

# Anomalous Rheological Behavior of Polyethylene Melts in the Gross Melt Fracture Regime in the Capillary Extrusion: Effect of Long-Chain Branching

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**ABSTRACT:** During a capillary extrusion with several different polyethylenes, we observe an abnormal rheological behavior. The nominal viscosity of some polyethylene melt in the gross melt fracture regime does not change with the temperature. Several metallocene-catalyzed linear low density polyethylene are investigated. Among them, polyethylenes, which have long-chain branches in their main chain, show this abnormal rheological behavior. By capillary extrusion experiments with various dies of different  $L/D$  ratios, it is inferred that the abnormal rheological

behavior is originated in the die land, not die entrance nor die exit. From various experiments, we notice that this abnormal phenomenon may be used to detect long-chain branch of PE. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2350–2355, 2008

**Key words:** gross melt fracture; sharkskin; polyethylene extrusion; abnormal rheological behavior; metallocene polyethylene; long-chain branching

## INTRODUCTION

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 (SMF)]. 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 (GMF) or wavy fracture]. GMF typically involves diameter variations of 10% or more. GMF occurs in many classes of materials including both linear and branched morphologies.<sup>1</sup>

So far, many studies on the 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 wherein 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.<sup>2</sup> Excellent reviews on the sharkskin<sup>3,4</sup> and GMF<sup>2,5</sup> are found elsewhere.

In our previous study,<sup>6</sup> in which we explored the nature of GMF during a capillary extrusion, we observed an abnormal rheological behavior of metallocene-catalyzed linear low density polyethylenes (mLLDPE). The flow curves of the mLLDPEs in the GMF regime show no-temperature and even no-molecular weight dependency. We investigated the rheological properties of three different metallocene catalyzed poly(ethylene-co-octene)s. Two of them have similar level of octene contents (~10 mol %) but different molecular weights. The other mPE has lower level of octene content (5.5 mol %) than those of another PEs. In all PEs investigated, the shear stress at the GMF regime maintains same value even though melt temperature increases. More interestingly, the shear stress at the GMF regime shows even no molecular weight dependency when two PEs have similar octene contents. From various experiments, we speculated that this abnormal phenomenon is relevant to the change of melt flow pattern as the melt temperature increases.

To find out more precise causes for this abnormal behavior, we perform and show capillary extrusion experiments with various PEs including mLLDPE (with wider range of octene contents than those of previous study), conventional Ziegler-Natta-catalyzed HDPE and LDPE.

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## EXPERIMENTAL

### Materials

Six mLLDPEs were investigated in this study. The relevant physical and molecular properties of these resins are tabulated in Table I.

### Apparatus and method

Capillary extrusion experiments described in this work were carried out using a piston-driven home-made capillary rheometer. Temperatures for the extrusion experiments vary from 140 to 200°C. Several different capillary dies, which have various  $L/D$  ratios, are used. Details of experiment and apparatus are described elsewhere.<sup>6</sup>

To assess the effect of long-chain branching (LCB) on the abnormal rheological behavior, degree of LCB was estimated by the rheological method.<sup>8</sup> Dynamic storage and loss moduli,  $G'(w)$  and  $G''(w)$  are determined with a strain-controlled rheometer (ARES from TA Instruments) in dynamic mode with a parallel-plate configuration of 25-mm diameter at temperatures ranging from 140 to 200°C.

## RESULTS AND DISCUSSION

The flow curves (wall stress versus apparent shear rate) of EOC4, EOC7, EOC10, and EOC13 obtained from a capillary die of  $D = 1.0$  mm and  $L = 20.2$  mm at various temperatures are shown in Figure 1. Figure 2 is the master curve constructed by time-temperature superposition principle. The filled symbols shown in Figure 1 indicate the onset of GMF determined by the appearance of the extrudate, that is, severe and chaotic distortion. A stick-slip or spurt flow regime accompanied by a typical flow curve discontinuity is not observed for these EOCs unlike many LLDPE.<sup>9,10</sup>

Same abnormal phenomenon with our previous study (in which rheological properties of EOC10 were investigated mainly) is observed for EOC4, EOC7, and EOC 13. In the GMF regime for all EOCs,

the measured flow curve is independent of temperature. Generally, the shear stress at constant shear rate decreases with the temperature of polymer melt, because the viscosity decreases with the melt temperature. It is also noticed that the lack of superposition begins above the critical shear rate for the onset of GMF. Hereafter, we denote this abnormal rheological behavior as flow curve coincident.

Figure 3 shows the flow curves for all EOCs at 140°C. In our previous study,<sup>8</sup> it was observed that when two different EOCs have similar octene contents and molecular weight distributions, they show the same flow curves (i.e., same nominal viscosity) at the GMF regime even though they have different molecular weight. However, EOCs investigated in this study show different shear stress-shear rate relationship at GMF regime when they have different octene contents. We do not know the exact cause for this abnormal experimental result. We just speculate that the chain structure of PE plays critical role in the rheological behaviors at GMF regime. It is also noted that the shear stress at the GMF regime tends to increase as the octene content in mLLDPE increases.

Figure 4 shows the flow curves of EOC10 from various capillary dies of different  $L/D$  ratios. Except zero die, all dies shows the flow curve coincident at GMF regime, implying that the abnormal rheological behavior is originated in the capillary die land not die entrance or die exit. In our previous study, we showed by Mooney analysis that this abnormal behavior is not due to a slip at polymer melt/die wall interfaces. Our speculation for the reason of the abnormal behavior is that the chaotic (turbulentlike) flow pattern of die land in the GMF regime becomes less chaotic as the temperature increases. Because the flow pattern changes with the temperature, the time temperature supposition rule fails at the GMF regime as shown in Figure 2.

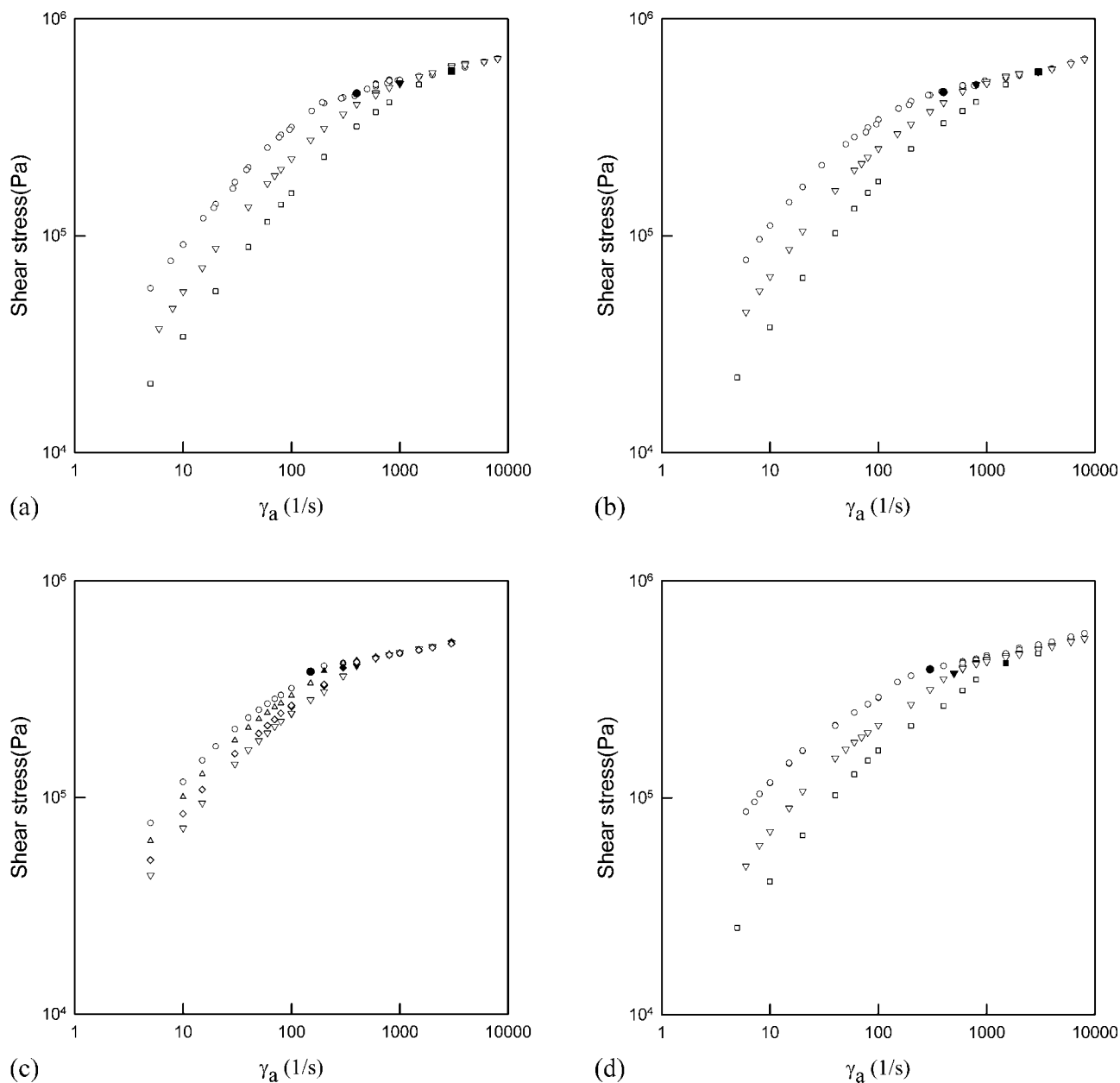
As seen in all flow curves, the slope of the flow curve decreases suddenly at the onset of GMF, which implies the turbulentlike flow in the GMF regime lower the stress level from that of pure laminar flow

TABLE I  
Characteristics of Polymers Used in this Study

Code	Materials	Trade name	Supplier	PDI	Melt flow index (°/min)	Comonomer and contents (mol %)	DRI
EOC4	mLLDPE	EG8480	DOW	2.0 <sup>a</sup>	1.0	Octene 4.1	2.90
EOC7	mLLDPE	EG8003	DOW	2.0 <sup>a</sup>	1.0	Octene 6.8	1.76
EOC10	mLLDPE	EG8100	DOW	1.9 <sup>b</sup>	1.0	Octene 9.8	0.86
EOC13	mLLDPE	EG8841	DOW	2.0 <sup>a</sup>	1.0	Octene 12.5	0.53
EOC10-L	mLLDPE	EG8200	DOW	1.9 <sup>b</sup>	20	Octene 9.8	0.40
E3132	mLLDPE	3132	Exxon mobile	2.0 <sup>7</sup>	1.2	Hexene	–

<sup>a</sup> From company catalog.

<sup>b</sup> Measured by GPC.

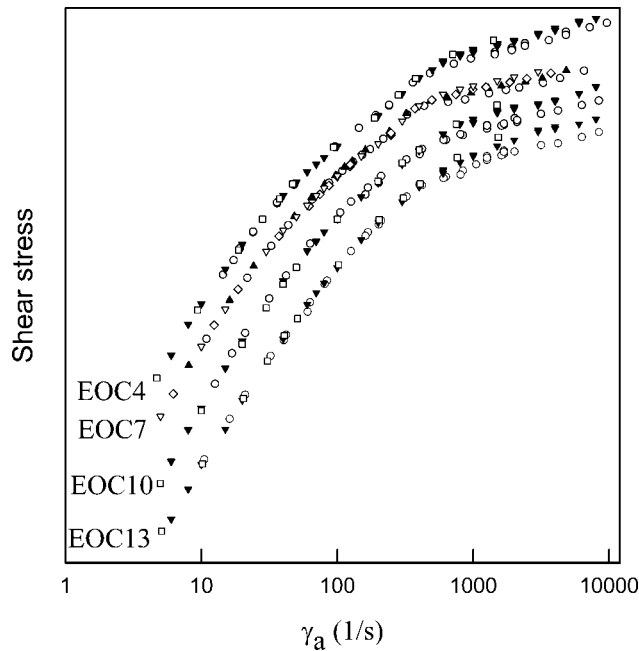


**Figure 1** Flow curves of EOC4 (a), EOC7 (b), EOC10 (c), and EOC13 (d) obtained from steel die of  $D = 1.0$  mm and  $L = 20.2$  mm at various temperatures:  $\circ$  140°C,  $\triangle$  150°C,  $\diamond$  160°C,  $\nabla$  170°C, and  $\square$  200°C. Filled symbols indicate onset of gross melt fracture.

at the same shear rate. The chaotic flow in the GMF regime is known to originate from the elastic nature of polymer melt.<sup>12</sup> Because the 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 decrease the

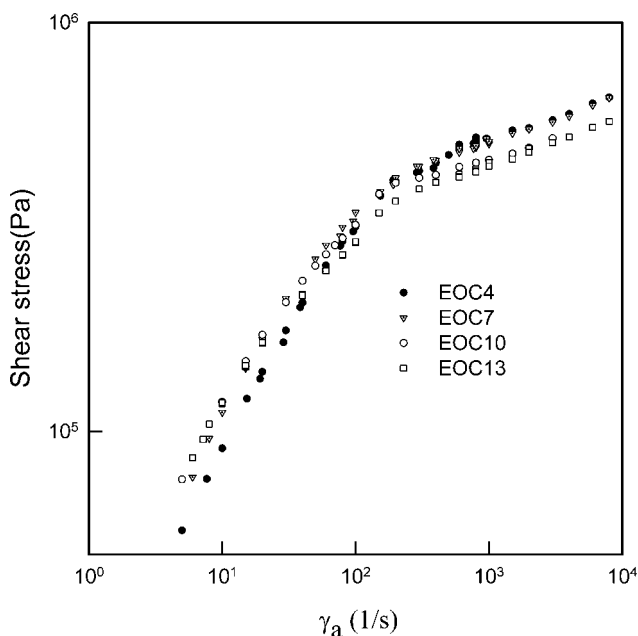
stress level as mentioned previous paragraph. As a result, both effect offset each other and consequently the stress is maintained at the same level though the melt temperature increases.

Figure 5 shows the flow curves of EOC10 obtained from a tungsten carbide capillary die of  $D = 1.0$  mm and  $L = 30.0$  mm at various temperatures. The rheometer for this test is a commercial capillary rheometer (Gottfert Rheo-Tester 2000). Same flow curve coincident is clearly seen for the die made of tungsten carbide. We also perform the capillary extrusion

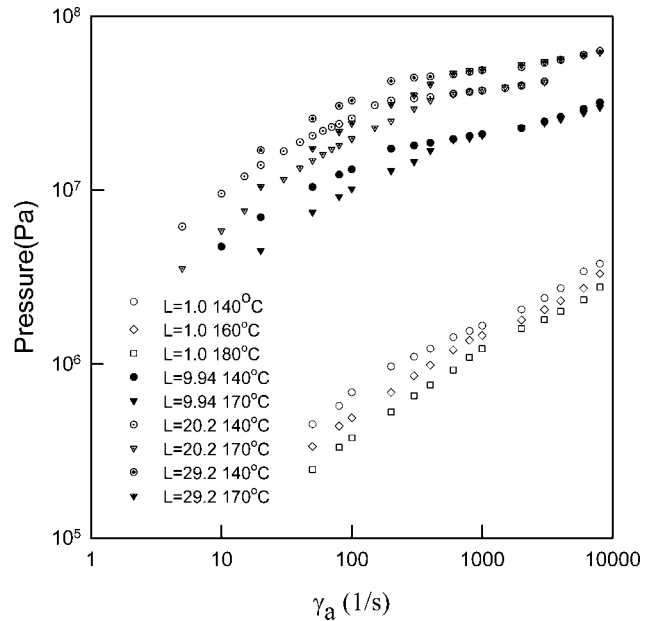


**Figure 2** Master curves constructed by the time temperature superposition principle from Figure 1. Reference temperature is 170°C. Scale for shear stress is arbitrary to avoid crowded. ○ 140°C, △ 150°C, ◇ 160°C, ▽ 170°C, and □ 200°C.

experiments with dies made of aluminum and bronze. Flow curve coincident is observed through the shear stresses at GMF regime are slightly different for each die of different materials. It is inferred that the interface between die and polymer melts is not relevant to the abnormal behavior, because the



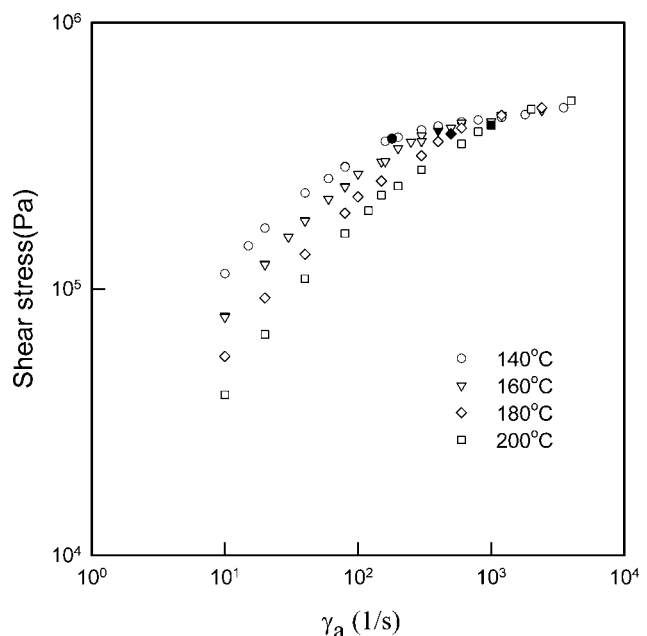
**Figure 3** Flow curves of EOC4 (a), EOC7 (b), EOC10 (c), and EOC13 (d) obtained from steel die of  $D = 1.0$  mm and  $L = 20.2$  mm at 140°C.



**Figure 4** Flow curves of EOC10 obtained from steel die of  $D = 1.0$  mm and various die length.

different die materials are known to alter an interfacial force between die and the polymer melts. This experimental result may support that there is no slippage between die wall and mLLDPE melts investigated in this study.

Because all EOCs discussed earlier have same melt flow index (1.0°/min), it is expected that these EOCs have similar average molecular weight. According to the literature,<sup>13</sup> EOC4, EOC7, and

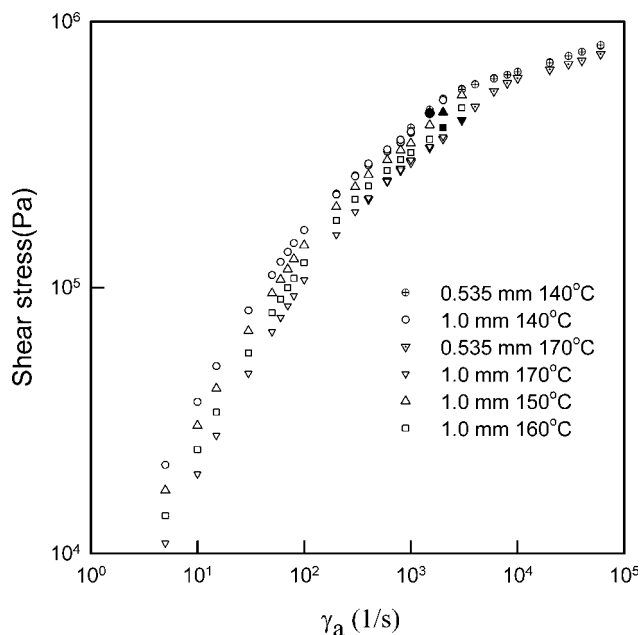


**Figure 5** Flow curves of EOC10 obtained from tungsten carbide die with  $L/D = 30$  mm/1.0 mm at various temperatures.

EOC10 have very similar average molecular weight and molecular weight distribution. Our previous study indicates that EOC10 (Dow Engage™ 8100) and Engage™ 8150 (MFI = 0.5°/min and same octene content with EOC10) show same flow curves at the GMF regime. From this observation, we concluded that EOCs, having same octene contents, show even no molecular weight dependency on the flow curve at the GMF regime.

To investigate this issue (no molecular weight dependency on the flow curve at GMF regime) in detail, we perform the capillary extrusion experiment with EOC10-L (which has same octene content with EOC10, but lower viscosity). The result is shown in Figure 6. Unlike our expectation, EOC10-L does not show the flow curve coincident though shear stresses at 140 and 170°C and tend to approach each other with the increase in the shear rate. Possible reason for this unexpected result may be difference of the molecular structure between EOC10-L and EOC10. We speculate that the degree of LCB is responsible for the flow curve coincident. To prove this speculation, we estimate the degree of LCB by the rheological method.<sup>8</sup> Lai et al.<sup>8</sup> found that for linear PEs prepared using single-site catalysts the Cross equation gives a reasonably good fit to viscosity data. They further showed that the characteristic time,  $\lambda$ , is proportional to the zero shear viscosity:

$$\eta_0(\text{Pa} \cdot \text{s}) = 3.65 \times 10^5 \lambda \text{ (s)} \quad (1)$$



**Figure 6** Flow curves of EOC10-L obtained from steel dies of  $L/D = 20.2 \text{ mm}/1.0 \text{ mm}$  and  $L/D = 9.94 \text{ mm}/0.53 \text{ mm}$  at various temperatures. Filled symbols indicate onset of gross melt fracture.

They noted that the Cross model could also be fitted to the viscosity data for similar polymers into which a small level of LCB had been introduced but that the presence of the branches caused a departure from the above relationship. Therefore, they proposed the use of this departure as an indicator of the level of long chain. They defined the Dow rheology index (DRI) as follows:

$$\text{DRI} = \frac{3.65 \times 10^5 (\lambda/\eta_0) - 1}{10} \quad (2)$$

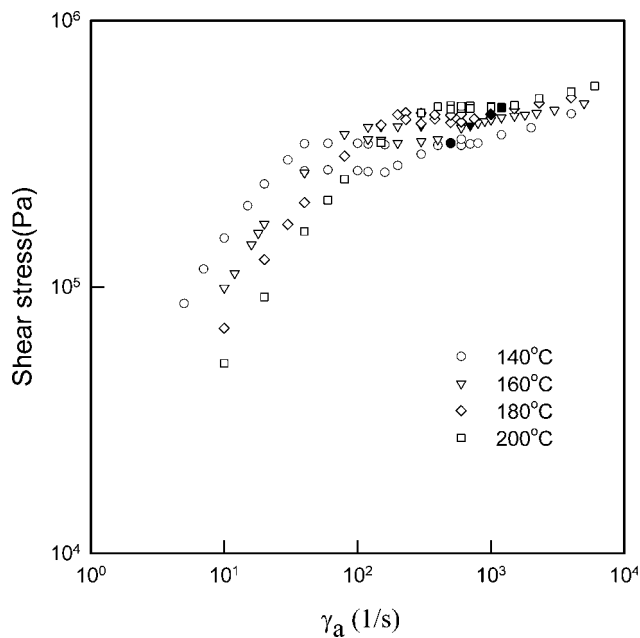
For a linear PE obeying eq. (2), the value of the DRI is zero, and Lai et al.<sup>8</sup> found that the introduction of LCB produces positive values of the DRI, with the value increasing with the level of LCB.

DRI values thus obtained are listed in Table I. According to this estimation, the degree of LCB for EOC10-L is lowest among all EOCs discussed earlier or may be zero, though we do not get the absolute value for LCB (degree of LCB). It is observed that LCB of mLLDPE tends to decrease with the octene comonomer content when the molecular weights of mLLDPEs are similar. More careful looking into the flow curve of EOC13 shows that the shear stress of GMF regime at 170°C is always lower than that obtained at 140°C at all shear rate ranges although they are very close. On the contrary, for EOC4, 7, and 10, the shear stress of the GMF region obtained at 170°C is same with that at 140°C or even slightly higher.

Figure 7 shows the flow curves of E3132 (from Exxon mobile) obtained from a tungsten carbide capillary die of  $D = 1.0 \text{ mm}$  and  $L = 30.0 \text{ mm}$  at various temperatures. The E3132 is a metallocene-catalyzed hexene-ethylene copolymer and is known to contain no LCB.<sup>13</sup> The rheometer for this test is a commercial capillary rheometer (Gottfert Rheo-Tester 2000). The flow curve coincident is not observed for this polymer.

From the earlier discussions, it is evident that the LCB of mLLDPE plays a critical role in the flow curve coincident. It seems that a linear PE without LCB (or very sparsely branched PE) does not show the flow curve coincident.

The influence of LCB on the viscoelastic/mechanical behavior of polymers is remarkable. Therefore, the characterization of LCB is very important. There are several methods detecting the LCB, including SEC-MALL, NMR, and rheological methods.<sup>14</sup> Among these methods, the rheological method is known to be most sensitive for the low level of LCB. Common problem for most rheological methods is that the increase of LCB and increase of polydispersity provide the same rheological effect.<sup>14,15</sup> As a consequence, it is very difficult to distinguish LCB effect from broad molecular weight distribution.



**Figure 7** Flow curves of E3132 obtained from tungsten carbide die with  $L/D = 30 \text{ mm}/1.0 \text{ mm}$  at various temperatures.

In this study, we see the possibility that the flow curve coincident may be used to detect LCBD of mLLDPE. More detailed discussion will be made in our subsequent publication.

### CONCLUSION

In this study, we observe that some mLLDPEs show no-temperature dependency on the rheological properties at the GMF regime. When two different PEs

have the same degree of shot-chain branching, they show the same stress level in the GMF regime regardless of molecular weight and temperature. By capillary extrusion experiments with various dies of different  $L/D$  ratios, it is inferred that the abnormal rheological behavior is originated in the die land, not die entrance or die exit. The mLLDPE having certain degree of LCB shows the abnormal rheological behavior whereas a linear PE without LCB (or very sparsely branched PE) does not. We see the possibility that the abnormal rheological behavior may be used as an indicator of the level of long chain.

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### References

1. Denn, M. M. *Annu Rev Fluid Mech* 2001, 33, 265.
2. Kim, S.; Dealy, J. M. *Polym Eng Sci* 2002, 42, 482.
3. Inn, Y. W.; Fischer, R. J.; Shaw, M. T. *Rheol Acta* 1998, 37, 573.
4. Migler, K. B.; Son, Y.; Qiao, F.; Flynn, K. *J Rheol* 2002, 46, 383.
5. Kim, S.; Dealy, J. M. *Polym Eng Sci* 2002, 42, 495.
6. Lee, H.; Kim, D. H.; Son, Y. *Polymer* 2006, 47, 3929.
7. Wang, W.; Yan, D.; Charpentier, P. A.; Zhu, S.; Hamielec, A. E.; Sayer, B. G. *Macromol Chem Phys* 1998, 199, 2409.
8. Lai, S.; Plumley, T. A.; Butler, T. I.; Knight, G. W.; Kao, C. I. *SPE ANTEC Conf Proc* 1994, 40, 1814.
9. Wang, S. Q.; Drda, P. A.; Inn, Y. W. *J Rheol* 1996, 40, 875.
10. Kalika, D. S.; Denn, M. M. *J Rheol* 1987, 3, 815.
11. Groisman, A.; Steinberg, V. V. *Nature* 2000, 405, 53.
12. Patham, B.; Jayaramana, K. *J Rheol* 2005, 49, 989.
13. Doerpinghaus, P. J.; Baird, D. G. *Rheol Acta* 2003, 42, 544.
14. Piel, C.; Stadler, F. J.; Kaschta, J.; Rulhoff, S.; Muenstedt, H.; Kaminsky, W. *Macromol Chem Phys* 2006, 207, 26.
15. Ye, Z.; Alobaidi, F.; Zhu, S.; Subramanian, R. *Macromol Chem Phys* 2005, 206, 2096.