

Influence of Reverse Pressure on the Shear Viscosity of Hydrophilic Poly(ethylene terephthalate) Melt^{*}

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Abstract The effect of reverse pressure on rheological behavior has been studied. The apparatus is a capillary rheometer with counter pressure chamber being held at a high reverse pressure by means of a cock. The results show that with the increase in temperature, the shear viscosity of hydrophilic PET is reduced. It is different that the effect of temperature on shear viscosity is varied under the condition of all shear rates or all pressures, and the effect is more prominent at 50 MPa or at 216 s⁻¹. At the same time, the pressure coefficients decrease with increasing the shear rate and the temperature and tend to reach a constant value nearly at the temperature of 290 °C.

Keywords: Hydrophilic PET; Shear viscosity; Pressure; Temperature; Shear rate; Pressure coefficients.

INTRODUCTION

Wide ranges of pressure, temperature and shear rate are encountered in polymer processing operations, as for example, in injection molding. While the temperature (shear rate) dependence of shear viscosity has been widely studied, the pressure dependence has not. It is, therefore, necessary to understand the dependence of the shear viscosity of the materials to be processed on pressure for polymer processing and shaping, especially in the design of injection moldings or in the choice of injection pressure. Moreover, it is of great significance for the study of polymer processing, and researchers concerned this problem gradually since 1950s. As early as 1957, Maxwell's team carried out an experiment with a modified capillary rheometer, which was equipped with two barrels and two pistons. In addition, the pistons can be controlled independently, so that the melt in the capillary should suffer the pressure from two directions. Their research indicated that the shear viscosity might increase one or two orders of magnitude in the injection molding process^[1]. Choi^[2] proved that the apparent shear viscosity of polystyrene (PS) increased by 135 times at a temperature of 195 °C, when the pressure was increased from 0 to 125 MPa, but little change in shear viscosity was detected at high shear rates^[3]. Penwell *et al.*^[4–6] studied the nonlinear pressure drop with different lengths of capillary. Emjonow^[7] had shown that the shear viscosity of PS was 2.2 times that when it was at atmospheric pressure when it was at a shear rate of 40 s⁻¹ and a pressure of 100 MPa. Hellwege *et al.*^[8] and Herrmann *et al.*^[9] used an apparatus designed by Semjonow^[7] consisting of a pressurized concentric cylinder geometry in which a Couette type of flow was

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generated by rotation of the outer cylinder and measured the torque exerted on the inner cylinder. They investigated polystyrene (PS) and poly(methyl methacrylate) (PMMA) and found that for both materials a temperature and pressure invariant plot, *i.e.* a master curve, can be obtained. Using the same apparatus, Christmann and Knappe^[10] measured low-density polyethylene and PMMA. The zero shear viscosity of both polymers was described by an exponential relation for the pressure effect and an Arrhenius expression for temperature dependency. Christmann and Weber^[11] also investigated the pressure effect on the shear viscosity for high-density polyethylene (HDPE). Lord^[12] presented data for polycarbonate (PC) measured by Westover *et al.*^[13]. Laun^[14], using flush minuted pressure transducers, made direct measurement of the pressure gradient in a slit die. He observed a slight curvature in the pressure profile, which he attributed to the effect of pressure on viscosity. He analyzed his data using a simple equation to determine the viscosity pressure coefficient. However, his analysis neglected compressibility, viscous heating and heat transfer, which can be significant at the mass flow rates investigated. Johanna and Seppo^[15–17] investigated the relationship between the viscosity of polymer (PS, PP, PC) and pressure by a capillary rheometer and reverse pressure chamber assembly. Chakravorty^[18] put forward a new method for measuring the effect of pressure on shear viscosity of PS and studied the influence of pressure on shear viscosity at a temperature of 200 °C. In addition, Sedlacek^[19] and Fernandez^[20] used the PVT to estimate the dependence of viscosity on the reverse pressure. In recent years, researchers who study the effect of reverse pressure on the rheological properties of the polymer are mainly concentrated on PE, PS, PMMA, PC and PP^[21–41]. However, few studies are focused on the effect of reverse pressure on shear viscosity of hydrophilic PET.

In this paper, for developing a good understanding of the correlation between reverse pressure, temperature, shear rate and the shear viscosity, different routes will be explored, and this study plays an important role in the study of hydrophilic PET processing under high pressure.

EXPERIMENTAL

Materials

The material studied is a commercial hydrophilic polyethylene terephthalate, which has been used in several other rheological studies. The hydrophilic polyethylene terephthalate is obtained from the China Textile Academy. The intrinsic viscosity of the hydrophilic PET measured at 25 °C in a 50/50 mixture of phenol and tetrachloroethane is 0.64 dL/g.

Instruments and Experimental Conditions

The basic instrument is a RHEOGRAPH 25 capillary rheometer and a reverse pressure chamber component (Göttfert Werkstoff-Prüfmaschinen GmbH, German), modified in such a way that high pressures (up to about 50 MPa) could be developed in the capillary. This is done by building a capillary assembly with the reverse pressure chamber component in which a reverse pressure could be developed by means of a cock (see Fig. 1). The pressure is measured with a pressure sensor with a range of 0–100 MPa. The capillary and reverse pressure chamber component are kept at isothermal conditions by means of several band heaters, controlled by a variac. Various gasketing materials are tried, with silver gaskets finally providing the necessary seals. Runs in the temperature range from 280 °C to 300 °C are made. The diameter of capillary is 1 mm ($L_0/D_0 = 40$), while the shear rates range is from 216 s⁻¹ to 1080 s⁻¹ and the Bagley method^[42] is used to correct for end effects. Prior to experiment the hydrophilic PET is vacuum-dried at 80 °C for 2 h in order to minimize the hydrolysis in the melt during processing, and then the temperature was raised to 130 °C and kept for 10 h.

Rheological Properties Testing and Data Processing

Figure 1 shows that at the end of the counter pressure chamber, there is a cock, which would control the outlet pressure of capillary and make the melt in the capillary under different pressure levels.

There is a pressure sensor at both the inlet and the outlet of the capillary separately to obtain inlet pressure P_{in} and outlet pressure P_{out} of the capillary. Then the pressure (P_m) of the flowing melt can be characterized with the average of P_{in} and P_{out} .

$$P_m = \frac{P_{in} + P_{out}}{2} \quad (1)$$

The formula of shear stress (σ_a), shear rate ($\dot{\gamma}_a$) and apparent viscosity (η_a) are described as follows.

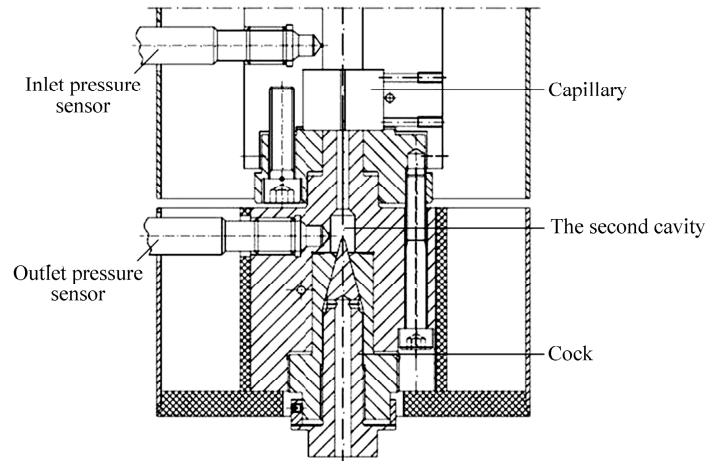


Fig. 1 Schematic of the counter pressure chamber fitted beneath a standard capillary rheometer

$$\dot{\gamma}_a = \frac{4Q}{\pi R^3} = \frac{D_p^2 \cdot V_p}{R^3} \quad (2)$$

$$\sigma_a = \frac{\Delta P \cdot D_0}{4L_0} \quad (3)$$

$$\eta_a = \frac{\sigma_a}{\dot{\gamma}_a} \quad (4)$$

In addition, D_p is the barrel diameter of the rheometer, V_p is the speed of the piston, R is the capillary radius, L_0 is the length of capillary, D_0 is the diameter of capillary, ΔP is pressure drop of the capillary, which is described as $\Delta P = P_{in} - P_{out}$.

RESULTS AND DISCUSSION

Effects of Different Temperature on Shear Viscosity of the Polyester at Constant Pressure

From Figs. 2(a) to 2(e), it was shown that the shear viscosity of hydrophilic PET decreased with increase of temperature at different shear rates or different pressures. There are two methods to explain the dependence of viscosity on temperature. One explanation is dynamics, and the other is the free volume theory. From the dynamic perspective, the thermal motion of hydrophilic PET molecular chains increases along with the increase in temperature, decreasing the interactions between molecular chains and reducing the shear viscosity. As for the free volume theory, the free volume between hydrophilic PET macromolecules increases with a rise in temperature, which results in the improved motion ability of hydrophilic PET macromolecular chains. As a result, the shear viscosity of hydrophilic PET decreases.

Effect of Different Shear Rates on the Shear Viscosity of the Polyester at Constant Pressure

The variation of shear viscosity with the temperature at the pressure of 30 MPa was analyzed in detail. The results under different shear rates shown in Fig. 2(f) were obtained using the RHEOGRAPH 25 capillary rheometer and reverse pressure chamber. It was shown that the shear viscosity of hydrophilic PET decreased at a different rate with the increase of temperature at the same rate at different shear rates.

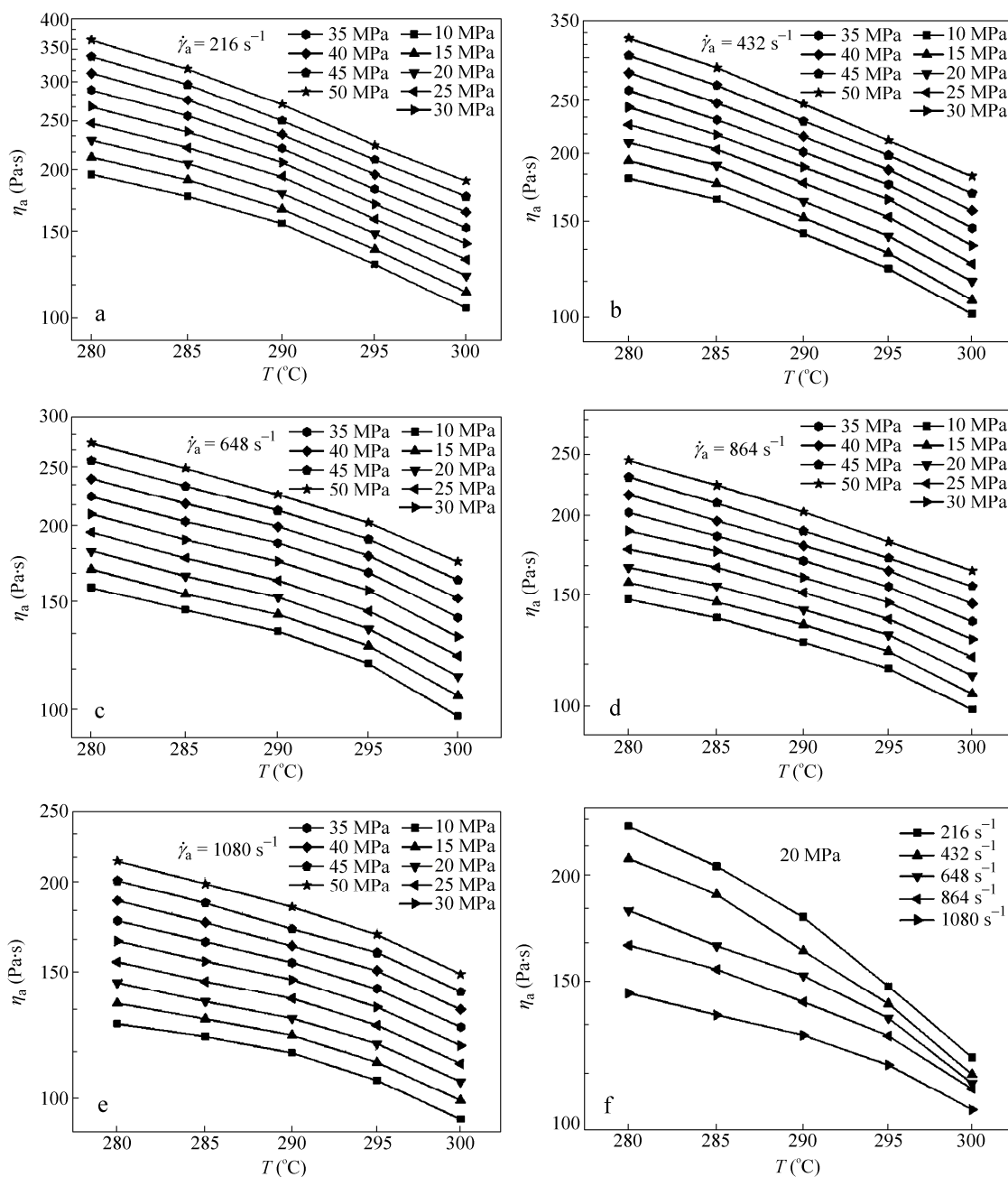


Fig. 2 The relationship of η_a and T of hydrophilic PET: (a) at 216 s^{-1} , (b) at 432 s^{-1} , (c) at 648 s^{-1} , (d) at 864 s^{-1} , (e) at 1080 s^{-1} and (f) at 20 MPa

Figure 3 shows shear viscosity measured by the capillary rheometer and reverse pressure chamber component against shear rate under constant pressure of different levels. Particularly while the temperature is 280°C , the shear rate is 216 s^{-1} and the reverse pressure is 50 MPa , the shear viscosity is 2.03 times as large as that at normal experiment, and slightly lower than that of PS mentioned in the text^[7]. Apart from this, during the normal experiment the pressure (P_m) was gradually increased from 3.53 MPa to 14.05 MPa , while the shear rate changed from 216 s^{-1} to 1080 s^{-1} , and the (P_m) of the reverse pressure experiment was about 3.56 times as large as that of the normal experiment. It was found that shear-thinning behavior occurred at different pressures and

this phenomenon becomes especially more significant while it was at high pressures. This can be attributed to the fact that free volume is decreased and the activity of chains is weakened at high pressures, and the glass-transition temperature (T_g) is increased. The effect of pressure on the shear viscosity should also be explained with the WLF equation.

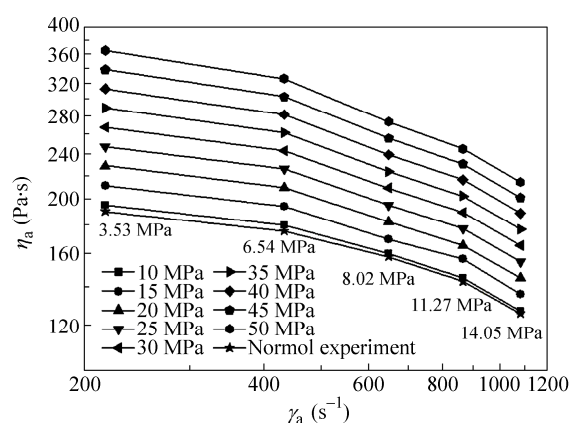


Fig. 3 The relationship of η_a and $\dot{\gamma}_a$ under different pressures at 280 °C

From Table 1, the shear viscosity difference of hydrophilic PET showed a decreasing trend as the shear rate increased, and the effect of temperature on shear viscosity under high pressures had a great degree of significance under the same shear rate. When the shear rate increased, the conformation of hydrophilic PET changed, and because of the shear stress, disentanglement appeared and at the same time polymer chains oriented along the direction of the flow, thus leading to a decrease in shear viscosity. This process has alleviated the tendency of shear viscosity to increase due to a rise in pressure. Shear-thinning behavior of the molecules showed that, with the increase in shear rate, the number of the entangled points between macromolecules was gradually reduced. This was also the reason for the decrease in shear viscosity in response to the increase in shear rate.

Table 1. $\Delta\eta_a$ of hydrophilic PET from 280 °C to 300 °C at different pressure levels and shear rates

P_m (MPa)	$-\Delta\eta_a$ (Pa·s)				
	216 s ⁻¹	432 s ⁻¹	648 s ⁻¹	864 s ⁻¹	1080 s ⁻¹
10	90.39	78.38	60.59	48.68	33.45
15	98.21	86.42	64.39	52.11	36.45
20	106.72	92.94	68.43	53.77	39.67
25	115.98	99.96	72.73	57.67	43.15
30	126.04	107.54	77.30	61.82	46.88
35	136.98	115.72	82.15	66.25	50.88
40	148.87	124.53	87.32	70.97	55.19
45	161.79	134.03	92.80	75.99	59.81
50	175.82	144.28	98.64	81.35	64.77

Effect of Different Pressures on the Shear Viscosity of the Polyester

It was also observed from Figs. 2(a) to 2(e) that with increasing temperature, the shear viscosity of hydrophilic PET showed a decrease while it was dependent on shear rate and pressure. In order to represent this phenomenon, the variation of shear viscosity ($\Delta\eta_a$) with a temperature change between 280 °C and 300 °C was obtained as follows (Table. 1). A further study was carried out to acquire the result about shear viscosity dependence on temperature. The results showed that at each shear rate, the shear viscosity of hydrophilic PET was on the rise as the pressure increased. Besides, the free volume between polymer chains and the molecular chain activities were decreased. There was an enhancement in interactions between macromolecular chains, and

the entanglement-disentanglement rate of the macromolecular chains also decreased. Balanced migration was accelerated because of the increase of shear rate. Thus, the dependence of shear viscosity on temperature under high pressures was of great significance. When the pressure is increased, according to the polymer free volume theory, the free volume of the hydrophilic PET molecular chains decreases. On the contrary, the interaction between the molecular chains increased, resulting in the increase of shear viscosity. It was interesting to note that these actions and the temperature played the same role in this process. When the temperature decreased, the thermal motion of macromolecules was reduced and the process of entanglement and disentanglement among the macromolecular chains was relatively slow. Therefore, it eased balanced migration. This shows why in the rheological properties of the polymerization process, cooling and increasing the pressure can be considered as equivalent. Then the effect of pressure on the shear viscosity of the polyester melt was equivalent to the effect of temperature on the shear viscosity of the polyester melt.

Effect of Reverse Pressure on the Pressure Coefficient

Commonly the pressure dependency of shear viscosity is often expressed by means of a pressure coefficient (β)^[42], in which i is either the shear rate $\dot{\gamma}_a$ or the shear stress σ_a . The pressure coefficient is often defined in terms of constant shear rate^[9, 22, 43–45] and that is adopted in this paper.

$$\beta = \left[\frac{d \ln \eta}{dP} \right]_{T, \dot{\gamma}_a} \quad (5)$$

It was possible to calculate β as the slope of the curves of the logarithm of the shear viscosity at a given shear rate plotted versus the mean pressure in the capillary, and the results are shown in Table 2. Such an approach can lead to coefficients that depend not only on pressure and temperature but also on shear rate. From the known inlet pressure and outlet pressure for every data point, the corresponding arithmetic mean pressure was calculated. In order to reduce the error, the pressure coefficients at different temperatures and shear rates were averaged.

Table 2. β of hydrophilic PET at different temperatures and shear rates

$\dot{\gamma}_a$ (s ⁻¹)	β (GPa ⁻¹)				
	280 °C	285 °C	290 °C	295 °C	300 °C
216	14.82	14.40	12.50	12.43	12.39
432	13.63	13.30	12.45	11.65	11.52
648	12.37	12.26	11.70	11.51	11.21
864	11.78	11.88	10.65	10.93	10.89
1080	11.55	10.99	10.44	10.75	10.72

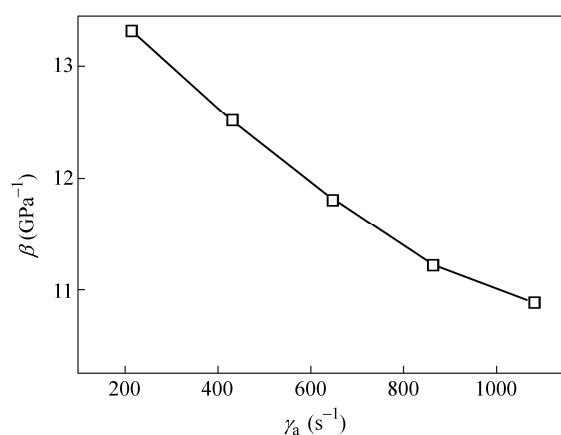


Fig. 4 The relationship of average β and $\dot{\gamma}_a$

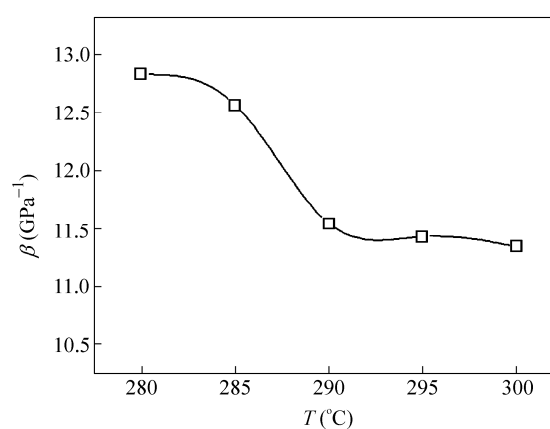


Fig. 5 The relationship of average β and T

It can be noted that the data showed a slight downward curvature with respect to the linear regression line in Fig. 4. The pressure dependence of the shear viscosity gradually reduced when the shear rate ranged from 216 s^{-1} to 1080 s^{-1} . The relationship of average β and T is shown in Fig. 5. Moreover, it was clear that the pressure coefficients decreased with increasing temperature and tended to reach a constant value nearly at the temperature of 290°C in the power law region of the viscosity curves.

CONCLUSIONS

The experiments of the present work were made in a capillary rheometer and a counter pressure chamber, which allowed measurements at high pressure but which presented several experimental difficulties in practice. The difficulties were that we had to deal with the entrance and exit effects, and not all of which were resolved definitively in the present work. The behavior of hydrophilic PET melts at high pressure was not simple. At low shear rates, there was a rough analogy between increasing the pressure and decreasing the temperature, both of which caused the shear viscosity to increase. According to the results, with the increase of temperature, the shear viscosity of hydrophilic PET was reduced. The effect of temperature on shear viscosity was and dependent on the shear rate and pressure, and the effect is more prominent at 50 MPa or at 216 s^{-1} . The shear viscosity of hydrophilic PET decreased at each temperature and pressure, when the shear rate increased, both showed the phenomenon of shear thinning. At the same time, the pressure coefficient showed a downward trend with the increase of the shear rate and the temperature and tended to reach a constant value nearly at the temperature of 290°C in the power law region of the viscosity curves.

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