ANNUAL TRANSACTIONS OF THE NORDIC RHEOLOGY SOCIETY, VOL. 15, 2007

Validation of empirical rules for a standard polymer solution by different rheological tests

Joerg Laeuger, Patrick Heyer

Anton Paar Germany GmbH,
Helmuth-Hirth-Str. 6, D-73760 Ostfildern / Germany
Phone: +49-711-72091-0, Fax:+49-711-72091-50
Info.de@anton-paar.com, www.anton-paar.com

ABSTRACT

Discrepancies to the certified values of a standard polymer solution (SRM 2490) have been found. Different rheological tests are performed and the data are checked by the use of different rules and relation. All data are consistent thus strongly indicating that the measured results are correct.

INTRODUCTION

For polymeric systems many empirical or semi-empirical rules exist. One of the most prominent is the Cox-Merz rule, which correlates the shear viscosity at a given shear rate to the complex viscosity measured in a frequency sweep. A generalized Cox-Merz rule correlates the first normal stress difference (N_1) with the elastic modulus G'. From definitions and due to requirements from continuum mechanics it follows:

$$\eta(\dot{\gamma}) = \eta'(\omega); \quad as \quad \omega = \dot{\gamma} \to 0 \qquad (1)$$

The elastic part η''(ω) vanishes at small frequencies. At higher frequencies or shear rates the Cox-Merz-Rule holds:

$$\left|\eta^*(\omega)\right| = \eta(\dot{\gamma} = \omega) \qquad (2)$$

With: $\eta(\dot{\gamma}) = \tau(\dot{\gamma}) / \dot{\gamma}$ and $\left|\eta^*(\omega)\right| = \left|G^*(\omega)\right| / \omega$

it follows:

$$\left|G^*(\omega)\right| = \tau(\dot{\gamma} = \omega) \qquad (3)$$

In transient tests Gleissles mirror rule relates the transient behavior of the shear viscosity with steady state results:

$$\eta(\dot{\gamma}) = \eta^+(t); \quad as \quad t = 1/\dot{\gamma} \qquad (4)$$

The Lodge-Meissner rule gives a relation between N_1 and the shear stress in a step strain experiment:

$$N_{1,LM}(Pa) = \gamma \cdot \tau(Pa) \qquad (5)$$

In addition to these empirical rules with the theory of linear visco-elasticity of polymers and by employing the relaxation time spectra H(λ) it is possible to convert the relaxation module G(t) measured in a step strain experiment to the storage G'(ω) and loss modulus G''(ω) as long as the strain is within the linear visco-elastic limit. The relaxation modulus is calculated from the time evolution of the shear stress τ(t) after a step in the strain γ.

$$G(t) = \tau(t) / \gamma \qquad (6)$$

Moreover, conversions from G'(ω) and G''(ω) as measured in a frequency sweep into the relaxation modulus G(t). are expected to work as well.

$$G'(\omega), G''(\omega) \Leftrightarrow H(\lambda) \Leftrightarrow G(t) \quad (7)$$

For simple polymeric fluids all this rules and relations are expected to hold and they provide a rather straightforward check on the validity of rheological data. However, still literature is published in which these relations are not considered and the published results are doubtful. A recent example were the data listed in the original certificate to the Standard Reference Material SRM 2490 supplied from NIST in which for example the zero shear viscosity measured by a frequency sweep and a rotational test differ significantly[1]. Since in our initial measurements we found a significant difference to the data published in the original certificate the aim of this paper is a complete check of the above rules for SRM 2490.

In the meantime a new certificate has been published, which includes the data measured by the authors of this paper as information values[2].

METHODOLOGY

All data have been measured using a Physica MCR501 rheometer from Anton Paar. The Physica MCR501 is equiped with an air bearing supported electrically commuted synchroneous motor (EC-Motor). The rheometer allows to conduct measurements in shear stress, shear rate and shear strain control, respectively.

Temperature control was done with a Peltier temperature device (PTD 200), which consists of a Peltier controlled bottom plate and additional actively Peltier controlled hood. The Peltier hood assures an uniform temperature distribution in the sample without any significant temperature gradients throughout the sample[3]. The absolute temperature was calibrated by the means of a certified temperature sensor. Measurements at different temperatures within the range of 0° and 50°C have been performed.

The measurements of the first normal stress difference were done with the normal force sensor which is integrated in the air bearing of the rheometer. The principle of the normal force sensor is based on a technique of measuring the deflection of the air bearing by an electric capacity method[4]. The normal force sensor has a range from 0.01N up to 50N

A cone-and-plate geometry with 50 mm diameter and a cone angle of 1° has been used for all measurements, except for measurements of the first normal stress difference in step strain tests with large strains, for which a 25 mm cone with a 4° cone angles was employed.

RESULTS AND DISCUSSION

Fig. 1 shows the complex viscosity and the complex modulus as measured in a frequency sweep (dynamic shear) experiment and calculated form a flow curve (steady shear) measurement according to equations (2) and (3) at 0°C, 25°C and 50°C, respectively.

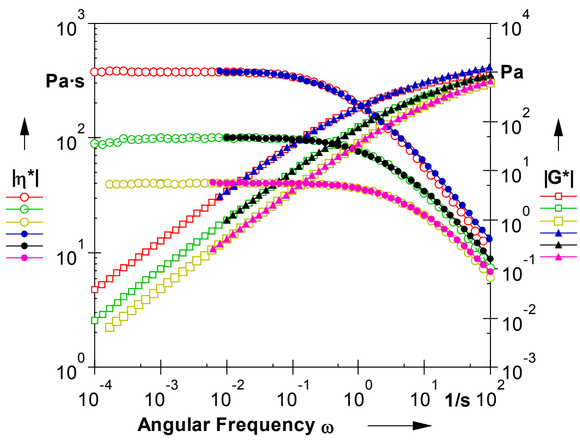

Figure 1. Complex viscosity and complex moduli obtained from frequency sweep (filled symbols) and flow curve measurements (open symbols). From top to bottom: 0°C, 25°C, 50°C.

As can be seen in Fig. 1 the dynamic and steady shear data correlate very nicely, indicating that the Cox-Merz rule is obeyed.

In Fig. 2 results from a steady shear flow curve over an extended shear rate range are converted according equation (4) (Gleissle mirror rule) and displayed together with transient viscosity data following steps in shear rate. The data from the steady shear flow is the limiting curve of the transient measurements as expected.

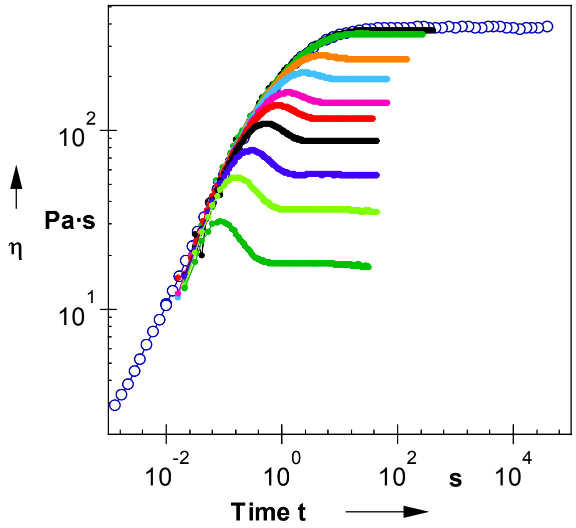

Figure 2. Transient viscosity after steps to different shear rates (filled sysmbols). From bottom to top: $50s^{-1}$, $20s^{-1}$, $10s^{-1}$, $5s^{-1}$, $3s^{-1}$, $2s^{-1}$, $1s^{-1}$, $0.5s^{-1}$, $0.1s^{-1}$, $0.05s^{-1}$. Open symbols represent shear viscosity data of a steady shear flow curve converted by equation (4) into the transient viscosity. Temperature: 0°C.

Fig. 3 shows the relaxation modulus G(t) = τ(t)/γ after step strains to various strains values. This test is commonly referred to as a step strain test or as a stress relaxation test. The strain values, which are also plotted in Fig. 3, are reached by the instrument after a rather short time interval of about 30ms without any overshoot in strain. This is important, since an overshoot represents not a single step in strain, but rather a larger step in strain followed by a second smaller step in the opposite direction.

At smaller strain values G(t) is independent of the applied strain, whereas at larger strains the relaxation modulus is shifted towards smaller values. The onset of a dependence of the relaxation modulus on the strain indicates the end of the so-called linear visco elastice range (LVE-range).

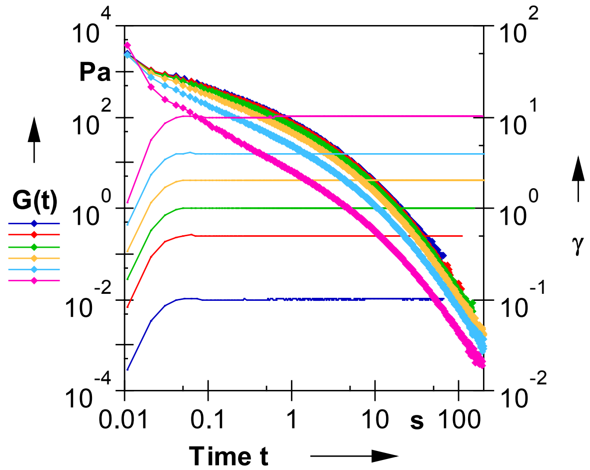

Figure 3. Relaxation modulus after steps in strain to different strain values of γ = 0.1, 0.5, 1, 2, 4, 10 at a temperature of 0°C.

The relaxation modulus after a step in strain well within the LVE-range (γ = 0.5) is converted according to Eq. 7 into the storage and loss moduli G'(ω) and G''(ω), respectively. The resulting moduli are plotted in Fig. 4 together with the moduli measured in a frequency sweep. A good agreement between the data form the stress relaxation test and the frequency sweep is observed.

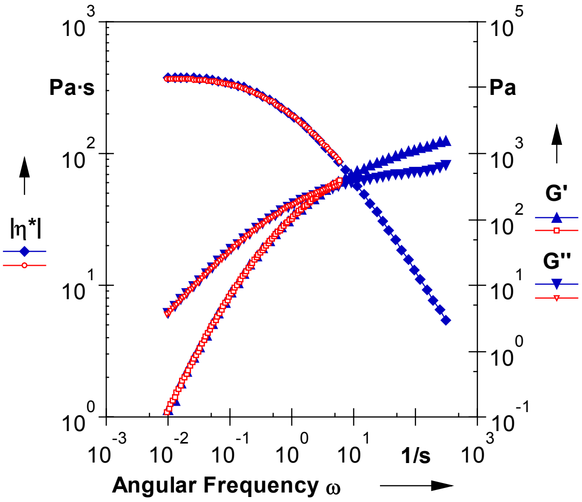

Figure 4. Comparison of data measured in a frequency sweep (closed symbols) and converted data from stress relaxation test with a strain $\gamma = 0.5$ (open symbols). Both the frequency sweep and the stress relaxation test were measured at a temperature of 0°C:

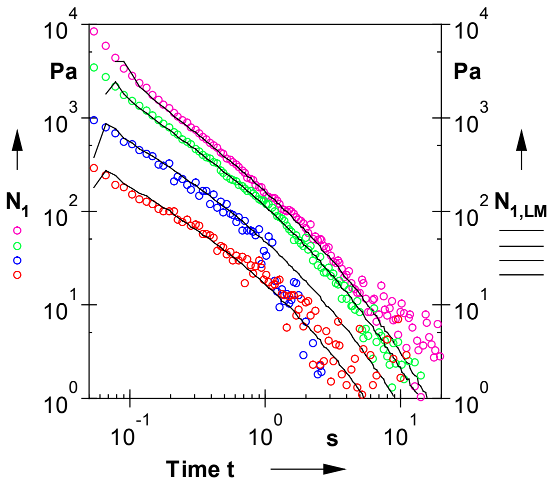

Figure 5. Measured N_1 (opens symbols) and $N_{1,LM}$ calculated according equation (5) (lines) following steps to different strains of 10, 5, 2, 1 (from top to bottom) at a temperature of 20°C.

In Fig. 5 data of the first normal stress difference (N_1) after steps with large strains are shown. In addition to the directly measured N_1-values $N_{1,LM}$-values calculated from the relaxation modulus following Eq. (5) are plotted. Although the SRM2490 relaxes very fast and therefore the lower limit of the normal force sensor is reached rather soon it can be seen that the Lodge-Meissner rule holds reasonably well.

CONCLUSIONS

All measured results form different tests like flow curve, step rate, step strain and frequency sweep are perfectly consistent and the Cox-Merz rule, the generalized Cox-Merz rule, Gleissles mirror rule, and the Lodge-Meissner rule are fulfilled, respectively.

The measured data and the inconsistency of the certified values with the Cox-Merz rule itself indicate that the published oscillatory data in the original Certificate to the SRM 2490 were wrong. Conversion form Dynamic into Steady Shear data (and visa versa) and the check of consistency is a valuable tool for validating experimental data.

REFERENCES

1. C. Schultheisz and S. Leigh, (2002), *Certification of the Rheological Behaviour of SRM 2490, Polyisobutylene Dissolved in 2,6,10,14-Tetramethylpentadecane*, Technical Technical Report 260-143, National Institute of Standards and Technology.

2. https://srmors.nist.gov/view_cert.cfm?srm=2490 (or https://srmors.nist.gov/ and search for 2490).

3. J. Läuger, M. Bernzen, K. Wollny, G. Raffer, *Accuracy in temperature control for rotational rheometers*, Proceedings of the 6th European Conference on Rheology, Erlangen, Germany (2002), S.493-494.

4. G. Raffer, (2001), US Patent No 6,167,752.