Stick-Slip Transition Behaviour of Two High Density Polyethylene Melts on Capillary Rheometer

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Abstract: The stick-slip transition behaviour of two high density polyethylene (HDPE) melts are studied experimentally by using a capillary rheometer with twin bores at different temperatures. The shear stress-shear rate curves are investigated by the capillary rheometer with two diameters. The results show that the flow curves break at a certain critical shear stress. The broken point of the flow curve implies the occurrence of the stick-slip transition. The critical shear stresses obtained by the two capillaries equal approximately, but extrapolation slip length increases with the diameter of the capillary. It is found that the critical shear stress increases proportionally with absolute temperature, which means increasing temperature can depress or delay the occurrence of slippage to a certain degree. Additionally it is found the slip section's slope of the shear stress-shear rate curve is lower than the sticky section's slope.

Keywords: Wall slip, critical shear stress, polymer melt, capillary rheometer, slope.

1. INTRODUCTION

The non-slip condition has been widely accepted for a long time, with which the macroscopic flow behaviour can be generally described. With the development of rheology and hydromechanics, wall slip or stick-slip has been discovered for not only polymer melts and solutions but also Newtonian fluids [1]. Especially in recent years in Micro-electromechanical Systems (MEMS) and Nano-electromechanical Systems (NEMS) the specific surface area (i.e. the ratio of the superficial area to volume of the cavity) is so large that the slippage of the fluid past solid boundaries can not be overlooked [2-4].

One of the slip mechanisms of polymer melts is proposed to be the entanglement/disentanglement between the polymer bulk chains and the polymer chains absorbed on the wall [5-7]. In suspension, a solvent layer forms because the suspended particles migrate from the bulk to the wall, thus slippage occurs between the bulk chains and the solvent layer. This slippage is an apparent slippage, not a true one [8]. The relationship between stick-slip defect and molecular slip at the wall for linear polymers was investigated by Allal and Vergnes [9]. Recently [6] gave a review on the wall slip of polymer melts. According to this review, a first weak slip then a strong slip happened between the melt and the wall. The mechanism of the weak slip is the detachment/desorption of the melt/wall, the mechanism of the strong slip is the entanglement/disentanglement of the bulk chains/absorbed chains on the wall.

Wall slip of polymer melts can be measured by various technical methods, for example, optical technique including a near field laser velocimetry technique, Plane Couette flow coupled with a video camera interfaced with a time lapse recorder, photographic techniques using tracer particles, the hot anemometer technique, Particle Image Velocimetry (PIV) [10, 11], etc. Also rheological methods can be applied to investigate wall slip, for instance, checking the dependence of flow curve on the dimension of flow passageway [12, 13], or checking the breaking or the slope of the flow curve. In our previous work [14], the break and wall slip for polymer melts on capillary rheometer are studied. In this work, the dependence of the flow curve on diameter of the capillary, the break of the flow curve and the change of the slope of the flow curve are investigated respectively.

2. EXPERIMENTAL

2.1. Materials

The polymer samples under investigation are two commercial high density polyethylene (HDPE 5306J and HDPE 2300J), both manufactured by Yangzi Petro. Co. Ltd, China. Table 1 lists the molecular parameters of the HDPEs measured by high temperature gelatin permeation chromatography (Waters-150-C-ALC/GPC manufactured in the United States).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE 5306J</td>
<td>$1.5\times10^4$</td>
<td>$9.4\times10^4$</td>
<td>6.1</td>
</tr>
<tr>
<td>HDPE 2300J</td>
<td>$2.2\times10^4$</td>
<td>$11.2\times10^4$</td>
<td>5.1</td>
</tr>
</tbody>
</table>
2.2. Rheometry

The experiments were done on a capillary rheometer RH2000 manufactured by Malvern Instruments Comp. The capillary rheometer is equipped with twin bores, i.e., a common capillary die (diameter = 1.0mm, length = 16mm; diameter = 0.5mm, length = 8mm) and a zero length capillary die (diameter = 1.0mm, length = 0.25mm; diameter = 0.5mm, length = 0.25mm). The shear rate and shear stress data were dealt with a Rabinowich and pressure drop correction, respectively. Before experiment the bores were cleaned carefully with liquid paraffin to eliminate possible contaminant or residual polymer chains.

2.3. Rheological Measurement

The experimental temperatures were 150, 170, 190 and 210°C for the HDPE melts respectively. Before rheological measurement the samples in the twin bores were pressed with 0.5MPa and 0.2MPa and with a speed of 2mm/min respectively twice and after each pressure 2, 4 minutes were lasted respectively when the samples were first melted in the rheometer at required temperature in order to remove the thermal and strain history and possible air bubbles. During the experiments, the temperature fluctuation did not exceed ± 0.2°C.

3 RESULTS AND DISCUSSION

On capillary rheometer, if wall slip occurs, the volume flow rate [6] is

\[ Q = \pi R^2 u_s + Q_{\text{no-slip}} \]  (1)

where \( R \) is the radius of the capillary die, \( u_s \) is the slip velocity on the wall of the capillary die, \( Q_{\text{no-slip}} \) is the volume flow rate without wall slip. The apparent shear rate is defined as \( \dot{\gamma}_d = 4Q / \pi R^3 \) or \( \dot{\gamma}_d = 32Q / \pi D^3 \), where \( D \) is the diameter of the capillary. The following equation is derived from equation (1)

\[ \dot{\gamma}_d = \dot{\gamma}_{\text{no-slip}} + \frac{8u_s}{D} \]  (2)

where \( \dot{\gamma}_d \) is the apparent shear rate when wall slip occurs, \( \dot{\gamma}_{\text{no-slip}} \) is the shear rate without wall slip. Equation (2) indicates that wall slip does not happen if

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Figure 1: Shear stress versus shear rate for HDPE 5306J with 0.5mm and 1.0mm diameter capillaries at (a) 150°C, (b) 170°C, (c) 190°C and (d) 210°C, respectively.
the apparent shear rate $\dot{\gamma}_d$ is independent on the diameter $D$ of the capillary, otherwise wall slip occurs. And the slip velocity $u_s$ can be obtained by calculating the slopes of the $\dot{\gamma}_d \sim 8/D$ curves.

The shear stress-shear rate curves of the HDPE 5306J measured using two capillary dies of different diameter at the temperature of 150, 170, 190 and 210°C respectively are presented in Figure 1. It can be seen that the flow curves break into two branches at a certain shear stress, which is in accordance with the reports [6, 16]. The breaking of the flow curves means the occurrence of stick-slip, i.e., the melt sticks on the wall before the breaking, but slips after that. Figure 1a and b show that the flow curves measured by two diameter capillary dies overlap before the breaking of the flow curves, which means wall slip does not happen. After the breaking, the flow curves by two capillary dies separate, which means wall slip occurs. And the shear rate measured by 0.5mm capillary is higher than that measured by 1.0mm capillary at the same shear stress, which accords with description of the equation (2).

Dividing two sides of the equation (2) by $\dot{\gamma}_{\text{no-slip}}$, the following can be attained

$$\frac{\dot{\gamma}_d}{\dot{\gamma}_{\text{no-slip}}} - 1 = \frac{8u_s}{(\dot{\gamma}_{\text{no-slip}} D)} \quad (3)$$

According to the definition of extrapolation slip length

$$b = \frac{u_s}{\dot{\gamma}_{\text{no-slip}}} \quad (4)$$

When slippage occurs, the critical extrapolation slip length $b$ is named as $b_c$. Then equation (3) turns into

$$\frac{\dot{\gamma}_d}{\dot{\gamma}_{\text{no-slip}}} - 1 = \frac{8b_c}{D} \quad (5)$$

where $b_c$ is the critical extrapolation slip length on the transition of stick-slip. The slip length $b_c$ can be calculated from equation (5), then the slip velocity $u_s$ can be calculated from equation (4). Figure 1 shows stick-slip transition occurs when the shear stress/shear rate approaches a critical value. The slippage means the transition of entanglement to disentanglement between the bulk chains and the adsorbed chain on the wall.

The shear stress-shear rate flow curves for HDPE 2300J at the temperature of 150, 170, 190 and 210°C are measured respectively, as shown in Figure 2. The flow curves at different temperatures break at a certain critical shear stress, which means stick-slip occurs.

![Figure 2](image.jpg)

**Figure 2:** Shear stress versus shear rate for HDPE 2300J with 0.5mm and 1.0mm diameter capillaries at (a) 150°C, (b) 170°C, (c) 190°C and (d) 210°C, respectively.
Similar to HDPE 5306J, the critical shear stress for HDPE 2300J increases with the increasing temperature. The critical shear stress measured with 1.0mm capillary die for HDPE 2300J at 150, 170, and 190°C is 0.211, 0.256, and 0.298 MPa (data is unavailable for 210°C), while the critical shear stress for HDPE 5306J at 150, 170, 190 and 210°C is 0.237, 0.283, 0.322 and 0.366 MPa, respectively, the latter is a little higher than the former. The critical shear stress values are consistent with the reported values [15, 16]. The critical extrapolation slip length at 1.0mm capillary is in the range of 0.17~0.23 mm for HDPE 2300J, and is in the range of 0.18~0.20 mm for HDPE 5306J. Both of them are in the approximately same range. It is worth noting there are some difference between the two curves measured by using 0.5 mm and 1.0 mm capillary. The reason is, on one hand, some measuring error exits, on the other hand, the molecular weight of HDPE 2300J is higher than that of HDPE 5306J, the former is more prone to slipping, so possible weak slippage happens before the transition.

The critical parameters corresponding to onset of stick-slip are listed in Tables 2 and 3. The critical shear stress increases with the increasing temperature, which means increasing the temperature can depress the wall slip. The critical shear stress predicted by the disentanglement model [5] is:

\[ \tau_c \propto vT \]  

where \( v \) is the number of chains per unit area grafted to the wall, \( T \) is the absolute temperature. According to the literature [9], the critical shear stress of stick-slip transition can be expressed as

\[ \tau_c = \frac{9C_{ad} \ln N_e}{4\pi} \frac{N_e \sqrt{M_g} nkT}{M_w a^3} \]  

where \( C_{ad} \) is a coefficient of proportionality, \( M_g \) is the monomer molecular weight, \( N_e = \frac{M_g}{M_0} \), where \( M_0 \) is the molecular weight between entanglements, \( M_w \) is the weight molecular weight, \( n \) is the number of entanglements in the volume \( a^3 \), which is a constant, \( a \) is the distance between entanglements, \( k \) is the Boltzmann constant and \( T \) the absolute temperature. Figure 3 shows the critical shear stress \( \tau_c \) is proportional to the absolute temperature \( T \) for the two

Table 2: Temperature Dependence for HDPE 5306J

<table>
<thead>
<tr>
<th>D / mm</th>
<th>T / °C</th>
<th>( \dot{\gamma}_s / s^{-1} )</th>
<th>( \dot{\gamma}_{n-s} / s^{-1} )</th>
<th>( \dot{\gamma}_{n-s} / s^{-1} )</th>
<th>( \nu' / cm \cdot s^{-1} )</th>
<th>( \tau_c / MPa )</th>
<th>( b_i / mm )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>150</td>
<td>3625.6</td>
<td>1513.9</td>
<td>12.2</td>
<td>0.244</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>170</td>
<td>10580.3</td>
<td>3587.9</td>
<td>43.7</td>
<td>0.287</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>190</td>
<td>14423.5</td>
<td>8138.7</td>
<td>39.3</td>
<td>0.332</td>
<td>0.05</td>
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<tr>
<td>0.5</td>
<td>210</td>
<td>34417.3</td>
<td>13921.2</td>
<td>128.1</td>
<td>0.357</td>
<td>0.09</td>
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<tr>
<td>1.0</td>
<td>150</td>
<td>3735.5</td>
<td>1508.6</td>
<td>27.8</td>
<td>0.237</td>
<td>0.18</td>
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<tr>
<td>1.0</td>
<td>170</td>
<td>9000.5</td>
<td>3496.4</td>
<td>68.8</td>
<td>0.283</td>
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<td>19883.1</td>
<td>7759.9</td>
<td>151.5</td>
<td>0.322</td>
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<tr>
<td>1.0</td>
<td>210</td>
<td>-</td>
<td>16554.4</td>
<td>-</td>
<td>0.366</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Table 3: Temperature Dependence for HDPE 2300J

<table>
<thead>
<tr>
<th>D / mm</th>
<th>T / °C</th>
<th>( \dot{\gamma}_s / s^{-1} )</th>
<th>( \dot{\gamma}_{n-s} / s^{-1} )</th>
<th>( \dot{\gamma}_{n-s} / s^{-1} )</th>
<th>( \nu' / cm \cdot s^{-1} )</th>
<th>( \tau_c / MPa )</th>
<th>( b_i / mm )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>150</td>
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<td>707</td>
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<td>0.197</td>
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<tr>
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<td>1473</td>
<td>12.4</td>
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<tr>
<td>0.5</td>
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<td>7670</td>
<td>3191</td>
<td>28.0</td>
<td>0.285</td>
<td>0.09</td>
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<tr>
<td>0.5</td>
<td>210</td>
<td>14092</td>
<td>7273</td>
<td>42.6</td>
<td>0.328</td>
<td>0.06</td>
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</tr>
<tr>
<td>1.0</td>
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<td>1622.6</td>
<td>687.9</td>
<td>11.7</td>
<td>0.211</td>
<td>0.17</td>
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<tr>
<td>1.0</td>
<td>170</td>
<td>3860.4</td>
<td>1541.6</td>
<td>29.0</td>
<td>0.256</td>
<td>0.19</td>
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<tr>
<td>1.0</td>
<td>190</td>
<td>10685.4</td>
<td>3766.9</td>
<td>86.5</td>
<td>0.298</td>
<td>0.23</td>
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<tr>
<td>1.0</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>
HDPE melts, which is consistent with equation (6) and (7). And the slope of the $\tau_s - T$ curve is approximately 0.002 for the two melts. Equation (7) does not indicate the effect of geometry and the polymolecularity on critical shear stress. From Tables 2 and 3, it can be found that the diameter of the capillary has little effect on the critical shear stress of stick-slip transition. Basically with the increase of temperature the slip velocity rises for the same capillary die, as shown in Tables 2 and 3. At the same temperature the critical extrapolation slip length and slip velocity measured with 1.0mm capillary is higher than that measured with 0.5mm capillary. This can be explained by equation (5), when the critical shear rate $\gamma_a$ and $\gamma_{\text{no-slip}}$ remain unchanged, as shown in Table 2, the larger the diameter $D$ is, the larger the slip length $b$ is.

The shear stress-shear rate curves for HDPE 5306J and HDPE 2300J at 150°C on 1.0mm capillary are shown in Figure 3a and b derived from Figure 1a and b, respectively. The flow curve before the stick-slip transition is the sticky section, the flow curve after the stick-slip transition is the slip section. The slope of the slip section is different from that of the sticky section, as shown in Figure 4. Figure 4a shows the slope of the sticky section for HDPE 5306J at 150°C is 0.505, and that of the slip section is 0.223. Figure 4b shows that the slope of the sticky and slip section for HDPE 2300J at 150°C is 0.408 and 0.232, respectively. It can be seen that the slope of the slip section is less than that of the sticky section. So a stick-slip transition can be inferred by the change of the slope of the flow curve.

4. CONCLUSIONS

The shear stress-shear rate data are measured by capillary rheometer for two high density polyethylene HDPE 5306J and HDPE 2300J. The critical rheological parameters at the stick-slip transition are investigated, and the results show as follows: The shear stress-shear rate curves for HDPE 5306J and 2300J break at a certain critical shear stress at various temperatures, which means the occurrence of stick-slip transition between the melt and the wall of the capillary die. The critical extrapolation slip length measured with 1.0mm capillary is in the same range of 0.17-0.23mm for both of the HDPE melts. The experimental results indicate that the critical shear stress for the onset of stick-slip transition increases proportionally with the absolute temperature. Thus improving temperature can depress the wall slip to some extent. The slope of the slip section is lower than that of the sticky section of the shear stress-shear rate curve, which indicates the occurrence of a stick-slip transition.
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SYMBOLS

\( a \) = the distance between entanglements, mm
\( b \) = extrapolation slip length, mm
\( b_c \) = the critical extrapolation slip length on the transition of stick-slip, mm
\( C_{ad} \) = a coefficient of proportionality
\( D \) = diameter of the capillary rheometer, mm
\( H \) = the gap of the parallel plates of the rotationary rheometer, mm

**HDPE** = high density polyethylene

\( k \) = the Boltzmann constant
\( K \) = material parameter
\( L \) = length of the capillary rheometer, mm
\( m \) = material parameter

\( M_e \) = the molecular weight between entanglements

\( M_0 \) = the monomer molecular weight

\( \frac{M_n}{M_w} \) = Number average molecular weight

\( \frac{M_n}{M_w} \) = weight average molecular weight

\( n \) = the number of entanglements in the volume \( a^3 \)

\( N_e \) = \( M_e / M_0 \)

\( Q \) = the volume flow rate, m\(^3\)/s

\( Q_{\text{no-slip}} \) = the volume flow rate without wall slip, m\(^3\)/s

\( R \) = the radius of the capillary die, mm

\( r \) = the distance between the fluid element and the center of the plate, mm

\( T \) = temperature, °C; absolute temperature, K

\( v^c \) = the critical slip velocity, cm/s\(^{-1}\)

\( \omega \) = the angular velocity of the disk of the rotationary rheometer, rad/s

\( u_s \) = the slip velocity on the disk of the rotationary rheometer, or the slip velocity on the wall of the capillary die, cm/s\(^{-1}\)

\( v \) = the number of chains per unit area grafted to the wall

\( \dot{\gamma}_{a,f} \) = the apparent shear rate on parallel plates, s\(^{-1}\)

\( \dot{\gamma}_R \) = the true shear rate on the radius of \( R \), s\(^{-1}\)

\( \dot{\gamma}_{n,R} \) = the nominal shear rate on the radius of \( R \), s\(^{-1}\)

\( \dot{\gamma}_{\text{app}} \) = The apparent shear rate when wall slip occurs, s\(^{-1}\)

\( \dot{\gamma}_{\text{no-slip}} \) = the shear rate without wall slip, s\(^{-1}\)

\( \tau_c \) = the critical shear stress, KPa or MPa

\( \tau \) = the critical shear stress, KPa or MPa

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