

Monitoring flow properties of food gels

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INTRODUCTION

Biopolymers are often used in the food technology for texturizing thus not only taking special advantage of their thickening effects but also of their characteristic gel forming properties. Gel forming biopolymers are gained from vegetable (e.g. starch, Carrageenane), animal (e.g. gelatin) or bacteria resources (e.g. Xanthan).

During the processing of aqueous gelling systems usually sol-gel transitions occur which are the reason for a very complex rheological behavior. Varying environmental parameters (time, temperature, concentration, etc.) often lead to dramatic changes in the viscoelastic behavior.

For the rheological characterization of such sol-gel transitions dynamic tests are performed which in contrast to shear measurements offer a good chance for non-destructive tests under small amplitude deformation to observe the structural changes. With such measurements the gel-forming kinetics [EIDAM et al. 1995] as well as the gel strength [REINHARDT et al. 1994; KULICKE et al. 1996] can be quantified.

In practice, an exact, extensive characterization of complex sol-gel cross-overs often requires intensive efforts of time and personnel. Strict criteria in the quality management increasingly require the optimization of rheological measuring methods by reducing the number of measurements and at the same time gain more information per time unit. For tests on self aggregating systems like gels the application of MultiWave seems to be a promising method, as recent discussions prove. [DOUBLIER et al. 1996].

Aim of this report is to show how an improved structure information can be obtained with MultiWave-tests (i.e. superposition of several frequencies) allowing a fast determination of the frequency dependency of viscoelastic quantities. This is shown on processes for

which time- resp. temperature-dependent changes of the viscoelastic behavior have so far only been determined at one constant frequency.

EXPERIMENTS

1. Biopolymers

A thermo-reversible gelling gelatin was selected as gel forming biopolymer. As substance a special commercial gelatin for the production of gel-coatings was used.

As test preparation the gelatin (containing 20% gelatin, 50% water, 30% glycerin) was melted in a water bath at a temperature of $T = 80^{\circ}\text{C}$.

2. Rheometry

The rheological measurements were performed with a shear stress controlled rheometer HAAKE RS150 and a plate-plate measuring system (35 mm diameter, gap 0.5 mm). Exact tempering was provided by the tempering system HAAKE TC80. AutoGap and ThermoGap ensured the exact position control during the measurements.

After being filled in the measuring system the substance was coated with liquid paraffin up to the upper rim in order to avoid a drying out during the measurements.

RESULTS AND DISCUSSION

The material functions gained from the mechanical sine wave measurements (storage modulus G' , loss modulus G'' , dynamic complex viscosity η^* , etc.) are often used as characteristic rheological quantities in order to simulate and describe the application behavior. Fig. 1 shows a schema of characteristic curves of storage and loss moduli as functions of time, temperature and angular velocity, deformation as well as the correlation with the application.

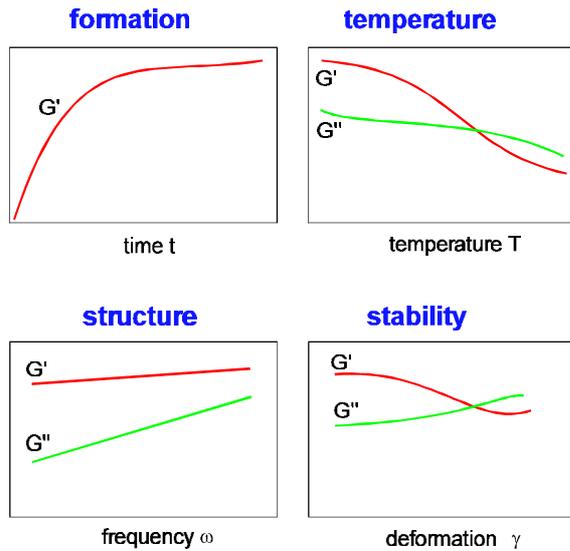


Fig.1: Schema of the storage moduli G' and the loss moduli G'' as function of various measurement parameters as well as the possibility of correlation with sol-gel characteristics.

Measurements for the characterization of time- and temperature-dependent structure changes are performed at a constant angular velocity ω or frequency f). A differentiated statement about the inner structure of the systems examined cannot be expected from this setup without investigating different stress energies.

The frequency dependency of viscoelastic properties cannot be investigated by a discrete frequency-sweep (subsequent measurements at different frequencies) during such processes since the substance is changing dynamically during the measurement which makes a meaningful status description almost impossible.

The other alternative, to repeat the measurements at constant, different frequencies multiplies the measuring effort.

Investigating the frequency dependency by MultiWave will significantly shorten the measuring time.

The MultiWave principle is based on a preset basic sine wave and higher frequencies modulated on it. This results in a complex shear stress setting which acts on the substance during the time of the basic sine wave.

The response function of the substance in the deformation level can again be transformed in the frequency domain with the Fourier analysis (FFT) resulting in a discrete deformation signal for each frequency [BRIGHAM 1995.]. The application of MultiWave is introduced on a thermo-reversible gelling gelatin.

3.1 Improved characterization of the temperature dependent gelling behavior by MultiWave

When investigating thermo-reversible gelling systems the temperature dependent gelling behavior is for many applications of utmost importance. Processing is done above the gel point temperature T_{GP} thus making use of the flowability of a biopolymer in its sol state. On cooling the system starts to gel and the flowability is gradually deteriorating until a viscoelastic solid body texture is reached.

From the rheological point of view this process is characterized as sine wave measurement where the temperature dependencies of the storage modulus G' and the loss modulus G'' are plotted at a small deformation amplitude and constant frequency. Fig. 2 shows such a measurement for the tested gelatin; the temperature of $T = 70^\circ\text{C}$ was cooled down to $T = 20^\circ\text{C}$ at a rate of $5^\circ\text{C}/\text{min}$.

It can be recognized that at higher temperatures the loss modulus G'' (stands for viscous portions) is higher than the storage modulus G' (stands for elastic portions) which documents the flowability of the substance. With decreasing temperatures this effect is gradually deteriorating and below the gel point temperature T_{GB} („cross-over,, - $G'=G''$) a reverse effect can be detected. Here the elastic properties of the substance prevail.

During this temperature ramp MultiWave measurements were added as measurement segments in 10K-intervals (see markers in fig. 2). As basic sine wave a value of 0.2 Hz was selected.

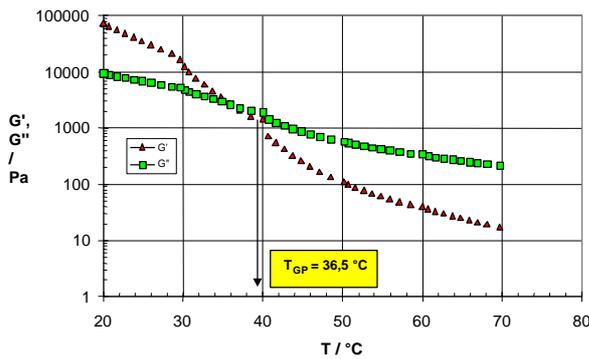


Fig. 2: Storage modulus G' and loss modulus G'' as a function of temperature T for the tested gelatin (angular velocity $w = 2,15$ Hz, cooling rate 5 K/min); every 10 degrees MultiWave-measurement ($0,215 - 10$ Hz).

Based on this basic sine wave this leads to a measuring time of 5 seconds which means considerable time savings compared with a traditional frequency sweep. Nine higher sine waves were modulated on this basic value so that a total of 10 logarithmically equidistant frequencies over two decades could be used for evaluation. The preset shear stresses for the temperature ramp as well as for the MultiWave measurements were selected that way that the resulting deformations stayed within the range of 0.1 and 1%. During pre-testing it was ensured that the tested substance reacts linearly viscoelastic within this deformation range.

With this combined method viscoelastic material functions can be obtained for the selected temperatures and for different frequencies. Fig. 3 shows the frequency dependency of the storage moduli.

It can be seen that on increasing cooling the absolute moduli values increase for every frequency which could already be seen from the simple temperature ramp.

Furthermore, the frequency dependency of the storage moduli allows a statement with regard to the polymer network structure of the gelling system at different stages of the gel forming process. At high temperatures a pronounced frequency dependency can be observed. This network structure where molecules can store

the applied energy elastically by moving modes (rotation, entanglement, etc.)

With decreasing temperatures the frequency dependency deteriorates until the end temperature of $T = 20^\circ\text{C}$ is reached where the storage modulus stays almost on one level which is due to a transition to an increasingly permanent network structure where the applied energy can only be stored to a limited extent between two fix network points. This macroscopic behavior corresponds to the changes on the molecular level. During the sol-gel transition polymer chains are associated which before could only interact through purely mechanical entanglements and form fixed three-dimensional orderly arranged structures („junction zones“). The momentum for this association are energetic interactions (H-H-bonding etc.), the effects of which can be seen at many biopolymers.

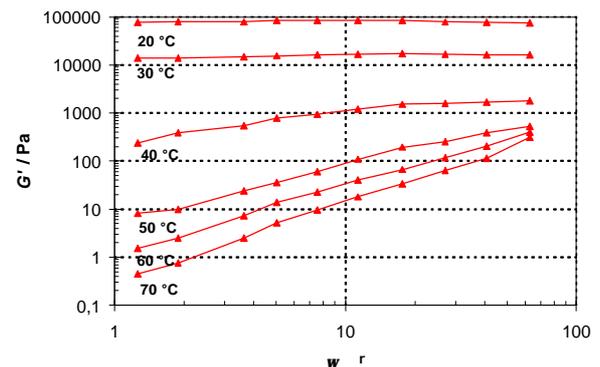


Fig. 3: Storage moduli G' as a function of angular velocity w at different temperature for tested gelatin (measuring results from MultiWave measurement ($0,215 - 10$ Hz)).

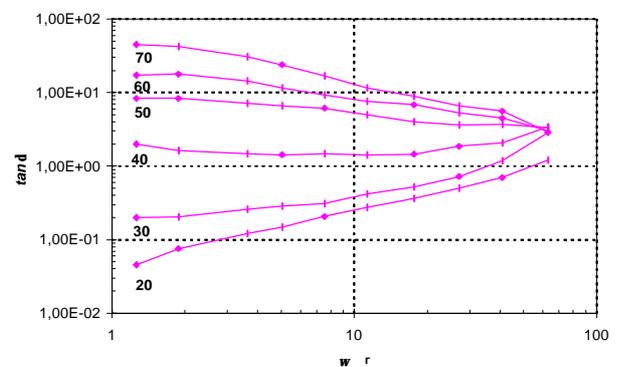


Fig. 4: Loss factors $\tan \delta$ as function of the angular velocity w at different temperatures T for the tested

gelatin (measuring results from the MultiWave measurement (0,215 - 10 Hz)).

Even when considering the total viscoelasticity a more extensive information on the tested sol-gel transition can be obtained.

For this the loss factor $\tan \delta$ can be investigated which as quotient from loss and storage modulus reflects the ratio between viscous and elastic properties. Fig. 4 shows the frequency dependency of this quantity from the MultiWave measurements.

Loss factor $\tan \delta = 1$ can be considered as characteristic limit; loss factors above 1 reflect mainly viscous, loss factors smaller than 1 mainly elastic behaviors.

From Fig. 4 can be seen that above the gel point temperature the viscous flow portions prevail in the sol state ($T = 50 - 70^\circ\text{C}$). The decreasing loss factor values at increasing frequency show the typical behavior of temporary network structures where the elastic portions grow stronger than the viscous ones with increasing stress energy.

A contradictory behavior can be observed in the gel state ($T = 30 - 20^\circ\text{C}$). Here the values of the loss factors are smaller than 1 (dominating elasticity). The increase of the loss factors with increasing frequency is characteristic for biopolymer gels which react increasingly viscous under increasing stress [EIDAM 1995].

In the transition range of the sol-gel cross-over, at a temperature of $T = 40^\circ\text{C}$, values of a bit over 1 without substantial frequency dependency can be observed reflecting a pasty behavior.

Besides the viscoelastic structural parameters one can also look at the pure viscosity behavior the temperature and frequency dependency of which allows conclusions regarding the texture of the substance.

Fig. 5 shows the frequency dependency of the dynamic complex viscosity η^* for different temperatures.

Fig. 5 does not only prove the expected result that with decreasing temperature the viscosity increases. Also, the dependency of the measuring frequency leads to additional findings: At temperatures of $T = 70^\circ\text{C}$ resp.

$T = 60^\circ\text{C}$ a Newtonian behavior can be observed.

Only below a temperature of $T = 50^\circ\text{C}$ it becomes slightly pseudoplastic. With decreasing temperature the frequency at which the dependency of the viscosity starts showing shifts to smaller values.

In the gel state ($T = 30^\circ\text{C}$ resp. $T = 20^\circ\text{C}$) there is no more zero shear range in the considered frequency range. The viscosity dependency of the frequency is substantial and extends in the MultiWave frequency range over more than one decade.

SUMMARY

The results presented in this report show that MultiWave measurements can be used to gain more information regarding complex structural changes like sol-gel cross-overs in a shorter period of time.

Although there are no new material functions available characteristic rheological data can be derived from the frequency dependency of the viscoelastic parameters reflecting the application behavior.

The table of Fig. 6 shows how the rheological material functions can be related to the application.

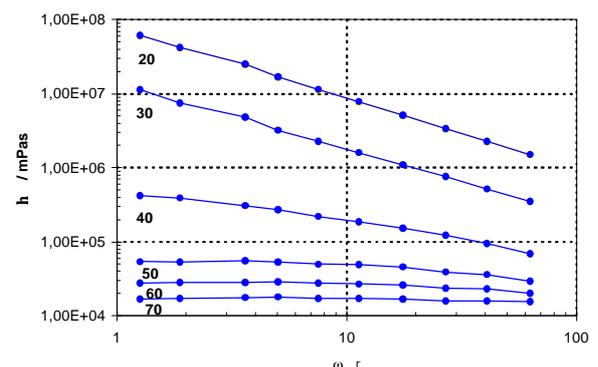


Fig. 5: Dynamic complex viscosities h^ as a function of angular velocity ω at different temperatures T for the tested gelatin (measuring results from MultiWave-measurement (0,215 - 10 Hz)).*

	Viscosity	Viscoelasticity
Additional information by frequency dependance	<u>flow curve</u> -zero shear viscosity -pseudoplasticity -slope of flow curve	<u>moduli</u> -viscoelastic behaviour at different time scales -network structures
Application	<u>processing</u> -transportation -filling	<u>texture</u> -gel strength -stability
Rheological Indices	$\eta^* = f(\omega)$	$G', G'' = f(\omega)$ $\tan \delta = f(\omega)$

Fig. 6: Additional information through frequency dependency at sol-gel cross-overs and relations to application conditions.

Besides the temperature dependency (gelling behavior) MultiWave measurements can also be used for the observation of the time dependent structural recovery of gelling systems. This offers a significant advantage for the detection of the gel forming kinetics especially for not reversibly gelling systems (e.g. native starches). Traditional „sweep“-measurements can usually not be performed on those systems because the substance changes during the measurement time.

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