

Shear Flow Behaviors of Poly(*p*-phenylene benzobisoxazole) Spinning Dope

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Received 26 January 2008; accepted 2 June 2008

DOI 10.1002/app.28820

Published online 30 July 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In this study, the shear flow properties of Poly(*p*-phenylene benzobisoxazole) (PBO)/poly(phosphoric acid) (PPA) spinning dope were studied by means of capillary rheometer. The effect of shear stress, temperature, PBO concentration, and PBO molecular weight on the apparent viscosity of PBO/PPA dope was discussed. The results showed that the apparent viscosity of the dope decreased with the increase of the shear stress and the temperature. The flow behavior index increased with the increase of tempera-

ture, which indicated that the non-Newtonian behavior of the dope became weaker at high temperature. Moreover, it was also found that at high shear stress, the apparent viscosity of the dope was insensitive to the temperature, PBO molecular weight, and PBO concentration. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1899–1904, 2008

Key words: poly(*p*-phenylene benzobisoxazole); shear flow; rheological properties; liquid crystal polymer

INTRODUCTION

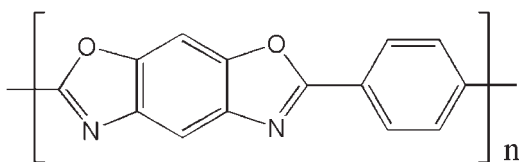
Poly(*p*-phenylene benzobisoxazole) (PBO) is a rigid-rod-like lyotropic liquid crystal polymer. PBO fiber has high modulus and high strength due to its high degree of axial chain orientation along the polymer backbone.^{1–4} The tensile modulus and strength of PBO fiber are significantly higher than most other high-performance fibers.⁵ Besides its excellent mechanical properties, it also shows excellent thermal stability and environmental stability.⁶ This material has received more and more interest in the reinforced materials and aircrafts.^{7–10} The chemical structure of the PBO molecule is shown in Scheme 1.

PBO fiber is usually prepared by PBO/poly(phosphoric acid) (PPA) dope. When the spinning dope is extruded from the spinneret under certain shear stress, the extrudate exhibit liquid crystalline structure with a high degree of molecular orientation.^{11,12} Then the extrudate are washed by water to remove PPA component, and the PBO fiber is formed. Therefore, the shear flow characterization of PBO/PPA dope is of crucial importance in industry applications as it can allow the choice of processing parameters and the estimation of spinning process.

Rheological properties of rigid-rod-like polymer solutions had been studied widely. Chow et al. studied poly(*p*-phenylenebenzobisthiazole) (PBZT) solu-

tion to examine the transient flow properties and shear-induced microstructure near the isotropic-nematic phase transition.¹³ Tan and Berry reported the rheo-optical and rheological behavior of rod-like poly(1,4-phenylene terephthalamide) (PPTA) and PBZT nematic solutions.¹⁴ Faraoni et al. used rigid-rod model to predict several rheological features of rod-like polymers in the nematic phase and formulated in terms of a nonlinear partial differential equation that describes the evolution of an orientational distribution function.¹⁵ Kupferman et al. solved the equations of transient shear flow for a model of a liquid crystalline polymer that contains a long-range interaction term in the nematic potential.¹⁶ Rheological behaviors of PBO/PPA solution had also been investigated previously, whereas most of these studies did not aim at the shear flow for spinning process. Shaffer et al. studied relative molecular weight distributions of PBO/PPA solution.¹⁷ The molecular weight for a dilute solution of PBO/PPA was determined by fitting the rheological data with a semiempirical polydisperse hybrid theory. Because the rheological data reported in the study was collected for a 0.05 wt % PBO solution, it was much different from the rheological behaviors of PBO/PPA spinning dope, which usually had the 10–15% weight ratio of PBO. Benoit and Morton reported the rheological properties of PBO/PPA solutions and found that liquid crystalline solutions of PBO/PPA exhibit linear viscoelastic response to strains of 5% and satisfy time–temperature superposition.¹⁸ The rheological behavior of the system is

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Scheme 1 The chemical structure of PBO.

suggestive of a weak gel-like structure with a small breaking strain at low frequencies. Meanwhile, the solutions are highly shear-thinning over the entire range studied. The conclusions reported by Benoit Ernsta were very valuable. However, in that investigation the rotational rheometer and oscillatory frequencies were used, the rheological behavior was different from the spinning process of PBO fiber to some extent.

In this study, we are interested in the shear flow behaviors of the PBO/PPA spinning dope in the capillary, from which we expected to simulate the shear flow for the dope in the tube and spinneret hole during spinning process. Using the apparatus described, we determined the flow curves of PBO/PPA spinning dope so as to acquire a greater knowledge of the shear flow behavior of the spinning dope and to study its optimum use in the transportation and spinning processes.

EXPERIMENTAL

Materials

All reagents, unless otherwise specified, were obtained from Aldrich and used as received. PPA was purchased from shanghai chemical reagent company and used without further purification. 4,6-diamino-1,3-benzenediol dihydrochloride (DAR) was obtained from commercial sources and purified before used. PBO was synthesized in the laboratory by polycondensation in PPA as solution following the procedure described in the Ref. 19. The concentration of PBO was 14% in the following discussion, unless it was pointed out specially.

Characterization

The shear flow properties of the PBO/PPA solution were performed on a capillary rheometer with a length-to-diameter ratio of 40/1. The Rabinowitch correction was used to determine the true shear rate. Rheological measurements were carried out at different temperatures, different PBO concentration in the PBO/PPA dope and different molecular weight of PBO. The molecular weight of all the polymers was tested by Intrinsic Viscosities method, which was measured in methanesulfonic acid (MSA) at 30°C by

using a modified device based on an Ubbelohde capillary viscometer.

RESULTS AND DISCUSSION

Flow curve and viscous flow activation energy

Flow curves of PBO/PPA solution for 180, 190, 200, and 210°C were shown in Figure 1. From the figure, it could be seen that with the increase of temperature, the curves descend. The possible reason was that the apparent viscosity of PBO/PPA dope decreased when the shear rate increased. That is to say the curves deviated from Newtonian behavior, and PBO/PPA dope showed a non-Newton fluid rheological behavior. This is similar to many other melting polymer systems without solvent.

The Ostwald-de Waele or the "power-law" is widely used as a model for non-Newtonian fluids,

$$\tau = \kappa \dot{\gamma}^n \quad (1)$$

where τ is shear stress (Pa), $\dot{\gamma}$ is shear rate (s^{-1}), κ is a viscosity related constant, n is an exponent (flow behavior index) that equals the slope of the $\log \tau - \log \dot{\gamma}$ in the flow curve. For Newtonian fluids, $n = 1$; for dilatant fluids, $n > 1$; for pseudoplastic fluids, $n < 1$. From Figure 1, this slope can be determined by means of regression calculations using the "power-law" equation. The flow behavior index (n) at temperatures of 180, 190, 200, and 210°C was calculated as 0.156, 0.165, 0.173, 0.175, respectively.

The effect of the temperature on the flow behavior index was also presented in Figure 1 and Table I. In Figure 1, the value of n is less than 1 for all temperatures under investigation, indicating the pseudoplastic nature of PBO/PPA solution under the above temperature. With the increase of temperature, the

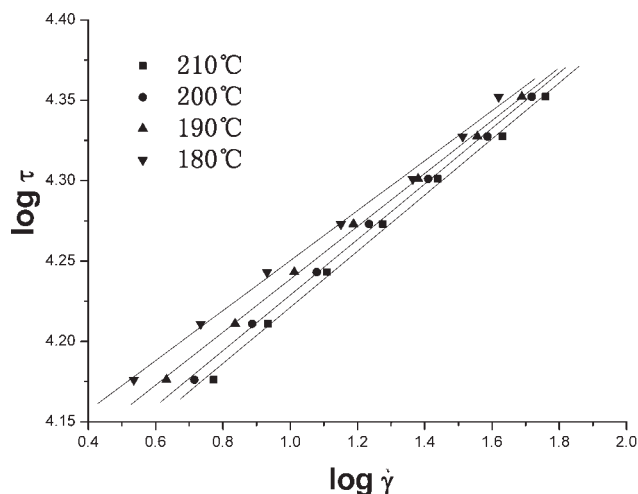


Figure 1 Shear stress versus shear rate for PBO/PPA dope at different temperatures.

TABLE I
The value of n for different temperatures

Temperature (°C)	180	190	200	210
N	0.156	0.165	0.173	0.175

flow behavior index (n) increased; this indicates that the non-Newtonian behavior of PBO/PPA solution became weaker. It was reasonable because with the raise of temperature, the polymer molecular mobility increased, and the viscoelastic behavior became weaker. Thus, the non-Newtonian behavior of PBO/PPA solution became weaker.

To indicate the relationship between apparent viscosity and shear stress of PBO/PPA dope, the viscosity of PBO/PPA dope was measured at different temperatures and different shear stress and was shown in Figure 2.

In Figure 2, the apparent viscosity at different temperature was decreased with the increase of shear stress. It was the typical pseudoplastic flow behavior. According to the classical theory,²⁰ the polymer melts or solutions in solvents have long chain molecules which in a random fashion loop and entangle with other molecules. This resulted in the strong intermolecular interaction as these long chain molecules do not act alone in an empty space but millions of similar molecules interlooped and entangled. These interloops and entanglements with molecule segments as connectors lead to the nonpermanent junctions at entanglement points. When suddenly suffered from high shearing forces, the fluid would initially show a solid-like resistance against deformation within the limits of the entanglement point network. Then, under the shear force the connector segments would elastically stretch and finally the molecules starts to disentangle, orient, and irreversibly flow one over the other in the direction of the shearing force. Moreover, as a kind of rigid-rod lyotropic liquid crystal polymer, PBO/PPA dope was slightly different from other typical polymer fluid as the intermolecular interaction and interloop between PBO molecules are more weaker because of their chemical constitutes and their rigid-rod structure. Thus, when the shear force rises, the disentanglement would be easier, and the decrease of viscosity is more obvious when compared with other polymer fluid.

Figure 2 also indicates the sensitivity of the viscosity of PBO/PPA solution to temperature. At a low shear stress, the viscosity of PBO solution was decreased dramatically with the temperature increasing from 180 to 190°C. From 200 to 210°C, the viscosity of PBO solution is decreased more slowly. The possible reason was that at low temperature the thermal energy supplied by environment approxi-

mately approaches or equals to the viscous flow activation energy, so the effect of temperature on the viscosity of PBO solution is more obvious. At high temperatures, the thermal energy exceeds the viscous flow activation energy of PBO solution; thus, the effect of temperature on the viscosity of system is not obvious.

There are two well-known equations to describe activation energy/temperature dependence of polymers: Arrhenius equation and WLF equation. The suitable model depends on the temperature range of investigation and the glass transition temperature of material. If the temperature is just above the glass transition temperature (T_g), the thermally stimulated flexibility of one polymer chain depends on its neighbors (known as a cooperative process). Whereas if the temperature is well above T_g , the thermal flexibility of chains is less cooperative. This difference in the physical behavior requires a different mathematical description.²¹ Under the temperature investigated in this study, system followed Arrhenius relationship rather than WLF relationship. Therefore, the viscous flow activation energy of PBO/PPA dope could be calculated by the Arrhenius equation,

$$\eta = A e^{\frac{E_\eta}{RT}} \quad (2)$$

where η is viscosity of the dope, E_η is viscous flow activation energy for the dope flow.

A plot of $\eta - 1/T$ is shown in Figure 3 and the viscous flow activation energy was calculated according to the slope of the straight line of $\eta - 1/T$. The results were summarized in Figure 4. From Figure 4, it could be seen that the viscous flow activation energy is higher at lower shear stress.

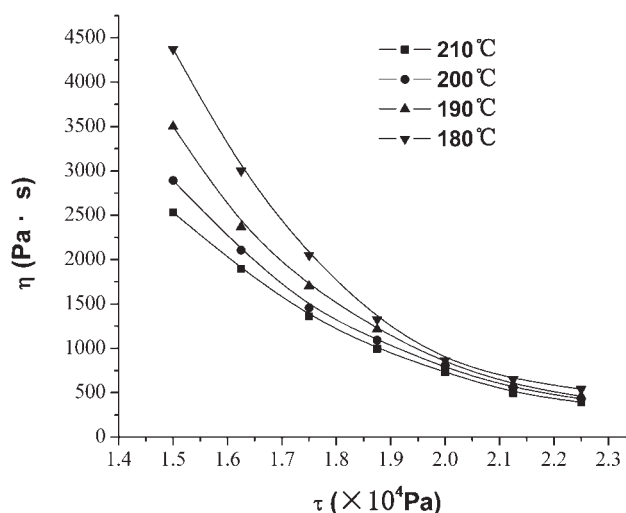


Figure 2 Apparent viscosity versus shear stress of 14% PBO/PPA dope at different temperature.

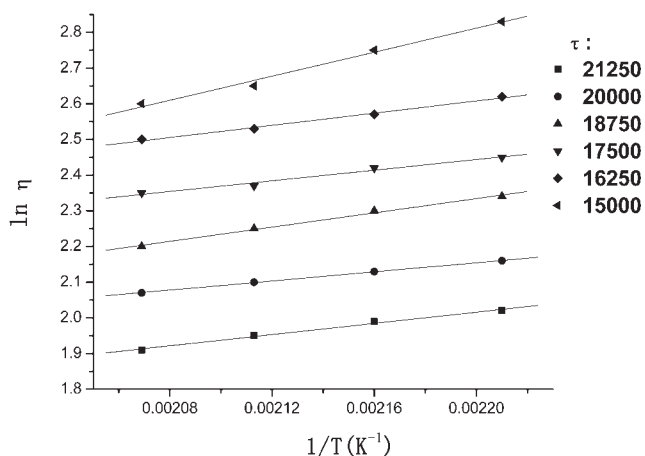


Figure 3 The temperature dependence of apparent viscosity for PBO/PPA dope.

Moreover, with the increase of shear stress, the viscous flow activation energy dropped sharply and then changed gently. The higher E_a at lower shear stress meant that the apparent viscosity was sensitive to temperature at lower shear stress, whereas the temperature effect on the apparent viscosity became weaker at higher shear stress.

The effect of molecular weight of PBO

The apparent viscosity versus shear stress curve of PBO/PPA dope with different molecular weight of PBO at 180°C was reported in the Figure 5.

From Figure 5, the viscosity curve for the PBO/PPA solution with lower molecular weight of PBO showed the three region behavior. The system with PBO M_w of 36,000 is a typical example. A plateau separates the curve to form three regions, i.e., the two shear thinning portions of the curve at low and

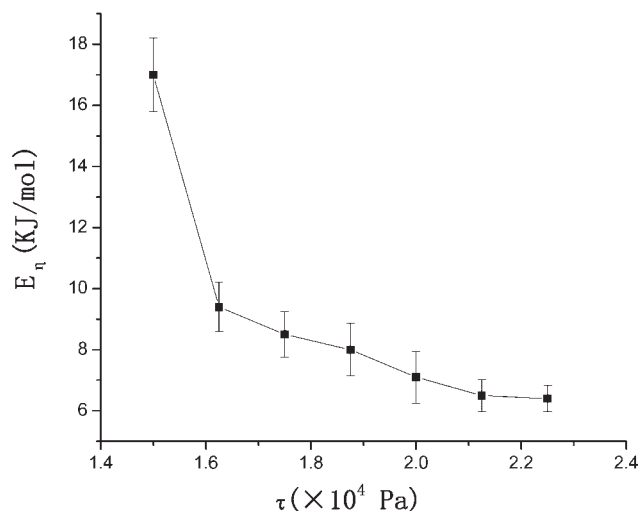


Figure 4 The relationship between viscous flow activation energy and shear stress.

high shear stress. The same qualitative feature of the viscosity curve was also found but was unapparent in that of the curve with the PBO M_w of 40,000, and also was reported in the Figure 5. A flattening of the viscosity curve is again observed at the lowest shear stress although the intermediate plateau was not clearly observed. However, this plateau was only existed in these two samples. The viscosity curve of the system with higher PBO molecular weight was completely different. As shown in Figure 5, a rather monotonously decreasing behavior was observed for the dope with high PBO molecular weight, corresponding to a single shear thinning region over the entire range of shear stress explored. No plateau or intermediate were found when M_w of PBO is 63,000 or 73,000. This plateau seemed to appear only in the system with low PBO molecular weight. As the molecular weight of PBO is increased, the two plateau regimes might be overlapped or disappeared, thus generating a monotonously decreased viscosity response.

To our knowledge, this viscosity curve was similar with the viscosity behaviors reported by Sigillo and Grizzuti in the lyotropic aqueous solutions of hydroxypropylcellulose.²² According to Sigillo and Grizzuti, a possible interpretation of these rheological results mentioned earlier could be proposed by considering the structured nature of the lyotropic liquid crystal system. The overall shear flow response of a liquid crystal system lies between two limiting situations. The high shear limit is dominated by the nonlinear molecular dynamics, whereas the low shear limit is linked to the fact that “less nematic” and “more isotropic” defect cores are needed to balance the torque of the tumbling nematic.

Moreover, from Figure 5 we could find that although the higher molecular weight system had much higher viscosity at the low shear stress, the

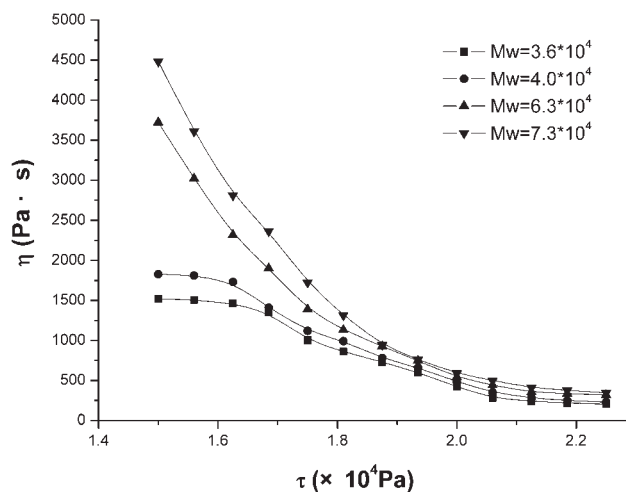


Figure 5 The effect of PBO molecular weight on the apparent viscosity of 14% PBO dope.

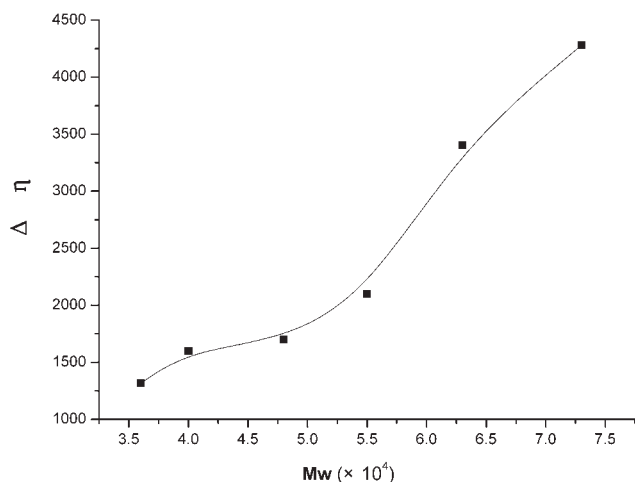


Figure 6 The margin of apparent viscosity for the dope with different PBO M_w .

difference of viscosity value between high PBO molecular weight dope and low PBO molecular weight dope became smaller at higher shear stress. When the shear stress increased, the drop of viscosity for the system became faster with the increase of PBO molecular weight. The results were summarized in the Figure 6. In Figure 6, the ordinate was the margin of apparent viscosity for the PBO/PPA dope at the shear stress of 15,000 and 22,500 Pa.

The effect of PBO molecular weight on the power-law index of the spinning dope was also investigated. Power-law index could be calculated by the slope of $\log \tau$ and $\log \gamma$ of the systems. All the $\log \tau$ and $\log \gamma$ curves gave a high degree of linear correlation, and the effect of molecular on the power-law index at 180°C was summarized in Figure 7. It is obvious that with the increase of molecular, the n fall sharply at first and then decreased gently. The power-law index is an important parameter for the spinning process. A decreasing power-law index make the spinning dope deviate the Newtonian fluid and affect the spinning process.

To summarize this section, it could be said that the change in molecular weight had important effects on the rheological behavior of PBO spinning dope. Although the absolute apparent viscosity was an increasing function of M_w , the apparent viscosities for the PBO/PPA dope with different PBO M_w at high shear stress seemed to be “closed” despite that the different of viscosity are greater at low shear stress for these system. This is of important value for the spinning process for the PBO spinning dope with higher PBO M_w .

The effect of concentration

As shown in Figures 8, the apparent viscosity of PBO dope with different concentrations is decreased

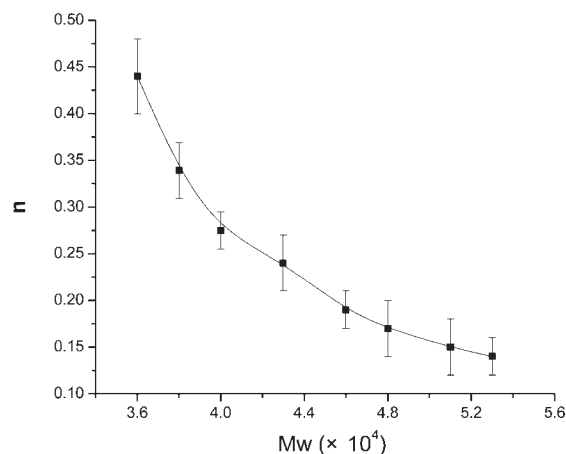


Figure 7 The change in n for the PBO/PPA dope with different PBO M_w .

with the increase of shear stress. Meanwhile, at the lower shear stress the viscosity of higher concentration PBO dope was obviously higher than that of lower concentration PBO dope, but the viscosity gap reduced with the increase of shear stress and even tended to be equal at high shear stress despite the difference of initial viscosity of PBO dope.

Two factors affected the viscosity of PBO dope: PBO concentration and PBO molecular weight. As PBO/PPA dope in this study were prepared directly by the polycondensation in PPA as solution, PBO M_w in the higher PBO concentration solution was higher than that of solution with lower PBO concentration (Table II). In the forenamed discusses we had already discussed the effect of molecular weight of PBO on the apparent viscosity. Moreover, the higher the PBO concentration for the dope, the more inter-loops and entanglements existed on the solution and the higher apparent viscosity was behaved. That

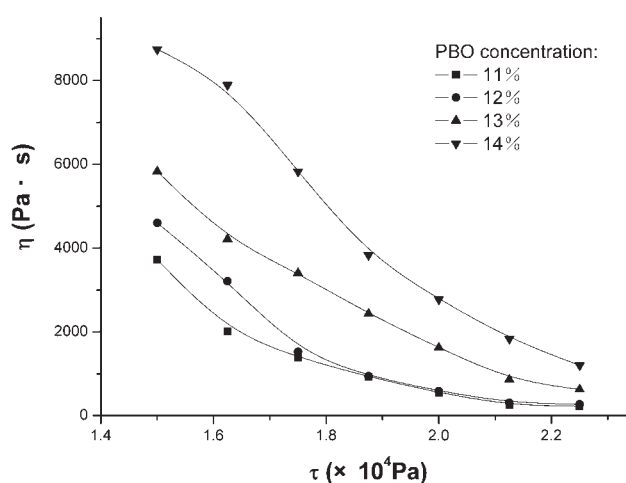


Figure 8 Apparent viscosity versus shear stress of PBO solution at various concentrations.

TABLE II
The relationship between PBO concentration and PBO molecular weight

PBO concentration (%)	11	12	13	14
PBO molecular weight ($\times 10^4$)	7.11	7.19	7.32	7.71

was to say, under low shear stress the higher viscosity of PBO solution might be caused by the higher PBO concentration and/or higher PBO molecular weight synchronously.

However, under high shear stress the effect of PBO molecular weight on the apparent viscosity was not obvious according to the forenamed discusses. Viscosity under high shear stress mainly lied on the effect of the number of PBO molecules within the dope (or the number of PBO molecules interloops and entanglements in the dope) on the viscosity. Comparing with other polymers, chains of PBO molecular are not very different in molecular weight, but they are typically rigid-rod-like and have less intermolecular interaction. Once the rigid rod highly oriented under high shear stress, the viscosity would be insensitive to the length of rigid rod (molecular weight) and the number of rigid rod (concentration) but be sensitive to the degree of orientation of rigid rod. The larger the shearing stress, the more rigid-rod-like molecules oriented; thus, the margin of apparent viscosity for the dope with different PBO concentration would become more unobvious.

CONCLUSIONS

The shear flow properties of PBO/PPA spinning dope was studied by means of capillary rheometer. The apparent viscosity of PBO/PPA dope was decreased with the increases of shear stress and temperature. With the increase of temperature, the flow behavior index increased and indicated that the non-Newtonian behavior of PBO/PPA dope became weaker. From the temperature dependence of the apparent viscosity of the dope, the viscous flow activation energy was calculated. Moreover, it was found that the apparent viscosity is sensitive to temperature at lower shear stress because of higher flow activation energy, and the temperature effect on the apparent viscosity becomes weaker at higher shear stress. The study of the effect of PBO molecular weight and the PBO concentration on the viscosity

showed that the apparent viscosity of PBO dope was sensitive to the PBO molecular weight and the PBO concentration under lower shear stress. However, despite the difference of initial viscosity for the dope with different PBO M_w or different PBO concentration under lower shear stress, the viscosity margin reduced with the increase of shear stress and even tended to equal at the high shear stress. At high shear stress the apparent viscosity of the dope was insensitive to the temperature, PBO molecular weight and PBO concentration. The possible reason was the high orientation of the rigid-rod PBO molecules under high shear stress.

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