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ORIGINAL CONTRIBUTION

Jörg Läuger
Klaus Wollny
Siegfried Huck

Direct Strain Oscillation: a new oscillatory method enabling measurements at very small shear stresses and strains

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J. Läuger (✉) · K. Wollny · S. Huck
Physica Messtechnik GmbH, Vor dem Lauch 6, 70567 Stuttgart, Germany
E-mail: laeuger@physica.anton-paar.com

Abstract As shown previously, a rotational rheometer equipped with an electronically commutated motor (EC-motor) allows one to conduct stress and strain experiments with the same rheometer in rotational mode. A new method has now been developed to improve further strain controlled oscillatory measurements by adjusting the strain directly within a single oscillation cycle. Generally, a strain controlled oscillatory test in a stress controlled rheometer consists of the following steps: applying one full oscillation cycle with an arbitrary stress amplitude, measuring the strain amplitude, adjusting the stress in the next oscillation cycle, and repeating this routine until the desired strain amplitude is reached. The newly developed direct strain oscillation mode employs a different approach. It does not require a full oscillation cycle but uses a real-time position control and adjusts to the desired strain directly on the sine wave. Therefore, the actual movement of the measuring system follows directly the required change in strain during each individual oscillation cycle.
This new oscillatory mode has several major advantages: (1) the possibility of conducting real strain controlled tests in oscillation, (2) the exact strain setting right from the first oscillation cycle, i.e., no or only very slight overshoot in strain, (3) faster data acquisition even within an oscillation cycle, (4) it allows the measurement at extremely low angular resolution and low torques. Due to the absence of strain overshoots and the ability of testing at small deflection angles and low torques this new method is especially helpful for measurements on samples with low viscosities and weak structures such as gels, emulsions, suspensions, colloids, and foams.

Keywords Rheometry · Oscillation · Strain control · Strain resolution · Stress resolution

Introduction

Historically there are two principles used for research grade rotational drag flow rheometers, the CR (controlled rate or controlled strain) and the CS (controlled stress) approach (see, for example, Macosko 1994). In CR devices the displacement or speed (strain or strain rate) is applied to the sample and the resulting torque (stress) is measured separately by the use of a transducer, whereas in CS devices a force is applied and the resulting displacement or speed is measured. Despite recent improvements, mainly due to the use of better and faster electronic components, the abilities of a conventional CR device to conduct CS tests like creep and creep recovery or of a CS machine to perform CR tests like step strain or strain sweep are still limited.

However, the need for more flexible instruments which can carry out CS and CR tests even with the same

sample and within the same measurement is increasing. Such a flexibility allows one not only to perform all standard rheological tests with a single instrument, but to create measurement profiles which are more complex and provide more possibilities for the direct simulation of practical applications, like the structure recovery after a high shear load.

It has been shown previously that a rotational rheometer equipped with an electronically commutated synchronous motor (EC-motor) enables stress and strain controlled rotational experiments to be performed with the same rheometer (Läuger and Huck 2000). Two different cases in which the CR capabilities of an EC-motor equipped rheometer were used are mentioned here as typical application examples: first, Nakken et al. (2001) employed speed or shear rate control to investigate polymer induced drag reduction which is an extremely important issue for pumping and pipe flow of crude oils; second, Archer (1999a, 1999b); Islam et al. (2001); Juliani and Archer (2001) used shear rate as well as strain control to measure transient effects and relaxation phenomena in polymer solutions and polymer blends.

The aim of this paper is the description of a new oscillation method which extends the strain capabilities of an EC-motor based rheometer to oscillatory tests.

Generally, a strain controlled oscillatory test in a stress controlled rheometer consists of the following steps: applying one full oscillation cycle with an arbitrary stress amplitude, measuring the strain amplitude, adjusting the stress in the next oscillation cycle, and repeating this routine until the desired strain amplitude is reached. The newly developed Direct Strain Oscillation (DSO) method uses a different approach. It does not require a full oscillation cycle but uses a real-time position control and adjusts to the desired strain directly on the sine wave. Therefore, the actual movement of the measuring system directly follows the required change in strain during each individual oscillation cycle.

This new oscillation mode has several major advantages including:

1. The possibility of conducting real strain controlled tests in oscillation
2. The exact strain setting right from the first oscillation cycle, i.e., no or only very slight overshoot in strain
3. Faster data acquisition even within one oscillation cycle
4. Measurements at extremely low angular resolution and low torques
5. The absence of a rotational drift

Due to the absence of strain overshoots and the possibility of testing at low strain and low stress levels, this new method is especially valuable for measurements on samples with low viscosity and a weak structure such as gels, emulsions, suspensions, colloids, surfactant solutions, lubricating greases, and foams.

Experimental

Method

The principle of an EC-motor has already been described in detail (Läuger and Huck 2000). The parts relevant to this study will be discussed briefly. An EC-motor uses an electronic commutation in which the motor is excited by special permanent magnets with a high flux density. The rotor field is therefore known and the EC control makes use of this knowledge. It is possible to adjust the electro-magnetic torque in such a way that it is linear to the total amount of the stator current, i.e., $M \sim I_s$. Under these conditions a change in the stator current will be followed by a change in the torque almost instantaneously.

Traditional strain oscillation with a stress rheometer. The frequency is fixed and a certain strain amplitude γ_{0d} is desired. As sketched in Fig. 1 in this case the instrument applies a full stress oscillation cycle $\tau(t) = \tau_0 \cdot \sin(\omega \cdot t)$ and the resulting deflection is measured. Since in a real experiment only a finite amount of discrete deflection angles can be measured by the rheometer electronics, a fast Fourier transformation (FFT) is conducted after each oscillation cycle. Normally only the resulting first harmonic is used giving a strain oscillation: $\gamma(t) = \gamma_0 \sin(\omega \cdot t + \delta)$, where ω is the preset frequency and δ the sample dependent phase shift. The resulting strain amplitude γ_0 is compared with the desired strain amplitude γ_{0d}. In the next oscillation cycle the stress amplitude τ_0 is adjusted to reach a γ_0 value which is closer to the desired strain amplitude γ_{0d}. This process is repeated until γ_0 and γ_{0d} are equal within a few percent. Depending on the sample and the torque which is required, the adjustment process can take many oscillation cycles. There is the additional risk that during the adjustment the strain can be much higher than γ_{0d}, i.e., a strain overshoot occurs and the actual strain is beyond the linear viscoelastic range of the sample. Thus a sensitive sample structure might be destroyed.

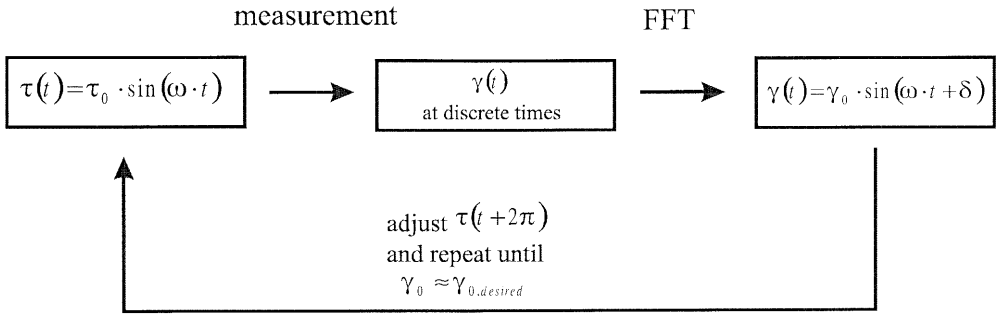

Fig. 1. Schematic diagram for the traditional oscillation with a stress rheometer

Direct Strain Oscillation (DSO). The desired strain is $\gamma_d(t) = \gamma_{d0}\sin(\omega \cdot t)$. In the direct strain oscillation mode a stress $\tau(t)$ is applied at the time t and the resulting strain $\gamma(t)$ is measured. Then the stress is adjusted to minimize $|\gamma_d(t+\Delta t) - \gamma(t+\Delta t)|$, i.e., that the actual strain follows the desired sinusoidal strain wave. Figure 2 shows the schematic diagram of this process. Depending on the frequency used and the sample properties, the length of the adjustment period differs but normally the adjustment is finished within half of the first oscillation cycle. The applied strain now directly follows the desired strain wave. The necessary stress values are used to calculate the stress amplitude τ_0 and the phase shift δ. Not only can this be done after a full cycle, but also within an oscillation cycle since there is no need for a Fourier transformation as in the traditional strain oscillation for stress rheometer. In other words, the adjustment routine of the direct strain oscillation mode gives an online determination of the stress amplitude and the phase shift.

Instrument

All measurements were conducted using the Direct Strain Oscillation (DSO) option on a Physica MCR 300 rheometer equipped with an EC-motor.

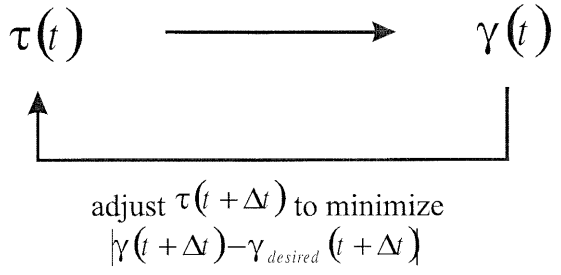

Fig. 2. Schematic diagram for the Direct Strain Oscillation (DSO)

Results

Amplitude and frequency sweeps

Figure 3 shows a strain sweep on a low viscous silicone oil (6.5 mPas at 20 °C). As can be seen, the viscosity is determined over five decades of the deflection angle, i.e., strain, and down to torque values of 0.01 μNm. For the cone-plate geometry (50 mm, 1°) used in this test the limits of the strain and stress are 0.5% and 0.25 mPa, respectively. The excellent agreement between the Direct Strain Oscillation data and the shear viscosity from a rotational test is shown in Fig. 4. For comparison purposes a shear rate was calculated from the oscillation data by the expression $\dot{\gamma} = \omega \cdot \gamma$.

Results of an oscillatory strain sweep at $\omega = 6.28\ s^{-1}$ on a polyisobutylene polymer solution are displayed in Fig. 5. The data prove that it is possible to set angular displacement amplitudes as small as 0.1 microradians and measure torques as low as 0.02 μNm. For the cone-plate geometry with 50 mm diameter and a 1° cone used for this measurement this means strain and stress amplitudes as small as 6×10^{-6} and 1 mPa, respectively.

The DSO method allows the measurement at different frequencies as well. Figure 6 shows results of a typical frequency sweep on the same polyisobutylene solution measured with the same cone-plate measuring geometry (50 mm, 1°) as for the measurement in Fig. 5. A fixed strain amplitude of 0.1 milliradians (strain $= 5.75\times10^{-3}$) was used. As can bee seen from Fig. 6 the angular frequency range started from $\omega < 0.07\ s^{-1}$ and went up to $\omega = 500\ s^{-1}$.

As a third example, Fig. 7 shows a strain sweep at an angular frequency of $\omega = 6.28\ s^{-1}$ on a gel-like food sample. Again, amplitudes starting from 0.1 microradi-

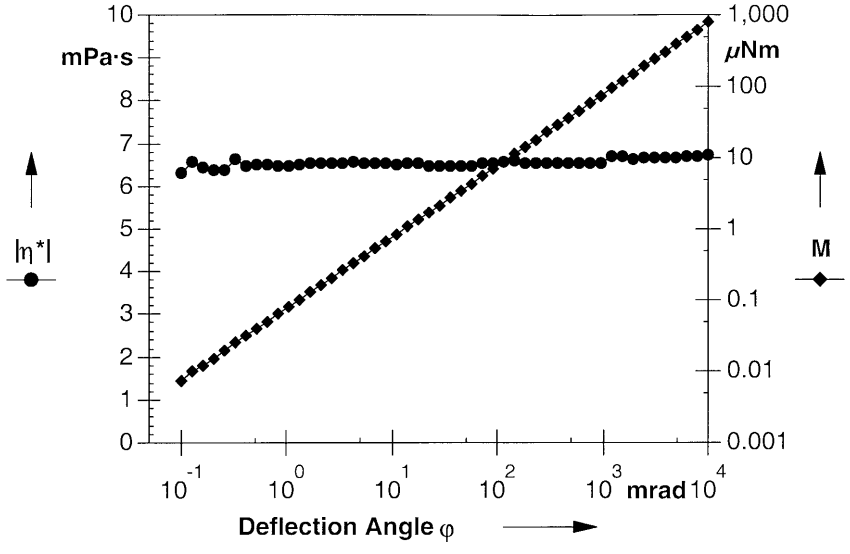

Fig. 3. Oscillatory strain sweep ($\omega = 6.28\ s^{-1}$) on a silicone oil with low viscosity at 20 °C. Cone-plate system 50 mm 1°

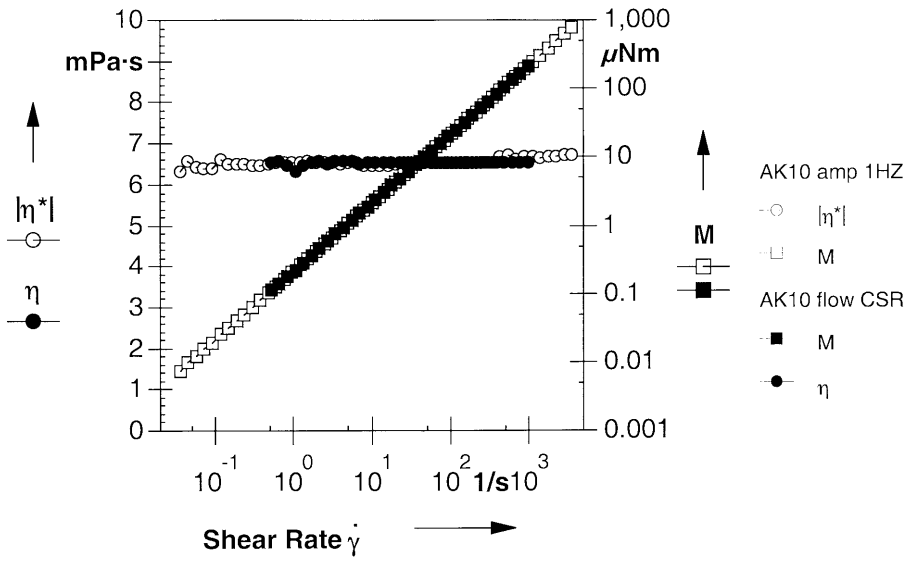

Fig. 4. Comparison of the complex viscosity measured with an oscillatory strain sweep and the shear viscosity from a rotational flow curve test on a silicon oil with low viscosity. Shear rate in oscillation: $\dot{\gamma} = \omega \cdot \gamma$ (see text)

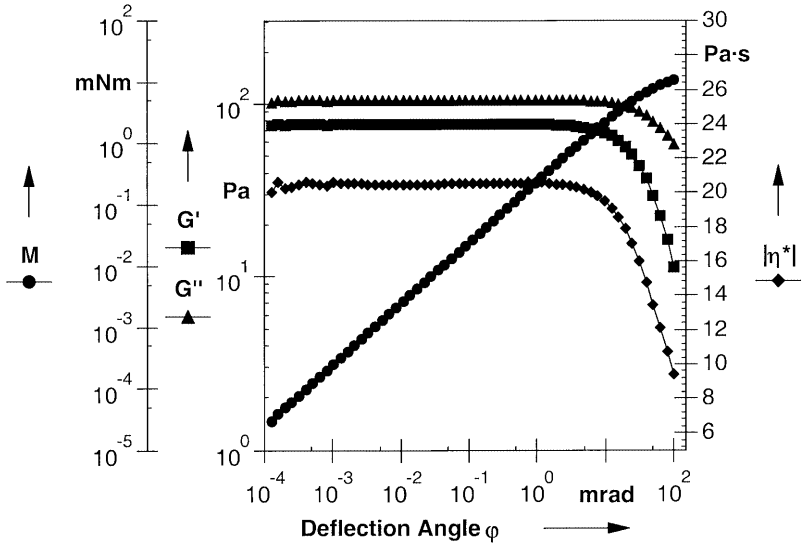

Fig. 5. Amplitude sweep ($\omega = 6.28\ s^{-1}$) on a polyisobutylene solution (NIST SRM1490) at 20 °C. Cone-plate system 50 mm 1°

ans were set and torques smaller than 0.02 μNm were detected, resulting in strain and stress of 4×10^{-6} and 0.23 mPa, respectively. The measuring system used was a plate-plate geometry with a diameter of 50 mm and a gap of 1 mm. As can be seen from Fig. 7, the measuring range covers almost eight decades in strain amplitude.

Fast oscillation measurements

Curing reaction

Figure 8 shows the measurement of a curing reaction of a powder coating at 180 °C. At the start of this experiment the sample viscosity is very low and drops further before the viscosity increases due to the onset of the curing reaction. The resulting torque at the viscosity minimum is well below 0.1 μNm, making it difficult to set the desired strain and measure the rheological properties using a conventional oscillation method. As can be seen in Fig. 8, the DSO method keeps the strain exactly at the desired value and allows the measurement of the whole curing reaction without changing any parameters.

Fast data at low frequencies

The ability of the Direct Strain Oscillation mode to produce valid data points even during one single oscillation cycle is demonstrated in Fig. 9. An oscillation measurement with a constant angular frequency of

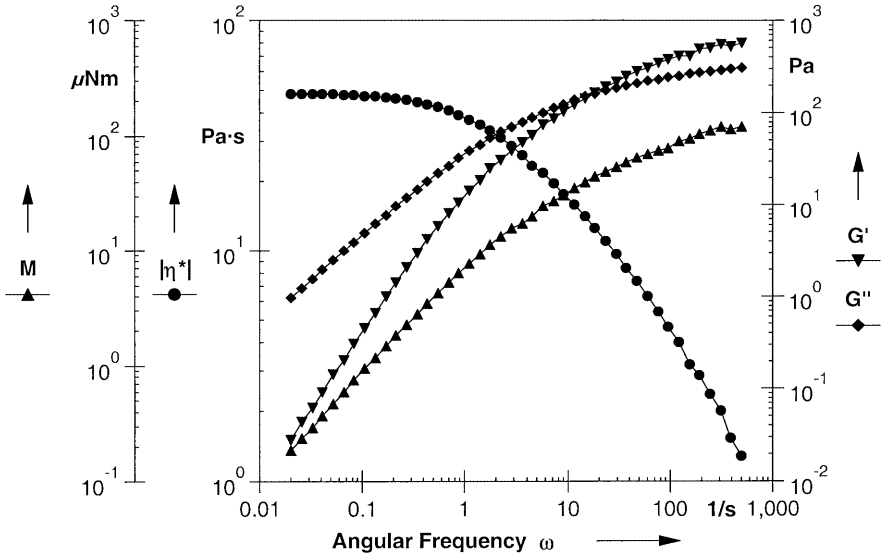

Fig. 6. Frequency sweep at 0.1 mrad (strain = 0.00575) on a polyisobutylene solution (NIST SRM1490) at 20 °C. Cone-plate system 50 mm 1°

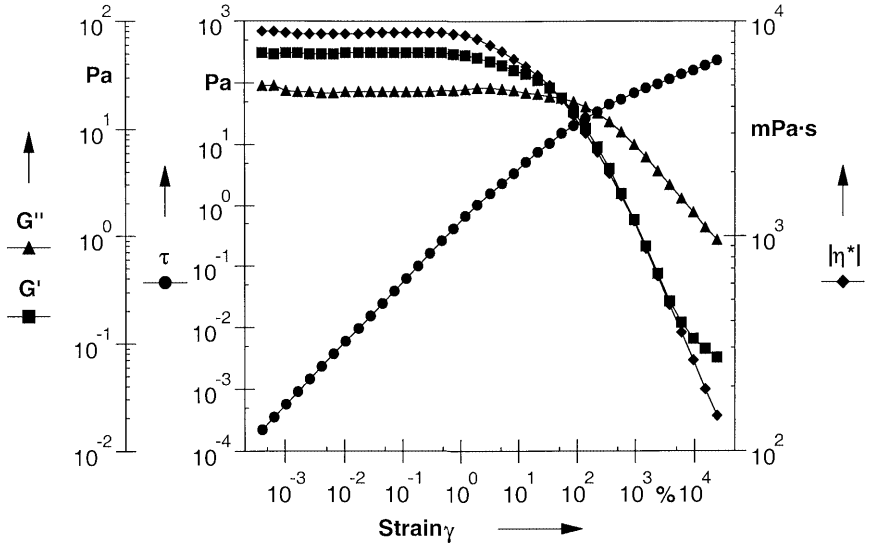

Fig. 7. Amplitude sweep ($\omega = 6.28\ s^{-1}$) on a starch based desert. Plate-plate geometry (50 mm)

$\omega = 0.0628\ s^{-1}$ (frequency f = 0.01 Hz) and a strain of 10% was carried out and data points were taken every 20 s, i.e., five data points per oscillation cycle. As can be seen the strain is already reached at the second data point, i.e., even before half of the first oscillation cycle has passed. Moreover, the resulting G′ and G″ values already have the final values before the first oscillation period is finished.

Structure recovery on low viscous samples with weak structures

Another interesting application of the Direct Strain Oscillation mode is the measurement of structure recovery, i.e., thixotropy, in samples with weak structures. It is well known that the amount and time dependence of structure recovery after a high shear load is crucial for a large variety of practical applications (see for example: Barnes 1997). Figure 10 shows an example with two chocolate milks. A three interval thixotropy test (3ITT) was performed. In the first interval a constant oscillation within the linear viscoelastic range is applied in order to measure the structure at rest. In the second interval a constant shear rate of 1000 1/s was applied for 50 s. In the third interval the structure recovery was followed by a constant oscillation ($\omega = 3\ s^{-1}$; $\gamma = 1\%$). As can be seen the two samples are very different. The first sample shows a fast recovery with a crossover of G′ and G″ after about 1.5 min, whereas in the second sample G″ remains below G′ over the whole measuring time indicating that

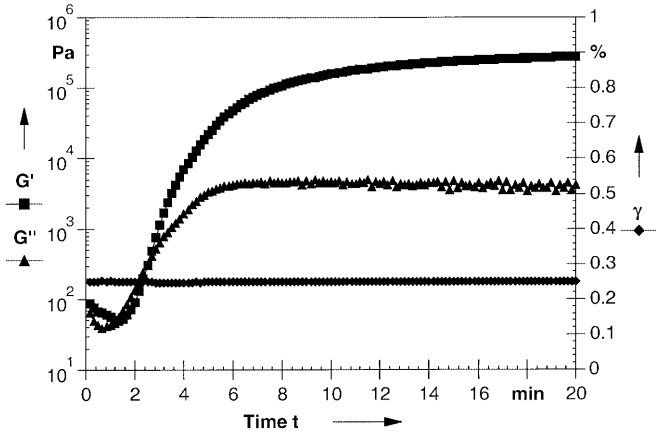

Fig. 8. Curing reaction of a powder coating. Strain: 0.25%, angular frequency: $\omega = 10\ s^{-1}$, plate-plate geometry (25 mm)

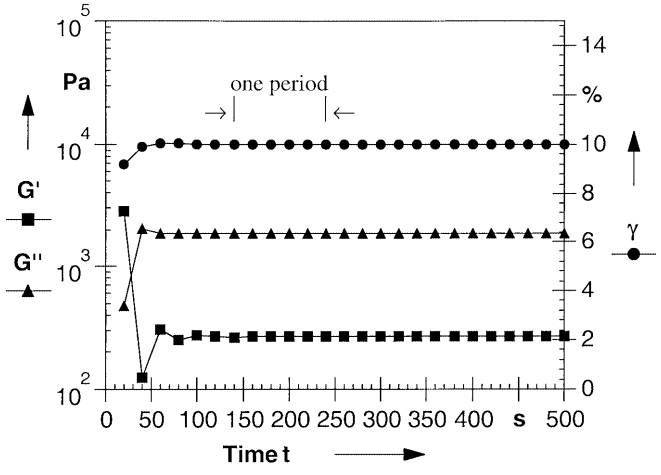

Fig. 9. Constant oscillation measurement on PDMS, $\gamma = 10\%$, $\omega = 0.0628\ s^{-1}$ (f = 0.01 Hz), 20 s measurement point duration, Plate-plate geometry (25 mm)

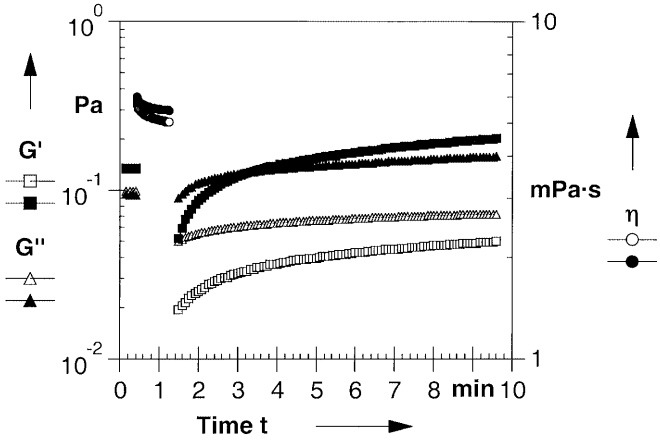

Fig. 10. Structure recovery (thixotropy) of two chocolate milks. $\omega = 3\ s^{-1}$, $\gamma = 1\%$, double gap geometry (42 mm)

this chocolate milk will display sedimentation after shaking the bottle.

Conclusions

It has been demonstrated that, by employing a new oscillation mode called Direct Strain Oscillation (DSO), a rheometer equipped with an EC-motor enables real strain controlled tests in oscillation. This new oscillation method extends the range of the rheometer to new test modes and applications. DSO is especially valuable for measurements at low torques (0.02 μNm) and small deflection angles (0.1 μrad) allowing rheological testing at extremely small shear strain and shear stress values and thus enabling the investigation of very weak structures. The absence of any rotational drift allows structure recovery measurements of low viscous samples with weak structures without destroying the structure during its rebuilding phase.

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