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Anomalous rheological behavior of polyethylene melts in the gross melt fracture regime in the capillary extrusion

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Abstract

During the capillary extrusion with several different polyethylenes, we observe an abnormal rheological behavior. The nominal viscosity of polyethylene melt in the gross melt fracture regime does not change with a temperature. All polyethylenes tested show same behaviors. More interestingly, the nominal viscosity in the gross melt fracture regime shows even no molecular weight dependency when PEs have similar molecular structures (degree of branching and co-monomer content). From various experiments, we conclude that this abnormal phenomenon is relevant to the structural change with the melt temperature.

Keywords: Melt-fracture; Sharkskin; Polyethylene

1. Introduction

Metallocene catalysts is known to synthesis polyethylene having well distributed chain branching and narrow molecular weight distribution, which consequently lead to different physical properties from those obtained by Ziegler–Natta catalysts [1,2]. However, metallocene-catalyzed PE is more prone to sharkskin and unstable capillary flow. Therefore, many efforts have been devoted to understand the origin of such instabilities [3–11].

In an extrusion process, when the throughput exceeds a critical value, small amplitude periodic distortions appear on the surface of extrudate (surface melt fracture or sharkskin melt fracture). These distortions have quite regular frequency and amplitude. As the throughput increases further, these take the more severe form of larger irregular distortions (gross melt fracture or wavy fracture). Gross melt fracture (GMF) typically involves diameter variations of 10% or more. GMF occurs in many classes of materials including both linear and branched morphologies [3].

So far, many studies on the sharkskin melt fracture (SMF) have been carried out because sharkskin occurs at relatively low throughput. It is generally accepted that SMF originates in the die exit region. On the other hand, GMF has received less attention. GMF is believed to originate at the die entrance where the melt undergoes uniaxial extension due to the flow contraction. GMF is reported to occur when the extensional stress at the entrance of a die exceeds a critical condition that seems to depend only on the polymeric fluid [12]. Excellent reviews on the sharkskin [9,11] and gross melt fracture [12,13] are found elsewhere.

In the experiment to explore the nature of GMF during a capillary extrusion, we observe an abnormal rheological behavior of polyethylenes. The flow curves of metallocene-catalyzed PEs in the GMF regime show no-temperature and no-molecular weight dependency. In this paper, we report on the unusual experimental results and possible causes for that phenomenon.

2. Experimental

2.1. Materials

Three metallocene-catalyzed linear low-density polyethylene (mLLDPE) were investigated in this study. The relevant physical and molecular properties of these resins are tabulated in Table 1. The metallocene-catalyzed polyethylenes are ethylene–octene copolymers marketed under the product name EG8100, EG8150 and PL1880.

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Table 1
Characteristics of polymers used in this study

Materials	Commercial name	Supplier	PDI	Melt flow index (g/10 min)	Comonomer and contents (wt%)
mLLDPE	EG8100	DOW	2.0	1.0	Octane, 38
mLLDPE	EG8150	DOW	2.0	0.5	Octane, 39
mLLDPE	PL1880	DOW	2.0	1.0	Octane, 19

2.2. Apparatus and method

Capillary extrusion experiments described in this paper were carried out using a piston-driven homemade capillary rheometer. A photograph and schematic diagram of the apparatus are shown in Fig. 1. A capillary die is held at the bottom of a barrel that is temperature controlled by three electrical heating bands and we estimate the temperature control within the barrel and die to be ± 0.2 °C. The barrel containing a capillary die is attached to a universal mechanical tester (Model Hounsfield H25KS) so that the force pressing a piston can be measured. The piston is advanced at a preset speed U_p (corresponding to a flow rate $Q = U_p \pi R_p^2$, where R_p is the radius of the piston, 6 mm) and the extrusion pressure is calculated from the force exerting the piston, which is measured using a load cell mounted in a universal mechanical tester, i.e. $P = F_p/(\pi R_p^2)$. The barrel diameter is 12 mm and a cylindrical stainless steel die is used, having an entrance angle of 180 °C and various L/D ratios. We compared the data obtained from our homemade rheometer with those obtained from a commercial capillary rheometer (Gottfert RheoTester 2000), and it is found that the data are consistent with each other.

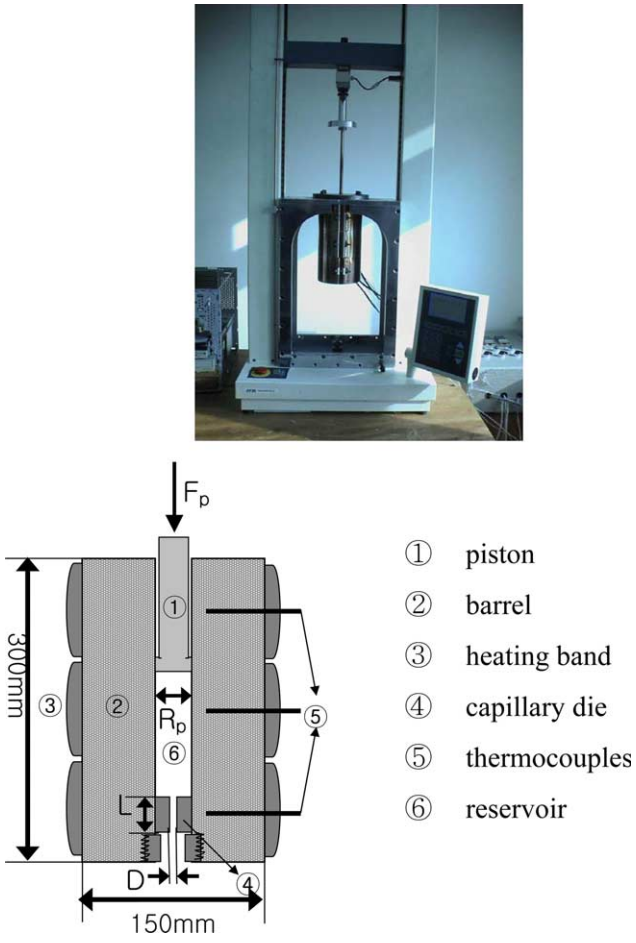

Fig. 1. Photograph of capillary rheometer used in this study and diagram of main part.

In one set of experiments, a fluoropolymer-coated capillary die is used to investigate its effect on the GMF. The coating involves repetitive introduction of a dilute mixture (1% mass fraction of fluoropolymer) of acetone and Dynamar™ FX9613 into a hot die (160 °C) and the subsequent evaporation of the acetone. The coated fluoropolymer achieves good adhesion with the stainless steel die upon heating to 180 °C for several minutes at the highest throughput.

3. Results and discussion

The flow curve (wall stress versus apparent shear rate) of EG8100 obtained from capillary die of $D = 0.535$ mm and $L = 9.31$ mm at various temperatures is shown in Fig. 2. Fig. 3 shows photographs of the extrudate obtained at the temperature of 140 °C. The filled and crossed symbols shown in Fig. 2 indicates the onset of SMF and GMF, respectively, at each temperature. The flow curve and fracture behavior of EG8100 agree with previous results reported by Migler et al. [11]. Initially, the extrudate is smooth and transparent. At the wall stress of 0.2 MPa, visible sharkskin begins to appear on the extrudate. The onset of the sharkskin melt fracture at the wall stress of 0.2 MPa agrees well with Ref. [14]. As indicated by Ramamurthy [8], this critical shear stress for the onset of SMF is almost independent of melt temperature within the experimental uncertainty. Analysis of the data for all capillary dies and at all temperatures investigated reveal no significant

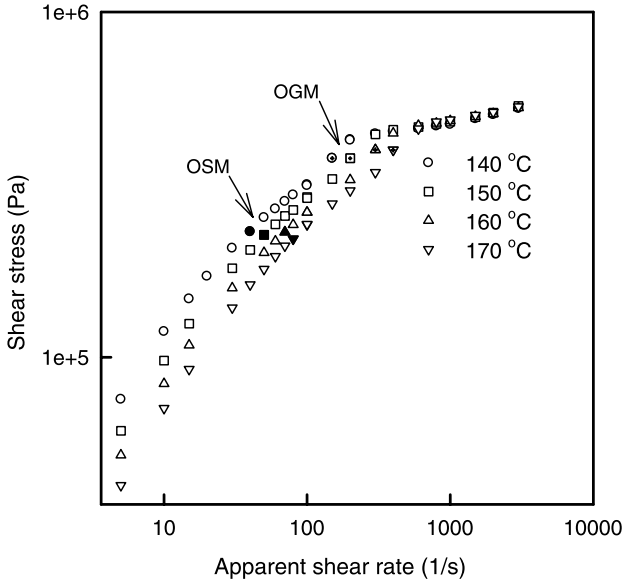

Fig. 2. Flow curves of EG8100 obtained from capillary die of $D = 0.535$ mm and $L = 9.31$ mm at four different temperatures. OSM; onset of sharskin melt fracture; OGM; onset of gross melt fracture.

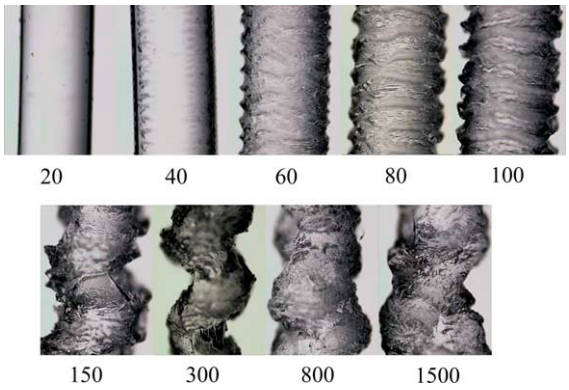

Fig. 3. Extrudates of EG8100 obtained at 140 °C. Numbers in each photo correspond to apparent shear rate in s^{-1}.

sudden change of slope at the onset of sharkskin, on the contrary to several reports [6–8]. The crossed symbols shown in Fig. 2 indicate the onset of GMF determined by the appearance of the extrudate, i.e. severe and chaotic distortion. A stick-slip or spurt flow regime accompanied by a typical flow curve discontinuity is not observed for EG8100 unlike many LLDPE [6,7]. Below the shear rate for the onset of GMF, the extrudate surface shows a typical sharkskin texture, i.e. a small amplitude and high frequency disturbance. Above the onset of GMF, the appearance of the extrudate changes dramatically, characterized by its wavy, rough and chaotic nature. In the GMF regime, an interesting and anomalous phenomenon is observed; the measured flow curve is independent of temperature. This result implies that the nominal viscosity of EG8100 in the GMF regime does not change even though the temperature increases.

We first presumed that this unusual phenomenon is due to a slip at polymer melt/die wall interfaces. Since, the slip is relevant to the elastic nature of polymer melt, it is most likely that the magnitude of slip increase as the melt temperature decreases, which lower the total stress. To investigate whether EG8100 displays any observable wall slip, the flow curves are obtained from dies of $L/D=20$ and various D ranging from 0.535 to 1.0 mm, i.e. Mooney analysis is performed as shown in Fig. 4. Data obtained from various die diameters are indistinguishable within the experimental error, which means that the wall slip of EG8100 is negligible at the shear rate range investigated in this study.

However, one can argue that there is a significant amount of slip in the GMF regime, but Mooney analysis may not be applicable in the GMF regime, because GMF shows turbulent-like flow pattern [15–18]. Basic assumptions for the Mooney analysis determining the slip velocity are laminar flow and steady state [19]. According to Refs. [15–18], at the onset of GMF the converging lamella flow pattern at the entrance becomes disturbed, the flow profile fluctuates and the axial symmetry of the streamline vanishes. As the flow rate increases further, the melt at the centerline of the entrance region fractures; the asymmetry and the fluctuation propagates to capillary die and consequently results in a chaotic appearance of the extrudates. This behavior looks similar to the turbulent flow of a non-elastic liquid. However, this turbulent-like flow pattern for a polymer melt occurs at very low Reynolds number and is believed to be caused by the elastic nature of the polymer melt. This is why GMF is often called elastic turbulence [20]. This turbulent-like flow pattern propagates into the die land and this may make the Mooney analysis not to be capable to detect slip velocity in the GMF regime.

To investigate this issue in more detail, we perform the capillary extrusion of EG8100 with modified dies by fluorocarbon elastomer (Dynamar FX9613) coating. Such a surface modification is known to greatly reduce the strength of polymer adsorption and yield stress-induced chain desorption and massive interfacial slip for polyethylene [21]. Fig. 5 shows flow curves of EG8100 obtained at 140 and 170 °C with and without Dynamar coating of the capillary die wall. Fig. 6 shows

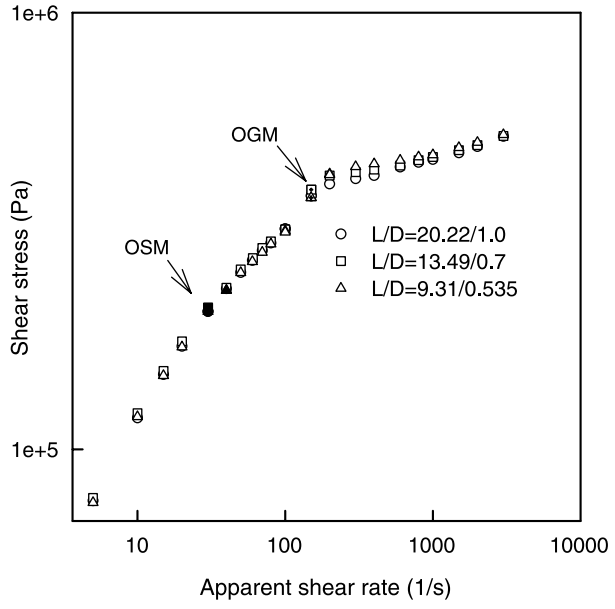

Fig. 4. Flow curves of EG8100 obtained from three different dies at 140 °C.

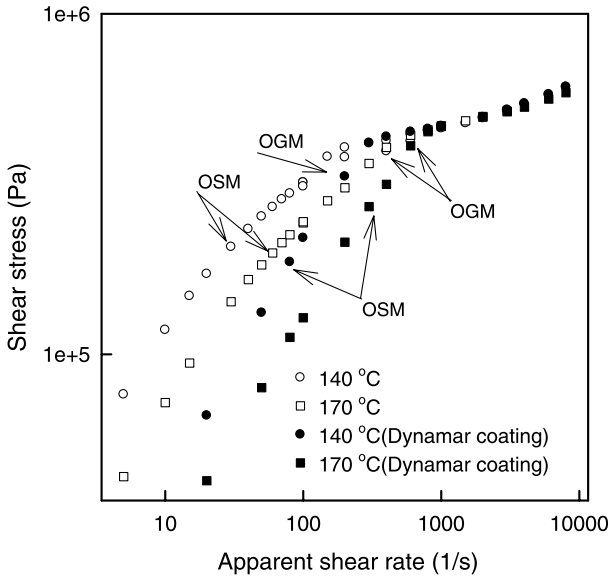

Fig. 5. Flow curves of EG8100 obtained from bare die (open symbol) and Dynamar coated die (filled symbol).

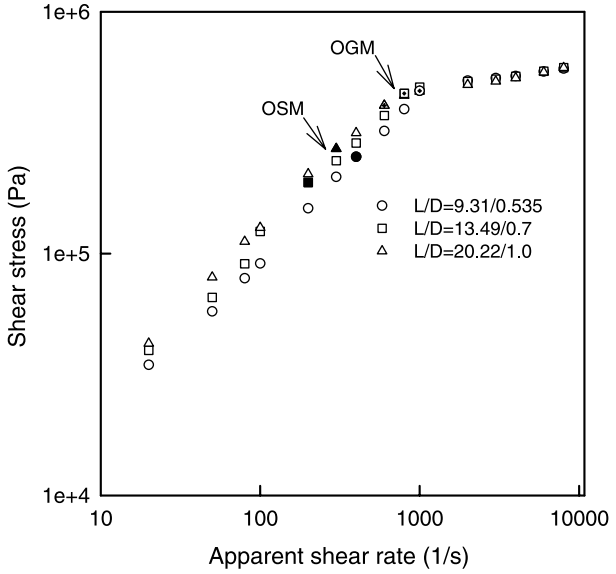

Fig. 6. Flow curves of EG8100 obtained from Dynamar coated die with different size.

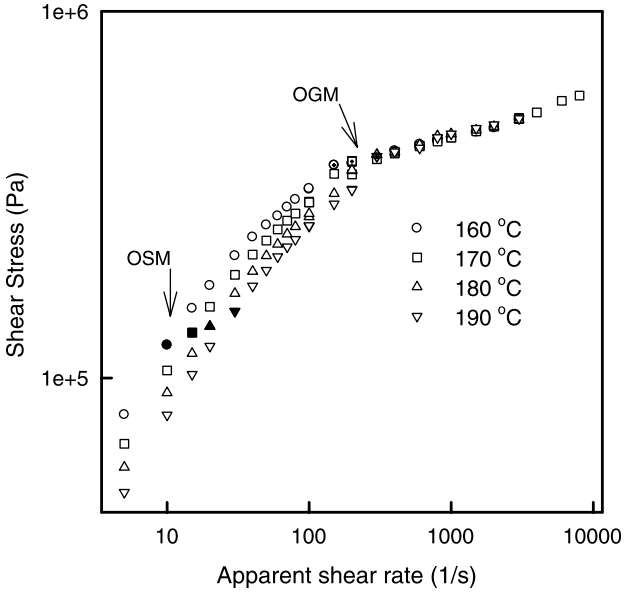

Fig. 7. Flow curves of EG8150 obtained from capillary die of $D=1.0$ mm and $L=20.2$ mm at four different temperatures.

the flow curves from Dynamar coated dies of $L/D=20$ and various D ranging from 0.535 to 1.0 mm. The Dynamar coating does not delay the onset of GMF. The comparison between two set of data in Fig. 5 indicates that there is some level of interfacial slip up to the critical shear rate for onset of the GMF. The experimental results seem to show that there is no interfacial slip even on the Dynamar coated die beyond the GMF regime. Interestingly again, the shear stress in the GMF regime is not dependent on the temperature and the Dynamar coating. Again, the fact that there is no diameter dependency on Dynamar coated die beyond the GMF regime suggest that there is no slip or Mooney's analysis may not be applicable in the GMF regime. However, if slippage occurs in the GMF regime, it is more probable that the stress obtained from Dynamar coated die is lower (or at least different with bare die) than that of bare die because the friction of bare die/polymer melts and the friction of Dynamar coated die/polymer melts are different. Similar experimental result was observed by Yang et al. [22]. They performed the capillary extrusions of PS, LDPE and ethylene vinyl acetate with bare and Dynamar coated dies. They found that the flow curves from bare and Dynamar coated dies approach each other as the shear stress increases, which means that magnitude of wall slip on Dynamar coated die (as measured by the extrapolation length) diminishes with shear stress. They attributed the diminishing magnitude of slip to shear thinning effect of polymer melt. The extrapolation length is proportional to the shear viscosity and inversely proportional to the friction coefficient [23]. The shear viscosity of polymer melt decrease with shear stress while the friction coefficient remains almost constant. Therefore, the magnitude of wall slip decreases with the shear stress. From these two graphs, we conclude that the slip is not the cause for the unusual phenomenon observed in this study.

In order to clarify whether this unusual phenomenon is coincidently observed only in EG8100, we perform same capillary extrusion experiment with various polyethylenes. Fig. 7 shows the flow curve of EG8150 obtained from capillary die of $D=1.0$ mm and $L=20.2$ mm at various temperatures, and Fig. 8 shows flow curves of EG8100 and EG8150 at 160 °C for comparison. Same experimental phenomenon is observed for EG8150, i.e. no temperature dependency of flow curve in the GMF regime. More surprisingly, the flows curves of EG8100 and EG8150 are coincident with each other in the GMF regime. According to the manufacturer's catalog, the difference between EG8100 and EG8150 is only molecular weight. The other characteristics of two polymers are same (octane content, polydispersity and degree of branching).

Fig. 9 shows the flow curve of PL1880 obtained from capillary die of $D=1.0$ mm and $L=20.2$ mm and Fig. 10

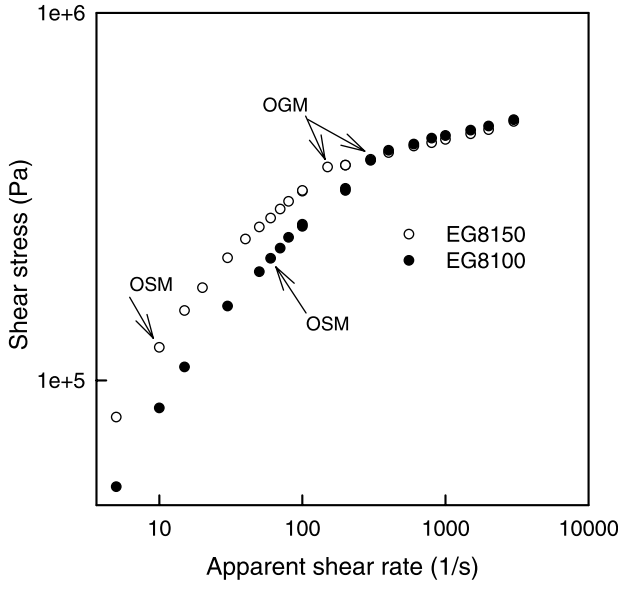

Fig. 8. Flow curves of EG8100 and EG8150 obtained at 160 °C.

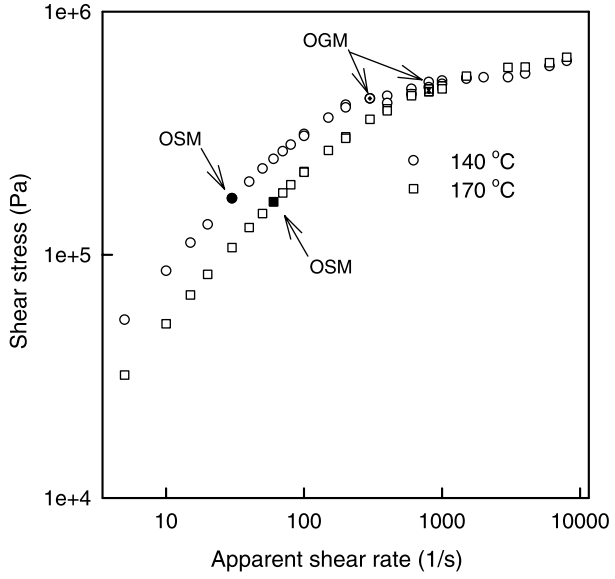

Fig. 9. Flow curves of PL1880 obtained from capillary die of $D=1.0$ mm and $L=20.2$ mm at two different temperatures.

shows flow curves of PL1880, EG8150 and EG8100 at 170 °C for comparison. Again the same unusual phenomenon is observed for PL1880. The flow curve of PL1880 in the GMF regime is slightly but significantly deviate from that of EG8100. The octane content of PL1880 is much lower than those of EG8100 and EG8150 as shown in Table 1. We think that the deviation of flow curves might be caused by the difference of octane content. From the experiments shown above, it is obvious that polyethylenes (at least for the metallocene-catalyzed PEs) having similar structures (i.e. co-monomer content, degree of branching and polydispersity) show no molecular weight dependency of flow curve in the GMF regime.

Now we assess the cause of this abnormal phenomenon. As mentioned earlier, the slippage between the polymer melt and die wall may cause this phenomenon. However, this possibility is already ruled out as shown earlier with Mooney's analysis and Dynamar coating experiments. Another possibility is the fact that the chaotic (turbulent-like) flow pattern of die land in the GMF regime becomes less chaotic as temperature increases. As seen in all flow curves, the slope of the flow curve deceases suddenly at the onset of GMF, which implies the turbulent-like flow in the GMF regime lower the stress level from that of pure laminar flow at the same shear rate. The chaotic flow in the GMF regime is known to originate from the elastic nature of polymer melt [20]. Since, an elasticity of polymer melt decreases with temperature, we speculate that the flow in the GMF regime becomes less chaotic with the temperature, and consequently stress level is less decreased, compared to that of more severe chaotic flow. Lower temperature increases an inherent viscosity of polymer melt (which tends to increase the stress level) and increases the degree of chaotic nature of flow (which tends to decreases the stress level as mentioned previous sentences). As a result, both effect offset each other and consequently the stress is maintained at same level though the melt temperature increases.

The explanation above is our speculation. At present, we do not know exact mechanism for this abnormal behavior, but we are sure that the phenomenon is not related to the slippage, but related to the structural change (the degree of the chaotic flow pattern) with temperature. The master curve from the data shown in Fig. 2 is prepared according to time–temperature superposition principle. The master curve is shown in Fig. 11. We notice that the time–temperature principle is valid below the critical shear rate for the onset of GMF. Generally, the time–temperature superposition rule is not valid for the materials of which structure changes with temperature such as immiscible polymer blends, liquid crystalline polymer, and etc. The fact that the time–temperature principle is not valid in

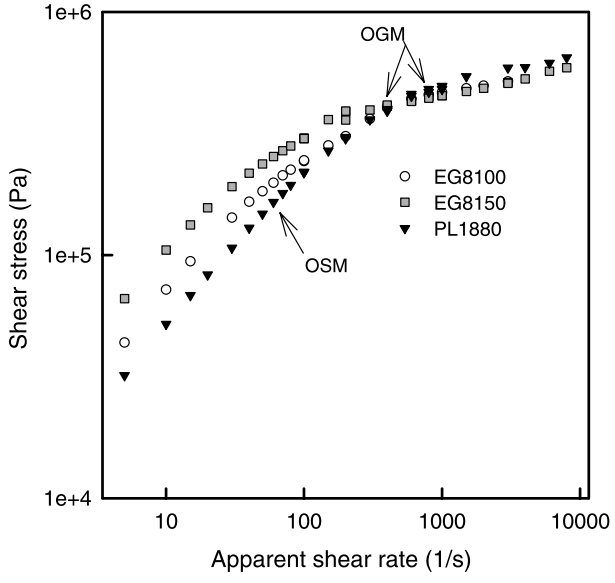

Fig. 10. Flow curves of EG8100, EG8150 and PL1880 obtained at 170 °C.

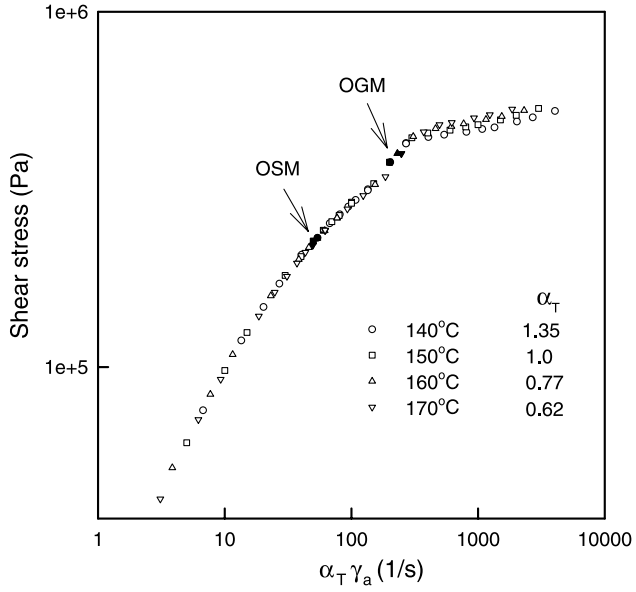

Fig. 11. The master curve prepared according to time–temperature superposition principle from data in Fig. 2.

the GMF regime implies that the something related to the degree of the chaotic flow pattern changes in temperature.

4. Conclusion

In this study, we observe metallocene-catalyzed LLDPEs show no-temperature dependency on the rheological properties at the GMF regime. When two different PEs have the same structures (degree of branching, the same co-monomer and composition), they show the same stress level in the GMF regime regardless of molecular weight and temperature. The flow curves, obtained from the dies of the same *L*/*D* ratio and different diameters, show no diameter dependency implying that there is no detectable slippage at the shear rate range investigated. Even the flow curve in the GMF regime, obtained from the die modified by fluorocarbon elastomer, is coincident with that from bare die. Both observations imply that the slippage is not origin of the abnormal behavior. When the master curve is prepared according to time–temperature superposition principle from the rheological data obtained at various temperature, it is noticed that the time–temperature principle is not valid at the shear rate for the GMF regime. From these facts, we conclude that this abnormal phenomenon is relevant to the structural change with the melt temperature.

Acknowledgements

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References

[1] Yano A, Akimoto A. In: Bendikt G, Goodall BL, editors. Metallocene-catalysed polymers: materials, properties, processing and markets. New York: SPE Plastic Design Library; 1998. p. 98.
[2] Parikh DR, Edmonson MS, Smith BW, Winter JM, Castille MS, Magee JM, et al. In: Bendikt G, Goodall BL, editors. Metallocene-catalysed polymers: materials, properties, processing and markets. New York: SPE Plastic Design Library; 1998. p. 113.
[3] Denn MM. Annu Rev Fluid Mech 2001;33:265–87.
[4] Tordellar JP. Unstable flow of molten polymers. In: Eirich ER, editor. Rheology, vol. 5. London: Academic Press; 1969. p. 57–92 [chapter 2].
[5] Cogswell FN. J Non-Newtonian Fluid Mech 1977;2(1):37–47.
[6] Wang SQ, Drda PA, Inn YW. J Rheol 1996;40(5):875–98.
[7] Kalika DS, Denn MM. J Rheol 1987;3(8):815–34.
[8] Ramamurthy AV. J Rheol 1986;30(2):337–57.
[9] Inn YW, Fischer RJ, Shaw MT. Rheol Acta 1998;37(6):573–82.
[10] Migler KB, Lavallee C, Dillon MP, Woods SS, Gettinger CL. J Rheol 2001;45(2):565–81.
[11] Migler KB, Son Y, Qiao F, Flynn K. J Rheol 2002;46(2):383–400.
[12] Kim S, Dealy JM. Polym Eng Sci 2002;42(3):482–94.
[13] Kim S, Dealy JM. Polym Eng Sci 2002;42(3):495–503.
[14] Doerpinghaus PJ, Baird DG. Rheol Acta 2003;42(6):544–56.
[15] Bagley EB, Birks AM. J Appl Phys 1960;31(3):556–61.
[16] Cook NP, Furno FJ, Eirich FR. J Rheol 1965;9(2):405–20.
[17] Tordellar JP. J Rheol 1957;1(1):203–12.
[18] Tordellar JP. J Appl Polym Sci 1963;7(1):215–29.
[19] Carreau PJ, De Kee DCR, Chhabra RP. Rheology of polymeric systems: principles and application. Munich: Hanser Publishers; 1997 p. 62–73 [chapter 3].
[20] Groisman A, Steinberg VV. Nature 2000;405(6782):53–5.
[21] Wang SQ, Drda PA. Macromol Chem Phys 1997;198(3):673–701.
[22] Yang X, Ishida H, Wang SQ. J Rheol 1998;42(1):63–80.
[23] de Gennes PG. CR Acad Sci Paris 1979;288B:219–20.