

Creep Recovery Measurements of Polymers^(*)

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ABSTRACT

Creep recovery measurements on anionic polymerized polystyrenes and commercial low density polyethylene have been performed with a new magnetic bearing rheometer. Due to the very small residual torque, a key feature of the magnetic bearing rheometer, small recoverable compliance values in the linear viscoelastic regime could be accurately measured. The equilibrium compliance J_e obtained is compared to the ratio of G'/G'' , evaluated from oscillation measurements in the terminal region (low frequency). Excellent agreement could be found for the narrow distributed PS with a molecular weight from 13 000 to 330 000 g/mol. Finally the shear compliance of a commercial PS was converted to the dynamic moduli G' and G'' using approximation formulas by Schwarzl to extend the frequency range of the oscillation data. The resulting data set represents a dynamic spectrum over a frequency range, large enough to fully describe the viscous and elastic behavior of the material.

SCOPE

The determination of the melt elasticity of thermoplastic melts is of major concern in regards to processing. Oscillatory shear measurements are usually performed to obtain the viscosity and elasticity of a polymer melt. The cross-over point method used with polypropylene, provides a characterization in terms of a viscosity and elasticity parameter. Whereas this method works well for PP, it is not sensitive for other materials such as HDPE. Measurements need to be performed at lower frequencies in the terminal region in this case. The

rheological parameter for elasticity is the equilibrium compliance J_e , and can be obtained from oscillation measurements by evaluating G'/G'' for $\omega \rightarrow 0$. In the terminal region, G' becomes much smaller than G'' , statistical noise and experimental errors reduce the accuracy of the storage modulus G' and consequently also the equilibrium compliance. A direct method to measure the equilibrium compliance J_e is the creep recovery test. The elasticity of the polymer melt is determined from the total recoverable deformation after previous steady state shear. In the following the accuracy of the measurement of J_e from the recovery experiment is demonstrated using a magnetic levitation bearing rheometer.

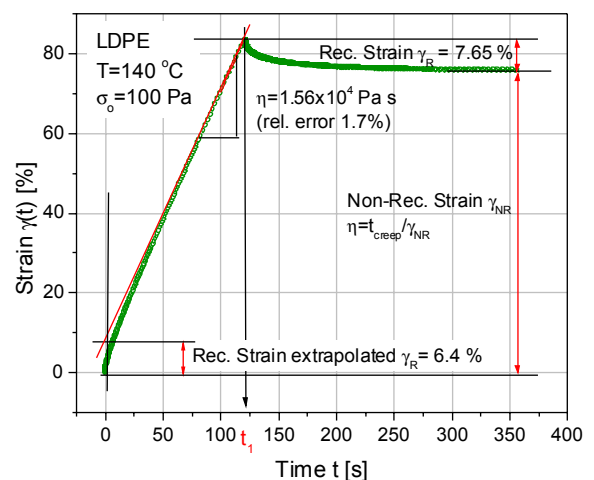


Figure 1: Time dependent strain of an LDPE polymer melt during creep and recovery. The total strain at t_1 can be split in a recoverable γ_R and a non recoverable γ_{NR} part

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SHEAR CREEP COMPLIANCE AND RECOVERABLE COMPLIANCE

$$J(t) = J_o + J_R \psi(t) + \frac{t}{\eta_o} \text{ with } \psi(0) = 0 \text{ and } \psi(\infty) = 1$$

$t > t_1$ recovery

$$\gamma_r(t) = \gamma(t_1) - (\gamma(t) - \gamma(t-t_1))$$

$$= \sigma_o J(t_1) - (\sigma_o J(t) - \sigma_o J(t-t_1))$$

$$\gamma_r(t) = \sigma_o (J_o + J_R \psi(t-t_1))$$

$$\lim_{t \rightarrow \infty} \gamma_r(t-t_1) = \gamma_R(t_1) = \sigma_o (J_o + J_R \psi(t_1))$$

steady state during creep $\psi(t_1) = 1$

$$\gamma_R(t_1) = \sigma_o (J_o + J_R) = \sigma_o J_e \text{ Equilibrium compliance}$$

$= 0$ for polymer melts

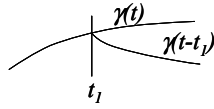
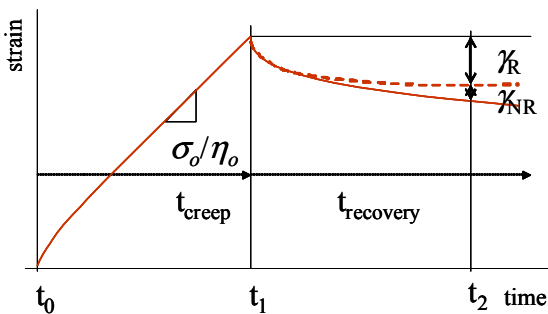


Table 1: Compliance, Recoverable compliance and Equilibrium compliance

THE CREEP RECOVERY TEST

Theoretical consideration

In a shear creep recovery experiment, a constant torque is applied to the sample and the resultant deformation measured as a function of time and applied stress. At a time t_1 , the torque is removed and the material recovers. The time and stress dependent recoverable shear deformation is the difference between the maximum deformation $\gamma(t_1)$ and the shear deformation at $\gamma(t)$ with $t > t_1$ (Figure 1). The total recoverable deformation γ_R for $(t-t_1) \rightarrow \infty$ is a measurement of the materials elasticity i.e. the mechanical energy stored in the sample during the creep phase. The total recoverable strain normalized with the applied stress, is referred to as equilibrium compliance $J_e = \gamma_R / \sigma_o$



Criterion:

$$\frac{|\gamma_V|}{\gamma_R} = \frac{(t_2 - t_1) \sigma_{res}}{\eta_o J_e \sigma_o} < 0.01 \text{ for } t_2 - t_1 = \tau_{max}$$

with $\eta_o J_e = \tau_{max}$

$$\frac{|\gamma_V|}{\gamma_R} = \frac{\sigma_{res}}{\sigma_o} < 0.01 \text{ for } t_2 - t_1 = \tau_{max}$$

Figure 2: Effect of the residual torque on the recoverable deformation and criterion for the applicability of the creep recovery test.

Phenomenologically, the time dependent strain in a creep test can be described as $\gamma(t) = \gamma_o + \gamma_r(t) + \sigma t / \eta$. For polymer melts, γ_o can be neglected and for $t \rightarrow \infty$, only the viscous term contributes to the deformation⁽¹⁾. Normalized with the applied stress σ_o , the compliance $J(t)$, (see table 1.) is obtained. J_R is the total recoverable deformation and $\psi(t)$ the delayed elasticity function. $\psi(t)$ is 0 at time zero and 1 for $t \rightarrow \infty$. The recoverable deformation $\gamma_r(t)$ obtained during the recoil experiment at $t > t_1$, is the difference of the strain $\gamma(t_1)$ at time t_1 , and the strain $(\gamma(t) - \gamma(t-t_1))$ for $t > t_1$, assuming $\gamma(t)$ is the linear viscoelastic response of the material and the sample recoil is only driven by the elasticity of the material. If steady state has been reached during the creep phase of the experiment (the viscosity term dominates and $\psi(t) = 1$), the recoverable deformation $\gamma_R(t_1) = \sigma_o (J_o + J_R) = \sigma_o J_e$ for $t \rightarrow \infty$. The total deformation $\gamma(t_1)$ can be divided into a recoverable γ_R and a non-recoverable γ_{NR} deformation. The recoverable part relates to the material's elasticity, the non recoverable part to the viscosity.

Benefit and limitation of the recoil experiment

In theory, the creep recovery test is the most direct measurement of material's elasticity. Practically however, it is impossible to isolate the sample such that only the energy storing mechanisms in the material are the driving the sample during recovery. The sample is held by the test fixtures and those are supported by a bearing. The bearing is not frictionless and generates residual torques, which are disturbing the recovery phase. The testing limit of the recovery test method is reached, when the deformation due to residual torque is on the order of magnitude of the recoverable deformation. The residual torque superposes a continuous flow on the material's recovery, increasing or decreasing the strain depending on the direction of the parasitic torque (Figure 2).

In order to quantify the operation range of the instrument and the applicability of the creep recovery test, a criterion for evaluating recovery tests has been formulated⁽²⁾. The assumption is that the ratio of viscous to recoverable deformation has to be equal or smaller than 0.01 (less than 1 %) after a recovery time $(t-t_1)$ equivalent to a maximum material retardation time. With $\eta_o J_{eo} = \tau_{max}$, the above criterion reduces to a simple relation, stating that

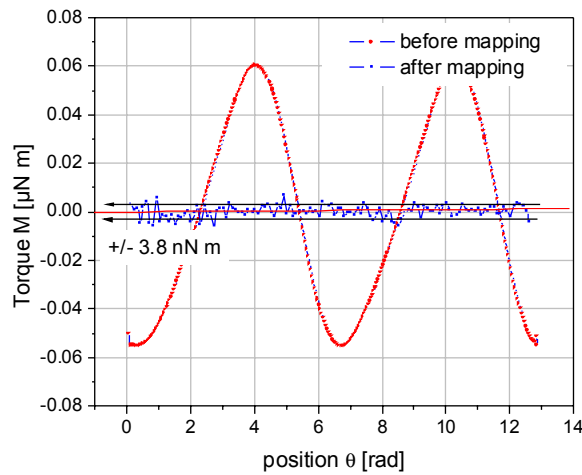


Figure 3: Residual torque of a typical AR-G2 bearing before and after mapping.

the residual torque must be no greater than 0.01 times the torque applied during the creep phase (Figure 2).

Note that the equilibrium compliance can be obtained only, when the creep time is longer than the longest material's retardation time ($\psi(t)=1$). The recovery test has to last double the time of the creep, so the effect of small residual torque contributions can be measured and corrected for. For measurements within the linear viscoelastic region, the stress has to be chosen such that a maximum shear of 1 is not exceeded during the creep phase.

EXPERIMENTAL

CMT rheometer with magnetic levitation thrust bearing

The creep recovery test is the native test for the CMT or stress controlled rheometers. In the early rheometers, a constant torque was applied during creep and removed during recovery in an open loop (no feedback). As such, no external forces except inertia and bearing friction were present. In order to improve the operation range, in today's rheometers the residual torque is actively compensated in a closed loop control. The method to measure residual torques in a bearing is referred to as "mapping". The mapping is applied during the recovery phase to correct for the imperfections of the support bearing, eliminating a substantial part of the residual torque contributions and as such increasing the torque range and improving the lower torque performance. A typical, good quality bearing generates a sinusoidal residual torque curve, an example of which is shown

in figure 3. Mapping removes this periodic variation of the torque. The residual torque is a strong function of the air pressure in the bearing and the imbalance of the shaft and the test geometries. When mapping is applied, the residual torque is reduced to a value in the order of ± 4 nN m, typical for the AR-G2 rheometer featuring a magnetic levitation thrust and air supported radial bearings.

Evaluation of residual torque

The best approach to validate an instrument and check the residual torque after mapping is to run a creep recovery experiment on a low viscosity Newtonian fluid and measure the drift of the strain during the recoil phase. Since the viscosity of the test fluid is known, the residual torque can be calculated from the slope of the angular position versus time (Figure 4). In the present example a residual torque of 3.3 nN m was obtained. This is in good agreement with what is expected from the mapping results shown in figure 3.

Note also that the residual is not a constant value and varies with position, but on the average should not be larger than the average residual torque after mapping.

Effect of instrument inertia

At the start-up of the creep experiment, due to the finite mass of the test fixture, a substantial part of the applied torque is used to overcome inertia. With a constant torque applied, the equivalent stress to deform the sample is not available instantaneous, but approaches its final value exponentially, as shown in figure 5. As a consequence, the deformation rate

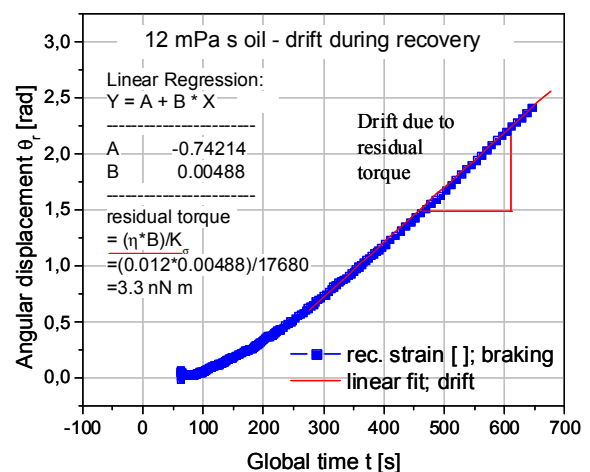


Figure 4: Measurement of the residual torque from the drift of the recoverable compliance for a 12 mPa s silicone oil

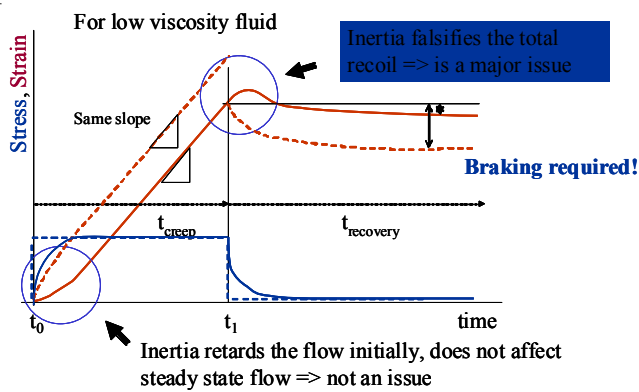


Figure 5: Influence of the instrument inertia on the system response in the creep and recovery experiment

increases slowly and the total deformation will be lagging the expected strain $\gamma(t)$. The energy to overcome inertia is not dissipated, but stored in the momentum of the rotating motor shaft. When the applied stress is removed at the end of the creep test, the fixture momentum is dissipated by the viscous flow of the sample with time. If the momentum of the rotating mass is significant in comparison to the elastic energy stored in the material and the energy dissipation capabilities of the viscous flow, the strain will continue to increase into the recovery zone. The measured recoverable strain will be erroneous and the equilibrium compliance not representative of the material's elasticity.

In order to minimize the inertial effects on the recoverable strain, an inertia braking technique is used to eliminate the momentum of the rotating shaft instantaneously at the beginning of the recoil experiment. Since rotation speed and inertia of the rotating mass are known, the momentum can be calculated and then compensated for by applying the

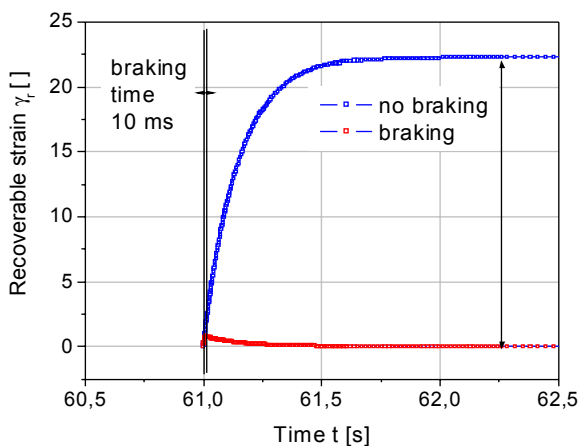


Figure 6: Recoverable compliance for a 12 mPa s silicone oil with and without braking

full instrument torque in the opposite direction for a given period of time (10-50 milliseconds) to stop the motor shaft.

This is demonstrated in figure 6 for 400 mPa s silicone oil. Since a Newtonian oil has no elastic component, the motor shaft is expected to stop dead immediately at the end the creep experiment, if braking is enabled. Without braking, the shaft continues to rotate for approximately 20 strain units before stopping. Low viscous elastic fluids require inertia braking, whereas for high viscosity polymer melts, the error on the recoverable deformation due to inertia usually can be neglected.

RESULTS FOR PE AND PS

Creep recovery experiments were performed on a low density polyethylene LDPE in a stress range from 10 to 5000 Pa at a temperature of 140 °C. The duration of the recovery section did last twice the time of the creep. For the LDPE under investigation, the total recovery is significant in comparison to the total deformation during creep (Figure 7). The applied stresses are ranging from 10 to 5000 Pa. Up to a stress of 1000 Pa, the creep compliance is independent of the stress. At a stress of 5000 Pa, a deviation from linear behavior occurs. Deviation from linear behavior can be seen in the recoverable compliance at a much lower stress of 500 Pa. The recoverable compliance is more sensitive and it is necessary to operate at lower stress in order to stay within the limits of the linear viscoelastic regime.

Much more challenging is testing materials with small values of the equilibrium compliance, such as narrow distributed polystyrene with low molecular

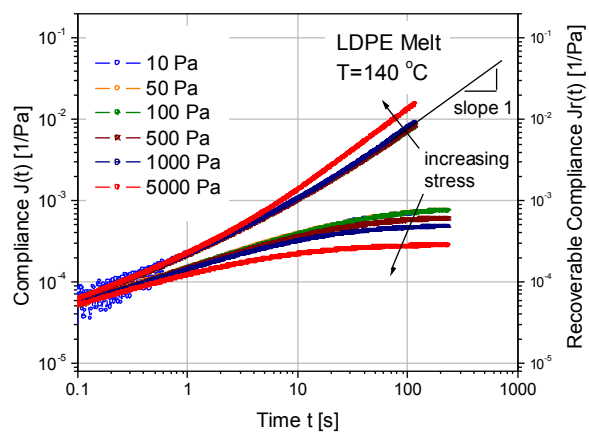


Figure 7: Creep and recoverable compliance for an LDPE at 140°C, measured in a stress range from 10 to 5000 Pa

	PS 13K	PS145K	PS330K
M_w [g/mol]	13 200	145 000	330 000
M_w/M_n	1.06	1.03	1.1
T [° C]	124	170	170
Creep: η_o [Pas]		8.8×10^4	1.8×10^5
Recovery: J_{eo} [1/Pa]	2.2×10^{-6}	1.1×10^{-5}	1.9×10^{-5}
Oscillation: η_o [Pas]		9.05×10^4	2.2×10^5
Oscillation: J_{eo} [1/Pa]		1.2×10^{-5}	2.1×10^{-5}

Table 2: Summary of molecular and rheological parameters for the PS13K, PS145K and PS330K

weight. Creep recovery measurements were performed on three narrow distributed PS and the results compared to the properties in oscillation. Table 2 summarizes key molecular and rheological parameters of the three polystyrenes; PS145K and 330K are samples with a MW above the entanglement point, PS13K has an MW below the entanglement MW.

All experiments were conducted without exceeding a maximum strain of 1 and a recovery time lasting at least twice the creep time. The figure 8 shows the results for the PS145K with the applied stress ranging from 10 to 10 000 Pa. The creep and recoverable compliance are independent of the stress within the testing range. The equilibrium compliance extracted from the recovery experiment is 1.1×10^{-5} 1/Pa. In order to verify this result, oscillation experiments at small strain were performed at different temperatures in a frequency range from 0.1 to 100 rad/s . The data are represented as a master curve referenced to 170 °C in figure 9. The elastic component was determined from the ratio G'/G'' in the terminal region (slope 2 for G' , slope 1 for G'') as a function of frequency and found to be approximately 1.2×10^{-5} 1/Pa. With $\omega \rightarrow 0$, G' becomes small compared to G'' as the phase angle approaches 90° . Under these conditions, G' is noisy and the ratio of G'/G'' as well. A slope of 2 for G' cannot be obtained in an experimental acceptable frequency

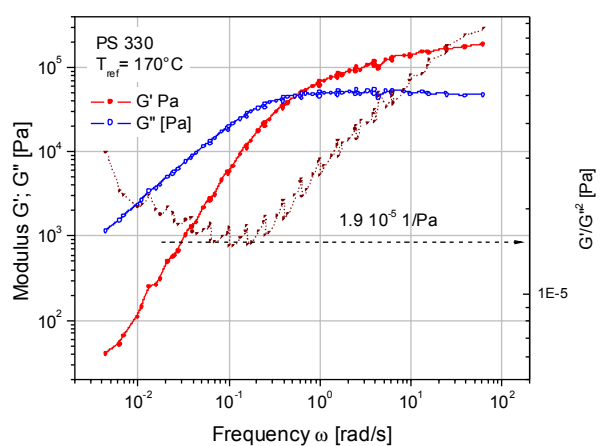
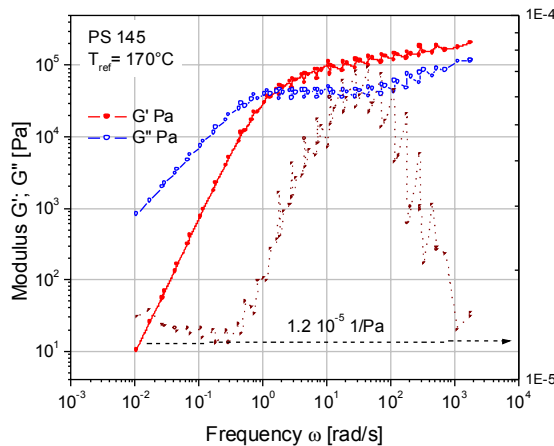
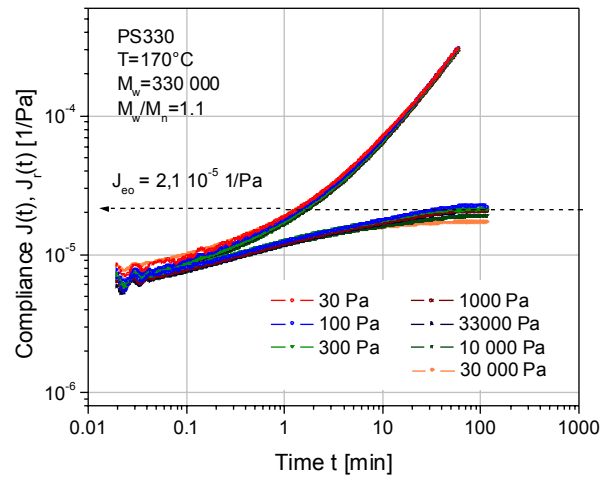
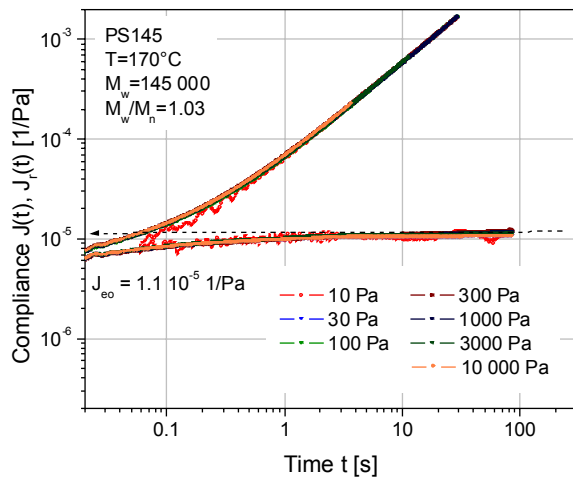


Figure 8: Creep and recoverable compliance for the PS145K at 170 °C in a stress range from 10 to 10 000 Pa.

Figure 9: Mastercurve of G' and G'' for the PS145K at 170 °C

Figure 10: Creep and recoverable compliance for the PS330K at 170 °C in a stress range from 30 to 30 000 Pa.

Figure 11: Mastercurve of G' and G'' for the PS330K at 170 °C

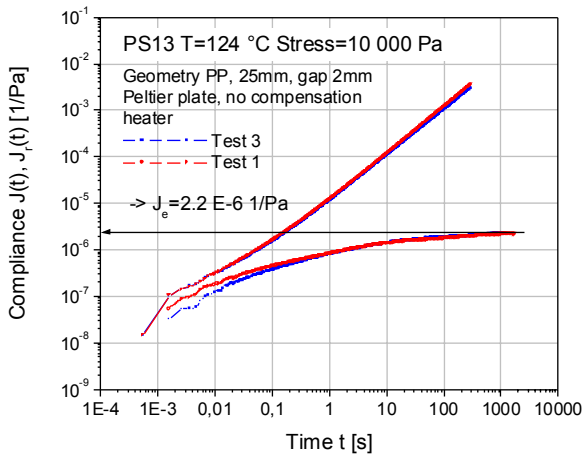


Figure 12: Creep and recoverable compliance for the PS13K at 124 °C

for polymers with broader molecular weight distribution. This fact and the uncertainty of the G' in the terminal zone are the main reasons, why oscillation measurements are not best suited to measure the equilibrium compliance. The viscosity, calculated from G''/ω reaches a plateau (zero shear viscosity) at higher frequency already and therefore is experimentally much easier accessible in an oscillation test.

For the narrow distributed PS145, G' shows a slope of 2 versus frequency already at 0.3 rad/s at 170 °C – thus the G'/G''^2 ratio obtained at this point coincides very well with the result from the recovery test at the same temperature.

The same analysis has been performed with the PS330K. Whereas the creep compliance remains

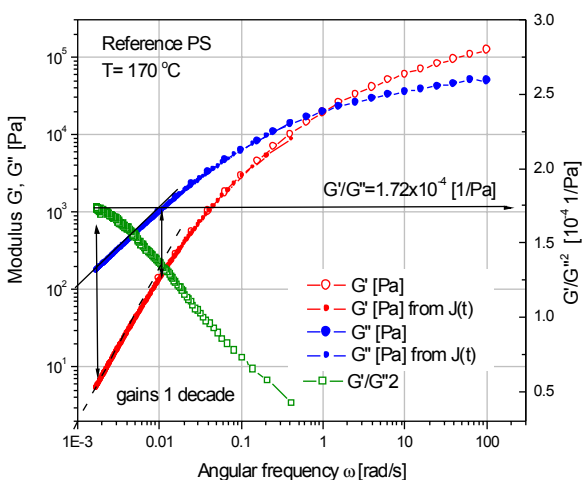


Figure 13: Oscillation data extended with the dynamic moduli G' and G'' converted from the creep recovery results in figure 14

independent of the stress in the range from 30 to 30 000 Pa in figure 10, does the recoverable compliance decrease above a stress of 300 Pa. The equilibrium compliance at the low stress limit is 2.1×10^{-5} 1/Pa. The equilibrium compliance J_e obtained from the dynamic moduli at a frequency of 0.3 rad/in figure 11 is 1.9×10^{-5} 1/Pa. Again good agreement has been achieved between the creep recovery and oscillation experiment. At lower frequency in figure 10, the ratio G'/G''^2 increase due to experimental errors in the measurement of G' .

The PS13K (13'000 g/mol) has a molecular weight below the entanglement molecular weight for PS and as such also very little elasticity. The recoverable compliance determined in a recovery experiment (Figure 11) is found to be approximately 2×10^{-6} 1/Pa, which is slightly higher than the literature

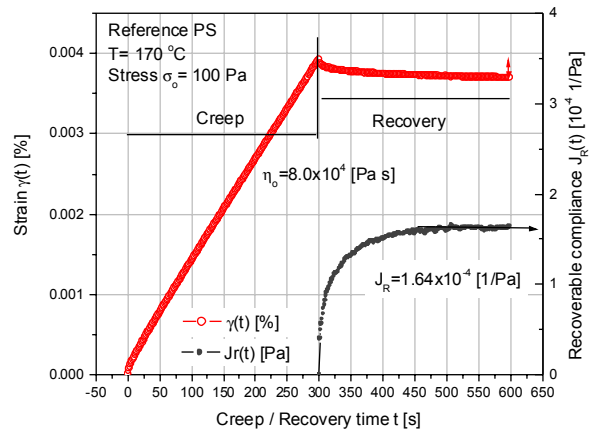


Figure 14: Creep and recovery of a commercial PS at 170 °C

values⁽³⁾. The reason for the discrepancies might be the sample's condition, as the amount of sample available was limited and the preparation of a good sample from powder difficult.

Creep recovery and oscillation experiments complement each other. The oscillation measurement provides the short time response of a material and the creep recovery test the long time response, necessary to determine the equilibrium compliance J_e and the zero shear viscosity η_0 . Within the framework of the linear viscoelasticity, the time dependent compliance can be converted into a frequency dependent compliance or modulus. This has been done and the results are shown in figure 13 and 14 for a commercial PS. The compliance $J(t)$ has been converted to G' and G'' data using approximation equations by Schwarzl⁽⁴⁾. The calculated

dynamic moduli agree very well with the experimental loss and storage modulus and extend the dynamic spectrum to the low frequency. The value of G'/G''^2 (1.72×10^{-4} 1/Pa) determined at 2×10^{-3} rad/s agrees well with the equilibrium compliance J_e (1.64×10^{-4} 1/Pa), obtained from the recovery experiment. The combination of these two tests provides a complete spectrum of relaxation times from low to high frequency without the need to perform the less accurate and time consuming low frequency measurements or the scans for temperature/frequency superposition.

CONCLUSIONS

Creep recovery measurements have been performed with narrow distributed polystyrenes to determine the equilibrium compliance. The results were found to be in good agreement with the equilibrium compliances, calculated from the dynamic moduli G'/G''^2 at low frequency. In order to obtain reliable compliance data in the recovery experiment, a magnetic levitation rheometer with minimum residual torque has been used.

For the commercial PS polymers, the compliance data obtained from the creep recovery experiment were converted to dynamic moduli and combined with the experimental oscillation results. The resulting composite curve describes the complete relaxation spectrum over a sufficient large frequency range to accurately extract the zero shear viscosity and the equilibrium compliance.

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