

Rheological Properties of Poly(trimethylene terephthalate) in Capillary Flow

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Received 2 October 2003; accepted 20 April 2004

DOI 10.1002/app.20917

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

ABSTRACT: The shear viscosity, extensional viscosity, and die swell of the PTT melt were investigated using a capillary rheometer. The results showed that the PTT melt was a typical pseudoplastic fluid exhibiting shear thinning and extensional thinning phenomena in capillary flow. There existed no melt fracture phenomenon in the PTT melt through a capillary die even though the shear rate was $20,000 \text{ s}^{-1}$. Increasing the shear rate would decrease the flow activation energy and decline the sensitivity of the shear viscosity to the melt temperature. The molecular weight had a significant influence on the flow curve. The flow behavior of the PTT melt approached that of Newtonian fluid even though the weight-molecular weight was below $43,000 \text{ s}^{-1}$ at 260°C . The extensional viscosity decreased with the in-

crease of the extensional stress, which became more obvious with increasing the molecular weight. The sensitiveness of the extensional viscosity to the melt temperature decreased promptly along with increasing the extensional strain rate. The die swell ratio and end effect would increase along with increasing the shear rate and with decreasing the temperature, which represented that the increase of the shear rate and the decrease of temperature would increase the extruding elasticity of the PTT melt in the capillary die. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 705–709, 2005

Key words: poly(trimethylene terephthalate); capillary rheometer; shear viscosity; extensional viscosity; die swell

INTRODUCTION

Poly(trimethylene terephthalate) (PTT) is an aromatic polyester made from the polycondensation of 1,3-propanediol (PDO) and a terephthalic acid (PTA), which was first reported by Whinfield and Dickson in 1941.¹ It was not until a great reduction in the manufacturing cost of PDO occurred in the mid 1990s that production commercially of PTT became possible. Because of its outstanding structure and mechanical properties, especially high elastic recovery, PTT has been intensively studied in recent years.^{2–7}

There are two fundamental rheological properties that are of primary concern in polymer processing, and they are the viscous and the elastic properties. These rheological properties in turn depend, among many things, on the polymer's molecular weight, molecular weight distribution, and also on processing conditions such as the melt temperature, pressure, and the flow rate. The rheological properties of the polymer melt are of great practical importance in the design of polymer processing equipment. PTT has found many applications in fibers, injection molding, and

film production. In fiber-spinning processing, the PTT resin is melted and extruded through a spinneret and the fluid threadlines solidify while passing through a cooling air cabinet. A better understanding of the interrelationships between the rheological properties and the processing conditions is essential for evaluating the processability of the PTT melt. Therefore, it is very important to investigate the flow behavior of the PTT melt in capillary die.

This investigation concentrates on the rheological and processing behaviors of the PTT melt in capillary flow, especially on the effects of the temperature and molecular weight on the shear viscosity, extensional viscosity, and die swell in capillary flow.

EXPERIMENTAL

Materials

The materials used in this study were PTT resins with different molecular weights shown in Table I. PTT was synthesized by direct esterification and polycondensation process. Sample 1 to sample 3 were synthesized by our laboratory, and sample 4 was Corterra 590200 manufactured by Shell Chemical Co. Sample 1 to sample 3 were used for studying the effect of the molecular weight on the rheological properties, while sample 4 was used in all cases alone.

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TABLE I
Main Specifications of PTT Resins Studied

Sample	Specifications
1	$[\eta] = 0.562 \text{ dl/g}$, $M_w = 3.17 * 10^4$, $M_w/M_n = 1.9$
2	$[\eta] = 0.681 \text{ dl/g}$, $M_w = 4.30 * 10^4$, $M_w/M_n = 2.0$
3	$[\eta] = 0.814 \text{ dl/g}$, $M_w = 5.71 * 10^4$, $M_w/M_n = 2.1$
4	$[\eta] = 0.935 \text{ dl/g}$, $M_w = 7.12 * 10^4$, $M_w/M_n = 2.0$

Procedures

PTT resin should be predried in vacuum and 90°C for 48 h to prevent thermal hydrolysis. The rheological properties were measured on a capillary rheometer (model RH7, Rosand Inc.) equipped with a computer for data acquisition and handling. The pressure sensor was located at the capillary entrance with zero calibration. The die diameter was 0.25mm and the die length was 1mm. Shear rates from 2000 to 20,000 s⁻¹ were used. The temperatures of 240°C, 250°C, 260°C, and 270°C were chosen for the study. Die swell was measured with a laser scan diameter equipped on the capillary rheometer.

RESULTS AND DISCUSSION

Shear flow of the PTT melt in capillary die

According to Han,⁸ a pressure drop occurs at the entrance to the die section because the cross section of a capillary is generally much smaller than that of a reservoir section. There may be three flow regions when fluid enters a tube from a large reservoir: (a) the entrance region, (b) the fully developed region, and (c) the exit region. Flow behaviors of the fluid in the fully developed region and the exit region are of importance for studying rheological properties. Assuming that there is no slippage at the wall of capillary die, the apparent shear rate of the polymer melt flow in the steady, fully developed flow could be calculated as:

$$\dot{\gamma} = \frac{Q(3n + 1)}{\pi nr^3} \quad (1)$$

where Q is the volume flow rate, n is a non-Newtonian exponent, and r is the die radius. The shear stress at the wall could be obtained from the ΔP :

$$\sigma = \frac{\Delta Pr}{2L} \quad (2)$$

where ΔP is the pressure difference in the fully developed region and L is the die length.

The shear viscosity of the polymer melt could be described as a function of the shear rate in terms of a power law model. The apparent shear viscosity is then defined as:

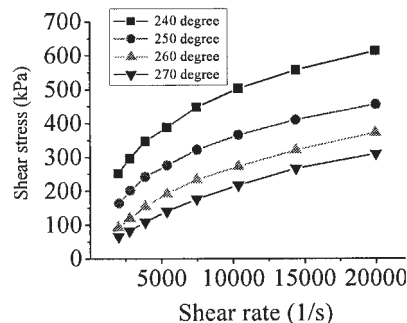


Figure 1 Shear stress versus shear rate of sample 4.

$$\eta_a = \frac{\sigma}{\dot{\gamma}} = K \dot{\gamma}^{n-1} \quad (3)$$

Figure 1 and Figure 2 show both the shear stress and the apparent shear viscosity versus the shear rate of sample 4 at four temperatures, respectively. With the increase of the shear rate, the shear stress increases and the apparent shear viscosity decreases, respectively. At the low shear rate region, the slope of the curve is higher than at the high shear rate. When the shear rate is below about 5700 s⁻¹, the shear stress increases and the apparent shear viscosity decreases promptly along with the increase of the shear rate. But at high shear rate over 5700 s⁻¹, the shear stress increases and the apparent shear viscosity decreases gradually along with the increase of the shear rate. This is typical for the PTT melt exhibiting a shear thinning phenomenon. It is obvious that the PTT melt is a pseudoplastic fluid, which corresponds with the power law model. The higher the temperature of the PTT melt, the lower shear stress and apparent shear viscosity at constant shear rate. The shear stress versus the shear rate curve is commonly used to identify the existence of the melt fracture and the wall slip. When a melt fracture occurs, the curve could have a discontinuity. There exists no such phenomenon in the PTT melt through a capillary die even though the shear

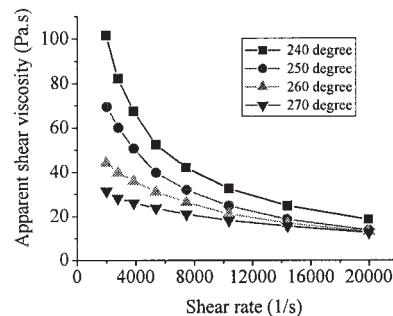


Figure 2 Apparent shear viscosity versus shear rate of sample 4.

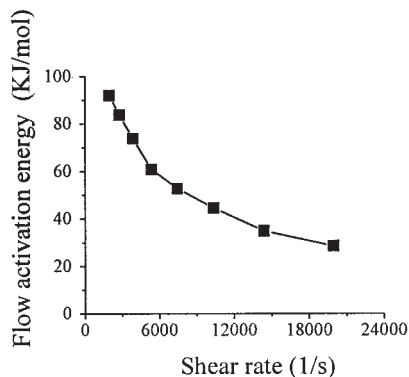


Figure 3 Flow activation energy versus shear rate of sample 4.

rate is $20,000 \text{ s}^{-1}$, which means no melt fracture is seen in the shear rate range studied.

The correlations between $\ln \eta_a$ and $1/T$ have a good linear relationship that corresponds well to Arrhenius equation at the shear rate range studied. The flow activation energy of the PTT melt in the shear flow could be deduced from the slope of the Arrhenius equation. Figure 3 shows that the flow activation energy of the PTT melt decreases with the increase of the shear rate. Increasing the shear rate will decrease the flow activation energy of the PTT melt and incline the sensitivity of the shear viscosity to the temperature, so as to improve the stability of spinning processing of the PTT melt.

According to the power law, there are significant correlations among the power law exponent ($n = \text{d} \ln \eta_a / \text{d} \ln \dot{\gamma} + 1$), temperature, and the shear rate. Figure 4 and Figure 5 show that the power law exponent increases linearly with the increase of the temperature at constant shear rates; while it decreases with the increase of the shear rate at constant temperatures, which is quite different from other polymer melts. The melt behaves like a Newtonian flow when the power law exponent approaches 1. Therefore, increasing the temperature and decreasing the shear rate will make the PTT melt approach that of the Newtonian fluid.

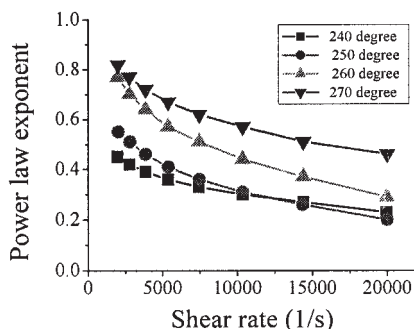


Figure 4 Effect of temperature on the power law exponent of sample 4.

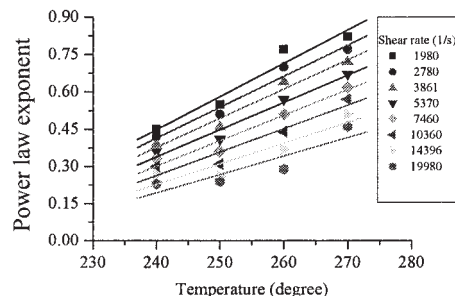


Figure 5 Effect of the shear rate on the power law exponent of sample 4.

Figure 6 shows the effect of the weight-molecular weight on the flow curves of the PTT melt at 260°C . The weight-molecular weight has a significant influence on the flow curve of the PTT melt. The lower the weight-molecular weight, the lower the apparent shear viscosity is at the same shear rate. The difference between the apparent shear viscosities becomes minor when the weight-molecular weight is reduced. The flow behavior of the PTT melt approaches that of Newtonian fluid when the weight-molecular weight is below $43,000$ at 260°C .

Extensional flow of the PTT melt in a capillary die

The effect of pressure on the extensional viscosity is included in the end effect. From the end effect, the η_e as a function of the extensional rate ($\dot{\epsilon}$) can be calculated based on the equations derived by Cogswell.⁹⁻¹⁰ In his analysis it was assumed that the polymer melt adopts a conicylindrical flow pattern as it passed from the reservoir into the capillary and that this pattern corresponded to a minimum entrance pressure drop. Following this analysis, the extensional stress, σ_e , the extensional viscosity, η_e , and the extensional strain rate, $\dot{\epsilon}$, may be calculated as, respectively:

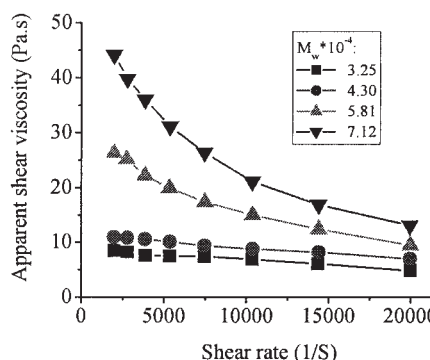


Figure 6 Effect of weight-molecular weight on the flow curves for the PTT melts.

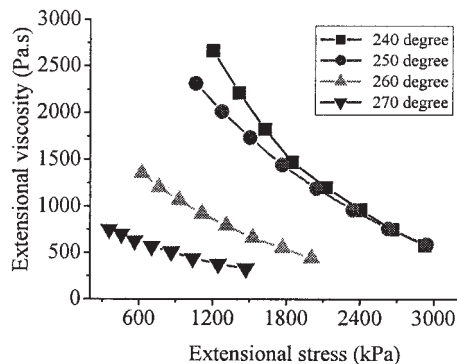


Figure 7 Extensional viscosity versus extensional stress of sample 4 at different temperatures.

$$\sigma_e = \frac{3(n+1)\Delta P_e}{8} \quad (4)$$

$$\eta_e = \frac{9}{32} \frac{(n+1)^2 \Delta P_e^2}{\eta_a \dot{\gamma}^2} \quad (5)$$

$$\dot{\epsilon} = \frac{4\eta_a \dot{\gamma}^2}{3(n+1)\Delta P_e} \quad (6)$$

where ΔP_e is the pressure drop at the entrance to the capillary, and n , η_a and $\dot{\gamma}$ are as previously.

Figure 7 and Figure 8 show that the PTT melt exhibits a typical extensional thinning phenomenon in a uniaxial extension. The extensional viscosity decreases with the increase of the extensional stress, which becomes more obvious with increasing the molecular weight of the PTT melt. According to the flow mechanism of macromolecular chains through an extensional flow, the extensional stress would either destruct the entanglement of macromolecular chains and result in decreasing the extensional viscosity, or it would increase the orientation of macromolecular chains so as to increase the extensional viscosity. For

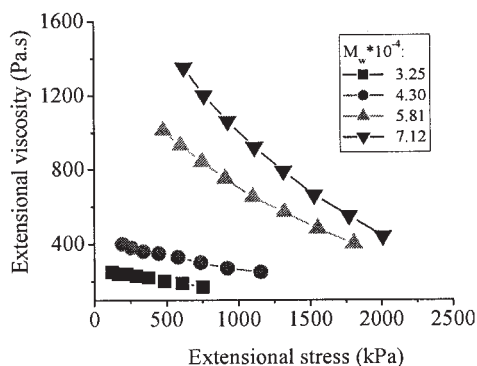


Figure 8 Extensional viscosity versus extensional stress of the PTT melt with different weight-molecular weights (at 260°C).

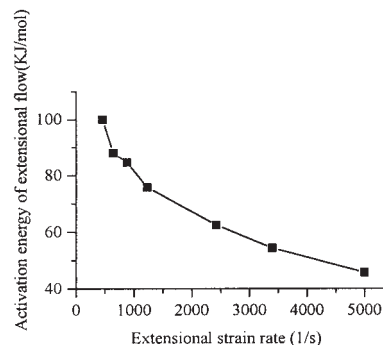


Figure 9 Activation energy of extensional flow versus extensional strain rate for the PTT melt.

the extensional thinning fluid as the PTT melt, increasing the extensional stress would destruct the entanglement of macromolecular chains and result in decreasing the extensional viscosity. Furthermore, a high temperature will drop the slope of the extensional viscosity versus extensional stress curves. When the temperature drops to 240 and 250°C, the two curves are close to each other and even become overlapped at a higher extensional stress region. Moreover, it is easier to produce the draw resonance in the melt-spinning processing. So it is very important to decrease spinneret draft in the melt-spinning processing of the PTT melt to decrease draw resonance and improve the spinnability.

Correlation between $\ln \eta_e$ and $1/T$ is linear, which corresponds well to the Eyring–Frenkel relation. Activation energy of the extensional flow, E_{η_e} , can be calculated from the slope of the curves. Figure 9 shows the significant dependence of activation energy of the extensional flow on the extensional strain rate. With the increase of the extensional strain rate, activation energy of the extensional flow will decrease significantly. This indicates that the sensitiveness of the extensional viscosity to the temperature decreases promptly along with increasing the extensional strain rate. Increasing the extrude speed can decrease the influence of the environmental conditions on the melt-spinning processing and improve the spinnability.

Elastic behavior of the PTT melt in a capillary die

Figure 10 shows die swell ratio versus the shear rate of the PTT melt at different temperatures. It can be seen that die swell ratio increases gradually with the increase of the shear rate and with the decrease of the temperature. From the rheological point of view, it is believed that die swell occurs as a result of the recovery of the elastic deformation imposed in the capillary. The major contribution of die swell is the elastic component at high shear rate. It is clear that a deformed element of the fluid exhibiting retarded elasticity will

not recover its elastic deformation instantaneously as it emerges from a capillary. Instead, while recovery is proceeding, it will travel some distance from the exit and cause die swell. In this investigation, die swell ratios at the lower shear rate of 305 s^{-1} are about $1.02 \sim 1.20$ at four different temperatures; while at the higher shear rate of 3078 s^{-1} , die swell ratios rise to $1.20 \sim 1.42$. These represent that the increase of the shear rate and the decrease of the temperature will increase the extruding elasticity of the PTT melt in the capillary die.

Using the relationship between the entrance pressure drop and the end effect, the end effect, e , can be calculated as per the following equation:

$$e = \frac{2^{3/2}}{3(n+1)} (\eta_e / \eta_a)^{1/2} \quad (7)$$

It can be seen that the pressure dependence of the end effect depends on both η_e and η_a , which means the extruding elasticity for polymer melt. A larger e value represents the higher elastic for polymer melt. Figure 11 shows the dependence of the end effect on the shear rate at different temperatures. This behavior indicates that the elastic behavior of the PTT melt depends, at constant temperature, on the shear rate. Decreasing the temperature will increase the viscosity of the PTT melt, which will retard elastic recovery and increase the extruding elasticity of the PTT melt.

CONCLUSION

Rheological behaviors and properties of the PTT melt were studied through a capillary rheometer. The PTT melt was a typical pseudoplastic fluid exhibiting shear

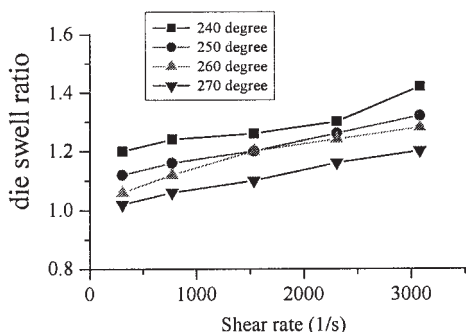


Figure 10 Die swell ratio versus shear rate for the PTT melt.

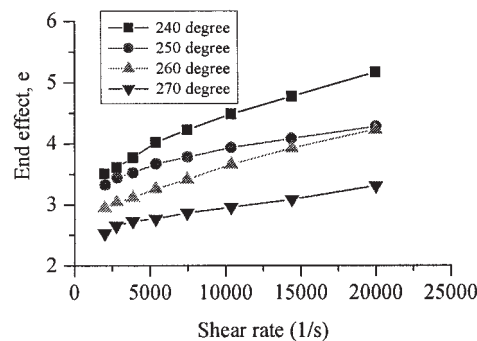


Figure 11 End effect versus shear rate for the PTT melt at different temperatures.

thinning and extensional thinning phenomena in a capillary flow. There existed no melt fracture phenomenon in the PTT melt through a capillary die even though the shear rate was $20,000 \text{ s}^{-1}$. Increasing the shear rate would decrease the flow activation energy and decline the sensitivity of the shear viscosity to the melt temperature. The molecular weight had a significant influence on the flow curve. The flow behavior of the PTT melt approaches that of Newtonian fluid when the weight-molecular weight is below 43,000 at 260°C . The extensional viscosity decreased with the increase of the extensional stress, which became more obvious with increasing the molecular weight. The sensitiveness of the extensional viscosity to the melt temperature decreased promptly along with increasing the extensional strain rate. The die swell ratio and the end effect increased along with increasing the shear rate and with decreasing the temperature, which represented that the increase of the shear rate and the decrease of the temperature would increase the extruding elasticity of the PTT melt in the capillary die.

References

- Whinfield, J. R.; Dickson, J. T. Br. Patent 578,097, 1941.
- Brown, H. S.; Chuah, H. H. Chem Fibers International 1997, 47(1), 72.
- Scott, A. Chem Week 1998, 160, 21.
- Chuah, H. H. Macromolecules 2001, 34, 6985.
- Ng, T. H.; Williams, H. L. J Appl Polym Sci 1986, 32, 4883.
- Huang, J. M.; Chang, F. C. J Polym Sci, Part B: Polym Phys 2000, 38, 934.
- Traub, H. L.; Hint, P.; Herlinger, H.; Oppermann, W. Die Angewandte Makromolekulare 1995, 230(4055), 179.
- Han, C. D. Rheology in Polymer Processing; Academic Press: New York, 1976.
- Cogswell, F. N. Trans Soc Rheol 1972, 16, 383.
- Cogswell, F. N. Polym Eng Sci 1972, 12, 64.