Rheometers

The HAAKE RheoScope Module built in a HAAKE MARS 60 Rheometer.

Investigating changes in food structure with RheoMicroscopy

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Keywords

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Abstract

To gain information about the reasons for certain changes in rheological properties, a special accessory for the Thermo Scientific™ HAAKE™ MARS™ 40/60 Rheometers is available. It combines a temperature control module for cone-plate or plate-plate measuring geometries with an optical microscope. In this report the Thermo Scientific™ HAAKE RheoScope™ Module is presented, and example data from different applications is shown.[1]

Introduction

Rheology is a “macroscopic” method, which tells us how a material behaves under certain conditions, but never why. For an understanding about the reasons why a certain behavior 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- and Raman spectroscopy or microscopy. Running two independent measurements on different instruments, however, doubles instrument 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 be correlated without hesitation as they were collected at the same time from the same sample.

The HAAKE RheoScope Module

The HAAKE RheoScope is designed as a compact module and can be mounted into the HAAKE MARS 40/60 Rheometers (and predecessor models) like any regular temperature control module. To guarantee an even temperature distribution and to make temperature ramps between -5 and +120 °C possible (up to +300 °C in combination with an active upper temperature control module), the whole lower plate rests on a heat exchanger.

The sample is viewed through a small window in the heat exchanger. Below this window the lens of the microscope can be moved along the radius of the bottom plate to select the best spot for sample observation (Figure 1).

On top of being part of a modular rheometer system the HAAKE RheoScope Module is modular itself. Lens, camera, light source, lower glass plate and the upper cone or plate (with a polished surface finish, up to 60 mm in diameter) can be selected to suit the respective application.

Apart from the data collection and data evaluation (Figure 2) the control of the HAAKE RheoScope Module is fully integrated into the Thermo Scientific™ HAAKE™ RheoWin™ Software. All optical settings like radial position, focus, integration time, contrast and the activation of polarizing filter can be saved and recalled for later routine measurements, for example.

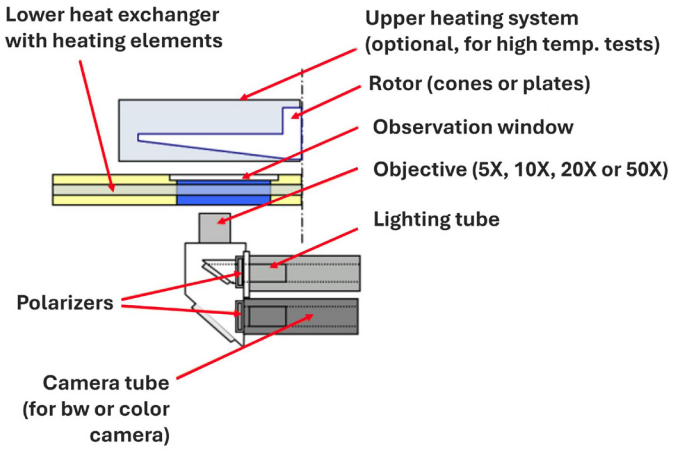

Figure 1. Schematic setup of the HAAKE RheoScope Module

Application examples

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 structure, starch is cooked in water to obtain 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.

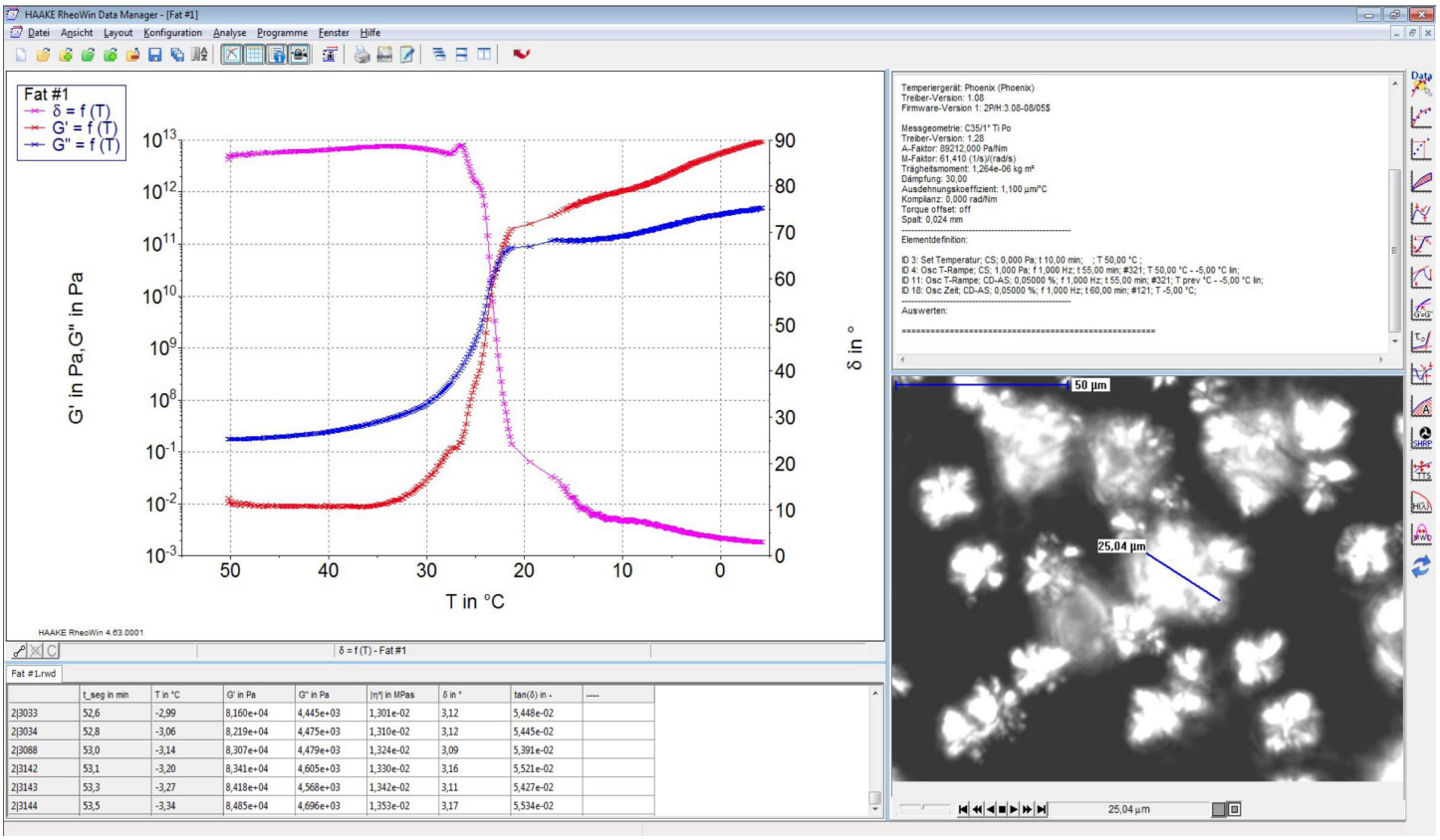

Figure 2. Rheological data and microscopic images are handled by the HAAKE RheoWin Software and are linked to each other. Size evaluation with the images can be done directly in HAAKE RheoWin Software.

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 in a process called retrogradation. The HAAKE RheoScope Module was used to look at the starch grains during the cooking process and at the structure of the final starch solution. The visual changes in the starch granules were correlated with the viscosity.

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 using the built-in crossed polarizers.

Figure 3 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 its maximum and the inhomogeneous solution after cooling down to 20 °C.

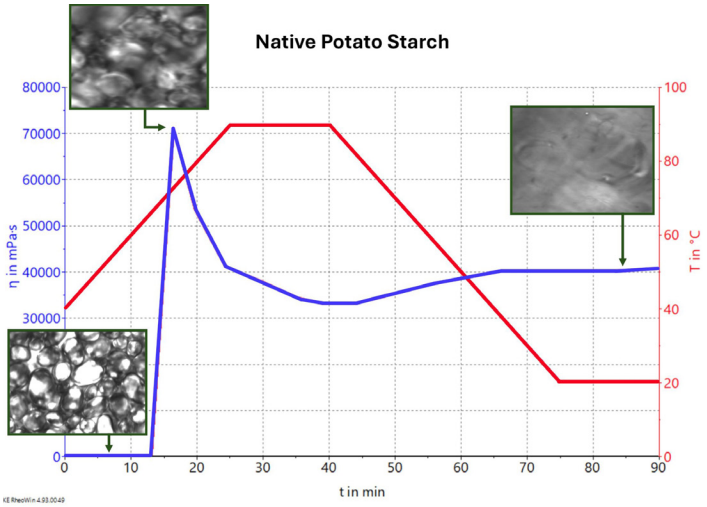

Figure 3. Native potato starch (5 % in water): Images show the starch crystals at the beginning, the swollen crystals at the peak viscosity and the inhomogeneous solution after cooling down..

Running the same cooking program with hydroxypropylated potato starch shows the viscosity maximum shifted to a lower temperature indicating a better water solubility (Figure 4). 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 (image No 3 in Figure 4).

Wheat starch in water shows a completely different behaviour. The viscosity shows a second local maximum before a temperature of 90 °C is reached (Figure 5). The microscopic images show that the starch particles at the beginning of the test

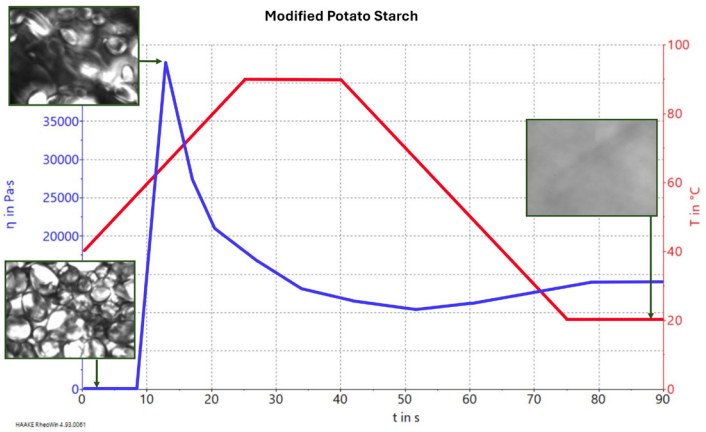

Figure 4. Modified potato starch (5 % in water): Images show the starch crystals at the beginning, the swollen crystals at the peak viscosity and the homogeneous solution after cooling down.

look different from the potato starch in its original state (image No 1 in Figure 5). Image No 2 Figure 5 confirms, that the first maximum corresponds with the maximum found, when testing potato starch, since here we also can see the fully swollen starch grains. Image No 3 Figure 5 shows an almost homogeneous solution. Why this structure corresponds with another maximum in the viscosity still needs to be investigated. When cooling down to 20 °C, the wheat starch solution becomes inhomogeneous again as can be seen in image No 4 in Figure 5.

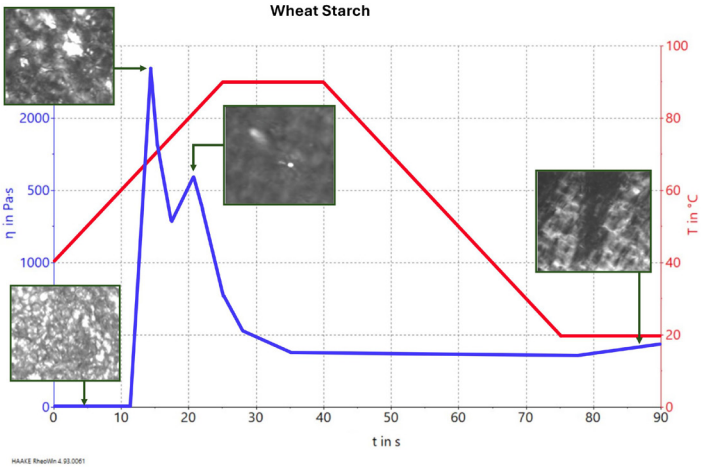

Figure 5. Wheat starch (5 % in water): Images show the starch crystals at the beginning, the swollen crystals at the peak viscosity, an almost homogenous solution at the second local maximum and the inhomogeneous solution after cooling down.

Using the HAAKE MARS Rheometer with the HAAKE RheoScope Module, it was possible to follow the changes in viscosity during the cooking process of starch in water. The images 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 key factors for the success of a food product, is the mouth feeling. When talking about solid or at least semi-solid

foods 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 crystallization temperatures can easily be determined with rheological methods or differential scanning calorimetry (DSC). Fats often show a more complex behaviour where several crystal phases have crystallization temperatures close to each other. In 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 crystallization cannot be regarded separately.

The mechanical oscillation put onto a sample in a dynamic mechanical method like a rheological oscillatory 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 Rheometer equipped with the RheoScope Module. After melting the fat in the cone & plate-geometry, a temperature ramp going down from +50 °C to -5 °C with 1 °C/min was run while recording the changing rheological properties of the fat with a constant small deformation oscillation 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 a decrease of the loss angle δ, respectively. At the same time the growth of different crystals can be observed.

Fat #1 shows a very steep drop in δ between 27 °C and 21 °C plus another weaker drop between 21 °C and 13 °C (Figure 6). At the end of the temperature program, fat #1 consisted of round crystalline domains embedded in an isotropic matrix (Figure 7, right image).

Fat #2 also crystallizes in 2 steps, but compared to fat #1 the crystallization happens very fast (Figure 8). First, a homogeneous melt is present down to a temperature of approx. 32 °C. Then a sudden appearance of small crystals together with a sharp decrease of δ is observed.

In a second step beginning at around 20 °C, another smaller drop in δ occurs and bigger, needle-shaped crystals are formed (Figure 9, right image). These needles grow until they fill the whole sample volume. Overall, it is possible to distinguish the two samples by the shape, size and speed of growth of the crystals or crystalline domains and to correlate this data with their corresponding rheological behaviour.

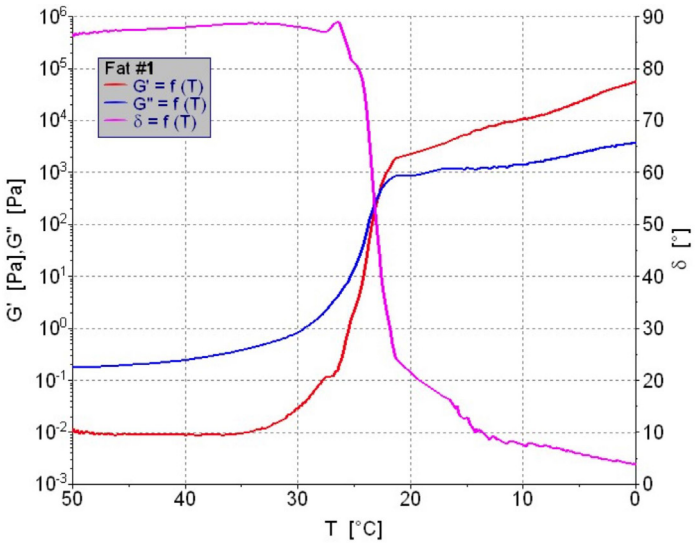

Figure 6. Crystallization of fat #1 in 2 slower steps.

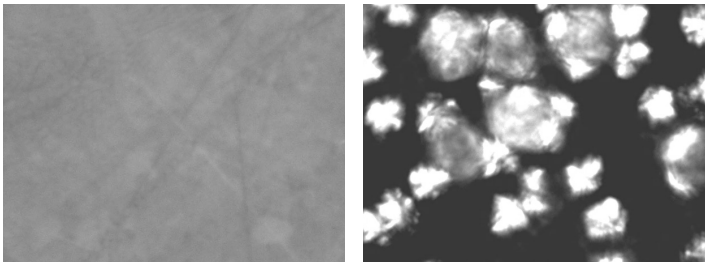

Figure 7. Microscopic images of fat #1 homogeneously molten (left) and after crystallization has begun (right).

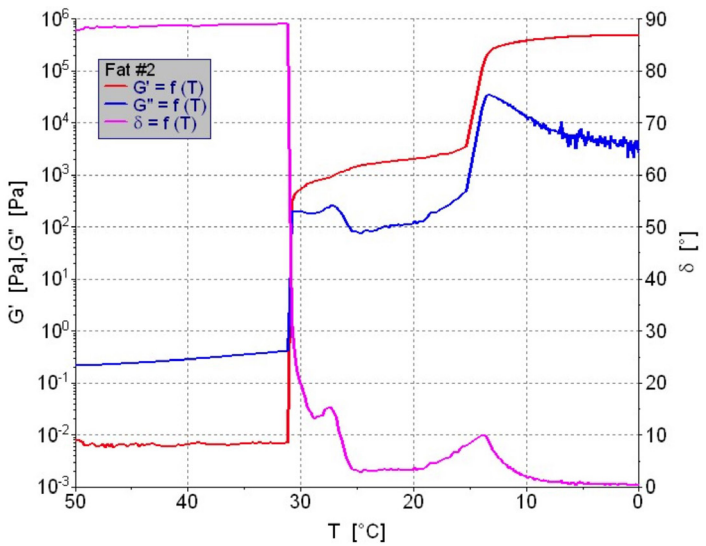

Figure 8. Crystallization of fat #2 in two fast steps.

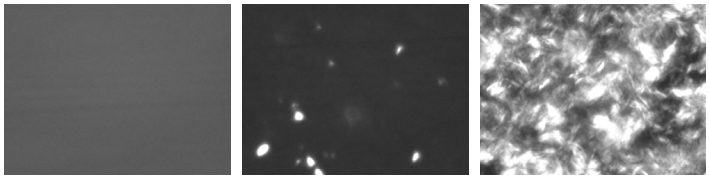

Figure 9. Microscopic images of the homogeneous melt of fat #2 (left), a first crystal phase formed below 32 °C (middle) and a second crystal phase formed below 20 °C (right)..

Conclusion

The RheoScope Module combines all characteristics of a compact temperature control module and a fully software controlled, optical microscope. It can simply be added to a HAAKE MARS 40/60 Rheometer (and predecessor models) without the need for any prior modifications or compromising any other functionalities of the rheometer. The performance of the temperature control is not affected by the microscope function. Therefore, it is possible, 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 a sample.

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

Acknowledgment

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

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

Reference:

1. Cornelia Küchenmeister-Lehrheuer, Fabian Meyer, HAAKE RheoScope Module for HAAKE MARS 40/60 Rheometers, Thermo Scientific Product Information PR085

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