for every data point the picture, which has been taken simultaneously can be displayed. Simple evaluation of the pictures can be directly done in HAAKE RheoWin.

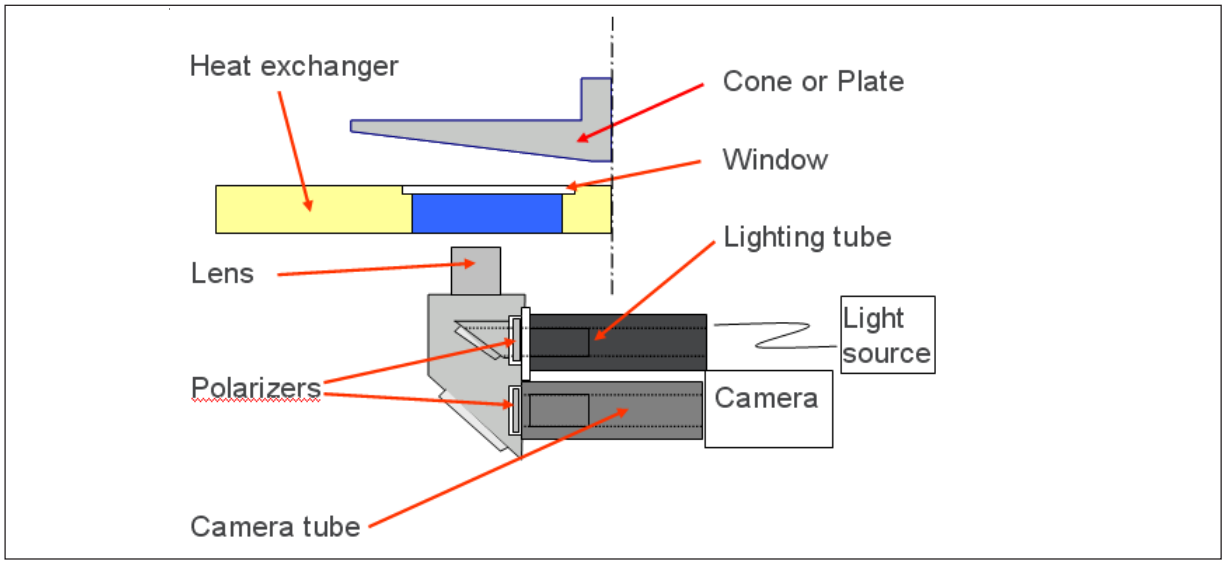

Fig. 4: Pictures are taken through a small window in the heat exchanger guaranteeing good temperature distribution.

Apart from the data collection and data evaluation (Fig. 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.

Fig. 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.

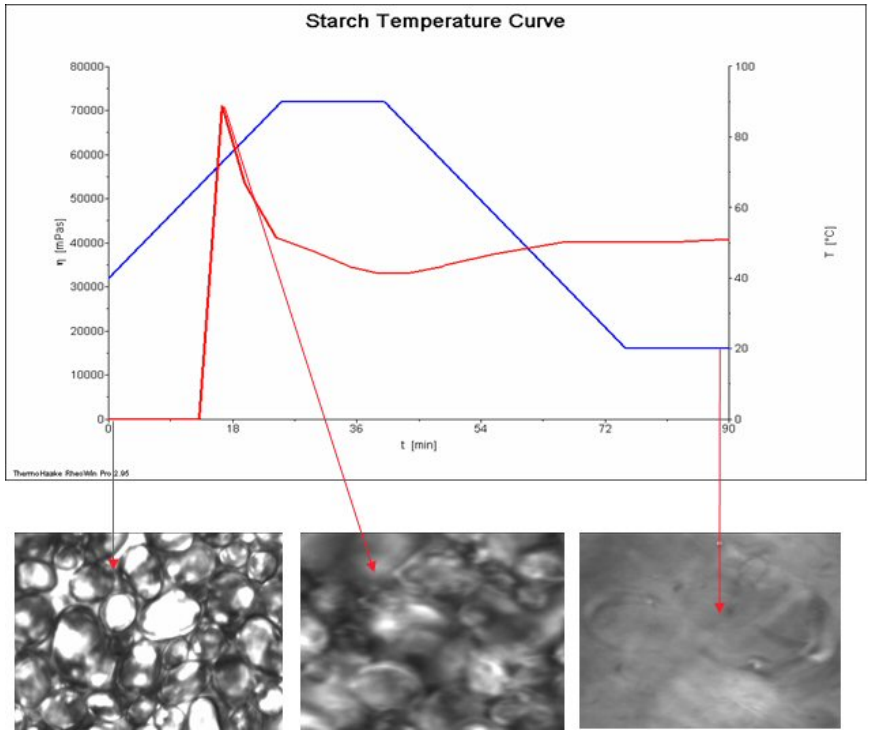

Fig. 5: Native potato starch (5 % in water): Photos show the starch crystals in the beginning, the swollen crystals at peak viscosity and the inhomogeneous solution after cooling down.

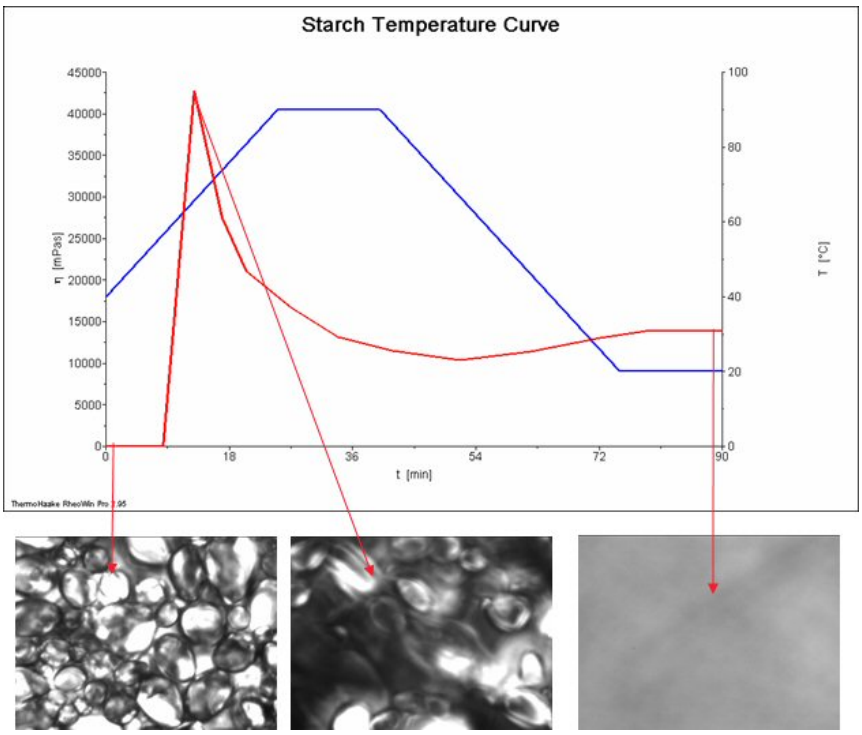

Fig. 6: Native potato starch (5 % in water): Photos show the starch crystals in the beginning, the swollen crystals at peak viscosity and the inhomogeneous solution after cooling down.

Running the same cooking program with hydroxypropylated potato starch shows the viscosity maximum shifted to a lower temperature indicating a better water solubility (Fig. 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 Fig. 6).

Wheat starch in water shows a completely different behaviour. The viscosity shows a second local maximum before 90 °C are reached (Fig. 7). The microscopic pictures show that already the starch particles at the beginning of the test look totally different (photo #1 in Fig. 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 Fig. 7.

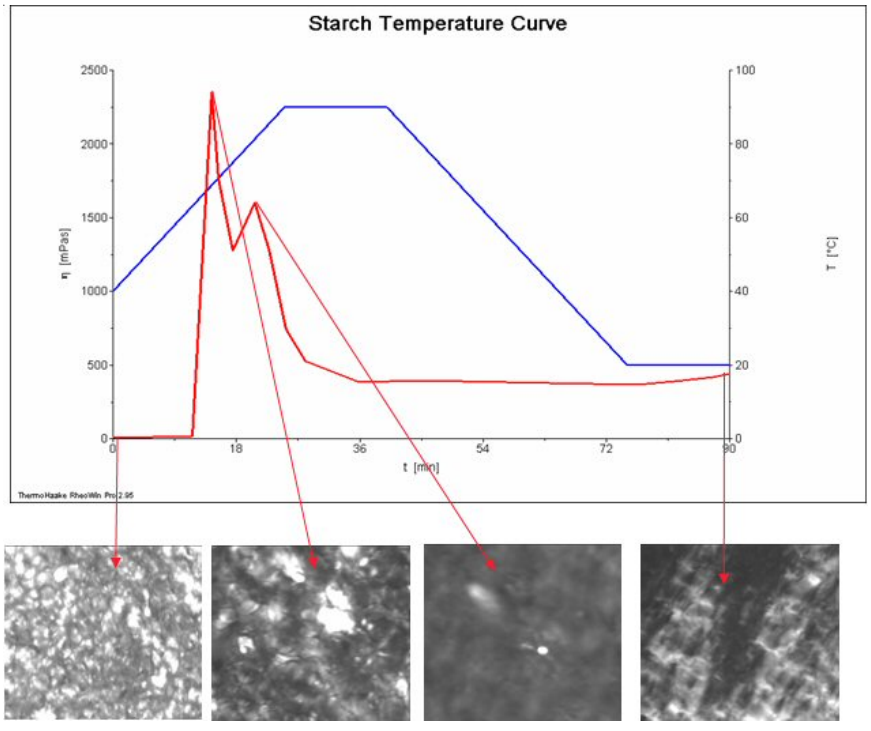

Fig. 7: Wheat starch (5% in water): Photos show the starch crystals in the beginning, the swollen crystals at peak viscosity, an almost homogenous solution at the second local maximum and the inhomogeneous solution after cooling down.

Using the HAAKE MARS 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 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 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 δ. At the same time the growth of different crystals can be observed.

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

Fat #2 also crystallizes in 2 steps but compared to fat #1 the crystallization happens very fast (Fig. 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 (Fig. 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.

Conclusions

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 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 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.

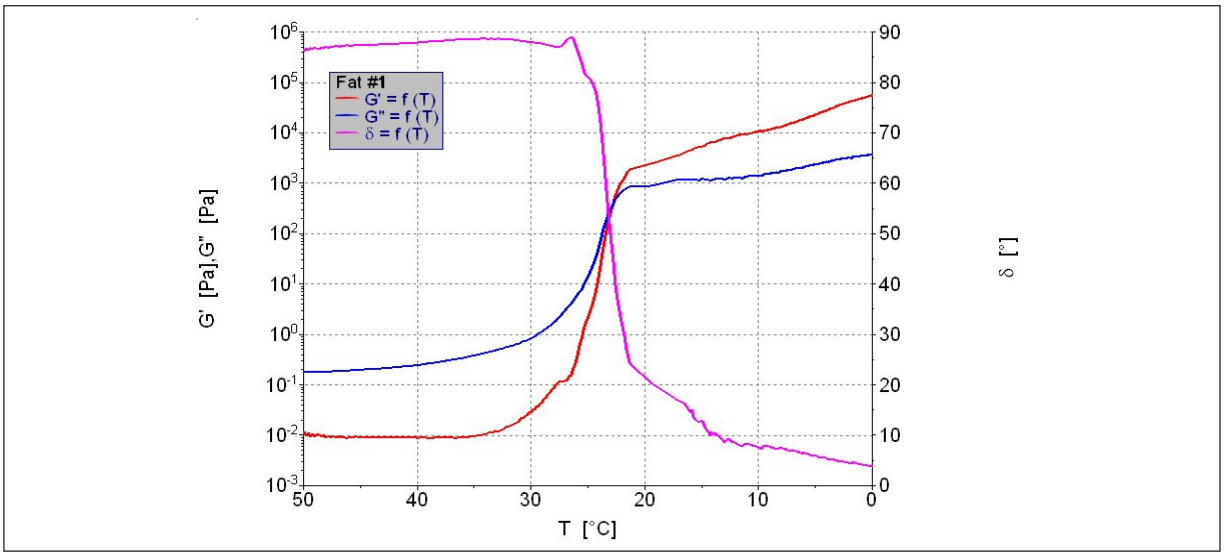

Fig. 8: Crystallization of fat #1 in 2 slower steps.

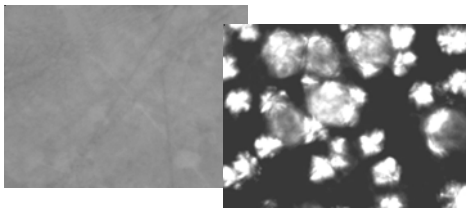

Fig. 9: Microscopic pictures of the homogeneous molten fat #1 (left) and the same are after crystallization has begun (right).

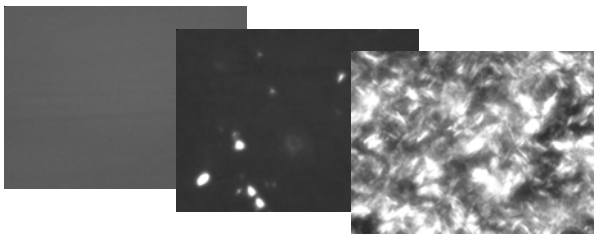

Fig. 10: Microscopic pictures of the homogeneous melt of fat #2 (left), a first crystal phase formed below 32 °C (middle) and a second crystal phase formed below 20 °C (right).

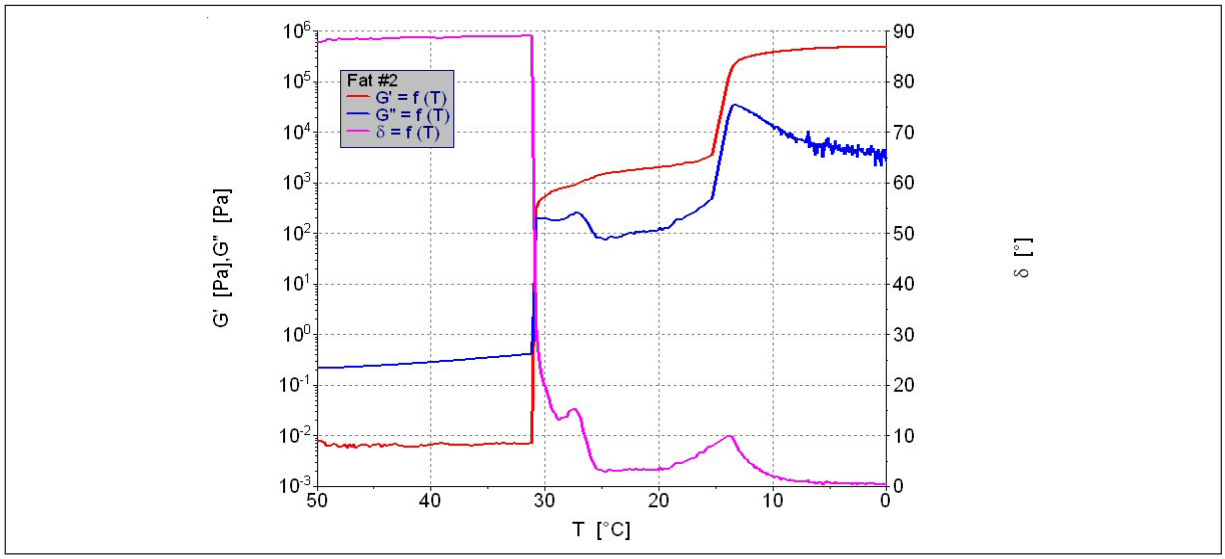

Fig. 11: Crystallization of fat #2 in 2 fast steps.

Acknowledgment

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

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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

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.

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).

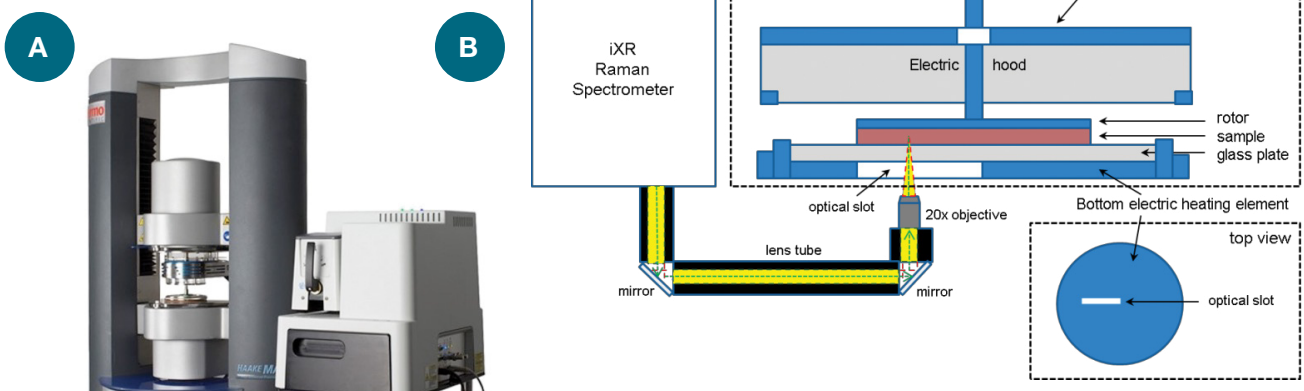


Figure 1. (a) The Thermo Scientific™ HAAKE™ MARSXR RheoRaman System. **(b)** Schematic diagram of the MARSXR RheoRaman system (showing side and top views of the rheometer sample stage). The iXR Raman spectrometer is free-space coupled to the MARS rheometer using lens tubes and mirrors that direct light 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.

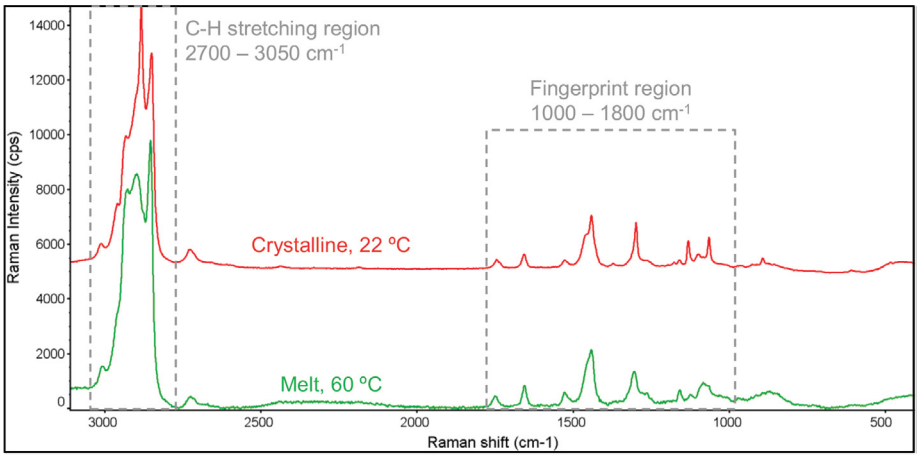
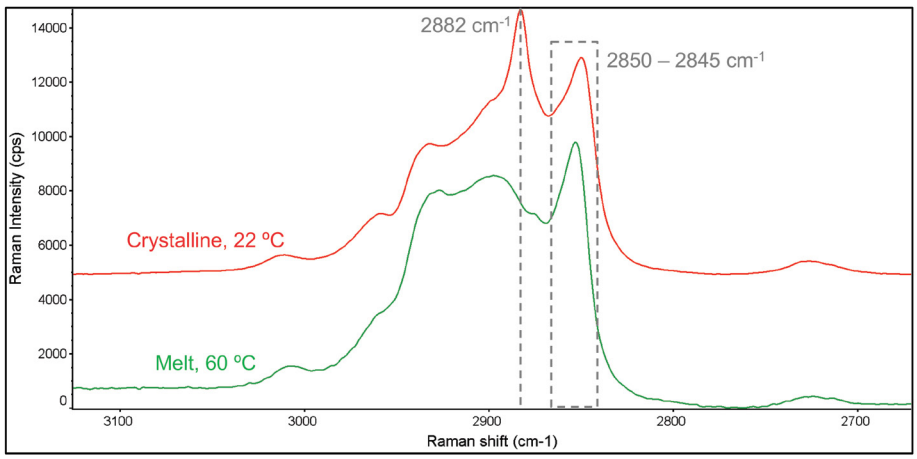


Figure 2. The full Raman spectra of melted and crystalline cocoa butter.

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.

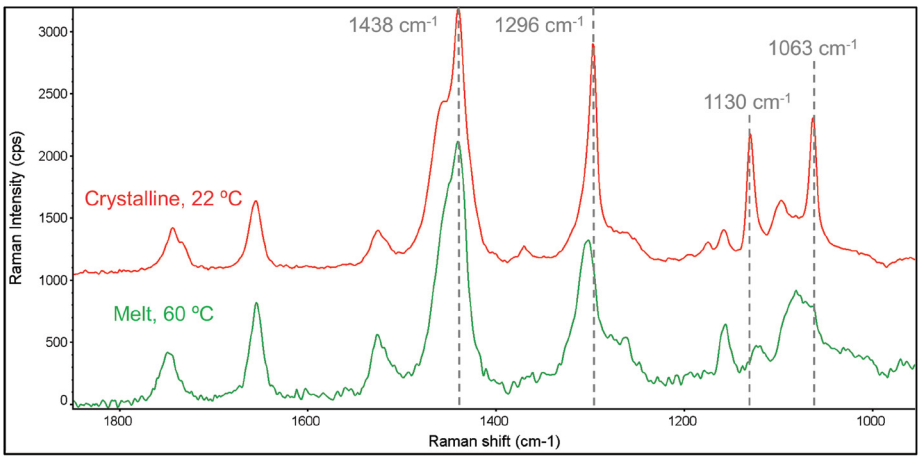


Figure 4. The 1000–1800 cm^{-1} Raman spectral range for melted and crystalline cocoa butter.

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.

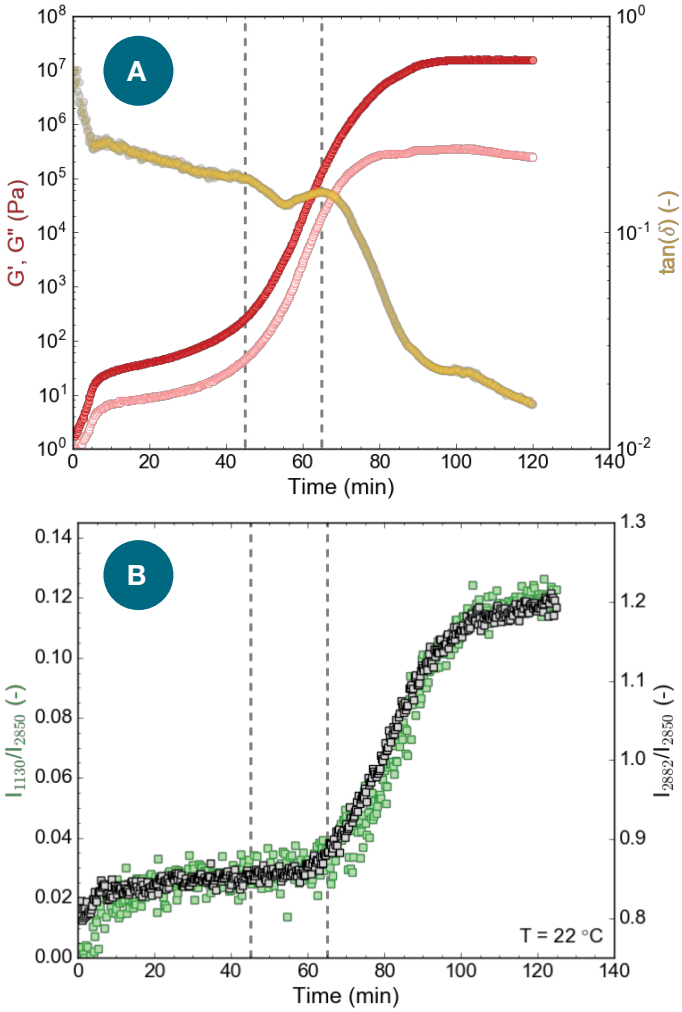


Figure 5. (a) Rheology: G' and G" (filled and open circles, respectively; plotted on the left y-axis) and tan(δ) (plotted on the right y-axis) and **(b)** Raman: the I_{1130}/I_{2850} (left y-axis, green) and I_{2882}/I_{2850} (right y-axis, black) peak intensity ratios for CB during isothermal crystallization 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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Food design by extrusion

In today's food production and processing, extrusion has established itself as a technology that is routinely used to create high-quality, tasty, attractive in price and, above all, safe products for humans and pets alike.

Starting materials for food extrusion processes are usually starch- or protein-based materials. But secondary sources, challenging to handle with other processes, also make a good ingredient for a high-value extruded food product. Among such materials are dark flours, wheat bran or broken rice.

As the processing range within an extruder is very wide, and the die and screw geometry is exchangeable, there is almost an infinite number of products (in shape and texture) that can be designed using modern twin-screw equipment. A subsequent treatment of the extrudates such as drying, roasting or coating helps to give polish to the end product.

Typical extrudated products used for human nutrition are*:

Type of product	Example
Directly expanded	Breakfast cereal, corn curls
Unexpanded	Pasta
Half-products	Potato pellets
Co-extruded	Fruit-based cereals, Jelly-filled cores
Modified	Starches, fat mimics
Texturized	Meat analogs
Candy	Licorice, chewing gum

*Karwe, Mukund V. (2008). "Food extrusion". Food Engineering 3. Oxford Eolss Publishers Co Ltd. ISBN 978-1-84826-946-0.

The raw materials entering the extrusion process are typically powders, e.g., derived from starch or a protein source. Depending on the desired end product properties, other powder materials, e.g., vitamins or colorants, are added as a dry-mix. Inside the extruder, liquids or semi-solids (such as syrups, fats, oils, water) are added and mixed together.

The shear energy and elevated temperature of the extruder barrel can induce a cooking process that can be precisely controlled at required levels. As pressure also builds up inside the instrument, the required processing time is comparatively small, so sensitive products are less prone to denaturation. This process is usually referred to as high-temperature-short-time (HTST) or extrusion cooking and performs the desired protein denaturation or starch gelatinization.

Being pressed through the extruder die at the end of the process, the material usually puffs out and changes its texture. Then it is cut into desired length and subsequently treated as required for the desired final result. Modern benchtop twin-screw extruders can help to mimic the full potential of extrusion-based food processing at a laboratory scale.

For more information about our extruders, visit thermofisher.com/foodextrusion or thermofisher.com/extruders for small and pilot scale extruders.

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APPLICATION NOTE

No. LR-81

Small scale extrusion solution for meat analogues

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Executive summary

Reducing the carbon footprint by producing "meat-like" structures from vegetal proteins has been a processing challenge until now. Taste, flavor and structure are all three needed to mimic the "meat-like" characteristics of analogue meat.

With Thermo Scientific™ compounding solutions combined with a new cooled sheet die for meat analogues, fibrous "meat-like" structures can be successfully made from vegetable proteins.

The compact design of the Thermo Scientific™ Process 11 Hygienic extruder allows you to optimize the process and develop new meat analogue formulations on a lab scale. This is due significantly reduced test time, sample size and waste from small sample volume of grams versus the kilograms of sample that are required by larger extruders.

The challenge with meat analogues

The increasing population and development in the world has caused a growing demand for meat. The resulting increased meat production from animal proteins has a significantly high impact on the carbon footprint (i.e., producing 1 kg of beef produces about the same amount of CO2 emission as driving 100 km or over 63 miles in a car).

It also takes about 15 kg of vegetable feed to produce just 1 kg of animal protein. That means plant-based proteins are an essential component in feeding the earth's growing population and reducing the carbon footprint at the same time.

Thermo Scientific Process 11 Hygienic Extruder with cooled slit die.

To get consumers to accept meat analogues based on vegetable proteins, it is necessary to improve the mouth-feel of such products. Meat analogues need to have a certain texture and appearance to feel like real meat in the mouth, and to ensure a similar eating experience.

Challenge solved

The ideal solution for the mouth-feel challenge is a twin-screw extruder process combined with a special die head that can cool the extruded protein down in a long flow channel to generate a fibrous, structure similar to real meat.

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Special die for the extrusion of plant-based proteins samples.

Wheat gluten samples with different textures. From top to bottom: The samples develop the fibrous characteristic of meat by optimizing the extrusion conditions.

Process 11 Hygienic Extruder: Special features and benefits for food products

- Compact bench-top extruder with small footprint
- Intuitive process control via touch screen with data logging
- Allows setting up, performing test and cleaning by a single user in laboratory environment
- Eight electrical heated & actively cooled temperature zones for exact temperature control and temperature profiles. Cooking and cooling of the product as it goes through the system
- Seven positions along the process to feed multiple components like plant proteins, water, flavors, spices, oils, as well as minerals and vitamins. (Additives like powders, pellets and liquids can be accurately dosed)
- Possibility for PAT (like NIR measurement) to monitor parameters such as product moisture
- Flexible screw design with interchangeable mixing and conveying elements, to optimize the compounding of ingredients and structuring of the products
- Process adjustments for customization of meat structure for final target group
- Suitable for scale-up to industrial sizes

Further information

We invite you to get in contact with us and discuss how we can support you at thermofisher.com/foodextrusion.

Find out more at thermofisher.com/foodextrusion

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LR-81 0318

The influence of extrusion conditions on the processability of starch compounds

Matthias Jährling and Bernd Jakob
Thermo Fisher Scientific, Material Characterization, Karlsruhe, Germany

Introduction

Starch is a base material that is widely used in the food industry for snack foods, cereals and pet food products. The processing of starch with twin-screw extruders offers great flexibility in process design and in the final products derived from it.
Carefully choosing extruder parameters like screw set-up and processing temperature, as well as the liquid-to-solid ration of the raw materials enables the operator to greatly influence the resulting product properties.
This application note showcases the different process parameters that play an important role in influenand their influence on the final product quality.

Experiment

The Thermo Scientific™ Process 11 “Hygienic“ Parallel Twin-Screw Extruder was used for extrusion experiment. This small and fully scalable co-rotating twin screw extruder with a screw diameter of 11 mm is ideal for such a test series because it allows many different condition settings to be made in a very short time.
The extruder itself is built of hygienic grade steel and is therefore perfectly suited for the processing of food-based materials.
A 30 mm sheet die with a gap height of 1.0 mm was attached to the extruder.
The extruded starch sheet was taken off by a small conveyor belt.
To avoid any loss of sample humidity, 20 mm discs were immediately cut from the extruded sheet, and the rheological properties were determined without further delay.

Sample Material

The extruded food compound was a dry blend containing 75% potato granules with 25% potato starch. This dry blend was fed into the main feeding section of the extruder, by means of a twin-screw feeder. To this dry blend, 26% water was added into the secondary feed port of the extruder, using a peristaltic pump.

Extrusion Equipment

- Extrusion System:
  Process 11 “Hygienic“ Twin-Screw Extruder (see Fig.1)
- Cooling Circulator:
  Thermo Scientific™ Polar Series Accel 500 LC Recirculating Chiller

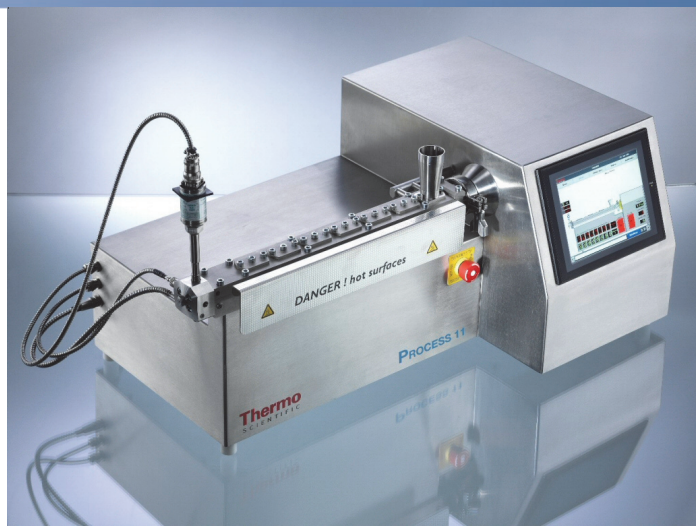

Fig. 1: The Process 11 “Hygienic“ Parallel Twin-Screw Extruder.

- Feeder for Premix:
  Gravimetric MiniTwin MT0 for Process 11 Extruders
- Feeder for Liquid:
  Thermo Scientific™ Masterflex P/S Pump Systems
- Extrusion Die:
  30 mm Sheet Die
- Take-Off System:
  Mini Conveyor Belt for Process 11 Extruders

Rheology Equipment

- Rheometer:
  Thermo Scientific™ HAAKE™ MARS™ 60 Rheometer
- Temperature control:
  Peltier temperature module
- Measuring geometry:
  20 mm Parallel plates

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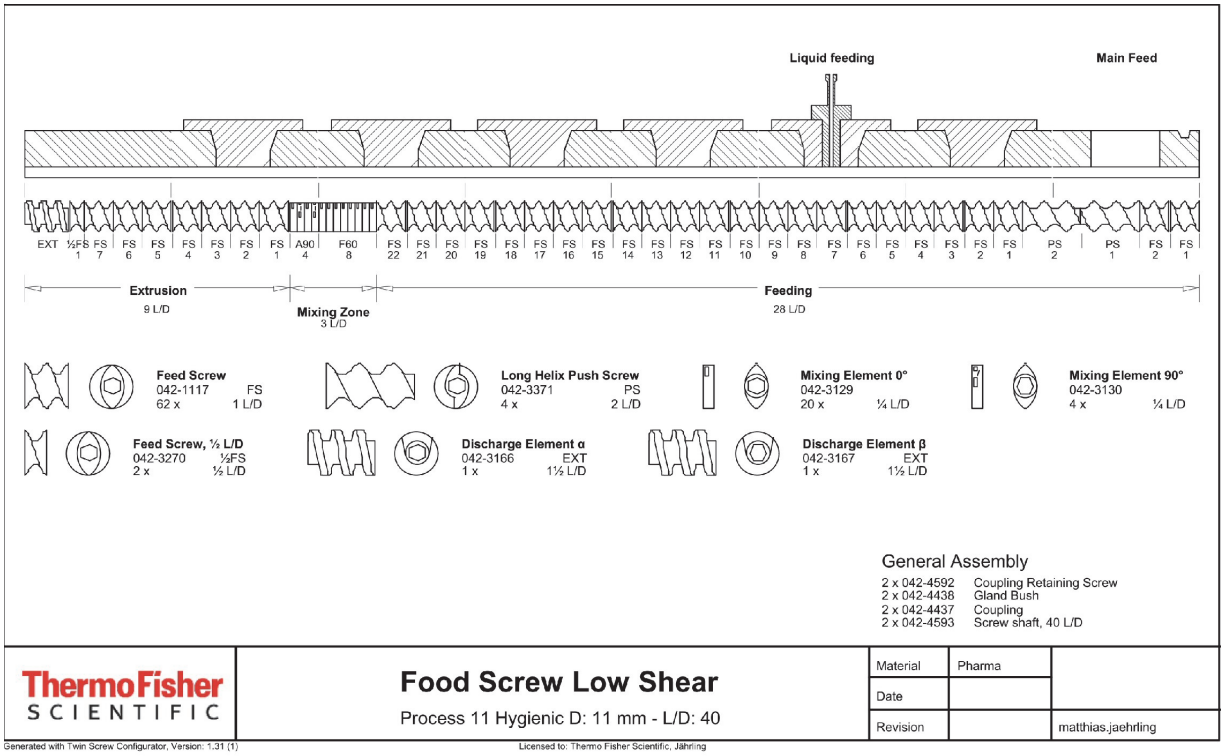
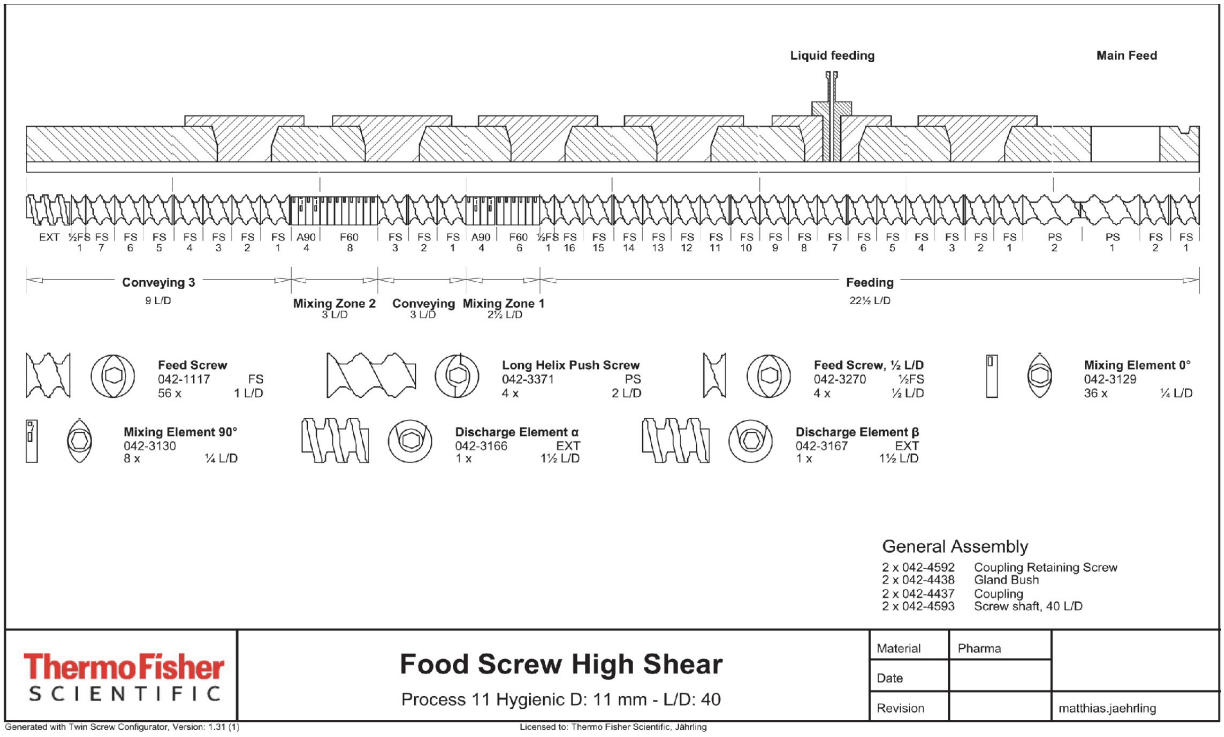
Extrusion Conditions

Variable 1: Screw-Configurations

a) Low shear screw (“LS“): One Stage Mixing



b) High shear screw (“HS“): Two Stage Mixing



Variable 2: Temperature Profiles

a) Low Temperature Profile (“80“)

Barrel Temperature Profile “80 °C“									
Zone	Die	9	8	7	6	5	4	3	2
	80 °C	80 °C	80 °C	80 °C	80 °C	70 °C	70 °C	50 °C	50 °C

b) High Temperature Profile (“120“)

Barrel Temperature Profile “80 °C“									
Zone	Die	9	8	7	6	5	4	3	2
	80 °C	90 °C	120 °C	120 °C	120 °C	70 °C	70 °C	50 °C	50 °C

Variable 3: Speed Extruder Screws

a) 200 rpm

b) 400 rpm

Variable 4: Feeding Rate

a) 540 g/h

b) 960 g/h

Process 11 Hygienic									
Sample No.	Screw config.	Speed [rpm]	mp [g/h]	Extrusion Temp.	TM [°C]	P [bar]	TQ [%]	RT [sec]	|η*| 10 Hz [Pa*s]
1	Low	200	540	80°C	87	31	24	95	15040
2	Low	400	540	80°C	94	25	25	78	12170
3	Low	200	960	80°C	93	41	33	58	15900
4	Low	400	960	80°C	99	33	28	47	12830
5	Low	200	540	120°C	113	35	26	99	20990
6	Low	400	540	120°C	117	32	28	91	20680
7	Low	200	960	120°C	107	50	28	63	24020
8	Low	400	960	120°C	115	48	27	51	29090
9	High	200	540	80°C	86	33	37	110	12960
10	High	400	540	80°C	98	24	32	92	9194
11	High	200	960	80°C	93	39	44	70	13970
12	High	400	960	80°C	99	31	39	56	12250
13	High	200	540	120°C	113	33	28	110	17300
14	High	400	540	120°C	119	38	27	75	13160
15	High	200	960	120°C	103	44	36	68	16830
16	High	400	960	120°C	115	37	32	57	15840

Discussion of the extrusion results

a) Residence Time

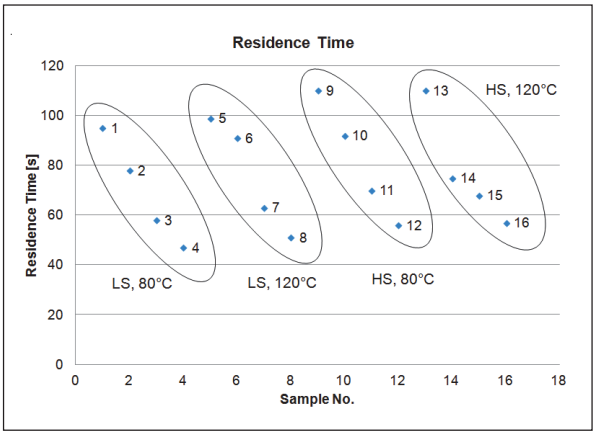


Fig. 2

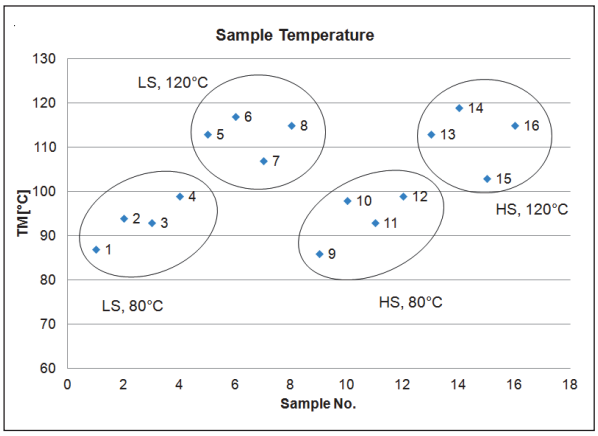


Fig. 3

The residence time was measured by means of a color tracer that was added into the main feed port. The time was stopped until a color change could be seen on the extruded sheet.
Fig. 2 shows the results of the residence time measurements. It can be clearly seen that the residence time gets shorter with increasing screw speed and with increasing feed rate, whereas the effect of the higher feed rate proved to have a much larger effect on the residence time.
It also can be seen, that the extrusion temperature had nearly no effect on the residence time. Finally, the effects of the different screw configurations are not very significant.

b) Sample Temperature

The sample temperature was measured with a melt thermocouple, which was placed at the die adapter at the end of the extruder.
As expected, Fig. 3 shows that the sample temperature increased, with a higher extruder temperature. In addition, the higher screw speed resulted in a higher sample temperature. The different screw configurations seemed to have no significant effect on the sample temperature.

c) Extruder Torque

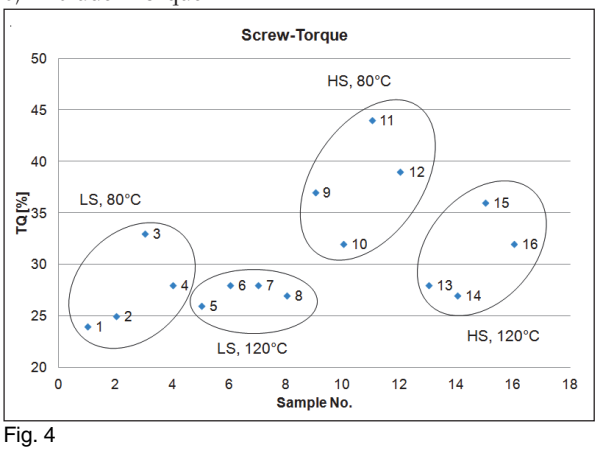


Fig. 4

The measurement of the extrusion torque showed a clear increase in torque when using the high shear screw configuration with the two mixing zones. It also can be seen that the torque is higher at lower temperatures. Higher feed rates with the same screw speed generate a higher torque whereas an increase of the screw speed decreases the torque.

d) Sample Viscosity

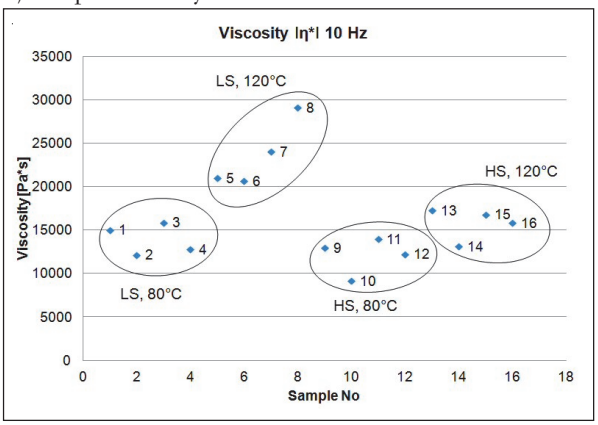


Fig. 5

The measurement of the sample viscoelastic behavior gave some interesting and unexpected results. The highest sample viscosity could be found with samples extruded at 120 °C with the low shear screw configuration. The viscosity measurements at 80 °C with the low shear screw configuration showed no significant difference to the samples prepared with the high shear screw at 80 °C and 120 °C. A possible explanation of this result may be that the sample wasn't yet fully gelated at 80 °C, but it was over-sheared with the high shear screw configuration so the structure already suffered a structural damage.

The test results indicate that extrusion with the low shear screw configuration, at 120°C, at the high feed rate, and at the high screw speed delivered the best gelation of the product.

Rheological Results

Rheological tests were performed on the samples with a HAAKE MARS 60 rheometer with a Peltier temperature module. All tests were conducted at 20 °C with a parallel plates measuring geometry: P20/Ti. All samples collected from the extruder were measured immediately. Test specimens were cut out of the extruded sheet with a 20 mm punch hole.

First an amplitude sweep from γ 0.5 to 50% at 1 Hz was performed to determine the linear viscoelastic range.

It is obviously in Fig. 6 that linear viscoelastic range extends to a deformation of about γ = 10%. For all the successive frequency sweeps, a deformation of γ = 2% was the set value for the tests with a frequency range of 0.02 to 46 Hz. To were repeatability, two fresh test specimens extruded at 80 °C were measured.

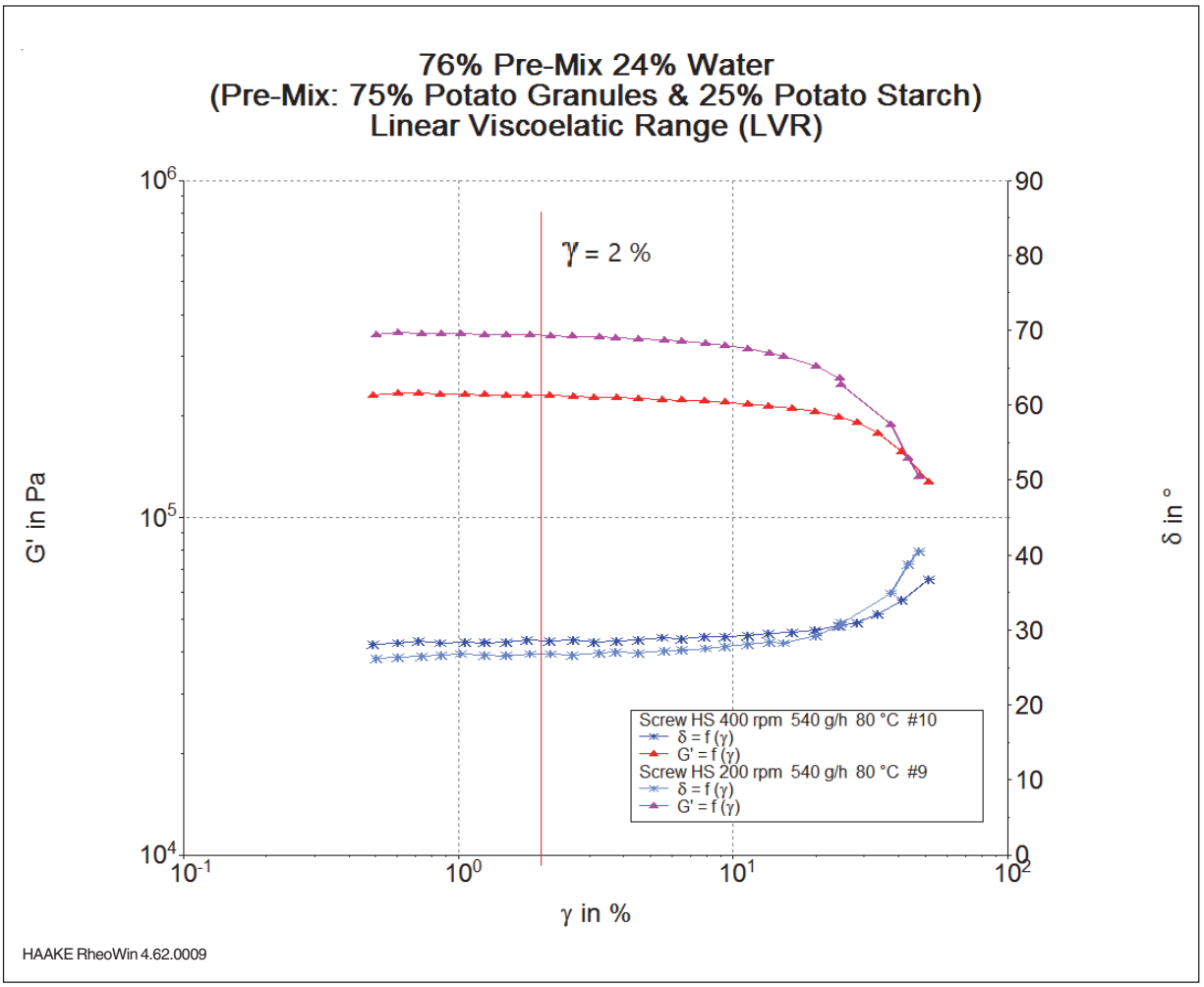


Fig. 6: Determination of the linear viscoelastic range. High shear screws, feed rate 540 g/h at 80 °C.

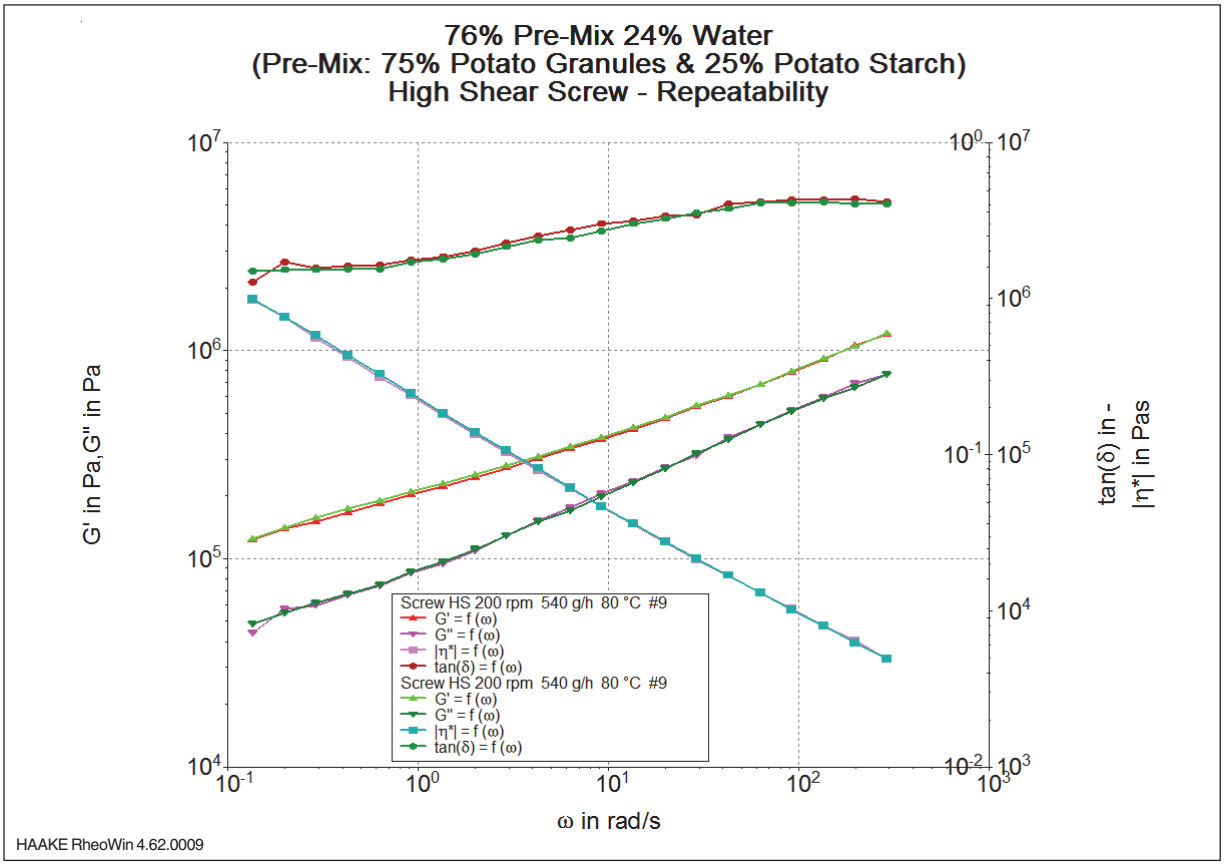


Fig. 7: Frequency sweep repeatability. High shear screws, feed rate 540 g/h at 80 °C.

In Fig. 7 the results of the two tests are plotted and show a reasonable repeatability. All test specimens show the same viscoelastic behavior; the elastic component G' is always higher than the viscous part G". In the frequency dependence of the complex viscosity |η*| a shear thinning of the sample is visible. This is also the typical trend of the quantities for all the other tests.

The four tests of the samples with low shear screws and the different feed rates at 120 °C are plotted in Fig 8. The complex viscosity |η*| and modulus |G*| of the samples with a feed rate of 540 g/h is almost independent of the screw speed. With an increase of the trough to 960 g/h, the values increase and the expected effect the of higher screw speed is visible. High feed rate and high screw speed of the low shear screws result in the highest viscosity and modulus which is an indication of the best gelation (see also Fig. 5).

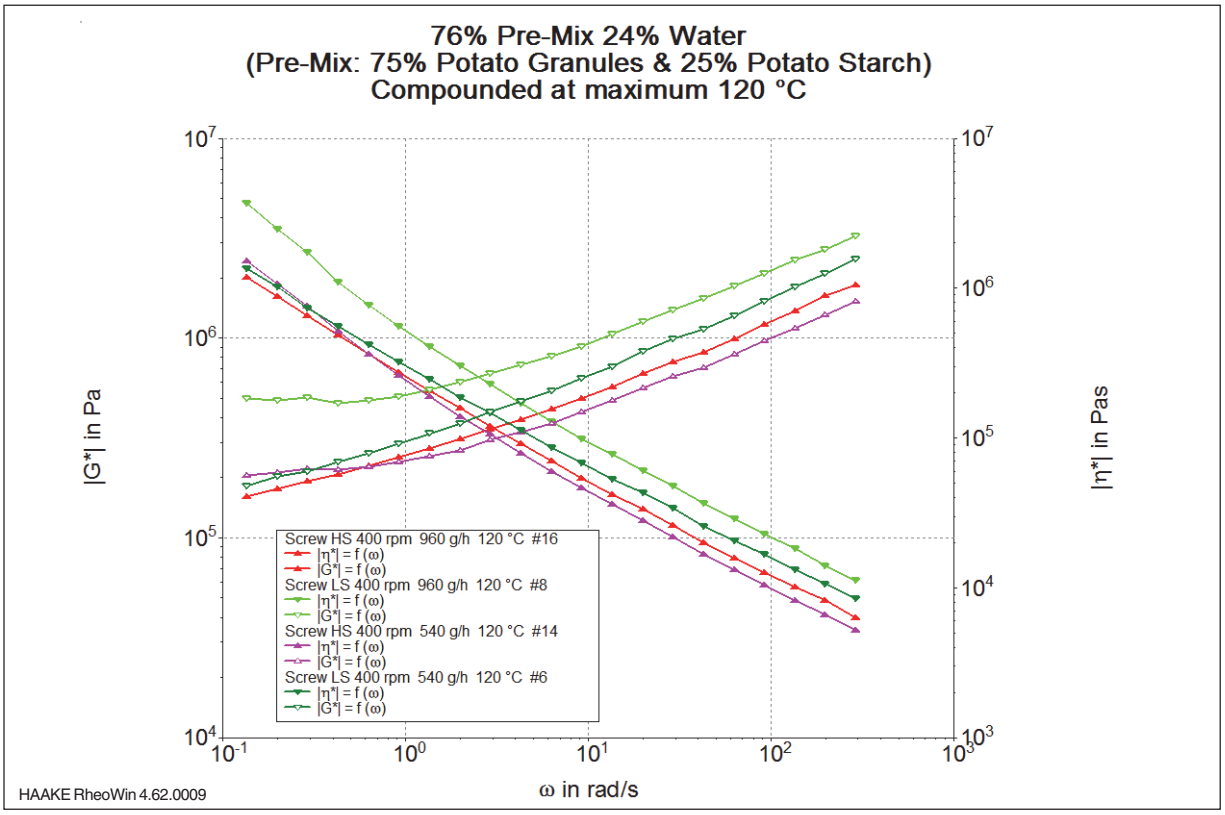


Fig. 8: Frequency sweep - high shear screws, different feed rates at 120 °C.

Conclusion

The gelation of starch is a complex process that is dependent on several variables. For water concentrations between 20% and 60%, the degree of gelatinization shows a strong dependency on the processing temperature [1]. The higher the temperature, the more complete the gelatinization is.
This effect can be observed in Fig. 5 where, using a liquid content of 26%, the viscosity is highest at 120 °C. Under the same conditions, the higher shear energy introduced into the system by the screw setup with two mixing zones degrades the three-dimensional network during the gelatinization process.
In summary, using twin-screw extrusion for production of a starch matrix offers a range of processing variables that enables the user to more adeptly design a starch matrix to required product properties. Twin-screw extrusion offers the user the ability to influence texture, stability and further processability of the final product. Combining extrusion with oscillatory rheology allows for defined, precise analysis of the end product and thus provides a workflow that enhances capabilities in today's food design.

Reference

[1] Fechner, Petra M. „Charakterisierung pharmazeutischer Hilfsstoffe“ 2005; Dissertation at Martin Luther Universität Halle-Wittenberg

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Encapsulation of Flavors and Ingredients Using a Twin-Screw Extruder

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Introduction

Flavors are sensitive and expensive additives used primarily in the food industry. Over the last decades these flavors and active ingredients have been encapsulated in a polymeric matrix for various purposes such as protection against oxidation, loss of flavor, taste masking, controlled release, or better product handling.
Possible matrix polymers include starch, different sugars, cellulose derivatives, lipids, proteins and special rubbers. The largest shares have of course starch and sugars. The traditional method of encapsulating flavors is based on a batch process, but it can be improved upon with twin screw melt extrusion.

Traditional Processing

The polymers are molten with the addition of water. Then the flavors or active ingredients are added, and mixed by vigorous kneading. Depending on the formulation, excess water may need to be removed under vacuum. Thereafter, the melt is cast as a plate and cooled down.
This process is very cumbersome and time-consuming. Also the required material amount is not flexible because it is predetermined by the size of the batch mixer.
Another popular traditional method for encapsulation of flavors is spray drying. A drawback of this complex, continuous process is the loss of flavors and active ingredients due to high process temperatures. The materials may oxidize, may have a shorter shelf life, and explosion protection measures may even have to be taken for some materials. The high energy consumption for drying in this process also makes it less favorable from an economic standpoint.

Encapsulation Using Twin Screw Melt Extrusion

Polymers are frequently processed with extruders, so it is an obvious choice to extend this technology for the encapsulation of flavors.
The flexible combination of dispersive and distributive mixing in a twin-screw extruder is perfectly suitable for continuous encapsulation of flavors. The twin screw extruder allows the temperature to be changed throughout

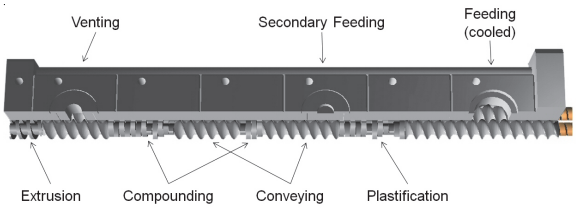

Fig. 2: Schematic of a Twin-Screw Extrusion.

Fig. 1: Process 11 “Hygienic“ Extruder with face-cut pelletizer.

the barrel zones, and it has a modular screw design to induce only the amount of shear and thermal energy needed for the process of encapsulation. This prevents unwanted degradation of the sensitive materials.
In the feeding section of the extruder (see Fig. 2; material flows from right to left) the polymer matrix material is metered and conveyed into the first mixing zone. Due to the heat and shearing, the polymer is transformed into a homogenous melt. In a secondary feed zone, the flavor is added by means of a liquid feeding pump.
In a further mixing zone, the flavor is now dispersed and evenly distributed into the polymer matrix. At the end of the extruder, the sample pressure is built up to press the compound through a die, and shape it to large number of small strands which are then directly cut into fine pellets by the rotating knife of a face-cut pelletizer. Another option is to extrude the melt directly onto chill-rolls which freeze it down and shape the material into flakes.
The Thermo Scientific™ Process 11 “Hygienic“ is the ideal instrument for testing the encapsulation process on a laboratory scale, because it combines the advantages of a compact bench-top extruder, with the full functionality of a production setup. Its modular design enables the optimal adjustment of the extruder barrel and screws to match the application and product needs. All product contact parts are made from stainless, hygienic-grade steel.

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As food products are often cleaned with water-based detergents, the high-grade steel provides an advantage over regular extruders which are normally used in polymer processes.

Testing Equipment

- Extrusion System:
  Process 11 “Hygienic“
- Cooling Circulator:
  Thermo Scientific™ Polar Series Accel 500 LC
- Feeder for Premix:
  Gravimetric MiniTwin MT0 for Process 11
- Feeder for Liquid:
  Thermo Scientific™ Masterflex P/S Pump Systems
- Downstream System:
  Face-Cut Pelletizer

For an encapsulation of a flavor in a sugar matrix, the Process 11 “Hygienic“ equipment setup was designed in a way that the sugar was metered into the cooled, first feeding zone of the extruder, with a gravimetric twin-screw feeder. The sugar was then conveyed by the extruder-screw, into the first mixing zone. There the sugar was molten due to the shear and heat generated by the kneading elements. These kneading elements were followed by conveying screw elements. In a co-rotating twin-screw extruder the conveying elements are not totally filled and the melt is not pressurized. As aresult the extruder could be opened again and the flavor was added into the molten sugar by the Masterflex P/S peristaltic pump.
Conveying screw elements then transported the mixture into two subsequent mixing sections, where the flavor was dispersed and evenly distributed in the sugar matrix.
At the end of the extruder the pressure was built up, and the final compound was pressed through the die head, into the face-cut pelletizer.

Designing the Final Product

Fig. 3 shows the final product, collected after cooling in the cyclone of the face-cut pelletizer.
Once the process is developed on the extruder, it is very simple to exchange of the downstream accessories to obtain differently shaped material. Fig. 4 shows flakes produced from the same process using a chill-roll (see Fig. 5) instead of the face-cut pelletizer. The molten material leaving the extruder is compressed and cooled down between two temperature-controlled rolls and formed into a thin sheet. The cooled sheet is then broken down into flakes by a kibbler device at the end of the chill-roll.

Conclusion

Using twin screw extruders for encapsulation of flavors and ingredients into a sugar or polymeric matrix offers several advantages over traditional processes.
The extruder is a continuous working instrument by nature so the amount of end-product is determined by run time and does not require adaptation via different sized production equipment as traditional batch operation does. Compared to the energy-hungry process of spray-drying, extrusion has milder process conditions and reduces the risk of product denaturation.
Finally the choice of downstream equipment (face-cut pelletizing or chill-roll) can help produce application specific end-product as required.

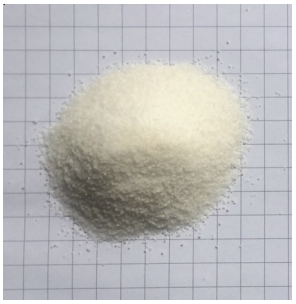

Fig. 3: Encapsulated flavor - pelletized.

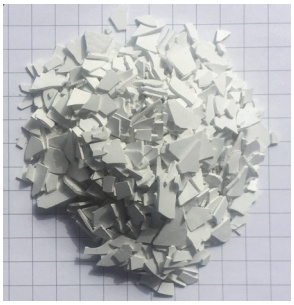

Fig. 4: Encapsulated flavor - Flakes from the chill-roll.

Fig. 5: Chill-roll with kibble.

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