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Abnormal Rheological Behavior of Linear Low Density Polyethylene Melts at High Shear Rate

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Summary

Abnormal rheological behavior is observed during capillary extrusion with a linear low density polyethylene (LLDPE). The nominal viscosity in the stick-slip flow regime and the gross melt fracture regime increase with a rise in temperature. This is attributed to slippage of the polymer melts. It is generally accepted that the occurrence of slippage can be detected by a Mooney analysis. However, it is found that the Mooney analysis is not applicable to detect the occurrence of slippage in the gross melt fracture regime. This is attributed to the main assumptions in the Mooney analysis being invalid in this regime, mainly due to the presence of a turbulent-like flow pattern. We suggest that failure of the time-temperature superposition principle can be used as an indication of slippage for polymer melts.

Introduction

Many extrusion-based polymer processes such as film blowing, melt spinning, and cast film extrusion are limited by flow instabilities [1-3]. It is generally observed that the extrudate becomes rippled, rough, twisted, and distorted as the throughput increases. The flow instability that occurs at relatively low throughput, is called a sharkskin melt fracture (SMF). It is generally accepted that SMF originates in the die exit region. The flow instability that occurs at the highest throughput is called a gross melt fracture (GMF). GMF typically involves diameter variations of 10% or more. GMF occurs in many classes of materials including both those having linear and branched morphologies whereas SMF typically occurs in linear polyethylene [3]. It is believed that GMF occurs at the die entry region.
For some linear polyethylenes, a “slip-stick” or “spurt” regime is observed at the shear rate range between SMF and GMF. This regime is characterized by pressure oscillations and alternating regions of sharkskinned and smooth extrudates; the sharkskinned regions correspond to ascending portions of the pressure curve while smooth regions correspond to descending portions [4, 5].
To date, many studies on the flow instability in a capillary extrusion have been conducted. However, most studies have focused on the sharkskin melt fracture, since

this instability occurs at relatively low throughput. The maximum shear rate has not been greater than 10^4 s^{-1} in most of these works. Slippage is frequently observed at high shear rates for many linear polyethylenes [3]. The slip velocity can be measured by either direct or indirect methods. The direct methods include laser Doppler velocimetry [6] and a particles tracer method [7], where the velocity of mixed solid particles in the polymer matrix is directly measured by deploying a high speed video camera. Both methods can provide clear evidence of the occurrence of slippage as well as the exact slip velocity, but the devices are relatively complicated and thus expensive. In addition, the measurement of slip velocity at very high shear rates is somewhat limited in terms of accuracy. On the other hand, the indirect method, known as the 'Mooney analysis' is very simple. On the assumption that the slip velocity is proportional to the shear stress regardless of the diameter of the capillary die, the pressure drop decreases with the diameter of the die upon the occurrence of slippage. The pressure drop does not show any diameter dependency when slippage does not occur. Many studies rely on this method to detect the occurrence of slippage [3]. In the present study, we investigate the rheological properties of LLDPE at various temperatures, focusing on very high shear rates up to 10^5 s^{-1}. Several interesting behaviors are observed at high shear rate. In particular, we found that the Mooney analysis is not applicable to detect the occurrence of slippage at very high shear rates. Experimental results and a discussion of these unexpected results are presented in this paper.

Experimental

Materials

Metallocene-catalyzed linear low-density polyethylene (ExxonMobil Chemical, Exceed™ 3518) was investigated in this study. This resin is a hexene copolymer

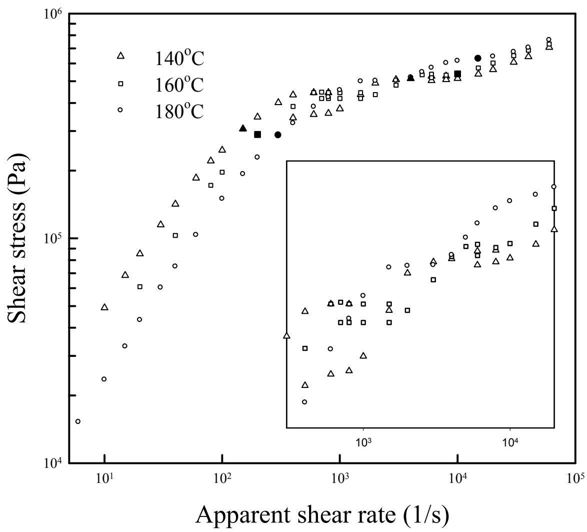

Fig. 1. Flow curves from a capillary die of D = 0.535 mm and L = 9.31 mm at three different temperatures. Filled symbols at lower shear rates represent the onset of sharkskin melt fracture, and those at higher shear rates represent the onset of gross melt fracture.

and, according to the supplier, contains no long chain branching. The relevant physical and molecular properties can be found on ExxonMobil's website [http://www.exceedmpe.com].

Apparatus and method

Capillary extrusion experiments were carried out using a piston-driven homemade capillary rheometer. Temperatures for the extrusion experiments vary from 140°C to 180°C. Three different steel capillary dies having similar L/D ratios and different diameters (0.535, 0.7, and 1.0 mm) were used. Details of the experiment and the apparatus have been described elsewhere [8].

Results and Discussion

Fig. 1 shows the flow curve (wall shear stress versus apparent shear rate) obtained from a capillary die of D = 0.535 mm and L = 9.31 mm at various temperatures. The filled symbols shown in Fig. 1 indicate the onset of SMF and GMF. Fig. 2 shows photographs of the extrudates and transient pressure curves at 140°C.

Below a critical shear rate for the onset of SMF, the extrudates are smooth and transparent. At a wall stress of 0.3 MPa, SMF begins to occur. The critical shear stress of 0.3 MPa for the onset of SMF is slightly higher than reported values [5, 9]. As indicated by Ramamurthy [10], the critical shear stress for the onset of SMF is almost independent of melt temperature. Above the critical shear rate for the onset of GMF, the extrudates show a morphology typically associated with GMF, i.e. wavy with severe and chaotic distortion.

Stick-slip or spurt flow regimes accompanied by a typical flow curve discontinuity are observed in shear rate ranges of 600 ~ 800 and 6000 ~ 8000 s^{-1}. Double data points at the same shear rate in the flow curves represent the stick-slip regimes. The maximum and minimum values in the pressure oscillation are presented in the flow curves. The

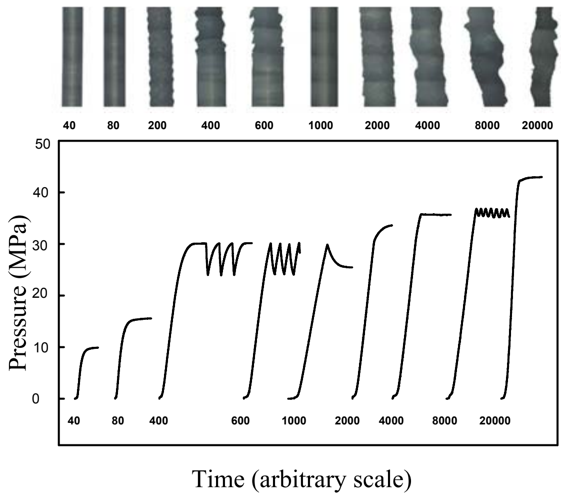

Fig. 2. Photographs of extrudates and transient pressure curves obtained at 140°C. Numbers correspond to apparent shear rate in s^{-1}.

stick-slip flows are frequently observed in many LLDPEs [11, 12]. However, the present observations are somewhat different with typical stick-slip flow behavior. It is observed that there are two distinct stick-slip regimes, separated by an intermediate stable region (no pressure oscillation). Similar phenomena have been observed elsewhere [12, 14].

It is observed that the amplitude of the pressure oscillation in the first stick-slip flow regime (appeared at lower shear rate) is larger than that in the second regime. In the first stick-slip flow regime, the extrudate has a typical stick-slip appearance, i.e. alternating regions of sharkskinned and smooth extrudates. It is well known that during the compression period (the ascending portion of the pressure oscillation), the polymer melts do not slip and the extrudate shows a sharkskinned appearance. During the relaxation period (the descending portion), the flow rate increases instantaneously, implying the occurrence of slip. As a consequence, the extrudate during the relaxation period is smooth and clean. The second stick-slip regime also shows pressure oscillation, but does not have a typical characteristic of alternating sharkskinned and smooth extrudates. The extrudates obtained in the second stick-slip regime are severely sharkskinned or wavy. The amplitude of the pressure oscillation decreases with a rise in temperature and the stick-slip phenomenon no longer appears at 180°C. Although the pressure oscillation is not observed in the flow curve obtained at 180°C, the flow curve at this temperature still shows a trace of the stick-slip flow.

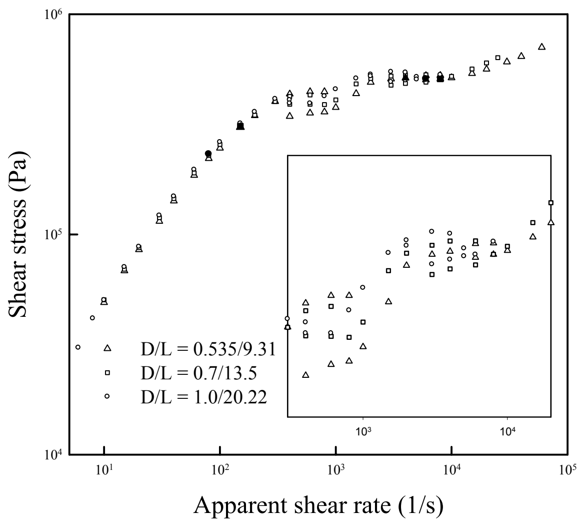

Fig. 3. Flow curves obtained from three different dies at 140°C. Filled symbols at lower shear rate represents the onset of sharkskin melt fracture, and those at higher shear rates represent the onset of gross melt fracture.

There are two regions where the slope of the flow curve, d log τ_w/d log $\dot{\gamma}_a$, is nearly zero (1500 ~ 3000 s^{-1} and near 15000 s^{-1}). This trace inherited from the lower temperature ancestor gradually diminishes as the temperature increases, as shown in Fig. 5. An intermediate stable region is observed between these two stick-slip regimes. The transient pressure curve in this region is noteworthy. For example, the pressure at a shear rate of 1000 s^{-1} increases initially and then reaches a maximum value followed by a sharp decrease until reaching a steady value. The sudden drop of pressure can be attributed to massive slippage, based on the following observations: (1) The extrudate obtained at 1000 s^{-1} is smooth and clean whereas that obtained at much lower shear rate (e.g. 200 s^{-1}) has a sharkskinned structure. It is known that the slippage eliminates or delays the sharkskin melt fracture [7, 15]. (2) The flow rate increases instantaneously at the initial stage of the pressure decrease. (3) The pressure as a function of temperature shows abnormal behavior beyond the intermediate stable region, i.e. the pressure increases with temperature. The last observation implies that massive slip occurs not only in the intermediate stable region but also in the second stick-slip regime and the GMF regime. This is consistent with the findings of other studies. Many studies have shown that there is large slip between the die wall and polymer melts beyond the stick-slip flow regime [6, 16].

Occurrence of slippage can be detected by a Mooney analysis [17]. The shear stress (or pressure) at a given shear rate (or flow rate) increases with the radius of the capillary die when slippage occurs. Fig. 3 presents flow curves obtained from three dies of same L/D and various D ranging from 0.535 to 1.0 mm at 140°C. All three dies show two stick-slip regimes and an intermediate stable region, but the shear rate for each region slightly depends on the diameter of the capillary die. For example, stick-slip regimes for D = 1.0 mm are observed at 600 and 3000 ~ 5000 s^{-1}, whereas those for D = 0.535 mm are at 400 ~ 800 and 6000 ~ 8000 s^{-1}.

The pressure obtained in a shear rate range of 1000 ~ 2000 s^{-1} increases with the diameter of the capillary die, implying that the Mooney analysis is applicable. However, above 2000 s^{-1}, the diameter dependency on shear stress is not consistent with the Mooney theory. At 3000 ~ 10000 s^{-1}, the pressures obtained from various die diameters are indistinguishable and the smallest die does not produce the lowest pressure drop, implying that there is no slip in this shear rate range. However, from the temperature effect on the shear stress, it is clear that slippage occurs at this high shear rate range.

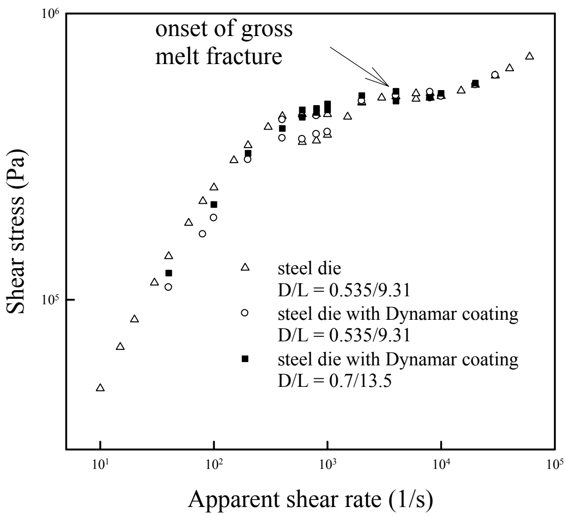

Fig. 4. Flow curves obtained from two different dies with and without the Dynamar coated die at 140°C.

To investigate this issue in more detail, we performed a capillary extrusion with modified dies by application of a fluorocarbon elastomer (Dynamar FX9613) coating. This type of surface modification is known to greatly reduce the strength of polymer adsorption and yield stress-induced chain desorption and massive interfacial slip for polyethylene [18]. Fig. 4 shows flow curves obtained from two different dies with and without Dynamar coating of the capillary die wall. The Dynamar coating does not delay the onset of GMF. A comparison between the two sets of data in Fig. 4 indicates that there is some level of interfacial slippage up to a shear rate of about 1000 s^{-1}, i.e. the shear stress from the Dynamar coated dies shows die diameter dependency. The experimental results indicate that there is no interfacial slip even on the Dynamar coated die at very high shear rate ranges. The absence of a diameter dependency on the Dynamar coated die at very high shear rates suggests that there is no slippage, or that Mooney's analysis may not be applicable in the GMF regime. It is known that the slip velocity is proportional to the shear stress and that the Dynamar coating enhances the slip phenomena. Therefore, it is likely that slip occurs on the Dynamar coated die even at very high shear rate. It is thus found that Mooney's analysis is not applicable at very high shear rates, e.g. the GMF regime.
Basic assumptions for the Mooney analysis in determining the slip velocity are laminar flow and steady state. According to findings reported in the literature [19-22], in the GMF regime, the converging lamella flow pattern at the entrance becomes disturbed, the flow profile fluctuates, and the axial symmetry of the streamline vanishes. Most likely, this turbulent-like flow pattern propagates into the die land and, as a result, the Mooney analysis cannot detect the slip velocity in the GMF regime. Another assumption for the Mooney analysis is that the same shear stress produces the same slip velocity regardless of the die diameter. In the GMF regime, this assumption may not be valid due to the turbulent-like flow pattern. To clarify this issue, direct measurement of slip velocity,y such as via the laser Doppler method [6] or a flow visualization method [7, 23] for the LLDPE investigated in this study, should be performed beyond the stick-slip flow regime. This presents an interesting research topic.

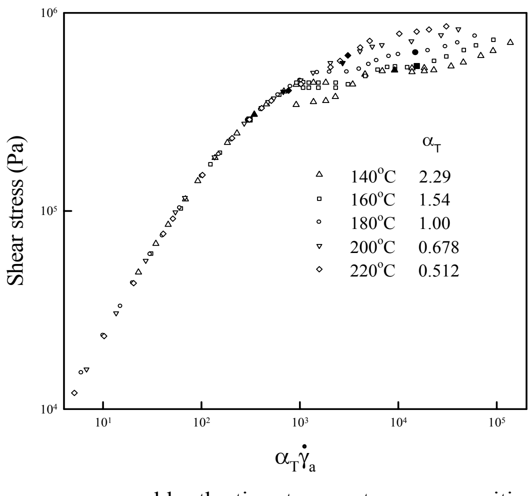

Fig. 5. The master curve prepared by the time-temperature superposition principle from data in Fig. 1.

Fig. 5 is a master curve constructed by the time temperature superposition (TTS) principle from the same data shown in Fig. 1. It is observed that the TTS principle is valid below the shear rate for the first stick-slip regime, but each flow curve begins to deviate from the master curve at a shear rate where the first stick-slip flow begins. Generally, the TTS principle is not valid for materials of which the structure or composition changes with temperature, such as immiscible polymer blends, liquid crystalline polymers, *etc*. [24, 25]. Given that the TTS principle is not valid beyond the first stick-slip regime, it infered that some aspect of the material changes with temperature. It is unlikely, however, that the structure or composition of the LLDPE investigated in this study changes with temperature. We believe that the change with temperature is related to the polymer melt flow or a boundary condition.

Slippage of polymer melts is known to originate from the elastic nature of the polymer melt [26]. Since the elasticity of the polymer melt decreases with temperature, it is clear that the slippage decreases with temperature. Therefore, it is inferred that the change of slip behavior with temperature leads to failure of the TTS principle. We suggest that the failure of the TTS principle may be used as an indication of slippage in LLDPE extrusions.

Conclusions

Nominal viscosity of LLDPE investigated in this study increased with a rise in temperature in the stick-slip flow regime and the gross melt fracture regime. From various investigations, it was found that this abnormal behavior can be attributed to the slippage of polymer melts. However, it was found that the Mooney analysis is not applicable to detect the occurrence of slippage in the gross melt fracture regime. This is because the main assumptions of the Mooney analysis are not valid in this regime. It was also found that the time-temperature superposition principle is not valid beyond the first stick-slip regime where massive slippage begins to occur. The failure of the TTS principle could potentially be used as an indication of slippage.

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