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 new special module for the 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 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

Since we presented the HAAKE RheoScope 1, the first combination of a rheometer with a microscope commercially available, technology has advanced significantly.
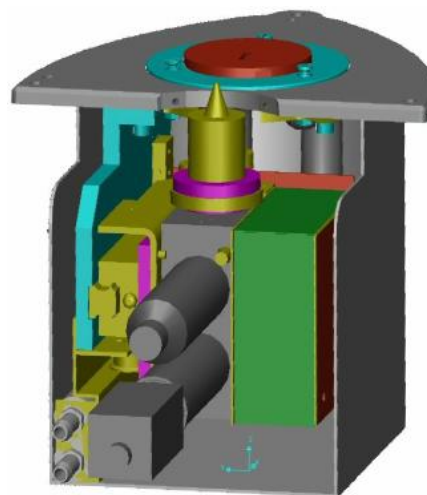

Figure 1. Inside the RheoScope module optical and mechanical components are arranged to give a high quality, fully software controlled microscope in addition to the temperature control unit.

Based on our experience with the HAAKE RheoScope 1, we designed a second generation microscope module by improving the microscope technology and
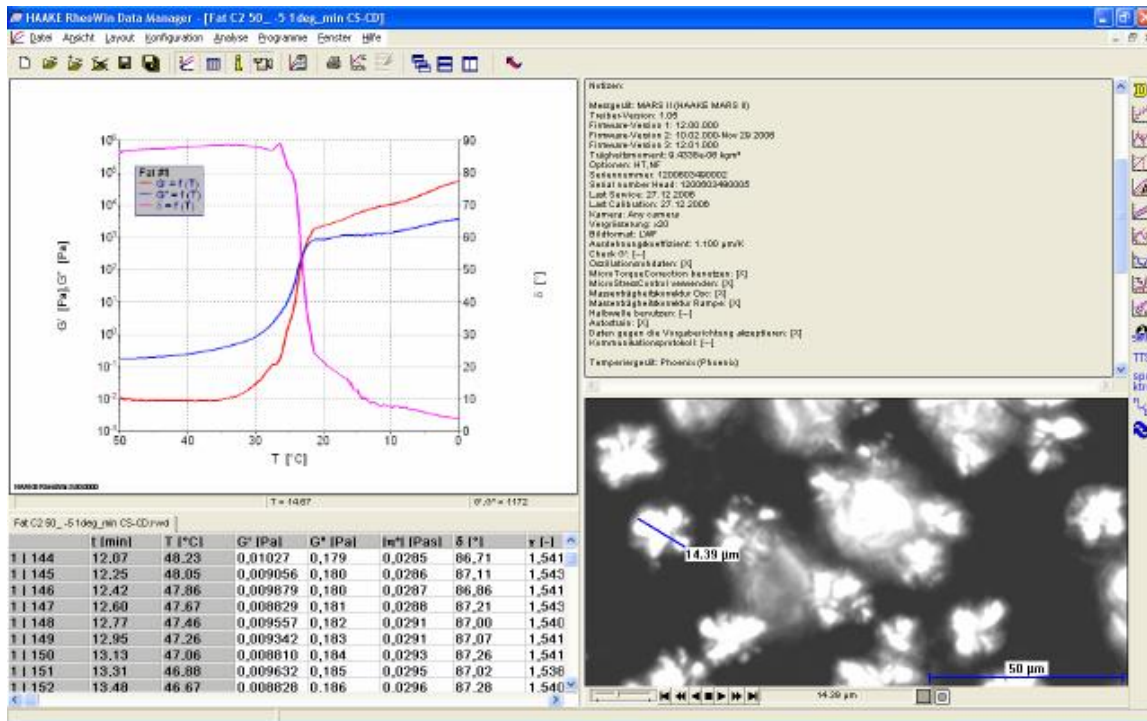
Figure 2.   Rheological data and pictures are handled by the HAAKE RheoWin software and are linked to each other, i.e. for every data point the picture, which has been taken simultaneously can be displayed. Simple evaluation of the pictures can be directly done in HAAKE RheoWin.

integrating it into a compact module (see Figure 1). This RheoScope module can be mounted into the HAAKE MARS like any other temperature control unit.

To guarantee an even temperature distribution and to make temperature ramps between -5 and 120 °C (optional 250 °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 Figure 3).

On top of being part of a modular rheometer system the RheoScope module is modular itself. Lens, camera, light source, lower glass plate and sensor (polished Titanium, up to 60 mm diameter) can be adapted to the individual application.
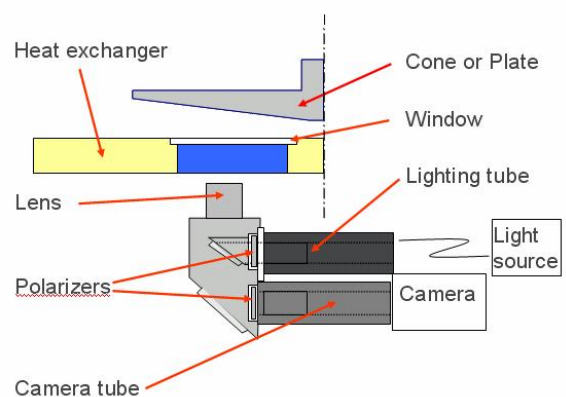
Apart from the data collection and data evaluation (Figure 2) the control of the RheoScope-module is fully integrated into the HAAKE RheoWin software. All settings like position, focus, integration time, contrast and using the polarizing filter can be saved and thus be recalled e.g. for later routine measurements. For advanced image analysis for e.g. a particle size distribution specialized software is available.

Figure 3.   Pictures are taken through a small window in the heat exchanger guaranteeing good temperature distribution.

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 amylase 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.
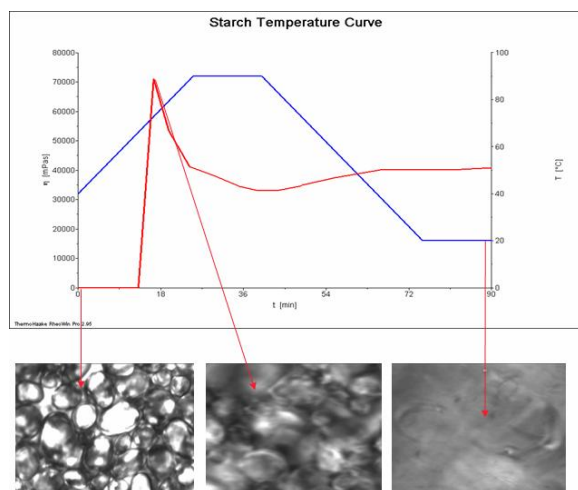

Figure 4.   Native potato starch (5 % in water): Photos show the starch crystals in the beginning, the swollen crystals at peak viscosity and the inhomogeneous solution after cooling down.

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

Figure 4 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 final inhomogeneous solution after cooling down to 20 °C.
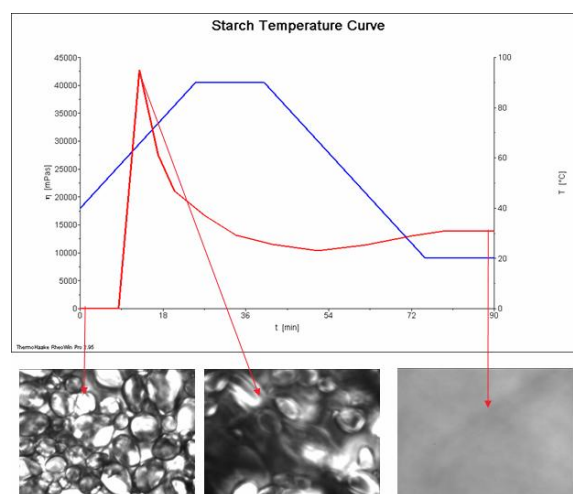

Figure 5.   Hydropropylated potato starch (5 % in water): Photos show the starch crystals in the beginning, the dissolving crystals at peak viscosity and the homogeneous solution after cooling down.

Running the same cooking program with hydroxypropylated potato starch shows the viscosity maximum shifted to a lower temperature indicating a better water solubility (Figure 5). This is confirmed by the pictures showing a high degree of swelling at viscosity maximum and a homogeneous solution after cooling down to 20 °C (photo #3 in Figure 5).

Wheat starch in water shows a completely different behaviour. The viscosity shows a second local maximum before 90 °C

are reached (Figure 6). The microscopic pictures show that already the starch particles at the beginning of the test look totally different (photo #1 in Figure 6). Photo #2 proves that the first maximum corresponds with the maximum found when testing potato starch since here we also can see the fully swollen starch "grains". Photo #3 shows an almost homogeneous solution. Why this structure corresponds with another maximum in the viscosity will be found by further work on this topic. When cooling down to 20 °C, the wheat starch solution becomes very inhomogeneous as can be seen in the 4th photo in Figure 6.
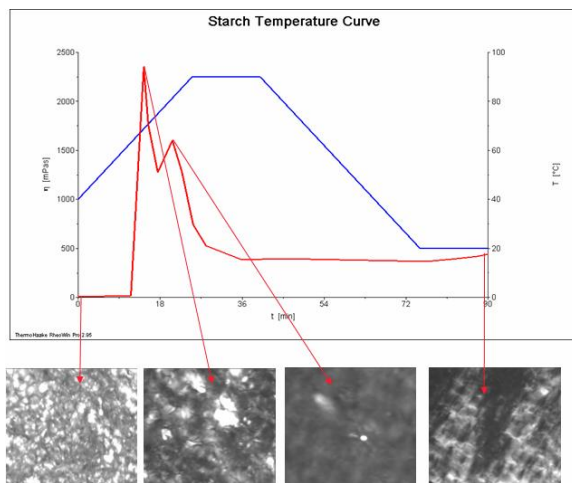

Figure 6. Wheat starch (5 % in water): Photos show the starch crystals in the beginning, the swollen crystals at peak viscosity, an almost homogenous solution at the second local maximum and the inhomogeneous solution after cooling down.

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 under-cooled 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.
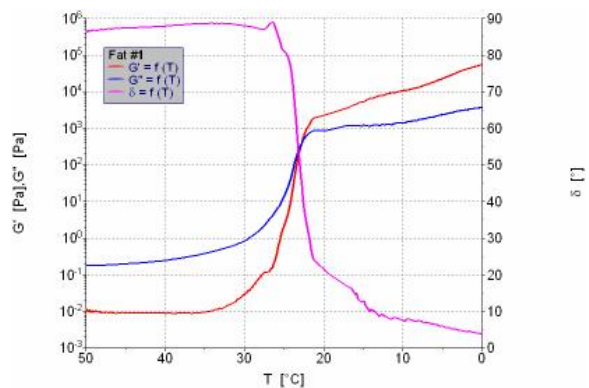

Figure 7. Crystallization of fat #1 in 2 slower steps

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 Figure 7). At the end of the temperature program, fat #1 consists of round crystalline domains embedded in an isotropic matrix (Figure 8, right photo).
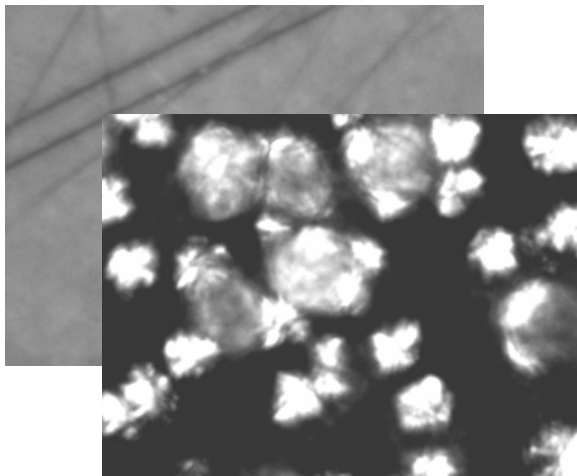

Figure 8. Microscopic pictures of the homogeneous molten fat #1 (left) and the same are after crystallization has begun (right)

Fat #2 also crystallizes in 2 steps but compared to fat #1 the crystallization happens very fast (Figure 9). First we have a homogeneous melt down to approx. 32 °C. Then we see a sudden appearance of small crystals together with a sharp decrease of δ. In a second step beginning around 20 °C we see another smaller drop in δ and now bigger, needle-shaped crystals are formed (Figure 10, bottom 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.
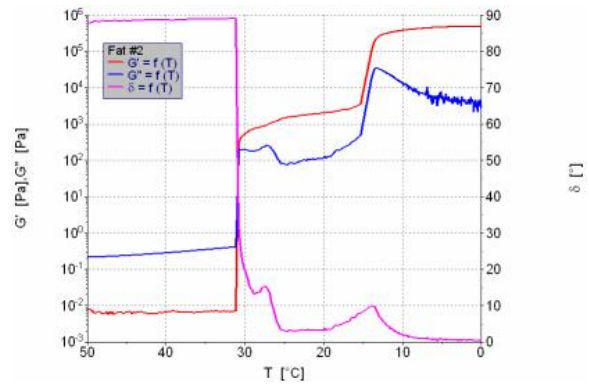

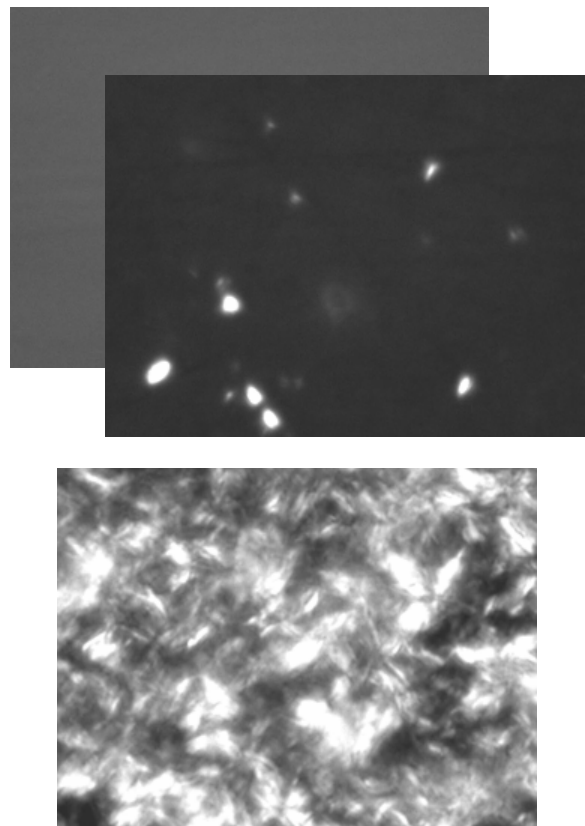Figure 9. Crystallization of fat #2 in 2 fast steps

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

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 RheoScope module enables the user to generate structure-property-relationships with measurements on the same sample and on one instrument only, saving time and money.