Getting the zero shear viscosity of polymer melts with different rheological tests

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ABSTRACT

The zero shear viscosity of a polymer melt was determined with different rheological tests like flow and viscosity curve, creep, frequency sweep and stress relaxation. All tests were performed with the same rheometer which was equipped with an electronically commutated synchronous motor allowing real controlled stress and controlled strain tests.

INTRODUCTION

At low shear rates polymer melts show a Newtonian behavior with a constant viscosity. The viscosity in the Newtonian regime is called the zero shear viscosity η_0. The zero shear viscosity gives valuable information on the molar mass: Above a critical molar mass M_C the empirical relation $\eta_0 \propto M_W^{3.4}$ is found to hold with M_W being the weight average molar mass. Molecular branching also has a strong influence on the zero shear viscosity. For example two polyethylene (PE) with the same average molar mass but different branching ratios might have zero shear viscosities which differ as much as two decades[1]. In addition the shear rate at which the Newtonian regime is reached can give information on the molecular structure. That means the value of the zero shear viscosity and the behavior of the viscosity curve at low shear rates are in general very crucial parameters for the characterization of polymer melts and of great importance for processing purposes.

In the following four different rheological methods are described and used to determine the viscosity function at low shear rates and the value of the zero shear viscosity of a polystyrene (PS) melt.

These tests include:

1. the direct measurement in a shear rate controlled flow curve experiment at low shear rates.
2. a creep experiment to determine η_0 as the viscosity in the stationary flow region.
3. a frequency sweep to determine η_0 from the low frequency limit of the complex viscosity $|\eta^*|$.
4. stress relaxation measurement after a step strain experiment and calculation of the complex viscosity $|\eta^*|$ and the zero shear viscosity η_0 via relaxation time spectra.

Tests 1 and 4 are typically associated with a controlled rate or strain (CR) instrument, whereas test 2 is a standard experiment for controlled stress (CS) rheometers. A frequency sweep experiment as described in test 3 can be done in stress or strain control. Being able to measure all four tests with a single rheometer requires an instrument which can be stress controlled, but uses a highly dynamic rheometer drive which is capable to cover a wide range of shear rates and to adjust to steps in strain in a very fast way.

INSTRUMENT AND SAMPLE

The measurements were conducted using a Physica MCR 300 rheometer equipped with an electrically heated temperature chamber. All experiments were carried out at 200°C. Sample degradation was prevented by the use of nitrogen as an inert gas. A plate/plate measuring system (∅ 25 mm) was used. The Physica MCR 300 was equipped with an electronically commutated synchronous motor (EC-drive) with a highly dynamic transient response, which allows controlled stress (CS) and controlled strain or controlled strain rate (CR) tests on the same rheometer[2]. Such a rheometer with a highly transient response is needed in order to adjust to steps in strain fast enough and therefore enabling stress relaxation measurements. For direct measurements of the viscosity curve the rheometer has to be able to control speeds down to 10^{-5} rpm very reliable.

The sample used was a polystyrene (PS) from BASF.

RESULTS

1. Flow curve at low shear rates

The flow curve of polymers is known to show a Newtonian regime at low shear rates with the viscosity being the zero shear viscosity in that range. Going to higher shear rates the viscosity is decreasing and a transition region starts. At even higher shear rates the slope of the viscosity curve, i.e. viscosity plotted versus the shear rate, is constant representing the so-called power law behavior. At very high shear rates it is believed that a second Newtonian regime starts. However, with a rotational rheometer which allows real strain rate control in most cases the first Newtonian, the transition and the power law regime are accessible.

Caution has to be taken with the measuring time. In order to be sure that the viscosity reaches a stationary value the measuring time per data point should be long enough. The exact time needed to reach a stationary value can be obtained by measuring the time dependence of the viscosity after a step from rest to low shear rate.

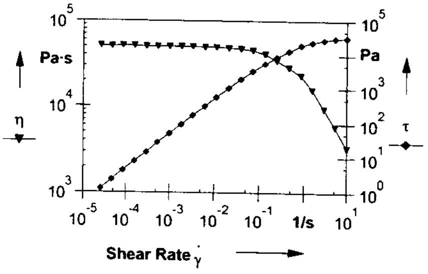

Figure 1. Flow and viscosity curve of the polystyrene sample.

Fig. 1 shows a flow and viscosity curve measured directly by applying a shear rate ramp. Rotational speeds starting from as low as 10^{-5} rpm have been used. The time for each data point was 60 sec. As can be seen from Fig. 1 this test and the control strain rate capabilities of an EC-motor equipped rheometer allow to measure the zero shear viscosity directly within a very short time. The zero shear viscosity obtained from Fig. 1 is $\eta_0 = 51300$ Pas.

2. Creep test

The creep test is a popular test in polymer research, since it allows the evaluation of long retardation or relaxation times by the measurement of long creep and creep recovery times, respectively. With a creep test a constant shear stress τ_0 is applied and the time dependency of the resulting strain γ is measured. In addition to the creep the creep recovery can be measured after the cessation of the shear stress at a time t_1. Quite often the creep compliance $J(t) = \gamma(t) / \tau_0$ and the creep recovery compliance $J_r(t) = \gamma(t>t_1) / \tau_0$ are plotted. In Fig. 2 a result of a creep and creep recovery experiment on the polystyrene sample is shown.

The zero shear viscosity can be obtained from the stationary flow region at the end of the creep phase. In that region the slope of the curve is constant yielding a constant shear rate $\dot{\gamma} = d\gamma / dt$. The zero shear viscosity is obtained as $\eta_0 = \tau_0 / \dot{\gamma}$.

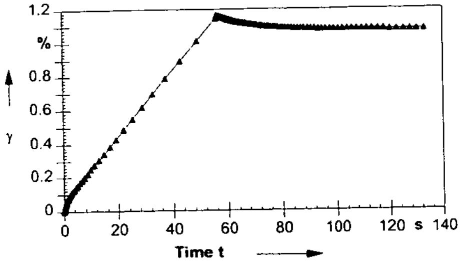

Figure 2. Creep and creep recovery measurement of the PS sample.

Different creep measurement with various different shear stresses from 2.5 Pa to 10 Pa were performed and a zero shear viscosity of η_0 = 51500 Pas was found in these tests. The shear rates in the stationary flow regime were between $\dot{\gamma} = 5x10^{-5} - 2x10^{-4}$ 1/s.

3. Frequency sweep

The frequency sweep is a widely used standard test in polymer rheology. In this test a sinusoidal stress or strain with a constant amplitude is applied and the oscillation frequency is varied. The resulting measuring parameters are commonly the storage modulus G'(ω) and the loss modulus G''(ω); ω represents the angular frequency. Other quantities as the complex viscosity $|\eta^*(\omega)|$ can be calculated from G' and G''. In Fig. 3 the result of a frequency sweep with a constant strain amplitude of 1% is shown.

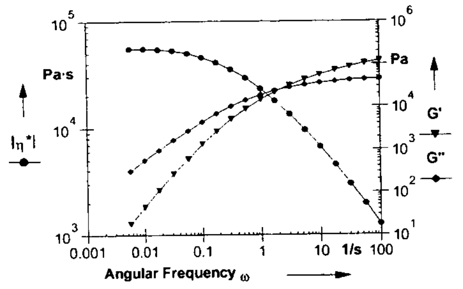

Figure 3. Frequency sweep of the Polystyrene sample.

For polymer melts it is well known that the empirical Cox-Merz-Rule holds:

$\eta(\dot{\gamma}) = |\eta^*(\omega)|$ for $\dot{\gamma}$ [1/s] equals ω [1/s], that means the complex viscosity is identical to the shear viscosity if the angular frequency is replaced by the shear rate. A zero shear viscosity of η_0 = 55000 Pas was found in the frequency test.

4. Stress relaxation after step strain

In Fig. 4 two step strain tests are displayed.

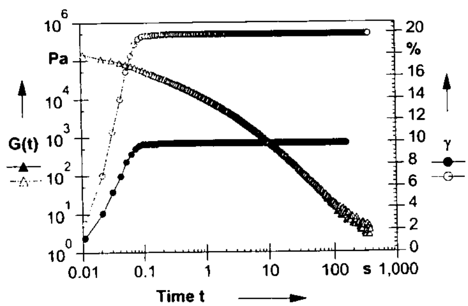

Figure 4. Two stress relaxation measurements after steps in strain. Filled symbols: 10% strain, open symbols: 20% strain.

In such an experiment a constant strain γ is applied and the time behavior of the shear stress τ is measured. Usually the relaxation modulus $G(t) = \tau(t) / \gamma$ is plotted. As can been seen in Fig. 4 the EC-motor equipped rheometer is able to set the strain to the desired value without any overshoot in less than 100 ms. The curves of the relaxation modulus coincide very well for the two applied strain values, indicating that the selected strain values are well within the linear viscoelastic region.

It is possible to calculate the storage modulus G' and the loss modulus G'' and therefore the complex viscosity $|\eta^*|$ from the relaxation modulus G(t) by use of the relaxation time spectra $H(\lambda)$ and a conversion calculation, i.e. $G(t) \rightarrow H(\lambda) \rightarrow G'(\omega), G''(\omega), |\eta^*(\omega)|$. The zero shear viscosity can be obtained from this calculated quantities as in the frequency test described in section 3. This procedure gives a zero shear viscosity of η_0 = 54500 Pas for the relaxation test.

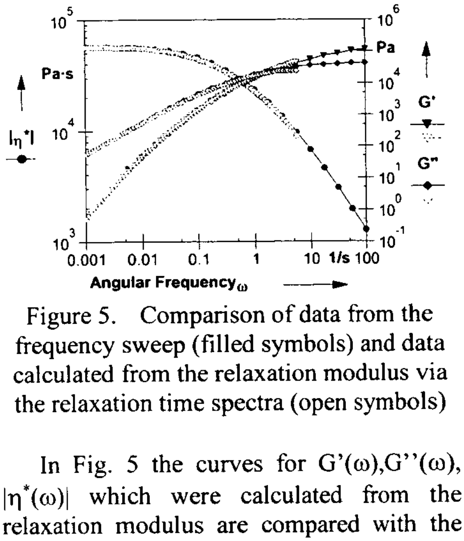

Figure 5. Comparison of data from the frequency sweep (filled symbols) and data calculated from the relaxation modulus via the relaxation time spectra (open symbols)

In Fig. 5 the curves for $G'(\omega), G''(\omega), |\eta^*(\omega)|$ which were calculated from the relaxation modulus are compared with the results of the frequency sweep described in test 3. As can be seen there is a good agreement between these data especially in the low frequency range.

The stress relaxation test is a very convenient way to get the value of the zero shear viscosity in a comperatively short time. The whole stress relaxation experiment only takes little more than 100s and provides extensive information about the sample behavior at low shear rates, whereas in a frequency test the measurement of every single data point takes at least that amount of time. The time saving aspect of the stress relaxation test is especially important for quality control purposes.

5. Comparison of results

In Table 1 the results of all four tests are listed. The average zero shear viscosity of the investigated polystyrene sample from all four test was η_0 = 53075 Pas, whereas the maximum of the deviation from the average value was 3.5%.

Test	Zero shear viscosity η_0 [Pas]
Viscosity curve	51300
Creep test	51500
Frequency sweep	55000
Stress relaxation	54500

Table 1. Comparison of the results.

CONCLUSIONS

It has been demonstrated that it is possible to get information on the zero shear viscosity and the viscosity curve at low shear rates by the use of four different rheological test. A good agreement between the results of the different experiments was obtained. The EC-motor equipped rheometer was found to be able to perform all described CS and CR tests.

REFERENCES

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2 J. Läuger, S. Huck, Proceedings of the XIIIth International Congress on Rheology, Cambridge, UK, 2000 to be published