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SUBCOMMITTEE ON STRUCTURE AND PROPERTIES OF COMMERCIAL POLYMERS\*\*

# GUIDELINES FOR RHEOLOGICAL CHARACTERIZATION OF POLYAMIDE MELTS

## (IUPAC Technical Report)

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# Guidelines for rheological characterization of polyamide melts

## (IUPAC Technical Report)

*Abstract:* Most producers of polyamide have their own characterization method to study the rheological properties of polyamide 6 (PA6). However, the measured rheological properties depend strongly on the sample preparation method, humidity regulation, and time-temperature history during the measurement and not least on the kind of rheometer being used.

This investigation is the result of an IUPAC project initiated by the Subcommittee on Structure and Properties of Commercial Polymers. Members of several industrial organizations, universities, and institutes cooperated, with the aim of formulating a guideline to measure reproducible rheological properties of PA6.

The results of the investigation show the changes in molecular weight during different kinds of rheological measurements due to hydrolysis and amidization reactions. A guideline is introduced which can be used to make comparable rheological measurements on PA6.

*Keywords:* polyamide 6; rheology; hydrolysis; amidization; molecular weight; IUPAC Polymer Division.

## INTRODUCTION

Although polyamide is an industrially important polymer, only a few scientific papers on its rheological properties have been published (e.g., [1–5]). An excellent overview of the viscoelastic behavior of polyamide is given in Laun's paper [2], where polyamide 6 (PA6) samples of different molecular weights were investigated by means of capillary viscometry, oscillatory rheometry, and using sandwich creep apparatus. The elastic properties were measured by means of normal force measurements and Bagley entrance pressure drop plots from capillary rheometry. Laun also discussed the influence of humidity on the results. It is suggested that rheological measurements be performed at a humidity lower than 0.1 % using relatively short measurement times.

In most of the scientific work on the thermal degradation of polyamide, the polymer was severely damaged at temperatures much above 300 °C [6,7]. The solid end-product can hardly be called polyamide any more. Only a few papers describe investigations on the thermal degradation of PA6 under milder conditions, i.e., at temperatures lower or not much higher than those at which the polymer is processed [8]. Other publications report studies at moderate temperatures, but with very long annealing times. The only systematic work we found on the influence of moisture on the rheological measurements of polyamide was performed by Khanna et al. [9] and by Acierno and Van Puyvelde [8]. Khanna et al. investigated PA 6, PA 6,6, and PA 12, while Acierno and Van Puyvelde studied PA 11.

The purpose of the present investigation was to find conditions that would allow reproducible and comparable rheological measurements to be made. The molecular structure of the polyamide should not change much within the time scale of these rheological experiments. The result should be a guideline or even standard method of performing rheological measurements on polyamide in the melt. These conditions for rheological measurements on polyamide should not necessarily be interchangeable with processing conditions, i.e., the proposed sample preparation method might be impractical and inefficient for processing large amounts of polyamide.

## EXPERIMENTAL

### Sample preparation

The sample used for this investigation was Durethan B30S, a medium-molecular-weight commercial grade of PA6 from Bayer Polymers (now Lanxess). The polyamide granules were dried at different times in a vacuum oven at 90 and 100 °C. The granules were compression molded at 240 °C. The maximum duration of heating and pressing was 150 s.

### Karl Fischer humidity determination

The humidity of the polyamide granules was determined in a Mitsubishi VA-06/CA-06. Measurements were made at 160 and 250 °C.

### Oscillatory rheometry

A Rheometrics ARES rheometer with a convection oven purged with nitrogen gas was used. The frequency range used was 0.01–10 Hz. The oven was preheated, and the rheological measurement was started 120 s after the sample was placed in the apparatus. Time sweep measurements were performed at a frequency of 1 Hz.

### Capillary rheometry

Capillary experiments were performed with a Goettfert 2003 capillary rheometer with a die length and die diameter of 30 and 1 mm, and a barrel length and barrel diameter of 300 and 15 mm. The viscosity values were corrected by means of the Rabinowitz procedure.

## RESULTS AND DISCUSSION

The complex viscosity of PA6 as measured after different drying times is shown in Fig. 1. This illustrates the difficulty of determining reproducible values. The sample dried for only 24 h has a much lower viscosity at all frequencies and shows an increasing viscosity toward lower frequencies. The physical reason for the apparent increase in viscosity for relatively humid PA6 can be seen in Fig. 2.

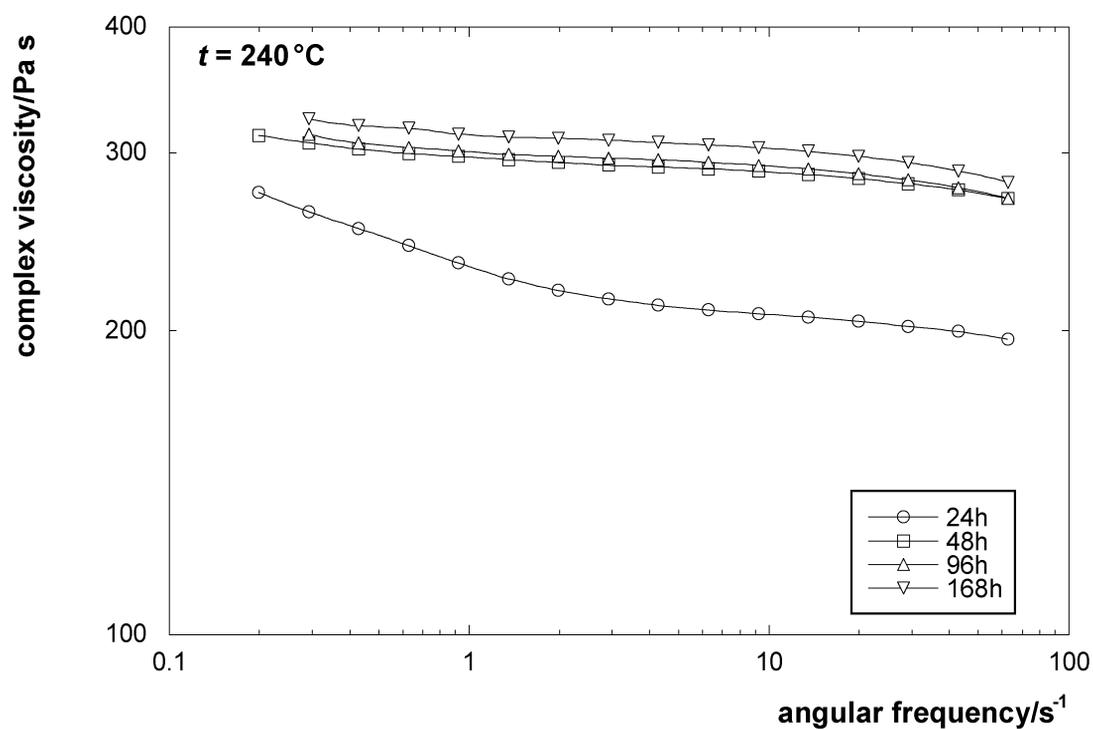


Fig. 1 Complex viscosity vs. angular frequency at 240 °C of PA6 at different humidities.

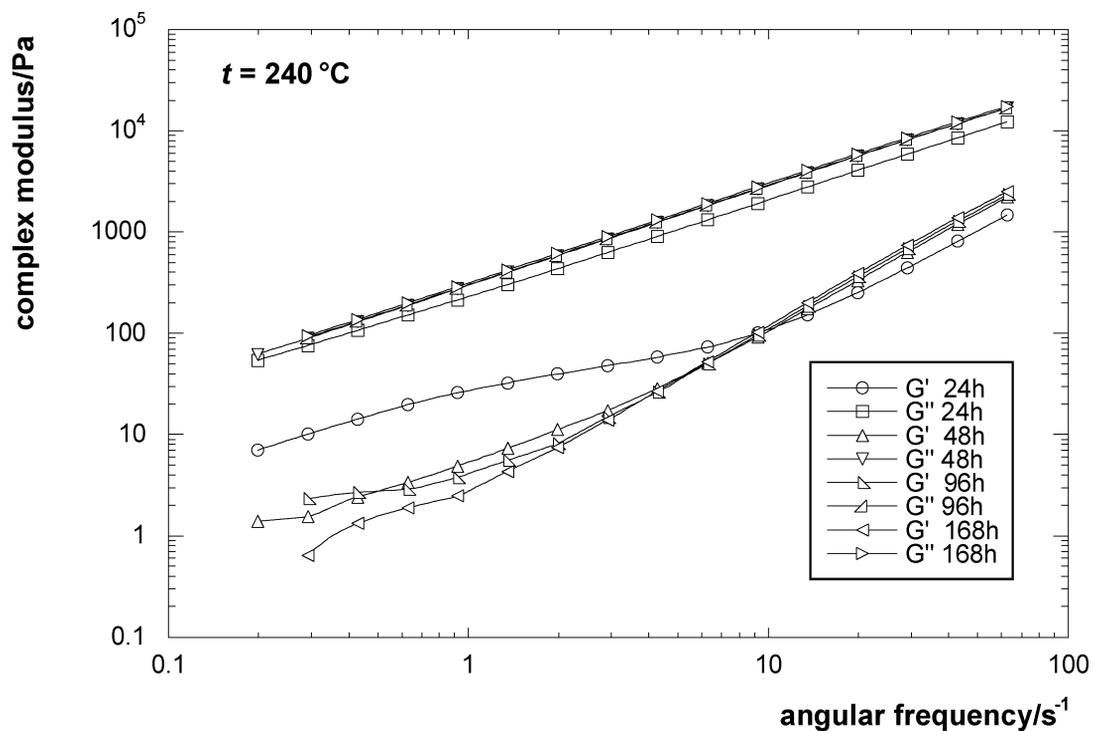


Fig. 2 Storage and loss modulus vs. angular frequency at 240 °C of PA6 at different drying times.

The increase in the complex viscosity is caused by an increase in the storage modulus. This phenomenon is often seen in foamy samples. The oscillating deformation changes the surface area of the bubbles, thereby changing the surface Gibbs energy and surface tension, which results in an increase in elasticity, i.e., storage modulus. This phenomenon, is of course, frequency-dependent, but the curve form might also be influenced by the measuring time since the frequency sweep is started at the highest frequency, i.e., the sample is being dried during the measurement. The time sweep made at a constant frequency of 1 Hz (Fig. 3) shows that the complex viscosity indeed increases with time for all samples. The relative increase in complex viscosity seems to be comparable for all measured humidities, only the absolute value of the viscosity is different for different levels of humidity. An increase in viscosity would mean an increase in molecular weight arising from further polycondensation, which would release additional water molecules (eq. 1). This shift in equilibrium position would be expected for very dry polyamide. However, an increase in viscosity was found even for relatively humid PA6, which is surprising.

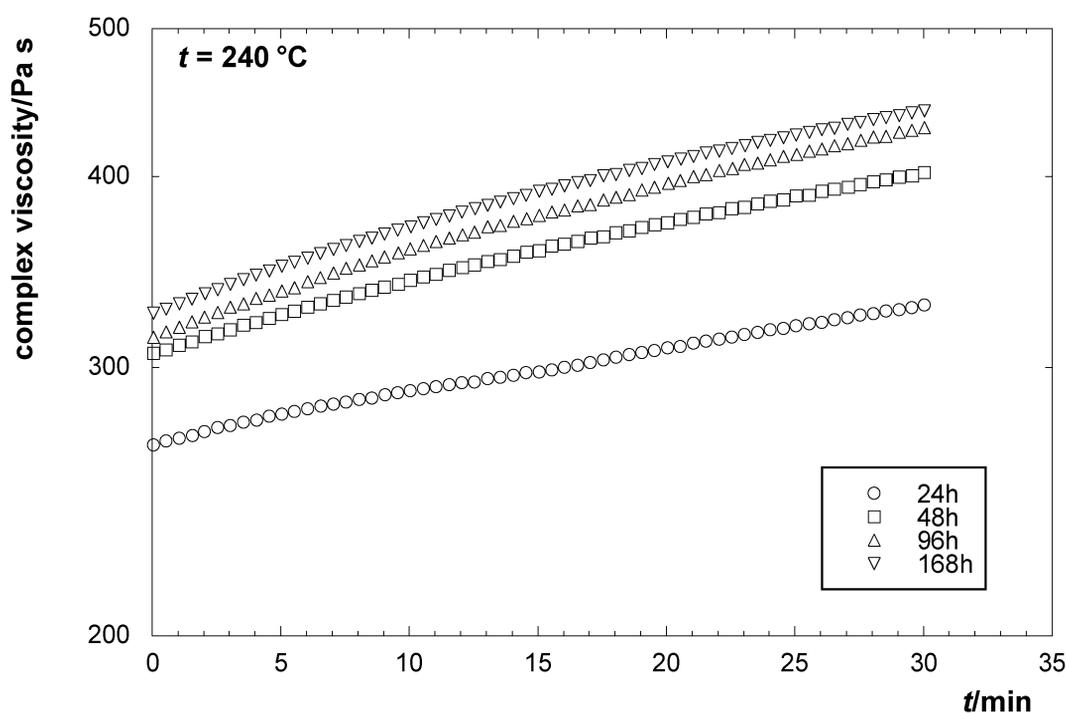
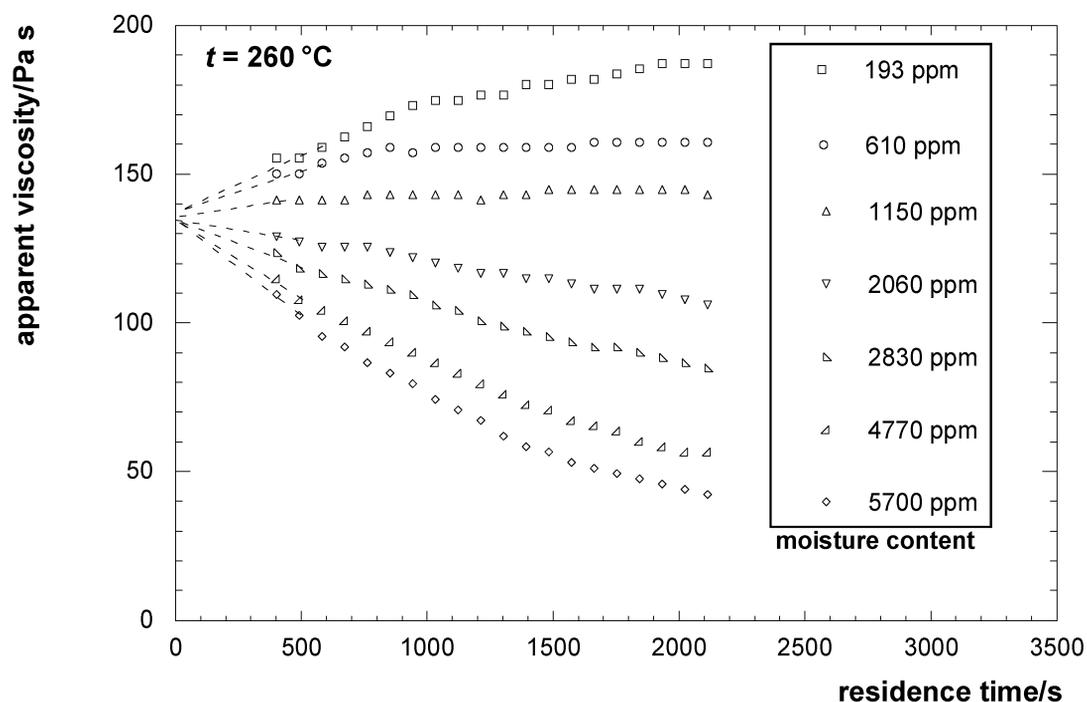


Fig. 3 Complex viscosity vs. residence time at 240 °C of PA6 at different moisture contents.

The capillary rheometry measurements show a totally different behavior from that seen in oscillatory shear. Figure 4 shows decreasing viscosities at high humidity content and increasing viscosity for very dry samples. This is exactly what one would expect from the equilibrium polycondensation reaction (eq. 1).



The Le Chatelier–Braun principle predicts the effect of a change in conditions on a chemical equilibrium. Higher water contents shift the equilibrium reaction to the left side of eq. 1, thereby reducing the water content and causing chain scission, i.e., reducing the molecular weight. On the other hand, at very low water content the reaction is shifted to the right side. The condensation reaction transforms



**Fig. 4** Apparent viscosity vs. residence time at 260 °C in capillary flow of PA6 at different initial moisture contents (Karl Fischer measurement at 160 °C).

two end groups into one peptide bond and one water molecule, respectively, thereby increasing the humidity and molecular weight of the sample. Figure 4 shows that at a water content of about 0.12 %, the viscosity, and by implication the molecular weight of the PA6 sample, remains constant at 260 °C. The equilibrium humidity concentration for constant molecular weight will depend on the concentration of reactive end groups of the polyamide and the operation parameters of the Karl Fischer measurement (e.g., temperature) and the capillary rheometer (e.g., the time and temperature needed to fill the cylinder).

A comparison between oscillatory and capillary rheometry explains the differences between these two methods. In oscillatory shear, the sample is more or less unpressurized, whereas in capillary flow the material is under large hydrostatic pressure. In the oscillatory rheometer, the water will be volatile and form small bubbles. The vapor pressure will depend on the surface tension of the polyamide melt. In the capillary rheometer, the water will be soluble in the melt due to the high hydrostatic pressure and no gas bubbles will be formed. Thus, the water molecules remain dissolved and may act as a plasticizer.

In capillary rheometry, the sample humidity will partly be lost due to evaporation during the sample filling step. As a consequence of the high temperature and hydrostatic pressure, the water that remains in the sample after the cylinder is filled and closed by the barrel will be dissolved in the polyamide melt, such that the flow curves (Fig. 5) will reflect both the change in molecular weight and the plasticizing effect of the dissolved water. In oscillatory rheometry, the humidity of the polyamide matrix will be almost independent of the initial water content. As soon as the experiment is started, the initially homogeneously distributed water molecules will form bubbles. The water concentration in the polyamide matrix will be almost entirely independent of the value before the measurement. Therefore, a time-sweep measurement will result in the same time-dependent increase in viscosity. Because of bub-

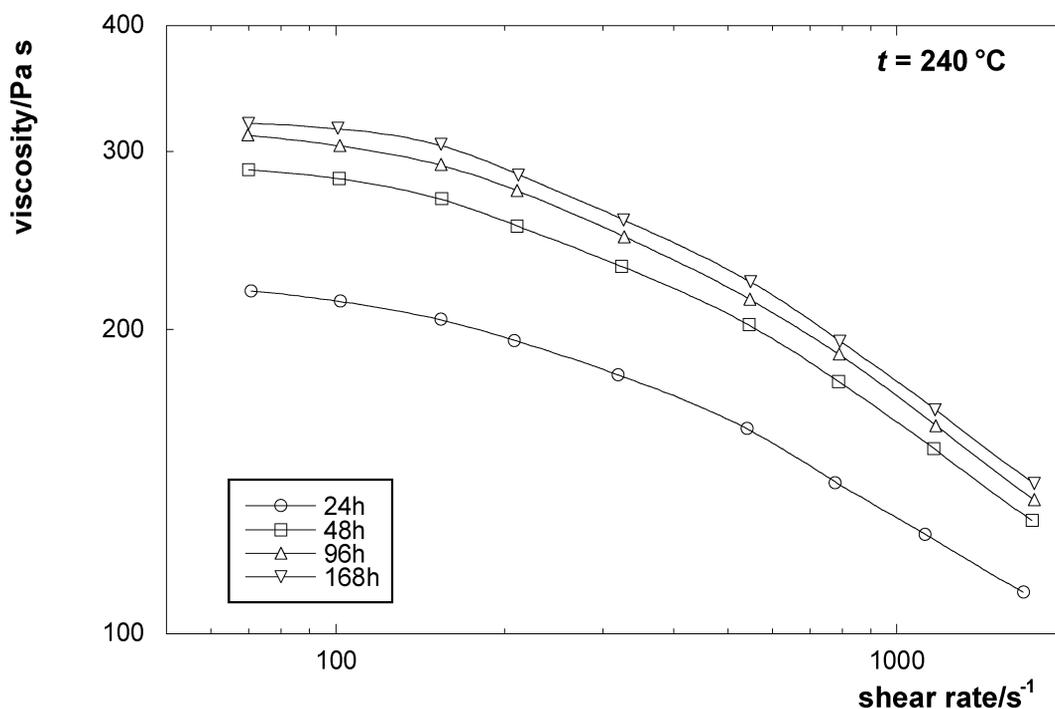


Fig. 5 Viscosity vs. shear rate at 240 °C in capillary flow of PA6 at different drying times.

ble formation, the absolute value of the measured viscosity will depend on the density of the melt (Fig. 3).

### A guideline for the standardization of rheological measurements

The experiments in the first part of this paper show that the measured rheological properties of PA6 depend strongly on the humidity of the sample and the experimental parameters of the method being used. The measured viscosity depends on changes in the molecular weight, gas bubbles, and the plasticizer effect.

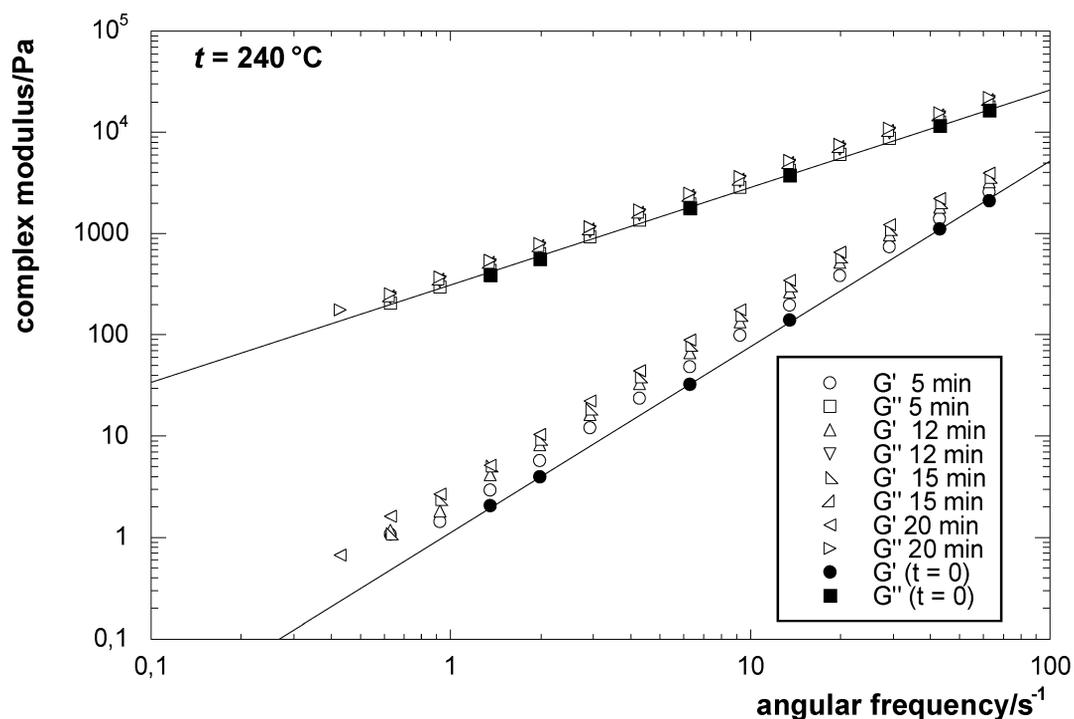
The aim in this IUPAC project was to develop a standard with which it is possible to make comparable measurements, i.e., it is not expected that the guideline will lead to the absolute value for the viscosity or the moduli of polyamide.

The easiest way to achieve comparable humidities is to make the polyamide sample as dry as possible. We tried this by performing non-increasing weight experiments and Karl Fischer measurements and found that at 90 °C very long drying times of up to 2 weeks are necessary in order to dry standard PA6 granules. The drying times are greatly reduced at 100 °C. The color of the polymer changes to light brown, but this did not change the rheological properties. However, the guideline should also be applicable to PA6 modified with fillers such as nanoclays. Fillers would dramatically increase the drying times necessary to attain very low water contents. Such a guideline would not be practical. It was also found that different types of ovens resulted in different water contents. Thus, drying times for discrete water contents are different for a convection oven, a vacuum oven, or a vacuum oven with inert purge gas. This would imply that the guideline should specify the type of oven to be used. Once again, this is not considered to be practical.

The viscosity, and therefore the molecular weight, changes with the residence time, as can be seen from Fig. 3. Extrapolation of the curve to time zero would give the viscosity of the sample before any

changes in molecular weight have occurred. The plasticizer effect in capillary rheometry might yield lower viscosities for high water contents. Therefore, extrapolation of the data of samples with very high water content might result in too low a viscosity value. However, Fig. 4 clearly shows that humidities up to 0.6 % still extrapolate to the same viscosity as the drier samples being investigated.

In Fig. 6, the measurement of oscillatory shear following 5 min equilibration is repeated after 10, 15, 20, and 25 min. For every frequency, the viscosity can be extrapolated to obtain those at time zero and these are also displayed in Fig. 6. This extrapolation procedure can also be applied to the values for storage and loss modulus. As explained above, the extrapolated values of viscosity, storage, and loss modulus should represent the initial molecular weight of the sample, and this should be independent of the humidity of the sample unless the water content is so high that the water molecules act as a plasticizer and reduce the viscosity.

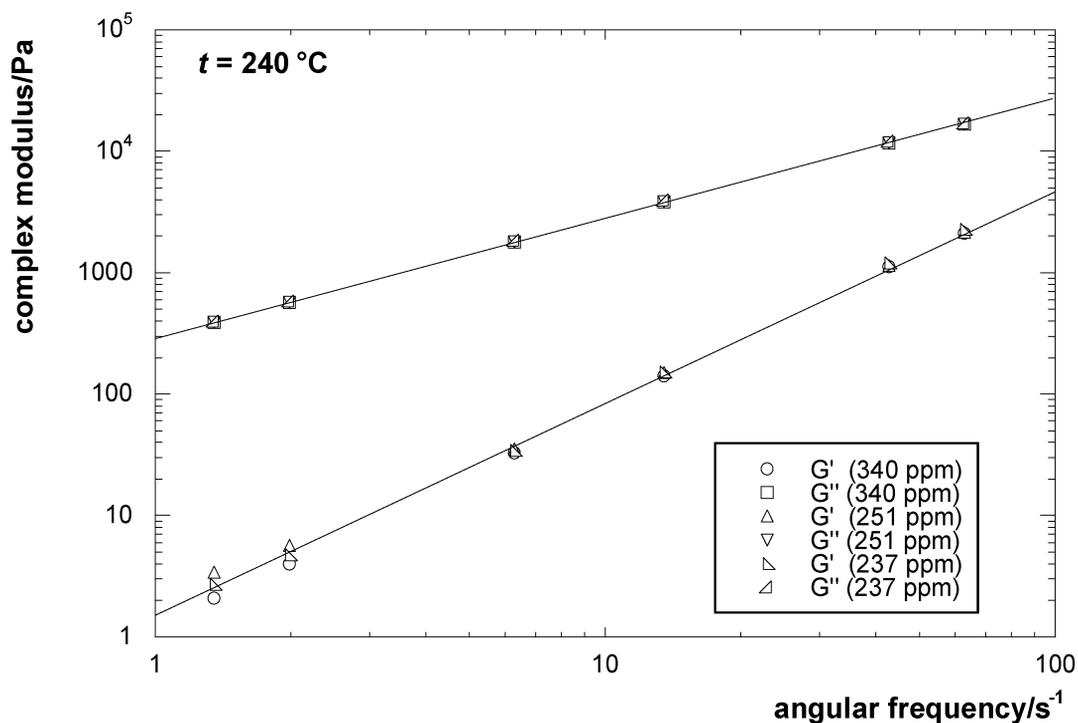


**Fig. 6** Experimental storage and loss modulus after different residence times in the rheometer together with the calculated extrapolated residence time  $t = 0$ .

In Fig. 7, the extrapolated storage and loss moduli of three samples with different but low humidities are shown. The extrapolated values are, with high accuracy, almost identical.

The extrapolation method seems to work very satisfactorily, such that one can conclude that the viscoelastic properties of PA6 can be determined using the procedure to obtain comparable and reproducible results.

As discussed above, Fig. 5 indicates that the extrapolation method might also work for capillary rheometry. For capillary rheometry, the time interval between subsequent measurements at different shear rates will be much larger than in oscillatory shear. Therefore, the exact time of the measurement should be taken for the extrapolation. Usually, the capillary data are corrected for the entrance pressure (Bagley correction) and non-Newtonian flow (Rabinowitz correction). Generally, for high values of the aspect rate of die length to die diameter, the entrance pressure drop will be much smaller than the pres-



**Fig. 7** Extrapolated values of storage and loss modulus for 3 samples with different humidities.

sure drop over the die such that a Bagley correction is not necessary. Using the newest versions of software for Goettfert capillary rheometers, it is possible to apply the Rabinowitz correction to experimental data after the extrapolation of apparent viscosities and shear rates to zero residence time.

A new high-frequency oscillating rheometer for linear viscoelasticity is now available from the Institute for Dynamic Material Testing (IdM) at the University of Ulm in Germany [10]. This piezoelectric rotary vibrator (PRV-rheometer) was used by one of the participants (Erik Wassner) to measure the high-frequency part of the curve in Fig. 8. At the overlap of both frequency ranges, the extrapolated viscosities from the PRV equipment are slightly lower than the data from the Rheometrics ARES oscillatory rheometer.

In Fig. 9, both the extrapolated data from oscillatory shear, capillary shear, and PRV are plotted together. The high hydrostatic pressure capillary shear and the pressure-less PRV show only slightly different curvature.

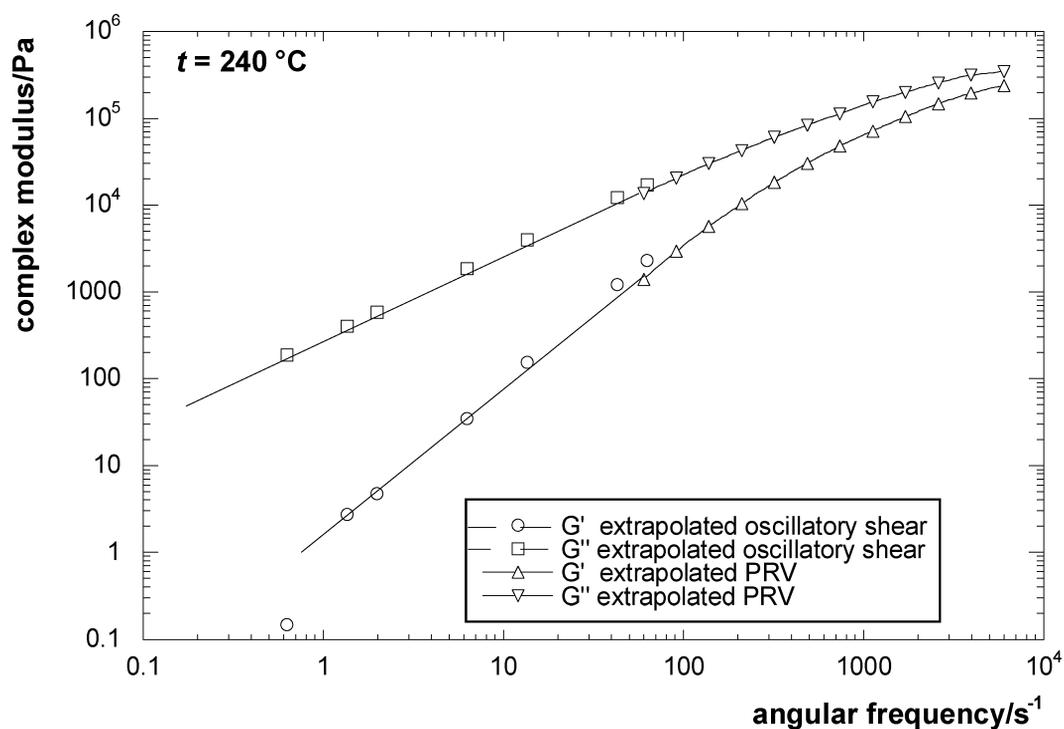


Fig. 8 Extrapolated storage and loss modulus from oscillatory shear and PRV measurements.

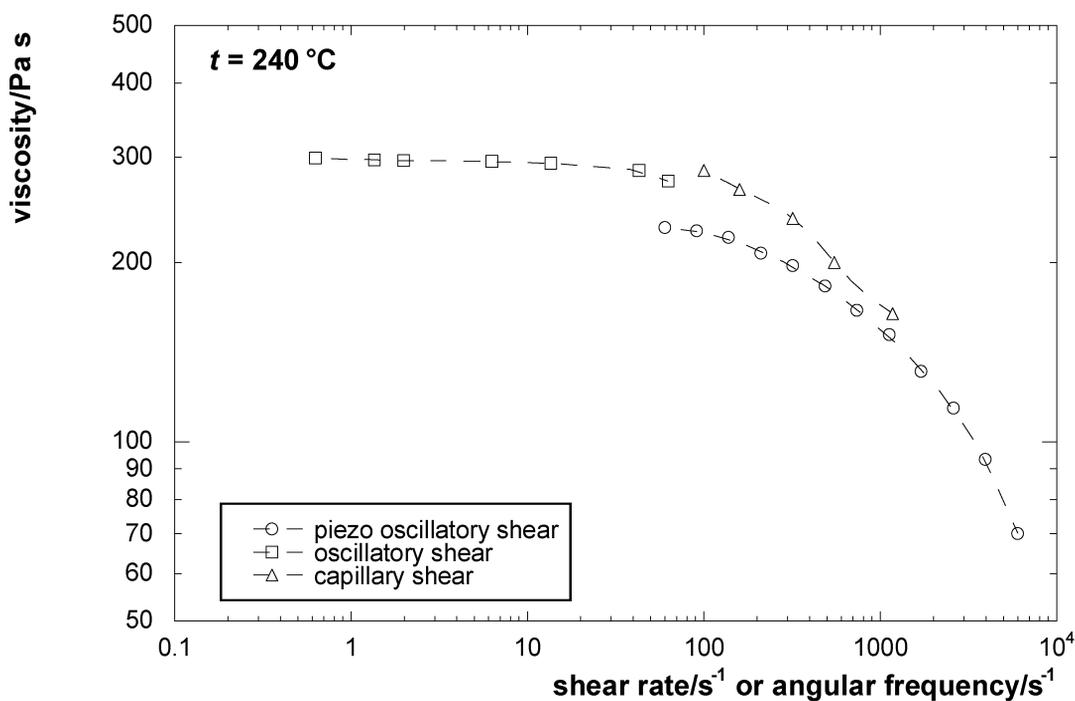


Fig. 9 Extrapolated viscosities from capillary, oscillatory, and PVR rheometry.

## CONCLUSIONS

The present investigation clearly shows that without any standardization, large differences in the rheological properties of PA6 can be obtained. Simply drying the polyamide does not solve this problem because the molecular weight of the polymer will also change for excessively dried material. Capillary rheometry showed an increase in viscosity for highly dried PA6 and a decrease in viscosity for higher humidities.

The proposed extrapolation method seems to work very satisfactorily and it was shown that the viscoelastic properties of PA6 determined in such a way gave comparable and reproducible results.

For capillary rheometry, the time interval between subsequent measurements at different shear rates will be much larger than in oscillatory shear experiments. Therefore, the exact time at each strain rate measured should be used for the extrapolation of capillary shear data.

The proposed back extrapolation method will be used to investigate different grades of PA6, other polyamide types and composites, e.g., nanoclay-modified PA6.

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