

Experimental investigation of the rheological behaviors of polypropylene in a capillary flow

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ABSTRACT: The rheological characterization of polymer melts is strongly related to their material properties. In this study, we focused on the rheological behaviors of a polypropylene (PP) melt through a capillary die. With an advanced twin-bore capillary rheometer with dies measuring 1.0, 0.5, and 0.25 mm in diameter, experiments were performed over a shear-rate range of 3×10^2 to 5×10^3 s⁻¹ at three temperatures, 210, 220, and 230 °C. The results demonstrate that the geometry dependence of the PP viscosity relied on the die diameter and the temperature of the PP melt. The viscosity values of the PP melt in the 0.25-mm diameter die were higher than were those in the 0.5- and 1.0-mm dies at 220 and 230 °C. However, the viscosity values in all of the tested dies were similar at 210 °C. The tendency for the viscosity to decrease as the temperature of the polymer melt increased weakened in the 0.25-mm diameter die. As a result, the pressure applied to the PP melt in the 0.25-mm diameter die increased; this caused a decrease in the free volume between molecules. On the basis of the Barus equation, the contribution of pressure to the changed viscosity in each die at each of the tested temperatures was calculated and was found to be as high as 32.86% in the 0.25-mm die at 230 °C. Additionally, the effect of the wall slip on the geometry dependence of the PP viscosity in the tested dies was investigated with a modified Mooney method. The values of the slip velocity revealed that wall slip occurred only in the 0.25-mm die at 210 °C. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43459.

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INTRODUCTION

The rheological characterization of polymer melts plays an important role in quality control, process design, simulation, and troubleshooting applications. Recently, the application of and research into the microscopic behaviors of polymeric melts have attracted attention because of the development of micro-electromechanical systems, and the demand for the molding of polymeric parts with micrometric structures has especially increased.^{1–5} Viscosity is a crucial rheological parameter of polymers; it is closely related to the flow properties of the polymer melt. Studies have confirmed that the viscosity of polymer melts in a microcapillary is different from that in a conventional one, and it is affected on different levels by factors such as the geometry characteristics, wall slip, molecular structure, shear rate, and even the heat-transfer behavior.^{6–9}

It is difficult to investigate the rheological behaviors of polymer melts on a microscale because of the lack of commercial

equipment and suitable devices.¹⁰ The literature presents large variations in the viscosity through a microchannel, depending on the method used or the shear-rate range under investigation, even for the same polymer. Eringen¹¹ suggested that the viscosity of a polymer melt on a microscale would deviate from that on a conventional scale when the mean square radius of gyration of the polymer molecular chain was not negligible compared with the channel size. A model of viscosity on the microscale was constructed on the basis of the nonlocal continuum mechanics of a viscous fluid. This predictive model indicates that the viscosity value of a polymer melt will increase as the channel size decreases in the mesostructure at a certain shear rate and temperature. Chen *et al.*¹² investigated the viscosity of the polymer melts with a slit rheometer in microchannels with various cross-sectional sizes on the mold. The results show that the shear viscosity of the molten polymer decreased with the reduction of the channel size at the same shear rate and temperature. Zhang *et al.*¹³ explored the effects of the mold

surface roughness on the filling flow of the polymer melt in microinjection molding with a disk insert, which had two halves with different surface roughness characteristics but the same roughness mean lines. The results indicate that the mold surface roughness resisted the cavity filling of the polymer melt in microinjection molding. The high mold temperature decreased the effect of surface roughness. Kelly *et al.*¹⁴ researched the high-shear strain rate rheometry of polymer melts. The data measured from wall shear strain rates of 10^{-1} to 10^7 s⁻¹ for a range of polymers through a 0.5-mm diameter die indicated that the shear viscosity resulted in different rheological behaviors over the tested shear-rate range. In some cases, the results show shear-thickening behavior at ultrahigh strain rates. More recently, Azuddin *et al.*¹⁵ focused on the observation of the microflow of melted polypropylene (PP) with a transparent poly(methyl methacrylate) (PMMA) mold. In their study, PMMA molds with channel diameters of 0.5, 0.8, and 1.0 mm were fabricated and injected with melted PP with a customized vertical plastic injection-molding machine. By comparing the experimental data with the results from the finite element analysis software MoldFlow Part Advisor, they found that the analysis software was not suitable for the prediction of the flow in the 0.5-mm diameter channel. Xu¹⁶ also investigated polymeric melt viscosity through microchannels with diameters of 0.355, 0.5, and 1.0 mm over a shear-rate range of 4×10^3 to 2×10^4 s⁻¹. Because of the geometry dependence of the viscosity of polymer melts and the viscosity of polymer melts in a conventional channel, a viscosity model was derived to predict the viscosity value in a microchannel. The results show that the predicted values were in agreement with the experimental ones. However, at the same shear rate and temperature, an uncertain predicted value of viscosity in a microchannel could be obtained when the size of the conventional channel referenced in the viscosity model was altered.

Particularly, the shear viscosity in a microscope capillary is closely related to the material properties, which result from different molecular structures and distributions of molecular weights. Chen *et al.*¹⁷ established a melt viscosity measurement system for a polyformaldehyde (POM) melt flowing through a microchannel. The calculated results were compared with those of a polystyrene (PS) resin to explore the effect of the structure on the viscosity characteristics of the polymers within microchannels. They emphasized that the rheological behaviors of the POM resin on a microscopic scale were different from those on a macroscopic scale. The wall slip for the PS resin within microchannels occurred more easily than that for the POM resin because of the positive effect of the molecular weight on the microflow of PS. Zhao *et al.*¹⁸ investigated the effect of wall slip between the polymer bulk and the wall surface on the shear viscosity on a microscale. They revealed that the entanglement–disentanglement slip mechanism was likely due to the geometrical viscosity of PMMA, but it was attributed to the adsorption–desorption slip mechanism for high-density polyethylene. More recently, Lin *et al.*¹⁹ studied the geometrical dependence of the shear viscosity with a twin-bore capillary rheometer. The results show the opposite geometrical dependence of the shear viscosity for PMMA between melt temperatures of 210 and 255 °C but a

similar geometrical dependence of the shear viscosity for high-density polyethylene between 190 and 260 °C.

Therefore, it would be reasonable to claim that the studies on the rheological behaviors of polymer melts through a microscope channel are currently identified on a case-by-case basis. Therefore, it is necessary to conduct further research on the rheological characterization of polymer melts on a microscale to aid the fabrication and simulation of polymeric components with microstructures.

The methods with high-efficiency and low-cost precision primarily involve the molding process of microinjection molding and microembossing extrusion to fabricate polymeric microstructures. The shear-rate range during the microembossing extrusion process is lower than that during microinjection molding.^{3,20} PP is a type of material commonly used to fabricate polymeric parts with microstructures because of its excellent properties; these properties include a good processability, heat resistance, and low density. In this study, the rheological behaviors of PP in microdies were investigated over a shear-rate range of 3×10^2 to 5×10^3 s⁻¹ with a twin-bore capillary rheometer. A series of experiments was performed for a PP melt through microdies with diameters of 1.0, 0.5, and 0.25 mm over the tested shear-rate range. The geometry dependence of the shear viscosity of PP through the tested dies was related to its temperature and pressure. In addition, the effect of wall slip on the geometry dependence of the shear viscosity at different temperatures was analyzed separately.

EXPERIMENTAL

In this study, an advanced twin-bore RH10 capillary rheometer (Malvern Instruments, United Kingdom) was used. Before each test, the polymeric material was fed into the two barrels. Two types of dies (long die and orifice die) with the same diameter as the flow channels were supported at the bottom of the barrels, which were composed of a tungsten carbide–cobalt alloy to maintain the geometric integrity. The ratio of the length to the diameter of the long die was 16, and that of the orifice die was less than 1. Dies with diameters of 0.25, 0.5, and 1.0 mm were used. Dual pistons with 15-mm diameters were used to drive the polymer melt through the two dies at different velocities corresponding to each of the shear rates. The polymeric material were subjected to a precompression pressure of 0.5–1.0 MPa and to a total preheating time of 540 s.¹⁴ The pressures at the entrances of the long die and the orifice die were measured separately by appropriate transducers during each test.

Commercial PP was used throughout the experiments, with a grade of R-301; it was supplied by Xiaoxing Corp. (Korea). The weight-average molecular weight, molecular weight distribution, and density of the PP melt were 430,996, 5.708, and 0.95 g/cm³, respectively.

The tests were repeated over the range of the apparent shear rate ($\dot{\gamma}_{app}$ s⁻¹) from 3×10^2 to 5×10^3 s⁻¹ through the 0.25-, 0.5-, and 1.0-mm diameter dies at 210, 220, and 230 °C. The real pressure drop of the long die was corrected for the energy required to converge the melt into the entrance of the die. According to the Bagley correction, the true value of the wall

Table I. Values of n of the PP Melt at 230 °C in the Tested Dies

Apparent shear rate (s ⁻¹)	410	561	766	1048	1432	1957	2676	3658	n_{ave} ^a		
Diameter (mm)	0.25	n	0.27	0.26	0.25	0.23	0.22	0.21	0.20	0.19	0.23
	0.50		0.50	0.46	0.42	0.39	0.35	0.31	0.27	0.23	0.37
	1.00		0.42	0.41	0.40	0.38	0.37	0.36	0.34	0.33	0.38

^a n_{ave} , average value of the power law index.

shear stress (τ_w ; Pa) can be calculated to modify the entrance loss as follows²¹:

$$\tau_w = \frac{R\Delta P}{2L} = \frac{(\Delta P_L - \Delta P_0) \times R}{2L} \quad (1)$$

where ΔP is the pressure drop through a capillary die ($\Delta P = \Delta P_L - \Delta P_0$). ΔP_0 denote the pressure drop (Pa) across the length of the die and at the die entrance, which are equal to the values of the pressure measured from the long die and the orifice die, respectively. L (m) and R (m) are the length and radius of the die, respectively

In contrast to the flow of Newtonian fluids with a parabolic velocity distribution, the flow of the polymer melts exhibits a pluglike pattern. Therefore, the real shear rate ($\dot{\gamma}_{true}$; s⁻¹) should be modified on basis of the Rabinowitsch correction²²:

$$\dot{\gamma}_{true} = \left(\frac{3n+1}{4n} \right) \times \dot{\gamma}_{app} \quad (2)$$

$$n = \frac{d(\ln \tau_w)}{d(\ln \dot{\gamma}_{app})} \quad (3)$$

where n is the power law index, which can be determined by eq. (3). The value n depends on the properties of the material, the shear rate, and the temperature. In this study, the values of n of the PP melt differed in the various dies, as listed in Table I; this indicated the geometry dependence of the PP viscosity on the microscale.

On the basis of eqs. (2) and (3), the apparent shear viscosity (η_{app}) and the real shear viscosity (η_{true}) were obtained as follows:

$$\eta_{app} = \frac{\tau_w}{\dot{\gamma}_{app}} \quad (4)$$

$$\eta_{true} = \frac{\tau_w}{\dot{\gamma}_{true}} \quad (5)$$

RESULTS AND DISCUSSION

Effect of the Temperature on the Geometry Dependence of the Shear Viscosity

The trend of the melt viscosity of PP shown in Figure 1 initially followed the typical pseudo-plastic shear-thinning behavior, and the shear viscosity decreased significantly when the shear rate increased from approximately 4×10^2 to 10^4 s⁻¹; this corresponded to an apparent shear-rate range of 3×10^2 to 5×10^3 s⁻¹. Then, the change in the shear viscosity tended to be flatter. The values of the PP viscosity increased as the die diameter decreased at 230 and 220 °C. Moreover, the increased values of viscosity showed different levels, as shown in Figure 1(a,b).

However, the viscosity values in the three types of dies at 210 °C were very similar, as shown in Figure 1(c), although differences remained among them. The geometry dependence of the shear viscosity of the PP melt through a microcapillary channel was clearly associated with its temperature.

It was interesting that the geometry dependence of the PP viscosity revealed in Figure 1 showed a large variation compared with the results reported in the literature,¹⁷ in which the rheological behaviors of a POM melt flowing through microchannels were investigated on the basis of a melt viscosity measurement system. The results shown in Figure 1 in this study were opposite to those in ref. 17, even over a similar range of shear rate. The following factors were analytically attributed to the difference. First of all, the microchannels of square cross section used in ref. 17 should have been converted into an equivalent radius if the capillary flow model was adopted. Therefore, the channel geometry was different from the circle cross-section dies used in this study. In addition, because of the higher flow resistance in the higher surface area of the square cross section compared to that in the circular cross-section channel, the equivalent radius must have been a multiple of a shape factor. Second, the channel surface roughness resists the polymer melt filling in the channel and impacts the measured pressure value at a certain level. Thus, the value of the polymer viscosity could have been affected by the different roughness characteristics. Last but not least, as reported in ref. 17, the effect of the morphological structure on the viscosity characteristics of the polymer within the microchannels was strongly related to the material properties.

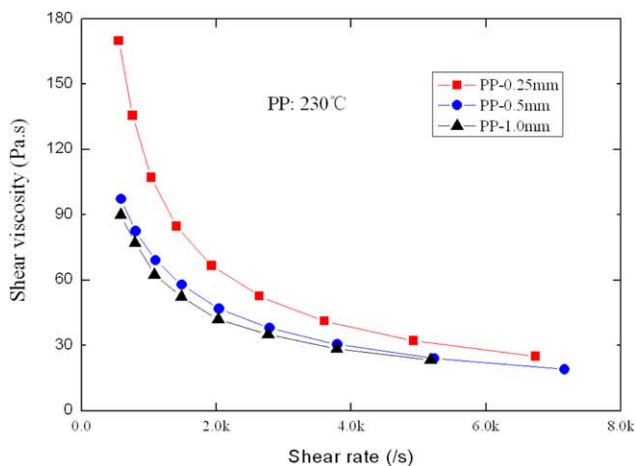
In the case of the PP melt in this study, it is well known that the shear viscosity decreases as the temperature of the polymer melt increases, as revealed in Figure 2(a,b). However, Figure 2(c) shows that the viscosity values in a 0.25-mm diameter die at all of the tested temperatures remained virtually unchanged, although there was a slight difference among them. Therefore, the shear viscosity of the PP melt through the three different dies showed different sensitivities to temperature.

To further investigate the geometry dependence of the shear viscosity at different temperatures, the deviations of the PP viscosity at 220 and 230 °C, that is, D_{220} and D_{230} , were calculated, whereas the viscosity at 210 °C was referred to as a basic value. D_{220} and D_{230} are defined as

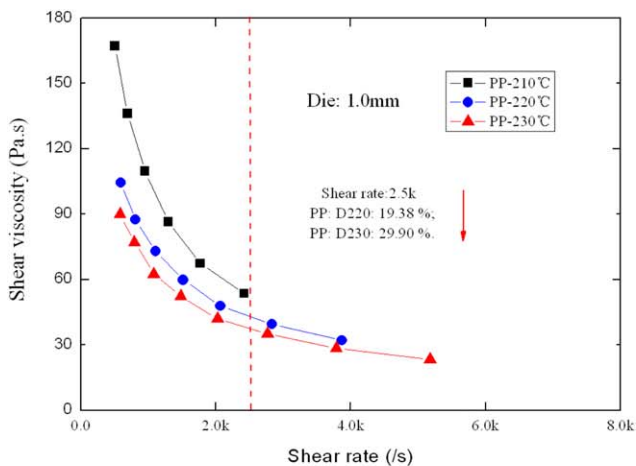
$$D_{220} = (\eta_{210} - \eta_{220}) / \eta_{210} \times 100\%$$

$$D_{230} = (\eta_{210} - \eta_{230}) / \eta_{210} \times 100\%$$

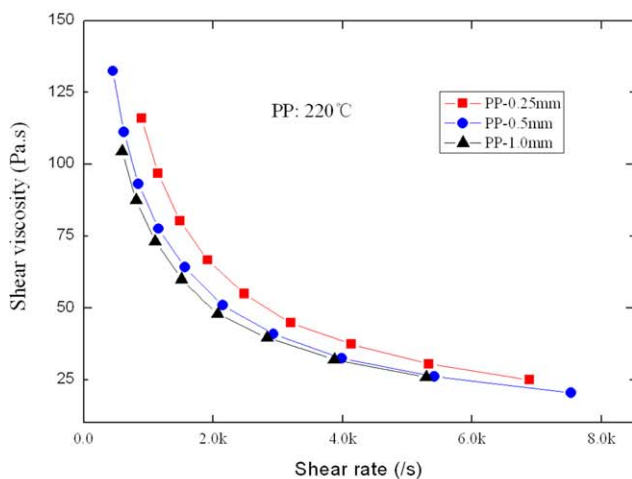
where η_{210} , η_{220} , and η_{230} denote the viscosity values of PP at 210, 220, and 230 °C, respectively. The deviation values of the



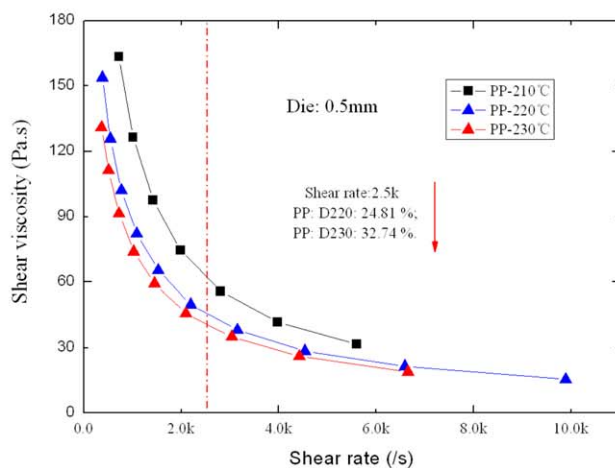
(a)



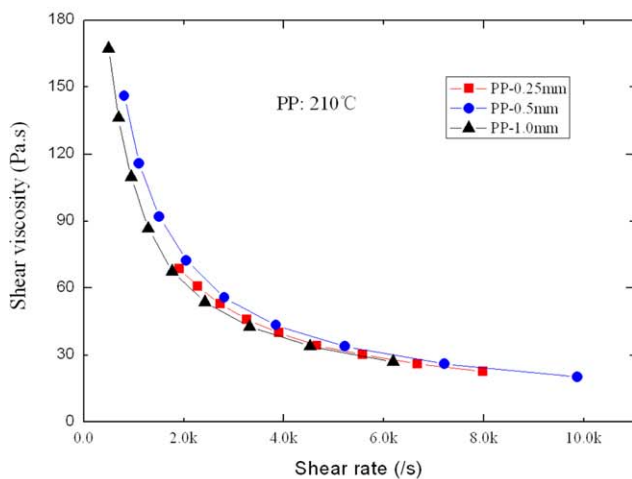
(a)



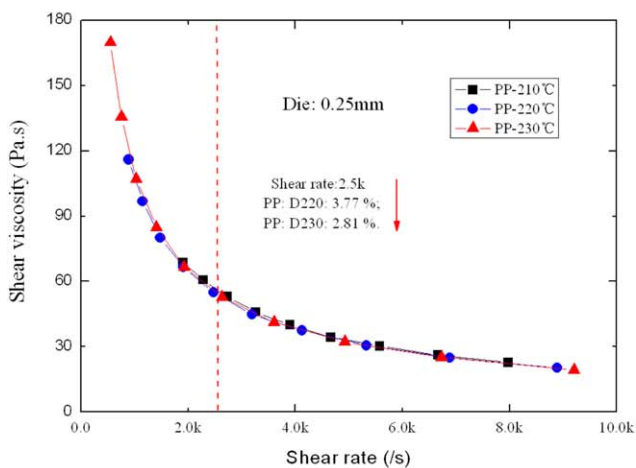
(b)



(b)



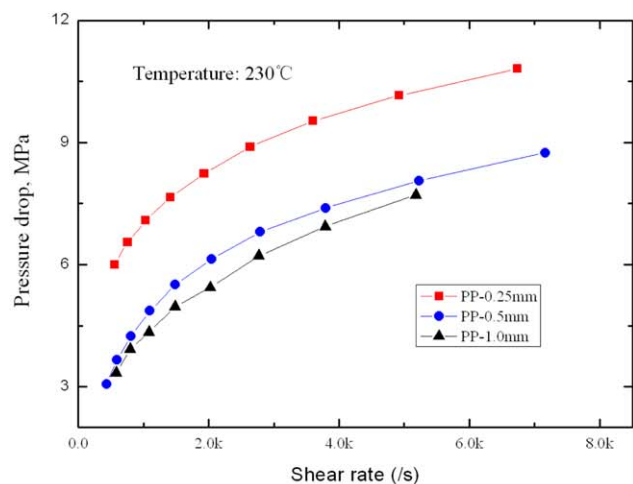
(c)



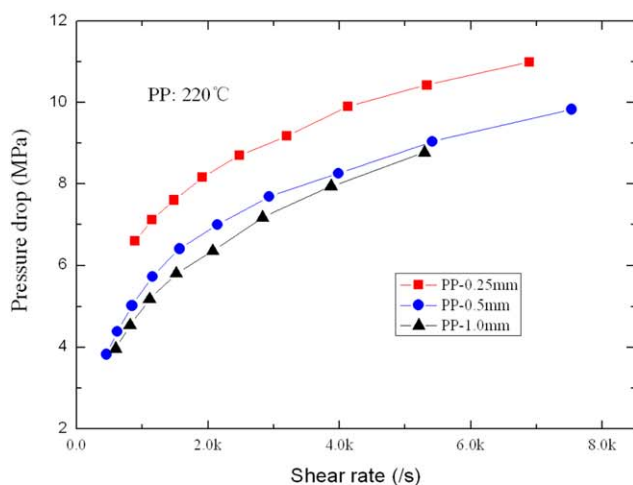
(c)

Figure 1. Comparisons of the shear viscosity in different dies at each temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

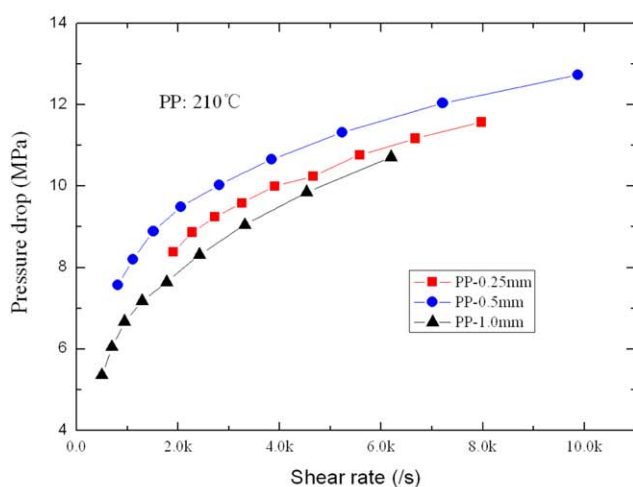
Figure 2. Comparisons of the shear viscosity in each die at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



(a)



(b)



(c)

Figure 3. Pressure drops in different dies at each temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

calculated viscosity (D_m) are revealed in Figure 1 at a shear rate of 2500 s^{-1} in each die at different temperatures. As expected, the calculated values of D_{220} were generally less than those of D_{230} in each die because the viscosity of the polymer melts decreased with increasing temperature. Meanwhile, the data shown in Figure 2 revealed that the deviations were different from each other. For example, the value of D_{230} reached nearly 30% in the 1.0-mm diameter die, but it was only 2.81% in the 0.25-mm diameter die. It appeared that the PP viscosity sensitivity to temperature became weaker as the die diameter decreased. Therefore, the geometry dependence of the PP viscosity on the microscopic scale was strongly related to its temperature.

As these results show, the PP viscosity typically presented a shear-thinning behavior and decreased as the temperature increased through each capillary die. Liang and Peng²³ investigated the viscosity of PP at low shear rates in the molten state with the temperature in the PP melt ranging from 180 to 280°C. The results show that the temperature dependence of the shear viscosity of the PP melt was consistent with the Arrhenius equation. However, the viscosity sensitivity to the temperature of the PP melt varied with the channel size of the capillary die in this study. Some factors had an opposite effect on the viscosity on the microscale and prevented the reduction of the shear viscosity with the increases in the shear rate and temperature.

Effect of the Pressure on the Geometry Dependence of the Shear Viscosity

Researchers have focused on the pressure sensitivity of the viscosity in studies on the rheological properties of polymer melts. In 1957, Maxwell and Jung²⁴ reported that the viscosity of branched polyethylene increased exponentially to 14-fold its value at atmospheric pressure when the pressure was increased to 168 MPa.

In this study, the role played by pressure in the viscosity behavior of the PP melt on the microscale was investigated.

The pressure drops were measured over the shear-rate range through the three dies at each temperature, as shown in Figure 3. The following points are stressed. First, the pressure drops decreased when the temperature of the PP increased, and the viscosity values of the PP through the 0.5- and 1.0-mm diameter dies were similar. Second, the pressure drops of the PP in the 0.25-mm diameter die at the three temperatures remained relatively stable, and all of their values were close to 12 MPa when the temperature increased from 210 to 230°C.

The temperature sensitivity of the shear viscosity of the polymer melt was easy to understand. The increasing temperature was attributed to an increase in intermolecular interactions, which were linked to the amount of free volume available to the molecular chain. Thus, the viscosity of the polymer melts decreased, and the polymer melt flowed more easily through the capillary die so that the value of the pressure drop decreased. However, the pressure drop situation in the 0.25-mm diameter die was different, and the values were much higher

Table II. D_m Values of the PP Melt in the 0.25- and 0.5-mm Diameter Dies at 230 °C

Apparent shear rate (s ⁻¹)	410	561	766	1048	1432	1957	2676	3658	D_{ave}^a
$D_{0.25}$	43.28	39.04	37.33	33.74	32.31	28.56	25.81	22.82	32.86
$D_{0.5}$	18.62	20.05	23.33	23.4	26.44	24.33	24.17	23.06	22.92

^a D_{ave} , average value of the viscosity deviation.

than those in the 0.5- and 1.0-mm diameter dies were at the tested temperatures.

Researchers have investigated the effects of the pressure on the shear viscosity of polymer melts.^{14,25–27} The results reveal that the increasing pressure of the polymer melt in the die led to a reduction of the free volume; this was related to the availability of space between molecules. As a result, the density of the polymer melt increased. The viscosity of the polymer melts increased with a corresponding growth of the intermolecular friction.

To explain the geometry dependence of the viscosity observed in this study, the effect of the pressure on the viscosity of PP was also investigated.

The influence of the pressure of the polymer melt on the viscosity (η) could be described by the Barus equation²⁸:

$$\eta = \eta^{(0)} e^{\beta P} \quad (6)$$

where $\eta^{(0)}$ is the viscosity at ambient pressure and β is the pressure coefficient. The experimental values of the viscosity in the 1.0-mm diameter die at different temperatures were generally considered to be the values of the PP on a conventional scale without the effect of the die geometry because of its larger diameter, and they are referred to as the calculated values of viscosity. Therefore, the viscosities in the 0.25- and 0.5-mm diameter dies could be obtained with the viscosity values in the 1.0-mm diameter die as follows:

$$\begin{aligned} \eta_m^{ca} &= \eta^{(0)} \cdot e^{\beta P_m^{ex}}, \eta_{1.0}^{ca} = \eta^{(0)} \cdot e^{\beta P_{1.0}^{ex}} \\ \frac{\eta_m^{ca}}{\eta_{1.0}^{ca}} &= e^{\beta \Delta P'}, \Delta P' = P_m^{ex} - P_{1.0}^{ex} \\ \eta_m^{ca} &= \eta_{1.0}^{ex} \cdot e^{\beta \Delta P'} \end{aligned} \quad (7)$$

On the basis of eq. (7), the deviation of D_m from the experimental value in the microdie could be evaluated as follows:

$$D_m = \frac{\eta_m^{ex} - \eta_m^{ca}}{\eta_m^{ex}} \times 100\% \quad (8)$$

where the superscripts ca and ex denote the calculated and experimental values of the viscosity and pressure drop, respectively. The subscript m and the value 1.0 denote dies that are 0.25/0.5 and 1.0 mm in diameter, respectively.

The values of $D_{0.25}$ and $D_{0.5}$ of the viscosity of the PP in the 0.25- and 0.5-mm diameter dies are listed in Table II, in which the average value of β was on the order of 20 GPa⁻¹, as reported in previous studies. Here, the value was taken as 21.5 GPa⁻¹.²⁵ As shown in Table II, the values of $D_{0.25}$ and $D_{0.5}$ over the shear-rate range appeared to be high, and the values of

$D_{0.25}$ were greater than those of $D_{0.5}$. Therefore, the varying viscosity of the PP melt was partially attributed to the increasing pressure on the microscale.

The values of D_m implied the results shown in Figure 2, which depicts the changed temperature sensitivity of the PP viscosity in different dies, as mentioned previously. As shown in Figure 2(c), the temperature seemed to have a limited effect on the viscosity of PP in the 0.25-mm die. The much higher $D_{0.25}$ was used to further analyze the results. It is well known that the polymer viscosity decreases as its temperature increases but increases with an enhancement in the pressure applied to the molten polymer. Kelly *et al.*¹⁴ pointed out that the mutually cancelling effects of pressure and temperature on the viscosity of polymer melts should be questioned for high shear rates. Similarly, the temperature effect on the viscosity of the PP melt in the different dies could be explored. The much higher D_m listed in Table II proved that the viscosity in the 0.25-mm die was due to the increasing pressure on the microscale. Therefore, because of the strengthened pressure effect in the 0.25-mm die, the temperature influence on the molten PP viscosity appeared to be consequently weakened.

Compared with the results reported by Lin *et al.*,²⁹ we found that the pressure sensitivity of the viscosity showed a close relationship with the molecular structure of the polymer melt. Because of the highly flexible molecular chains of PMMA, the effect of the pressure of PMMA on shear viscosity was much higher than that of PP. These results were in good agreement with the conclusion suggested by Couch and Binding,²⁵ who found that the viscosity sensitivity to pressure of polymer melts was directly related to the molecular structures, and the polymers with larger side chain groups had a higher viscosity sensitivity to pressure. Additionally, the effect of the pressure on the viscosity occurred in the order Polyethylene < PP < PMMA < PS in terms of the complexity of the molecular structures of the polymers.

Effect of Wall Slip on the Geometry Dependence of the Shear Viscosity

Wall slip is considered an important factor accounting for the change in the shear viscosity of polymer melts because of adhesive failure at the polymer–wall interface in a flow channel.

On the basis of the Mooney slip model for the steady-state flow of a Newtonian fluid under slip boundary conditions, the total volume flow rate (Q_{total} ; m³/s⁻¹) in a channel with a radius R (m) can be calculated as follows³⁰:

$$\frac{4Q_{\text{total}}}{\pi R^3} = \frac{4v_s}{R} + \dot{\gamma}_{\text{true}} \quad (9)$$

where Q_{total} includes the shear and slip volume flow rate (m^3/s^{-1}) under slip conditions and v_s is the slip velocity (m/s^{-1}).

The relationship between Q_{total} and the apparent shear viscosity ($\dot{\gamma}_{\text{app}}$) in eq. (4) can be determined as follows:

$$\dot{\gamma}_{\text{app}} = \frac{4Q_{\text{total}}}{\pi R^3} \quad (10)$$

Equations (9) and (10) indicate that $\dot{\gamma}_{\text{app}}$ can be expressed in a linear function of the coefficients of $1/R$, and that the gradient of the function is equal to four times v_s . From the plots of the apparent shear viscosity ($\dot{\gamma}_{\text{app}}$) versus $1/R$ under a series of constant shear stresses, the fitted gradients of curves were obtained; this enabled us to calculate the corresponding v_s values. Hatzikiriakos³¹ introduced additional details about the method to measure v_s .

On the basis of Hatzikiriakos's method, the slip velocities were determined under four constant shear stresses at the tested temperatures, as shown in Figure 4. In this study, the slip velocities in the PP flow from the microdies presented different patterns compared with those in the PMMA flow reported by Lin *et al.*²⁹

Because the fitted gradient of the curve of $\dot{\gamma}_{\text{app}}$ versus $1/D$ (D is the diameter of a capillary die) was directly linked to v_s , the negative slip velocities shown in Figure 4(a–c) indicated that no wall slip occurred in the 0.5- and 1.0-mm dies at the tested temperatures. Wall slip only existed in the 0.25-mm die at 210 °C, as revealed by the positive gradients of the curves (the negative values of v_s were omitted for clarity in Figure 4).

Hatzikiriakos proposed an expression for wall slip occurrence in a polymeric flow in which wall slip occurs when the shear stress exceeds a critical value because the shear stress overcomes the force that is attributed to the flow-induced chain detachment or adsorption at the polymer–wall interfaces in a flow channel and to the disentanglement of the polymer chains in the bulk from a monolayer of polymer chains adsorbed at the interface.³¹ In these cases for PP, it was reasonable that the shear stresses in the 0.5- and 1.0-mm dies at the tested temperatures were not strong enough against the adhesive force between the near-wall layer of the polymer and the wall in the capillary dies. However, the value of stress increased with increasing pressure in the 0.25-mm die; this was associated with the decrease in the diameter of the die and the temperature of the PP, as previously mentioned. Once the value was above the critical value of stress, wall slip occurred suddenly, as shown in Figure 4(c).

The different shear viscosity sensitivities to the temperature and pressure are proposed to have been responsible for the diversity of wall slip patterns among the polymer melts in the microdies. In addition, in our previous study, we found that the profile of the front of the polymer-filling flow in a capillary die with a diameter of less than 0.2 mm differed from that in a conventional die, as shown in Figure 5.³² The analysis indicated that the additional pressure accounting for surface tension slightly affected the filling flow in the microchannel. Meanwhile, wall slip occurred during the filling flow into the capillary, and v_s

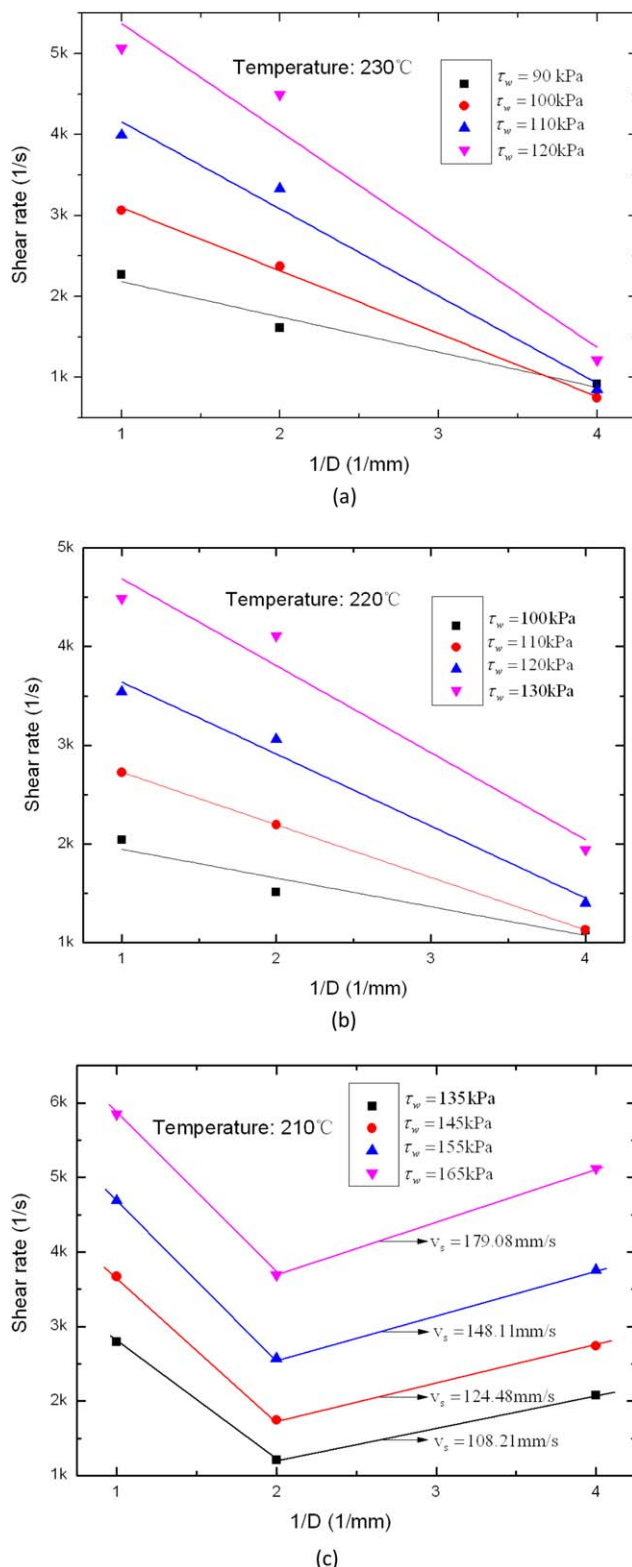


Figure 4. Analysis of the wall slip in capillary flow at each tested temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

increased as the size decreased. Kim *et al.*³³ explored the effect of the surface tension on the filling flow. A similar result was also reported in which the surface tension hindered the flow;

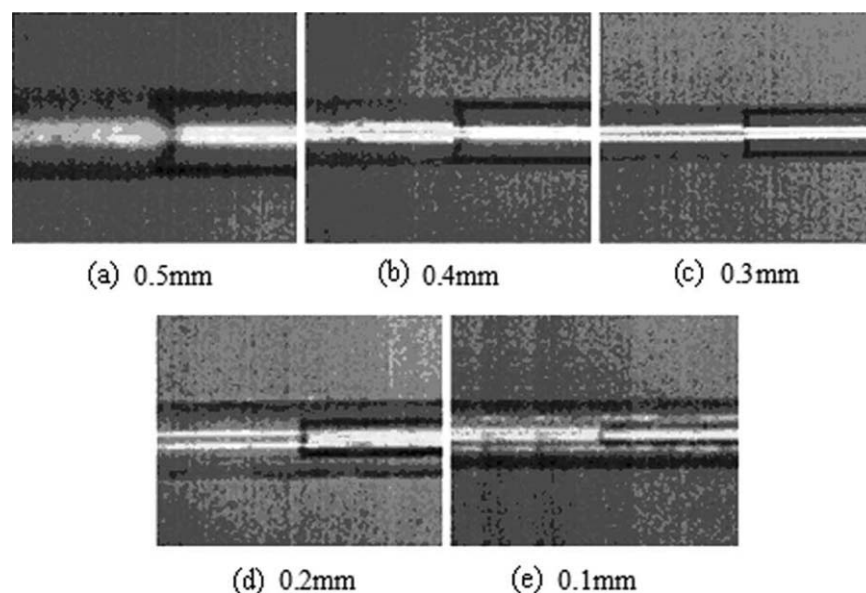


Figure 5. Various flow fronts in capillary dies with diameters of 0.1–0.5 mm.

the hindering phenomenon was especially clear in the small channel. Therefore, it appeared that the effects of the material properties, the temperature and pressure, on the shear viscosity of the PP melt were strongly related to each other.

CONCLUSIONS

A series of rheological experiments was performed for commercial-grade PP to explore its rheological behaviors through a microcapillary die. The results indicate that the PP viscosity in the 0.25-mm diameter die was greater than those in the 0.5- and 1.0-mm diameter dies at 210 °C but was close to those in the 0.5- and 1.0-mm diameter dies at 220 and 230 °C. The rheological behavior in which the viscosity of the polymer melts decreased as the temperature increased became weaker because of the geometry dependence of the viscosity in the microcapillary die. As a result, the pressure of PP in the 0.25-mm diameter die remained much higher than those in the 0.5- and 1.0-mm diameter dies; consequently, the free volume of the molecular chain decreased. The Barus equation was used to calculate the contribution of pressure to the increasing PP viscosity. The results reveal that the increasing pressure partially accounted for the enhancement of the PP viscosity through the 0.25-mm diameter die. Meanwhile, the effect of wall slip on the geometry dependence of the viscosity was examined, and the slip velocities of the polymer melt flowing through the tested dies were plotted with a modified Mooney method under slip boundary conditions. The results show that no wall slip occurred under the tested conditions, except for the PP flow through the 0.25-mm diameter die at 210 °C.

In summary, the rheological behaviors of polymer melts in a microchannel are complex and should be investigated comprehensively because of the close correlations with the polymer properties, including the channel size, temperature, and shear rate. Our study is expected to reveal a better understanding of

the rheological properties of PP melts on the microscale. Because of the geometry dependence of the shear viscosity of PP in the microdie, the analysis suggests that the deviation of the PP viscosity on the microscale from that on the conventional scale clearly depends on the size of the die and its temperature.

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REFERENCES

1. Becker, H.; Gartner, C. *Anal. Bioanal. Chem.* **2008**, *390*, 89.
2. Bernassau, A. L.; Garcia-Gancedo, L.; Hutson, D.; Demore, C. E. M.; McAneny, J. J.; Button, T. W.; Cochran, S. *IEEE Trans. Ultrason. Ferroelectr. Freq. Control* **2012**, *59*, 1820.
3. Brousseau, E. B.; Dimov, S. S.; Pham, D. T. *Int. J. Adv. Manuf. Technol.* **2010**, *47*, 161.
4. Chandekar, A.; Alabran, M.; Sengupta, S. K.; Lee, J. S.; Mead, J. L.; Barry, C. M. F.; Whitten, J. E.; Somu, S.; Busnaina, A. A. *Microelectron. Eng.* **2008**, *85*, 187.
5. Giboz, J.; Copponnex, T.; Mele, P. J. *Micromech. Microeng.* **2007**, *17*, R96.
6. Bissacco, G.; Hansen, H. N.; De Chiffre, L. *CIRP Ann. Manuf. Technol.* **2006**, *55*, 593.
7. Chen, C. S. *e-Polymers* **2008**, *39*, 43.

8. Chien, R. D.; Jong, W. R.; Chen, S. C. *J. Micromech. Microeng.* **2005**, *15*, 1389.
9. Ito, H.; Suzuki, H.; Kazama, K.; Kikutani, T. *Curr. Appl. Phys.* **2009**, *9*, E19.
10. Son, Y. *Polym. Test.* **2008**, *27*, 243.
11. Eringen, A. C. *Int. J. Eng. Sci.* **1995**, *33*, 2297.
12. Chen, S. C.; Tsai, R. I.; Chien, R. D.; Lin, T. K. *Int. J. Heat Mass Transfer* **2005**, *32*, 501.
13. Zhang, H. L.; Ong, N. S.; Lam, Y. C. *Polym. Eng. Sci.* **2007**, *47*, 2012.
14. Kelly, A. L.; Gough, T.; Whiteside, B. R.; Coates, P. D. *J. Appl. Polym. Sci.* **2009**, *114*, 864.
15. Azuddin, M.; Zahari, T.; Choudhury, I. A. *Mater. Manuf. Process.* **2011**, *26*, 255.
16. Xu, B.; Wang, M.; Yu, T.; Zhao, D. *Chin. J. Mech. Eng.* **2010**, *46*, 125.
17. Chen, C. S.; Chen, S. C.; Liaw, W. L.; Chien, R. D. *Eur. Polym. J.* **2008**, *44*, 1891.
18. Zhao, D.; Jin, Y.; Wang, M.; Song, M. *Proc. Inst. Mech. Eng. C: J. Mech. Eng. Sci.* **2011**, *225*, 1175.
19. Lin, X.; Kelly, A.; Woodhead, M.; Ren, D.; Wang, K. *J. Appl. Polym. Sci.* **2013**, *131*, 39982.
20. Schiff, H.; David, C.; Gabriel, M.; Gobrecht, J.; Heyderman, L.; Kaiser, W.; Köppel, S.; Scandella, L. *Microelectron. Eng.* **2000**, *53*, 171.
21. Bagley, E. B. *Appl. Phys.* **1957**, *28*, 624.
22. Rabinowitsch, B. *Z Phys. Chem. A* **1929**, *145*, 1.
23. Liang, J. Z.; Peng, W. *Polym. Test.* **2009**, *28*, 386.
24. Maxwell, B.; Jung, A. *Mod. Plast.* **1957**, *35*, 174.
25. Couch, M. A.; Binding, D. M. *Polymer* **2000**, *41*, 6323.
26. Sedlacek, T.; Zatloukal, M.; Filip, P.; Boldizar, A.; Saha, P. *Polym. Plast. Technol. Eng.* **2004**, *44*, 1328.
27. Binding, D. M.; Couch, M. A.; Walters, K. *Non-Newtonian Fluid Mech.* **1998**, *79*, 137.
28. Barus, C. *Proc. Am. Acad.* **1891**, *27*.
29. Lin, X.; Kelly, A.; Ren, D.; Woodhead, M.; Coates, P.; Wang, K. *J. Appl. Polym. Sci.* **2013**, *130*, 3384.
30. Mooney, M. J. *Rheol. Acta* **1931**, *2*, 210.
31. Hatzikiriakos, S. G. *Prog. Polym. Sci.* **2012**, *37*, 624.
32. Meng, L.; Wu, D.; He, X.; Zhuang, J. *Mater. Res. Innov.* **2014**, *18*, 1034.
33. Kim, D. S.; Lee, K. C.; Kwon, T. H.; Lee, S. S. *J. Micromech. Microeng.* **2002**, *12*, 236.