Short Communications

Free oscillatory shear measurements – an interesting application of constant stress rheometers in the creep mode*

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Abstract: A constant stress rheometer in the creep mode was used to perform free oscillatory shear measurements on soft solids. The results obtained are in good to excellent agreement compared to forced oscillatory shear measurement data. Depending on the rheologic properties of the sample and the moment of inertia of the rotating device of the measurement system, free oscillations are suited to confirm or supplemented forced oscillatory measurement results.

Key words: Free oscillations – forced oscillations – shear measurements – creep – soft solids – gels

Introduction

Forced oscillatory shear- and creep measurements with controlled stress- or controlled strain rheometers have become standard methods to investigate the rheologic behavior of viscoelastic materials. Besides the determination of material constants like the relaxation modulus and the steady-state shear compliance, these methods allow to investigate a sample's time dependent behavior, i.e., measurements of storage- and loss moduli as a function of the oscillatory frequency, or measurements of the creep compliance in the course of time. Theoretically, the free oscillatory shear- and the creep compliance measurements should yield equivalent results and one method should confirm the other. Practically, forced oscillatory measurements give more reliable results in the study of a sample's short-time/high-frequency behavior, whereas creep measurements are preferred in the long-time/low-frequency domain. The time domain where the results of both methods overlap is limited and usually covers the range of 1 – 100 s (Schwarzl, 1990). Particularly for a verification of the high frequency part of the oscillatory measurements the use of another measuring device is required.

In the course of our rheologic investigations on aqueous- and microemulsion mediated gelatin gels with a constant stress rheometer (Zölzer and Eicke, 1992) we observed free oscillations. These oscillations – disturbing typically the start of creep measurements on samples with relatively low damping – are generally undesirable, because they hamper a reliable determination of the important steady-state shear compliance by extrapolation to $t = 0$ (Schwarzl, 1990). On the other hand such free oscillations contain information on rheologic quantities like frequency and decrement. Thus, one can utilize such data to verify or supplement the results of forced oscillatory shear measurements, even in the higher frequency domain.

Experimental

Materials and sample preparation

Bis(2-ethylhexyl)sulphosuccinate sodium salt (AOT) was obtained from Fluka (MicroSelect) and used without further purification. Isooctane was also a Fluka product (puriss., p.a.) and used without further treatment. The water was deionized and then twice distilled. The gelatin was obtained from Sigma (G-2500, 300 Bloom, lot 60 H 0832).

The aqueous gelatin gel was prepared by dissolving 1.00 g of gelatin in 11.12 g of water at 60 °C, followed by cooling the solution to room temperature.

The microemulsion mediated gelatin gel was prepared from a mixture of 0.36 g gelatin and 1.14 g of

* Dedicated to Professor W. Nitsch on the occasion of his 60^{th} birthday.

water which was allowed to swell for 2 h at room temperature. Following 10.00 cm^3 of a 0.1 M AOT-solution in isooctane were added and the sample heated up to 60 °C. After extensive mixing and cooling to 20 °C a transparent gel was obtained.

Instrumental

The rheometer was a Carrimed CRSH 100 equipped with the release 5.1 controlling software. This software offers the possibility to perform forced oscillatory shear measurements up to a frequency of 40 Hz and to determine precisely the moment of inertia I of the rotating axis and measuring system, in our case 19.087 ± 0.005 μNms^{-2}. The measurement system was a home-made double cone geometry which is described in detail elsewhere (Zölzer and Eicke, 1992). The angles of the double cone system (outer cone 12 °, inner cone 14 °) were chosen small enough to enable a calculation of the rheologic quantities with the same formulas as used in connection with cone-plate geometries.* All measurements were performed within the linear viscoelastic region.

The free oscillations of the rotating system were recorded in the rheometer's creep mode. In this mode, 100 points are recorded within the first 0.1 s, then 10 points are taken every 0.1 s. The stress was applied for one second, but the oscillations have already vanished after about half a second. Thus, the oscillations recorded are superimposed by an additional stress component leading to asymmetric patterns of the graphs. This does not affect essentially the evaluation of the rheologic quantities because it can be adjusted for mathematically. The stress applied was just large enough to allow for recording of a few oscillatory cycles.

Free oscillations were also obtained after the removal of stress, i.e., in the creep recovery mode. It was possible to reproduce the radian frequencies ω and the damping constants β of the creep-mode experiments to within 2.4% and <0.1%, respectively.

Before applying the theoretical model to the data some of the data points recorded within the first 0.1 s were dropped in order to achieve a more even data point distribution. A damping controlled frequency shift was always neglected.

* Instruction Manual for the Carri-Med CSL Constant Stress Rheometer, Sect. 9, p. 2.

Theoretical considerations

The time-dependent elongation $x(t)$ of a damped oscillation can be described by

$$x(t) = x_0 e^{-\beta t} \sin(\omega t) \ , \qquad (1)$$

where β is the damping constant and ω is the radian frequency of the oscillation. After one period ($t = T = 2\pi/\omega$) the initial amplitude x_0 is reduced by $e^{-(2\pi\beta/\omega)}$. Generally, the ratio of two successive amplitudes is $e^{-2\pi\beta/\omega}$. The natural logarithm of $2\pi\beta/\omega$ is called the logarithmic decrement Δ.

From the forced oscillatory measurements, we obtain Δ by considering that

$$G''(\omega)/G'(\omega) = \tan\delta \ , \qquad (2)$$

and

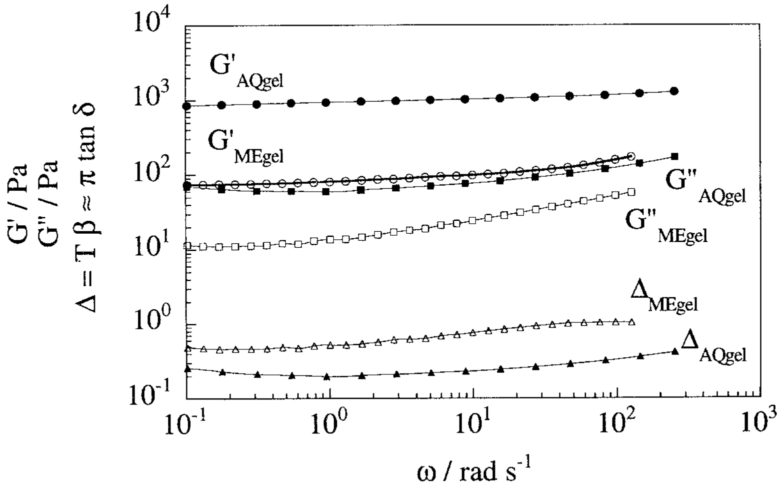

Fig. 1. Storage moduli (G'), loss moduli (G'') and the decrements (Δ) of the aqueous gelatin gel (AQgel) and the microemulsion mediated gelatin gel (MEgel) plotted against the radian frequency (ω). The compositions of the samples are given in the text, $T = 20$ °C

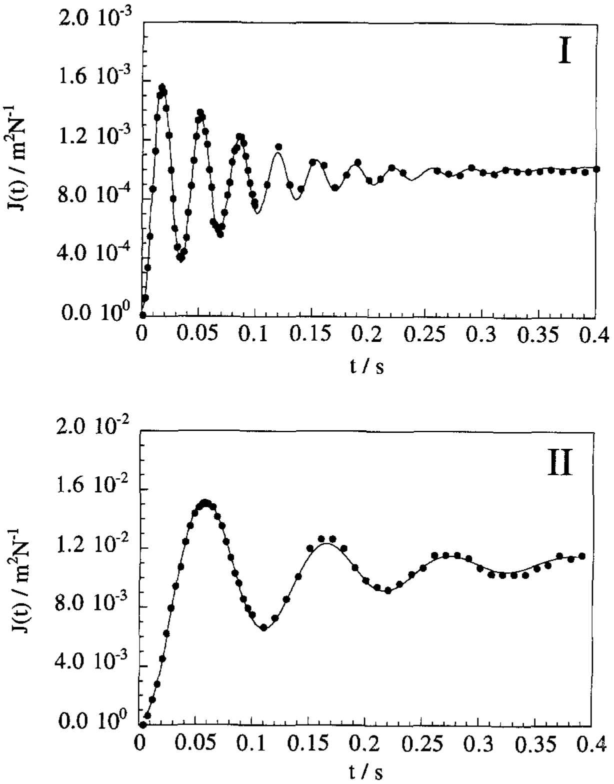

Fig. 2. Free oscillations of the aqueous (I) and the microemulsion mediated gelatin gel (II) induced by stresses of 30.0 Nm^{-2} (I) and 1.5 Nm^{-2} (II) in the creep mode, respectively, are plotted as creep compliances J against the time t; $T = 20\,°C$. The data points are the experimental results, the graphs were obtained by fitting the data to Eq. (1). The actual fitting had to be performed by considering a phase angle in the argument of the sinus and an additional constant amplitude term in order to describe the parallel shifts of the graphs along the two axes. The small asymmetric rise of the $J(t)$-values caused by the superimposed stress components required an additional linear time-dependent term

Table 1. Comparison of the results of free and forced oscillatory measurements. The values in italics were calculated from measured rheologic quantities listed in the same column.

Rheologic quantity	Microemulsion mediated gelatin gel		Aqueous gelatin gel	
	Oscillations		Oscillations	
	Free	Forced	Free	Forced
ω_c/rad s^{-1}	59	59	185	185
$G'(\omega)$/Pa	*139*	132	*1367*	1164
$G''(\omega)$/Pa	*40*	39	*184*	157
$\tan\delta$	*0.288*	0.295	*0.135*	0.135
β/s^{-1}	9.0	*9.1*	13.0	*12.4*
Δ	0.96	*0.97*	0.44	*0.42*

$$\Delta \approx \pi \tan\delta \quad (\tan\delta \ll 2\pi) \ . \tag{3}$$

A comparison of the Δ's may, therefore, serve to compare the results of free and forced oscillatory measurements, especially in those cases where the moment of inertia I of the rotating measuring system is not exactly known.

If I is known and if $\Delta \ll 2\pi$ (Schwarzl, 1990; Struik, 1967), it is possible to calculate separately G' and G'' at the frequency ω from free oscillatory data (Ferry, 1980) by

$$G'(\omega) \simeq (I\omega^2/b) \tag{4}$$

and

$$G''(\omega) = (I\omega^2/b)(\Delta/\pi) \ ; \tag{5}$$

$b = 2\pi r^3/3\theta$ is a form factor valid for cone-plate and double-cone geometries; it is obtained from r, the radius of the sample, and θ (in radians), the angle between the rotating and the fixed parts of the system.

Results and conclusions

Forced oscillatory measurements reveal that both the aqueous and the microemulsion mediated gelatin gels behave like weak solids (Fig. 1). The onset of stress in the creep mode causes the rheometer's rotating system to perform damped oscillations (Fig. 2). A comparison of the rheologic quantities obtained from both kinds of measurements (see Table 1) reveals that the agreement depends on the properties of the sample and can be considered as good to excellent.

In the case of the more elastic aqueous gelatin gel, oscillations with a frequency of about 30 Hz were recorded. Already this is higher than the maximum frequency usually accessible in free oscillatory shear measurements (25 Hz) (Ferry, 1980). Under the assumption that the moment of inertia could be further decreased, e.g., by application of measurement systems made from acrylic resin, even higher frequencies should be accessible. On the other hand if I is systematically increased, e.g., by attaching additional masses to the rotating axis, it should be possible to obtain a series of frequency-dependent data probably down to 0.1 Hz (Ferry, 1980).

On the whole, free oscillatory shear measurements with a constant stress rheometer seem to be appropriate to confirm or to supplement the results of forced oscillatory measurements, at least if the materials under investigation are soft solids.

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