

Oscillation Tests: Influence of the Applied Stress on the Gelation Process

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Introduction

“That works well, but...”

To find the perfect active ingredient like for example a perfume, a detergent or a pesticide is only half of the job to create a successful product the customers will like and buy, of course. The other part of the success is to offer the active ingredient to the customer in a form that fits the application or is simply liked by the customer.

With a viscosity like water a shampoo would be difficult to handle or a pesticide would be washed away by the next bit of rain. One approach to adjust the product to the application's needs is to put the active substance into a gel matrix to make the product stick, stand or easy to dose. For product development and quality control it is therefore crucial to be able to understand gelling processes and to characterize gels.

An oscillation test is the classical rheological method to follow the development of a network structure during gelation processes. Since they mainly involve small stresses or small defor-



Fig. 1: The sample hood made of polyoxymethylene (POM) can be used to minimize temperature gradients, to reduce solvent evaporation or to flush the sample with a shielding gas.

mations, oscillation tests are usually regarded to be non-destructive in general. Especially in the case of a more fragile network structure the question remains, whether this is always true.

The following tests have been done to evaluate if and to what extent the stress the sample is exposed to during an oscillation test can affect the gelation process.

Materials and Methods

For this test a polymer-solvent combination has been chosen, which shows a temperature-dependant reversible sol/gel-transition. A Thermo Scientific HAAKE MARS rheometer, equipped with a Peltier plate and a 35 mm plate geometry was set to 50 °C. To keep temperature gradients to a minimum, a sample cover made of POM (Fig. 1) has been used during the initial temperature equilibration and the tests.

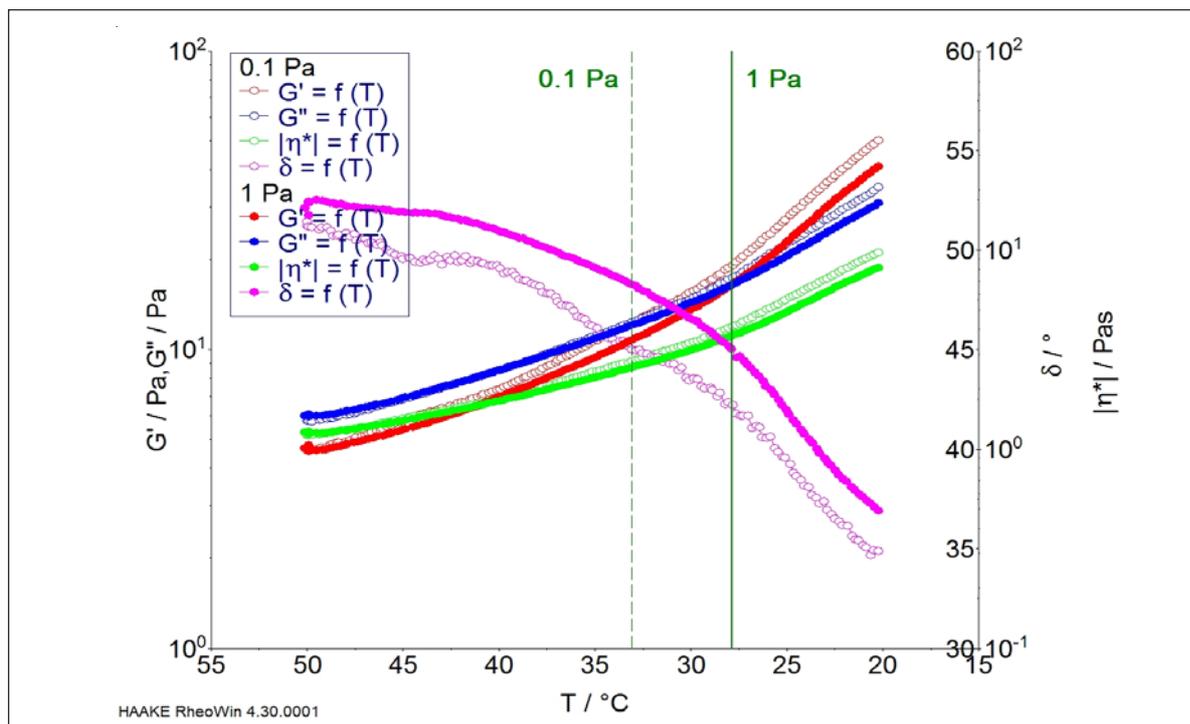


Fig. 2: Transition from sol to gel happens at 33.1 °C with 0.1 Pa (dotted line) and 27.9 °C with 1 Pa (solid line).

The liquid sample has been filled into the rheometer at 50 °C and was cooled down to 20 °C with -2 K/min. The transition from sol to gel was monitored by applying an oscillation with a constant frequency of 1 Hz and a constant stress and determining the cross-over temperature, where the properties of the sample change from mainly viscous to mainly elastic. For the constant stress, values of 0.1 Pa, 1 Pa and 20 Pa have been selected to detect the influence of the stress applied. After the gelation, the gels were characterized with a stress sweep. Using the unique capabilities of the measuring and evaluation software Thermo Scientific HAAKE RheoWin, the whole test program with all 3 stresses was cast into one test method including sample loading, cooling the sample, characterizing it with an amplitude sweep, determining the cross-over, reheating it and repeating the whole procedure with the other two stresses.

Results and Discussion

At 50 °C the sample is clearly a sol, its loss modulus (G'') is higher than its storage modulus (G') and thus the phase angle (δ) is above 45 ° (Fig. 2). With falling temperature the moduli and the viscosity increase, the difference between the moduli becomes less and around 30 °C the cross-over-point is reached. Below this temperature, G' is higher than G'' and δ is therefore below 45 °, in other words: the sample behaves mainly elastic.

This cross-over-point is often used as the gelation-point, where the sol/gel-transition happens.

The influence of the stress can immediately be seen during the cooling run. Comparing the results of the tests with 0.1 Pa and 1 Pa it can clearly be seen that the higher stress leads to a transition temperature 5 °C lower.

After the cooling run the gels have been tested using a stress sweep. The general shapes of the material functions shown in Fig. 3 are the same. In the linear viscoelastic range (LVR) δ is a bit higher than 30 °, well below 45 ° proving that a gel structure has been formed.

In the LVR, relative to the 0.1 Pa-gel, the 1 Pa-gel shows a viscosity approx. 10 % lower, its G' is about 11 % lower, its G'' is about 5 % lower and its δ about 5.5 % higher. These differences are indicating that under the higher stress a weaker gel-structure has been formed.

When a stress of 20 Pa is applied during the cooling of the sample, a totally different picture occurs. The viscosity still increases but under the influence of the bigger stress, the gelation is hindered to an extent that no network is established. As can be seen in Fig. 4, the viscosity of the sample is about half an order of magnitude lower compared to the two earlier tests. The phase angle δ stays almost constant around 80° during the whole experiment. No sol/gel transition happens.

Subsequently, the product behaves completely different during the stress sweep (Fig. 5). Compared to the 0.1 Pa-gel, the 20 Pa-gel has a 74 % lower viscosity, an 88 % lower G' , a 55 % lower G'' and a δ , which is more than twice as high around 67 °. Such a high value for the phase angle in the LVR is proof that no gel has been formed during the cooling run.

Summary

The stress applied during the gelation process influenced the development of the gel network. With increasing stress the gel stability was reduced down to the point that at the highest stress a gel structure throughout the whole sample could not be formed. The sample remained to be a mainly viscous liquid with a phase angle around 67 ° in the LVR.

These results lead to various consequences. Especially during the synthesis of fragile gels, the mechanical forces acting upon the developing gel structure have to be controlled to be able to run a reproducible gelation process. If a weaker gel has to be produced on purpose, a defined stress put on the material during the gelation could be an easy way to achieve this goal without changing the formulation.

The results have to be considered as well for the design of rheological tests aiming to describe the gelation process. Again, especially for more fragile gels it has to be avoided that

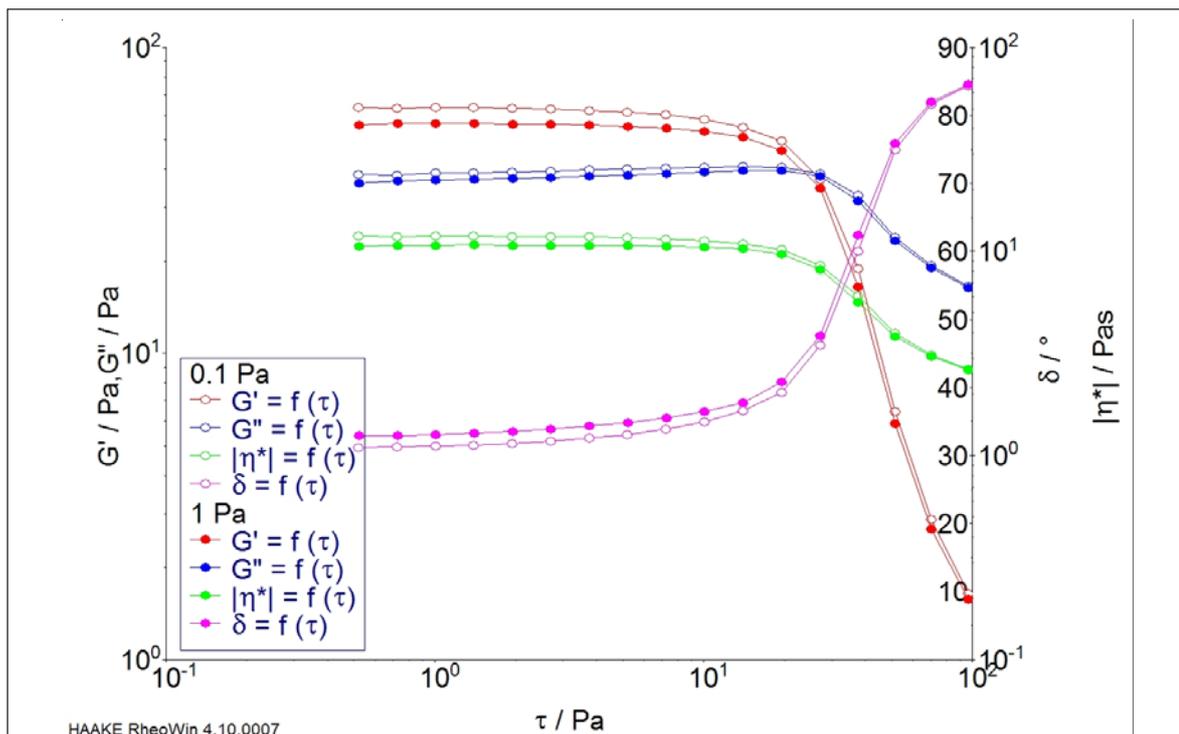


Fig. 3: Gel stability of the 0.1 Pa-gel (open symbols) and the 1 Pa-gel (filled symbols). The 0.1 Pa-gel shows a slightly higher viscosity and a slightly higher elasticity over the whole range of the test. The stresses at cross-over differ by only 1.6 Pa, which is too small to be significant.

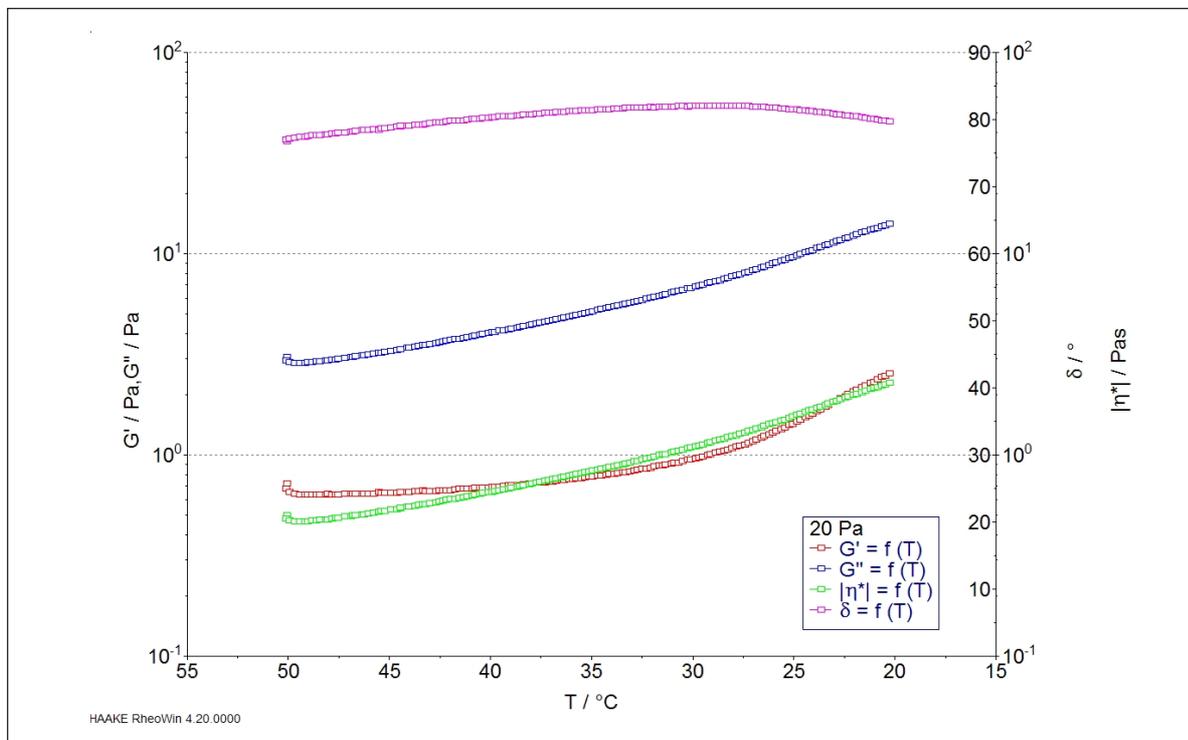


Fig. 4: Under an oscillatory stress of 20 Pa no sol/gel transition happens. The viscosity is about 10× lower compared to the 2 earlier examples. The phase angle is around 80° throughout the whole test.

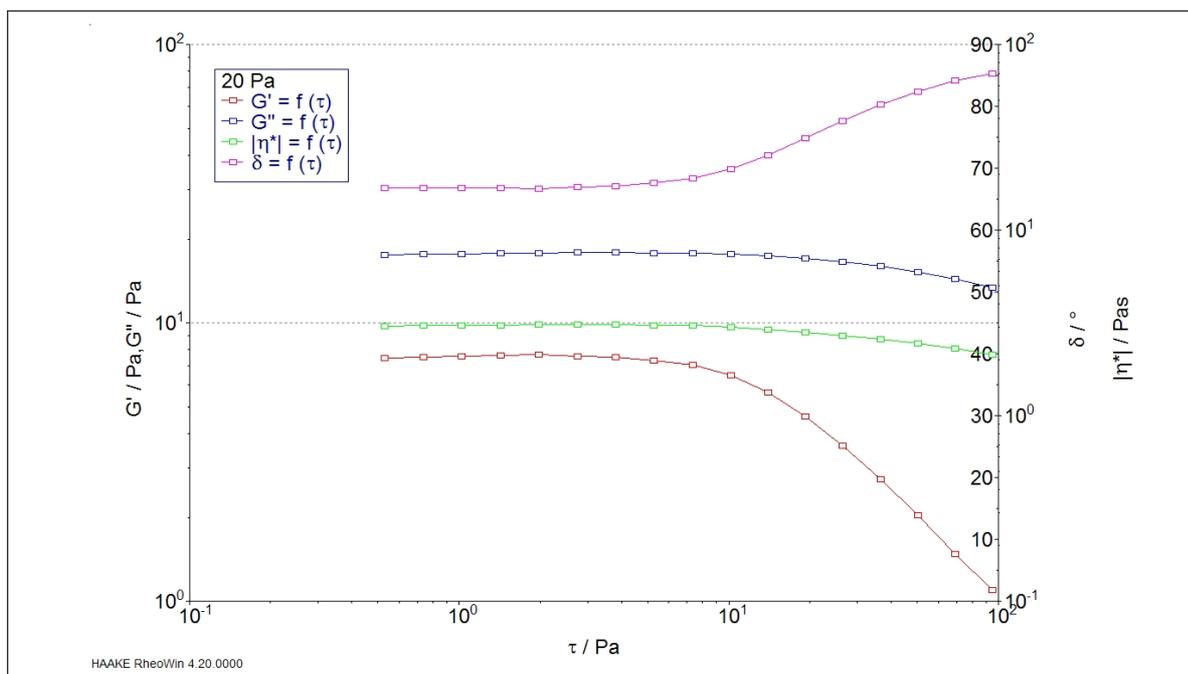


Fig. 5: The result of the stress sweep confirms that no gel has been formed under an oscillatory stress of 20 Pa. The phase angle in the LVR is around 67°, far above 45°, the sol/gel-transition point.

a stress accidentally chosen too high, will affect the test results. Before running for example a time sweep or a temperature sweep on a gelation formulation to the end that the results will be used to set up a production process, it has to be made sure that the test conditions reflect the conditions during production. Typically, gels are synthesized at rest to obtain the best gel strength possible. Thus, the rheological test must not disturb the development of the gel network. To be on the safe side, the tests to follow a gelation process or to characterize a gel should be performed with

the smallest stress or smallest deformation still yielding reliable rheological data.

The HAAKE Mars rheometer with its torque sensitivity down to the nano-Newton-metre-range is the perfect tool to characterize even weak gel-structures and their formation without inadvertently affecting them.

Using the capabilities of the HAAKE RheoWin software, the whole test program consisting of sample loading, temperature equilibration 3 cooling runs, 3 stress sweeps and the determination of the cross-over points was

written into one single test method, which ran unattended even saving the results of the individual tests into separate files.

Based on the degree of automation possible with HAAKE RheoWin, only a minimum of working time is needed to prepare and start a complex test program like the one described in this report. It is therefore suitable for the time-effective determination of the optimum testing conditions. Only if the gelation is not influenced by the test conditions, significant results can be generated, which describe the gelation process under production conditions correctly.

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