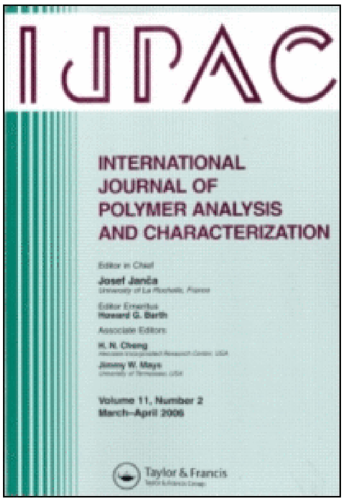

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Da-Peng Wang[a]; Cai-Yun Jiang[a]; Pei-Jun Li[a]; Shu-Gao Zhao[a]
[a] Key Laboratory of Rubber-Plastics, Ministry of Education, Qingdao University of Science and Technology, Qingdao, China

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Da-Peng Wang, Cai-Yun Jiang, Pei-Jun Li, and Shu-Gao Zhao
Key Laboratory of Rubber-Plastics, Ministry of Education, Qingdao University of Science and Technology, Qingdao, China

Abstract: Unique observations on the shear flow rheological characterization of nylon resins, especially in the high-shear-rate region, nylon 6 and its nylon 610 blends in particular, are reported. The main aims of our study were to deal with a deviation of nylon melt from the Ostwald-de Wale equation, well accepted for polymers to date. It was found that rheological data of nylons fit well with the logarithmic law. Such unique results, in contrast to those for polyethylene and polypropylene, were tentatively attributed to the rupture of H-bonding in nylon melts.

Keywords: Logarithmic law; Nylon; Rheological characterization

INTRODUCTION

The rheological characterization of linear flexible chain polymers has aroused considerable concern from both industrial and academic circles in recent years.[1] Rheological characterization is regarded as the essential to obtain plastic products with outstanding quality and improving production efficiency during extrusion molding and injection molding.

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Correspondence: Shu-Gao Zhao, Key Laboratory of Rubber-Plastics, Ministry of Education, Qingdao University of Science and Technology, Qingdao 266042, China. E-mail: zhaosg@hotmail.com

This has resulted in most of the literature concentrating on polyolefin melt rheology[2–4] and relatively little on condensation polymers,[5, 6] such as the nylons. It is well known that nylon 6 and nylon 610 are important commercial polyamides with good mechanical and rheological properties, and they are used in a large range of industrial fields. However, less attention has been paid to the rheological characterization of nylon 6/nylon 610 blends in the high-shear-rate region. Therefore, the purpose of this study is to investigate the rheological information of nylon matrix on normal stress, as well as rheology conformation formation. To the best of the authors' knowledge, this is the first report on the unique rheological characterization of nylon materials, although there have been a few reports on the melt rheology of nylon-based materials.

EXPERIMENTAL SECTION

Measurements were made on commercial polymers. Polycaprolactam (PA6) and poly(hexamethylene sebacamide) (PA610) were supplied by Hongrui Co. Ltd (China); before measurement, all the polymers were carefully dried at 80°C for 72 h under vacuum to give a water content of not more than 100 ppm. Nylon blends were prepared by melt blending in a twin-screw extruder at 235°C with a screw speed of 80 rpm; the extrudates were then cut into pellets. Neat nylon 6 was treated with the same procedure as the nylon blends for comparison. The pellets have a diameter of about 2 mm and were dried before using.

The rheological characterizations of the materials were made with a Rosand Precision rheometer (Bohilin Instrument, Malvern, UK) in the double-bore experiment mode. The length/diameter ratio of the capillary in one bore was 16/1; within the orifice die in the other bore was a zero-length capillary. The experiments were carried out at 230°C. The experimental results were processed with software from Bohilin Instrument, and all the rheological data obtained were subjected to Bagley and Rabinowitch calibration. All the tests were run under air atmosphere. Reproducibility of the measured parameters was tested with at least three samples of the same composition; the experimental curves obtained were similar to those reported here.

RESULTS AND DISCUSSION

Generally speaking, nylons exhibit very narrow temperature range for rheological tests so that adequate data cannot be obtained for generating a master curve.[1] PA6 begins to melt at 204°C and ends the melting event at about 227°C, as observed on the differential scanning calorimetry curve (not shown here). The equilibrium melting point (Tm) of PA610 is lower than that of PA6. Therefore, melt rheology measurement for PA6 and its blends was carried out at the temperature of 230°C in this study.

The steady shear response of polymer usually provides some useful information on the processability of the material. The steady shear response as measured by apparent viscosity (η_a) for neat PA6 and its blends with 5, 10, 20, and 40 wt% nylon 610 are shown in Figure 1(a). It is seen that the value of apparent viscosity decreases with increasing PA610 loading for the samples with 10, 20, and 40 wt% PA610, while the sample with 5 wt% PA610 has relatively similar apparent viscosity values when compared with the one with 10 wt%. This is believed to arise from the good flowability of nylon 610. Each flow curve displays a quite similar profile with an approximately linear relationship between η_a and γ at low-shear-rate region (e.g., less than $500\,s^{-1}$) and a deviation occurring at higher shear rates. Similar observation was reported for other nylon systems,[7,8]

The reproducible phenomenon mentioned above is attributed to the accurate linear relationship between η_a and log (γ) for neat nylon 6 and its blends, which has not been previously reported, as shown in Figure 1(b). To investigate the dependence of η_a on γ, the Ostwald-de Wale equation (see Equation (1)) and logarithmic equation (see Equation (2)) were employed to fit the non-Newtonian viscosity curve for neat PA6 and its blends, as shown in Figure 1 by the solid lines. It is seen that experimental data fit much better with Equation (2) than with Equation (1).

$$\eta_a = K_1 \cdot \gamma^{\dot{n}-1} \tag{1}$$

$$\eta_a = K_2 \cdot \log(\dot{\gamma}) + \eta_0 \tag{2}$$

Here, η_0 is the zero shear rate viscosity, γ is the shear rate, n is a dimensionless parameter, and K_1 and K_2 are the coefficients. Then, for Equation (1), the slope of η versus γ on a log-log plot in the power-law region is ($n - 1$), where n is called a non-Newtonian index, which usually decreases with increasing shear rate. However, Equation (2) shows that η_a follows a linear relationship with log(γ), and the slope of $\eta - \gamma$ on a linear-log plot is K_2, which is a constant coefficient that can quantitatively measure shear thinning characterization of PA6 and its blends when γ is more than 100/s. This equation may not accurately describe the melting fluid flow behavior of nylon 6 and its blends in a shear-rate range of $0 \sim 100$/s if K_2 remains constant, resulting in calculated values of η_0 that may be not accurate. The calculated values of K_1, K_2, and n (supposed as constant in order to examine the applicability of Equation (1)) are not the key point of this study, and thus they are not shown here. Determination coefficient (R^2) serves to evaluate the fitting degree of regression straight line with the experimental points. The closer to 1 R^2 is, the better fitting

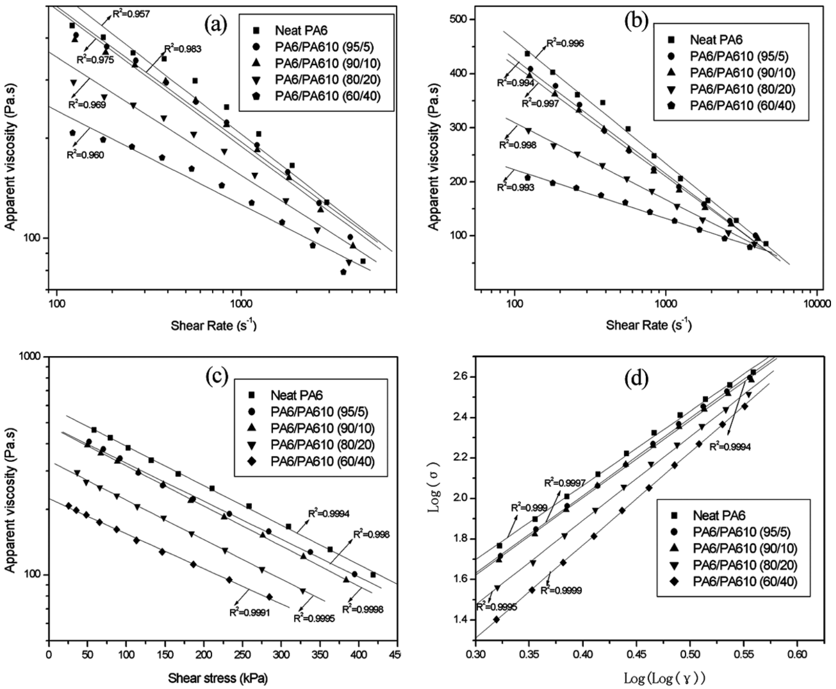

Figure 1. Melt shear flow response: apparent viscosity versus shear rate for neat PA6 and its nylon 610-based blends on the (a) log-log plot and on the; (b) linear-log plot; (c) apparent viscosity versus shear stress, and; (d) log(σ) versus log (log(γ) for neat PA6 and its blends. Symbols are the experimental data at 230°C, and solid lines from (a), (b), (c), and (d) are the fitting curves with Equations (1), (2), (3), and (4), respectively.

degree is obtained. The values of R^2 show that R^2 from Figure 1(b) is specifically closer to 1 than that from Figure 1(a) for each $\eta_a - \gamma$ curve of the nylon system, indicating that a logarithmic equation is better used for describing melt flow characterization of nylon matrix than the Ostwald-de Wale equation, especially in the high-shear-rate region (more than 500/s). It is considered that deviation occurring on a log-log plot means that a novel relationship occurs.

Combined with the melt flow response in the observed shear-rate range, η_a as a function of shear stress (σ) for nylon 6 and its blends is shown in Figure 1(c). To investigate the dependence of η_a on the σ, the logarithmic model (see Equation (3)) was employed to fit the non-Newtonian $\eta_a - \sigma$ curve for neat nylon 6 and its blends, as shown in Figure 1(c) (solid lines).

$$\log(\eta_a) = K_3\sigma + \log(\eta_0) \tag{3}$$

Here, σ is the shear stress and K_3 is the coefficient. The slope of log (η_a) versus σ is K_3, which remains constant. The lower K_3 is, the better fluidity of nylon melt is obtained. It has been found that log(η_a) is perfectly proportional to σ for nylon systems and the R^2 of each curve is more than 0.999. However, a distinct linear relationship never happens on the double-logarithm coordinates, which is not shown here. It is assumed that σ versus η_a is in accordance with logarithmic law for neat nylon 6 and its blends in the observed range of shear stress, a fact not previously reported in the literature. The $\eta - \sigma$ curve need not consider time-temperature superposition. In other words, the curve of η versus σ can avoid temperature effect, when compared with that of η_a versus γ.

When investigating the internal relations of experimental data from Figure 1(b) and (c), it is found that there is a specific relationship between σ and γ, described by the following scaling law:

$$\log(\sigma) \sim \log(\log(\dot{\gamma})) \tag{4}$$

This scaling law used in nylon melt flow is quite different than the Ostwald-de Wale power law equation, which is well known. Generally speaking, power law is suitable for a number of polymer materials (e.g., polyethylene and polypropylene) in a wide shear-rate range, whereas for nylon 6 and its blends, the suitability of logarithmic law is better than that of power law, especially in the high-shear-rate region (e.g., more than 400/s). Another advantage of the logarithmic law is that all of the parameters are constant, indicating that rheological characterization of nylon melt could be distinctly predicted in high-shear-rate region through monitoring the rheological behavior in the relative low-shear-rate region. Figure 1(d) shows that log(σ) linearly increases with log (log(γ)) for each nylon matrix. The R^2 of each $\sigma - \gamma$ curve is more than 0.999. The results indicate that the nylon matrix follows logarithmic law but does not fit well with the power law. Such unique results, in contrast to polyethylene and polypropylene, are tentatively attributed to the rupture of H-bonds in nylon melts, although the exact reasons why nylon matrices fit well with logarithmic law are not yet clear. It might be interesting to explore whether the logarithmic law is suitable for the rheological behavior of other polymer systems.

CONCLUSION

Melt rheological characteristics of nylon 6 and its blends have been studied in this work. It has been found that rheological data of nylon matrix fit well with logarithmic law. Compared with the classical theory (power law), in nylon systems log(η_a) is distinctly proportional to σ and η_a linearly increases with log(γ). It is assumed that the deviation occurring at high-shear-rate region on a log-log plot should be regarded as following the logarithmic law, which is useful to describe the rheological characteristics of nylon 6 and its blends. However, whether the logarithmic law is applicable only to nylon 6-based polymer material is not yet clear.

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