Effects of Long Chain Branching on Melt Fractures in Capillary Extrusion of Metallocene-Catalyzed Linear Low-Density Polyethylene Melts

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ABSTRACT: To investigate the effect of long chain branching (LCB) on melt fractures of metallocene-catalyzed linear low-density polyethylene (mLLDPE), we prepared a series of sparsely long-chain-branched mLLDPEs with well-defined degrees of LCB. Gross melt fractures were observed to decrease as the degree of LCB increases. This is in accordance with a prediction based on the observation that LCB enhances chain entanglement and consequently increases the melt strength of a polymer. However, sharkskin melt fracture (SMF) was observed to be more severe with the degree of LCB. There have been debates over the effect of LCB on SMF. According to a well-known mechanism of SMF, SMF is expected to decrease with the degree of LCB. Therefore, the majority of research groups believe that SMF decreases with the degree of LCB. This study clearly shows that the SMF becomes more severe with an increase of the degree of LCB and suggests another possible mechanism for the SMF. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: long chain branch; metallocene LLDPE; gross melt fracture; sharkskin melt fracture

INTRODUCTION

Metallocene polyethylene has attracted both academic and industrial interest because metallocene technology can produce polyethylene with tailored molecular structures. Metallocene linear low-density polyethylenes (mLLDPE), ethylene/α-olefin copolymers, have narrower molecular weight distributions (MWD) and more uniform comonomer distributions than the conventional Ziegler-Natta LLDPEs (ZN-LLDPE), whereas α-olefin in the ZN-LLDPE polymerization is preferably copolymerized in low molecular weight (MW) chains. The uniform distribution of the comonomer by the metallocene catalyst makes it possible to synthesize mLLDPEs with lower crystallinity and density. Thus, mLLDPEs are more transparent and elastomeric, which are beneficial properties for film applications and impact modifiers.

Metallocene LLDPEs were first commercialized by ExxonMobil in 1991 followed by the DOW Chemical Company in 1992.[1] Because these two companies adopt different catalyst systems, the produced mLLDPEs have different chain architectures. It is known that ExxonMobil's mLLDPE contains no long chain branches (LCBs) due to the nature of the ExxonMobil's Exxpol™ technology, whereas the Dow Chemical Company's mLLDPE contains a very small number of LCBs (less than two LCBs per 10^4 main chain carbons) due to the characteristics of the constrained geometry catalyst system.[1] Rheological behavior and many end-use properties are influenced by not only MW and MWD but also the existence of LCB. Therefore, considerable effort has been dedicated to controlling LCB in mLLDPE polymerization and detecting the degree of LCB. However, conventional analytical methods to detect LCB based on solution properties such as C^{13}-NMR and size exclusion chromatography (SEC) coupled with multiangle laser light scattering and viscosity detector (measuring the intrinsic viscosity, $[\eta]$) are very difficult for very sparsely long-chain-branched mLLDPEs. Many studies have attempted to correlate the rheological properties to the existence of LCB in polyethylene (PE), because rheological properties are very sensitive to small amounts of LCB based on previous studies. The findings described below reflect the general consensus on effect of LCB on the mLLDPEs.

The LCB increases the zero-shear viscosity (viscosity at Newtonian region).[2–4] This is due to the fact that LCB enhances chain entanglement. LCB also reduces hydrodynamic volume. These two factors have opposing effects on a polymer's rheological properties. At low shear rates, long-chain-branched polymers have higher viscosities than linear polymers due to enhanced chain entanglement. However, at high shear rate, polymer chains are disentangled and the LCB polymers have lower viscosities due to smaller hydrodynamic volume than linear polymers. Consequently, LCB polymers show a sharp transition from the Newtonian region to a power law region.

Raju et al.[2] established the following relationship between number average MW and zero-shear viscosity at 190°C for linear polyethylenes (PEs). The degree of LCB of an unknown PE can be estimated qualitatively by the extent of deviation from eq. (1).

$$\eta_o = 2.78 \times 10^{-15} M_n^{3.6} \tag{1}$$

It has been reported that the presence of LCB has a more pronounced effect on extensional rheology. The presence of LCB leads to significant strain-hardening behavior in mLLDPE resins. It was also reported that for the cases above, a Trouton ratio of $3\eta_o$, steady-state extensional viscosity increases as the degree of branching and polydispersity index increases.[5,6]

LCB PEs show higher activation energies of flow, E_a, than linear PE. It was observed that E_a increases from 6.5 kcal/mol °K for high density polyethylene (HDPE) to 14 kcal/mol °K for low density polyethylene (LDPE).[7–10]

One of the most difficult tasks regarding LCB PE is to quantify the degree of LCB with sufficient accuracy. To correlate the degree of LCB to rheological properties and to quantify the degree of LCB from rheological data, it is necessary to prepare a series of model polymers that have known degrees of LCB. To date, there have been many studies in which the rheological properties of a linear PE and a long-chain-branched PE are compared and investigated. However, there have been few studies on rheological properties of long-chain-branched PEs having various degrees of LCB.

There have been a few studies on the melt fracture behavior of sparsely long-chain-branched LLDPE.[11–20] Doerpinghaus and Baird investigated the melt fracture behavior of polyethylenes having various molecular characteristics.[11] When comparing the flow behaviors of two different mLLDPEs (one has sparsely long-chain-branched architecture while the other does not), they found that the spurt flow does not appear in the sparsely long-chain-branched mLLDPE. Onset stress of sharkskin melt fracture (SMF) for sparsely long-chain-branched

mLLDPE (0.17 MPa) is almost similar with that (0.16 MPa) of mLLDPE without any LCB, but the degree of SMF and gross melt fracture (GMF) is more severe in the branched mLLDPE.

Delgadillo-Velazquez and Hatzikiriakos investigated the processing behavior of LLDPE/LDPE blends.[12] They found that the stick-slip flow is greatly influenced by small amount of LDPE in LLDPE/LDPE blends. Amounts as low as 1 wt % LDPE reduced significantly the amplitude of pressure oscillations. However, the onset of sharkskin and GMF was not much affected by the addition of LDPE into LLDPE. Kim et al.[13] investigated the melt fracture behavior of mLLDPE/LDPE blends and obtained similar results on the spurt flow, i.e., small amount of LCB from LDPE influences significantly the amplitude of pressure oscillations.

Wang et al.[14] synthesized mLLDPEs that contained various degrees of LCBs and investigated their rheological properties. Their observations were consistent with previous findings except for the effect of LCB on SMF. According to a well-known mechanism for SMF,[15] SMF is expected to be delayed to high shear stress in accordance with the degree of LCB. This stems from increased extensional strength due to enhanced entanglement by the LCB. The Dow Chemical Company claimed that their unique catalyst system (constrained geometry catalyst) generates sparely long-chain-branched mLLDPE, and its melt fracture resistance is improved due to the LCB of their mLLDPE.[1]

There has been ongoing debate over the effect of LCB on SMF. Some studies have reported that LCB PE has higher resistance to SMF than linear PE,[16,17] whereas other studies reported the opposite results.[18–20] These studies did not investigate a set of sparsely long-chain-branched PEs but only compared the melt fractures of linear PE and one LCB PE.

In this study, we used two mLLDPEs (ethylene/butene copolymer) that have similar polydispersity and density (i.e., similar butene comonomer content). The difference between these mLLDPEs is the existence of LCB. One has a very small amount of LCB, whereas the other has no LCB. Several different mixtures were prepared and a series of mLLDPEs with various degrees of LCB was thus prepared. With these samples, we investigated the rheological characteristics of sparsely branched mLLDPE with an emphasis on the melt fractures including SMF and GMF. As most studies on the effects of LCB on rheological properties have been limited to low shear rate or dynamic rheology, the present investigation of capillary extrusion rheology is expected to be valuable.

EXPERIMENTAL

Materials

Two mLLDPEs were investigated in this study. mLLDPE manufactured by the Dow Chemical

TABLE I
Characteristics of Polymers Used in This Study

Material code	Commercial names	Suppliers	M_n[a] (g/mol) and PDI[b]	MFI[c] (g/10 min)	Density (g/cm³)
mLLDPE-LCB	ENR7340	Dow Chemicals	74,000 (2.3)	5.0	0.861
mLLDPE-no-LCB	DF605	Mitsui Chemicals	173,000 (2.35)	0.5	0.875

[a] Number average molecular weight.
[b] Poly disperse index.
[c] Melt flow index.

Company (trade name: ENR7340) is a butene copolymer and is believed to contain a small amount of LCB due to the catalytic nature of the Dow Chemical's product. Its rheological properties show typical long chain branched characteristics, i.e., strain hardening. The other mLLDPE manufactured by Mitsui Chemical (trade name: Mitsui DF605) is also butene copolymer, and is believed to contain no LCB. The relevant physical and molecular properties of these resins are tabulated in Table I.

Apparatus and method

The ENR7340/DF605 blends with various compositions were prepared by melt mixing in an internal batch mixer (Haake PolyLab QC Mixer 3000). The mixing was carried out at a rotor speed of 100 rpm with 40 g of polymer. Mixing temperature and time were 180°C and 10 min, respectively. After mixing operation, samples were removed from the batch mixer and quenched in ice water. Then, the blended samples were dried and crushed into small pieces.

Capillary extrusion experiments of two mLLDPEs and their blends were carried out using a piston-driven homemade capillary rheometer at 140–170°C. The capillary die used was 1.0 mm in diameter and 20.2 mm in length with 180° entrance angle. Entrance pressure correction was not made because the SMF begins at relatively low shear rate and L/D ratio of the die is large. Details of the experiment and apparatus have been described elsewhere.[21]

The existence of LCB for the two mLLDPEs was estimated by the strain hardening behavior in transient extensional rheology. Measurement of time-dependent elongational viscosity ($\eta^+_e(t)$) was carried out at 140°C by an extensional viscosity fixture in the advanced rheometric expansion system (ARES). Elongational rates for the measurement were varied from 0.05 to 4.0/s, respectively. The detailed features of the equipment have been reported elsewhere.[22]

The blended samples were compressed at 180°C to a sheet with thickness about 1 mm and cut into 25 mm disks for rheological measurements. All the rheological measurements were carried out at various temperatures on a strain-controlled rheometer (Physica MCR301 from Anton Paar) with a parallel plate fixture. The gap for all measurements were set to 1 mm. Oscillatory shear measurements were made at 30% strain, which was within the linear regime of all samples.

Fracture surfaces of the blend were prepared in liquid nitrogen. To observe any phase separation of mLLDPE-LCB and mLLDPE-no-LCB, morphology of fractured surface was examined with a scanning electron microscope (SEM, a JEOL JSM-6335F).

RESULTS AND DISCUSSION

The time-dependent elongational viscosities of two mLLDPEs are plotted in Figure 1. Mitsui DF605, which is known to contain no LCB, does not exhibit any indication of strain hardening. Thus, we denote DF605 as an mLLDPE-no-LCB. In contrast, DOW ENR7340, which is known to be slightly long-chain branched, exhibits a completely different time dependent elongational viscosity. It shows strain hardening at elongational rates above 0.25 s⁻¹. Thus, we denote ENR7340 as mLLDPE-LCB. One problem in correlating the strain hardening behavior to the existence of LCB is that very high molecular mass components can cause significant strain hardening even in a linear PE.[6] Both samples investigated in this study have similar MWD and relatively low
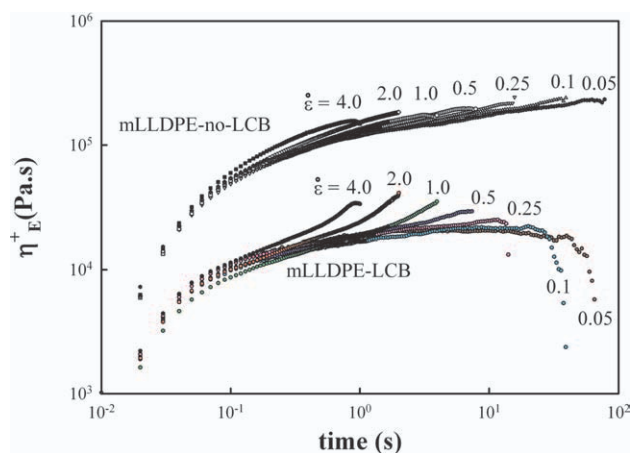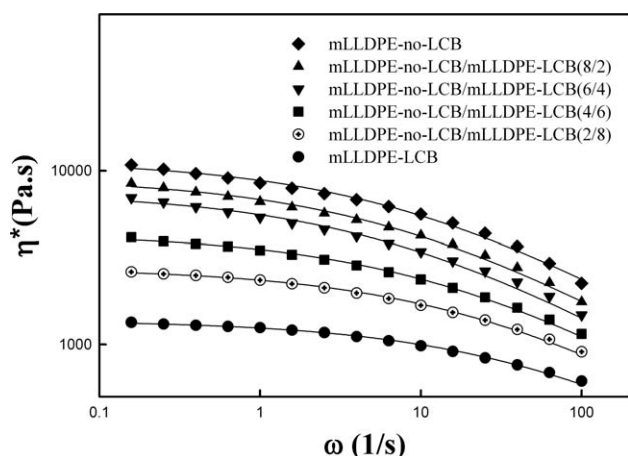

Figure 1 Time-dependant extensional viscosity of mLLDPEs used in this study. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

Figure 2 Complex viscosities (η^*) of mLLDPE-LCB, mLLDPE-no-LCB, and their blends at 230°C.

MWD. Thus, strain hardening behavior will represent the existence of LCB.

In this study, we prepared a series of mLLDPEs with various degrees of LCB by mixing the mLLDPE-no-LCB and the mLLDPE-LCB in various compositions. Control over the degree of LCB is extremely difficult in metallocene LLDPE polymerization and even the amount of LCB evaluated by the conventional analytical methods based on solution properties is not reliable when the degree of LCB is very low (typically below $1/10^4$ carbons.[20] On the contrary, our method can provide samples with exact orders of LCB degree. However, if mLLDPE-no-LCB and the mLLDPE-LCB investigated in this study are immiscible, the method preparing the series of mLLDPEs with various degrees of LCB to investigate effect of LCB on the melt fractures is useless. Thus, we investigated the miscibility of mLLDPE-no-LCB and the mLLDPE-LCB.
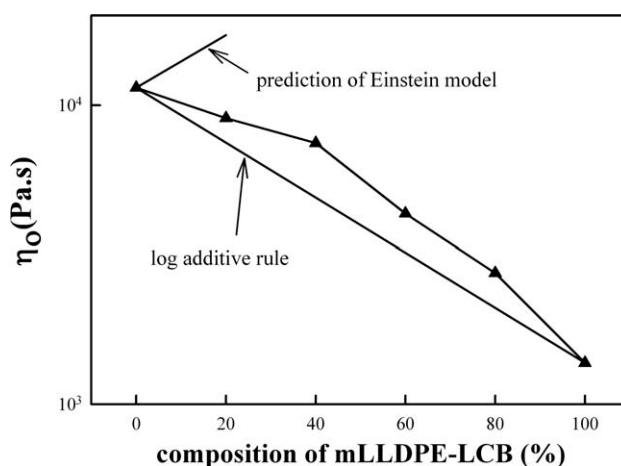
To assess the miscibility, we performed rheology tests of mLLDPE-LCB, mLLDPE-no-LCB, and their blends. Figure 2 shows complex viscosity, $\eta^*(\omega)$ of mLLDPE-LCB, mLLDPE-no-LCB, and their blends as a function of angular velocity, ω. In all ω ranges, the viscosities of the blends lie between the viscosities of the two pure components, as shown in Figure 2. According to the emulsion model based on the assumption of a Newtonian fluid, the addition of a less viscous component (here, mLLDPE-LCB) to a more viscous component leads to increased viscosity of their blends.[23] If the two polymers in this study are immiscible, blends containing a small amount of mLLDPE-LCB would show higher viscosity than that of mLLDPE-no-LCB at low ω.

The complex viscosity data were fitted to a cross model and the zero shear viscosities, η_0, were obtained. In Figure 3, the zero shear viscosity as a function of the composition is presented, together with the Einstein model, the upper limit for emul-

sion systems. The plot shows a weak positive deviation in a log additive rule. These results support that the two polymers are miscible in the melt state. Another simple way to assess the miscibility of polymer blends is to check the validity of the time–temperature superposition principle. Time–temperature superposition was applied to mLLDPE-LCB, mLLDPE-no-LCB, and their blends. The master curves (G' and G'' versus $\alpha_T\omega$) were prepared according to this principle and shown in Figure 4. As seen in Figure 4, G' and G'' obtained at three different temperatures fall into a single master curve implying that the mLLDPE-LCB and mLLDPE-no-LCB display a single phase at entire range of compositions.

Figure 5 shows SEM photographs of fractured surface of mLLDPE-no-LCB/mLLDPE-LCB(8/2) at a liquid nitrogen. Any indication of phase-separated structures is seen in the SEM photos. Other compositions also show similar type of surface structure, and this suggests that the mLLDPE-LCB and mLLDPE-no-LCB display a single phase at entire range of compositions.

As viscosities of two components (mLLDPE-LCB and mLLDPE-no-LCB) show one-order magnitude difference as shown in Figure 2, one can raise a question that the viscosity mismatch can cause the migration of low MW component (mLLDPE-LCB) to the surface of the extrudates at a high throughput and the migration can affect behaviors of the melt factures. To clarify this issue, we measured MW of mLLDPE-LCB/mLLDPE-no-LCB blends for a surface of extrudates and entire extrudates. A sharp razor blade was used to take small pieces from surface of the extrudates. If the migration of low MW component (mLLDPE-LCB) to the surface of the extrudates is serious, the MW of a sample taken from the surface of the extrudates at the highest throughput and the MW of entire extrudates would be different.

Figure 3 Zero-shear viscosity of mLLDPE-LCB, mLLDPE-no-LCB, and their blends.
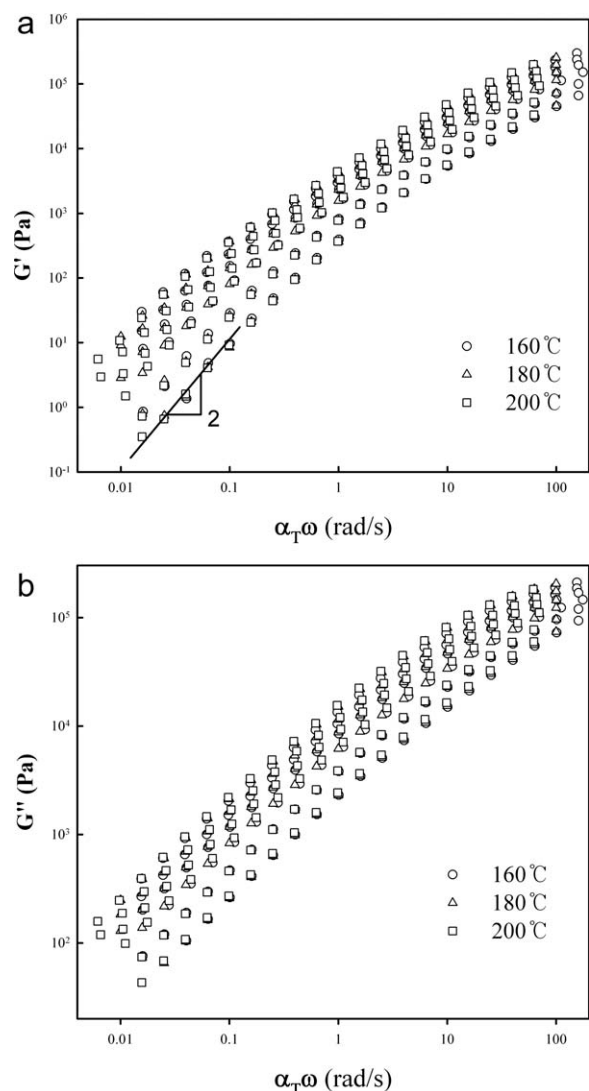
Figure 4 (a) Storage modulus (G') and (b) loss modulus (G'') versus angular velocity (ω). G' and G'' obtained at three different temperatures are shifted to a reference temperature (180°C) according to the time–temperature superposition principle. From the top, mLLDPE-no-LCB, mLLDPE-no-LCB/ mLLDPE-LCB(8/2), mLLDPE-no-LCB/ mLLDPE-LCB(6/4), mLLDPE-no-LCB/ mLLDPE-LCB(4/6), mLLDPE-no-LCB/ mLLDPE-LCB(2/8), and mLLDPE-LCB, respectively.

We measured the MW for several blends extruded at the highest extrusion rate and temperatures of 140 and 170°C. The measured MWs do not show any meaningful differences.

As mLLDPE-LCB and mLLDPE-no-LCB are observed to be miscible and do not show any segregation due to the large viscosity difference, it can be verified that the LCBs are distributed homogeneously in the mLLDPE-no-LCB/mLLDPE-LCB blends. It is, thus, meaningful to investigate the effect of LCB on the melt fracture of extrudates prepared in this study.

Figure 6 shows shear rate–shear stress curves obtained from a capillary rheometer at 140 and 170°C. mLLDPE-no-LCB shows a typical flow curve for a linear polyethylene. When the flow rate is low, the extrudate is smooth and clean. As the flow rate increases, a defect called sharkskin or surface melt fracture (SMF) appears at a shear stress of about 0.32 MPa. As the flow rate increases further, a "slip-stick" or "spurt" regime is observed at the flow rate between SMF and GMF, which is characterized by pressure oscillations and alternating regions of sharkskinned and smooth extrudates. At the highest flow rate, GMF is observed. On the contrary, the flow curve of mLLDPE-LCB does not show a spurt flow, and shear stress at the GMF regime is independent of the melt temperature, as can be seen in Figure 6(g), i.e., shear stresses obtained at 140 and 170°C fall onto the same curve at the GMF regime.
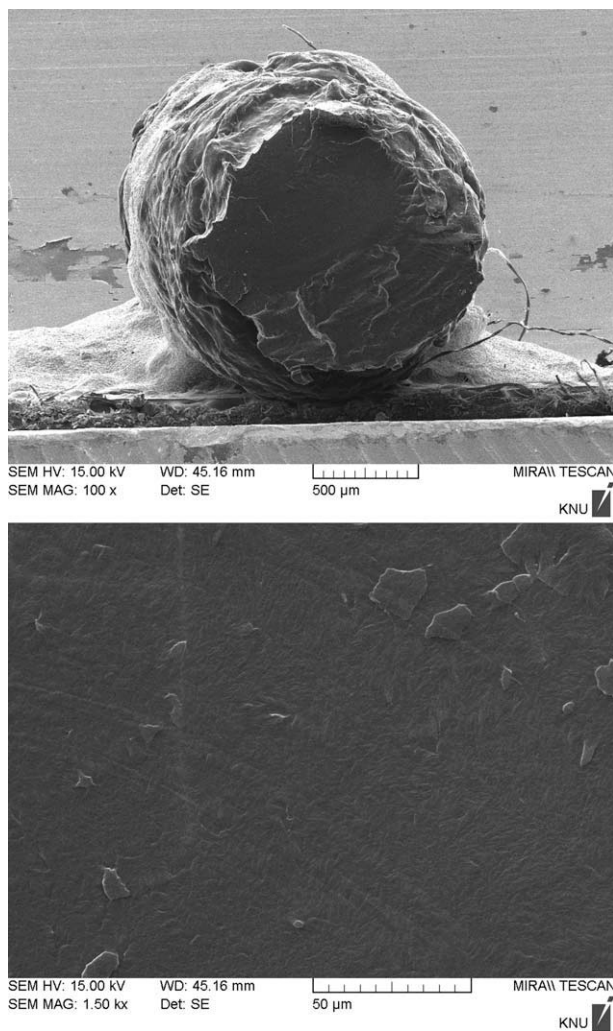
Figure 5 SEM photographs of fractured surface of mLLDPE-no-LCB/ mLLDPE-LCB(8/2). Bottom one shows 10 times magnified photos taken near surface of the extrudates.
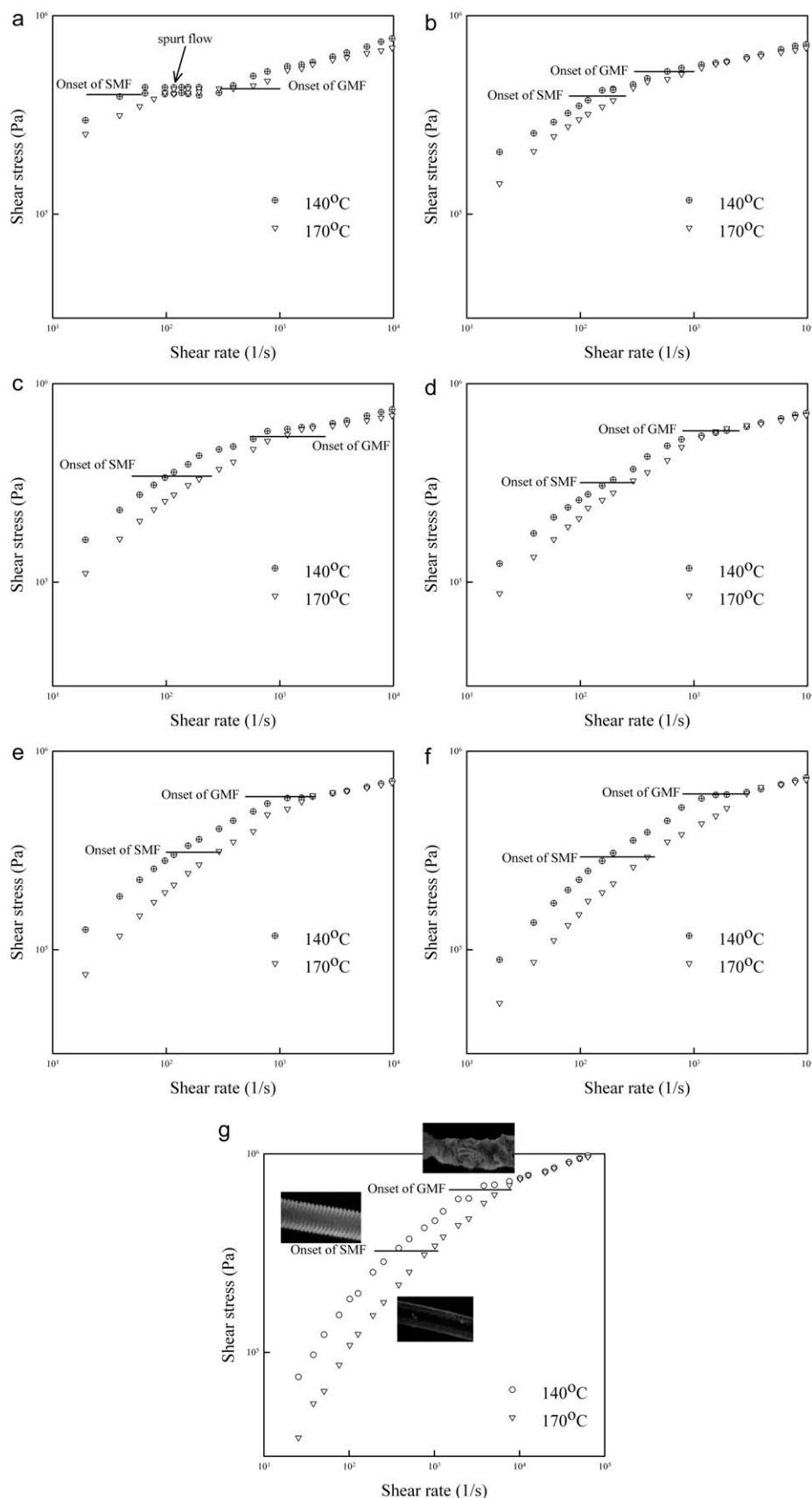
Figure 6 Flow curves of mLLDPE-LCB, mLLDPE-no-LCB, and their blends at various compositions. (a) mLLDPE-no-LCB, (b) mLLDPE-no-LCB/mLLDPE-LCB(8/2), (c) mLLDPE-no-LCB/mLLDPE-LCB(6/4), (d) mLLDPE-no-LCB/mLLDPE-LCB(5/5), (e) mLLDPE-no-LCB/mLLDPE-LCB(4/6), (f) mLLDPE-no-LCB/mLLDPE-LCB(2/8), and (g) mLLDPE-LCB.
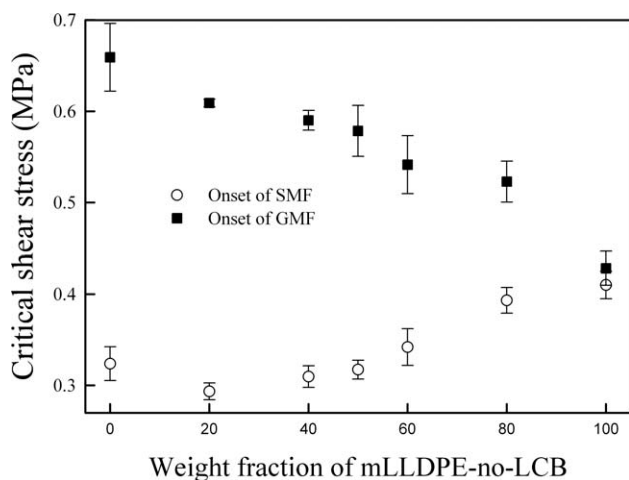
Figure 7 Onset of SMF and GMF as a function of weight fraction of mLLDPE-no-LCB.

Recently, we have been conducting capillary extrusion experiments with various metallocene catalyzed polyethylenes.[13,21,24,25] We observed very interesting rheological behaviors for these materials. The flow curves (shear stress versus shear rate relationship) at the GMF regime show temperature independency for sparsely long-chain-branched mLLDPEs; i.e., the nominal viscosity at the GMF regime does not show any temperature dependency. In addition, a long-chain-branched mLLDPE does not show spurt or stick-slip flow, which was frequently observed in linear PE.[26,27] Thus, we speculate that these two unusual behaviors are indicators of sparsely long-chain-branched LLDPE. However, our recent study[13] showed that blends consisting of LDPE (many LCB) and mLLDPE (no LCB grade) show temperature-dependent viscosity at the GMF regime. The amount of LDPE in the blends investigated is very low, and thus, the degree of LCB in the blends is comparable to that of sparsely long chain branched mLLDPE. The discrepancy between the sparsely LCB mLLDPE and the LDPE/mLLDPE blends investigated in our previous study is likely due to a heterogeneous LCB distribution and the immiscibility between mLLDPE and LDPE.

The spurt flow observed in the mLLDPE-no-LCB disappears with the addition of mLLDPE-LCB. The blends that contain mLLDPE-LCB of more than 20 wt % do not show any spurt flow. The mLLDPE-LCB/mLLDPE-no-LCB(2/8) blend shows only one data point that exhibits an oscillating pressure profile. It is also noteworthy that the shear stress at the GMF regime is independent of the melt temperature for the blends containing more than 50 wt % of mLLDPE-LCB. Again, it is likely that these two abnormal behaviors (the absence of spurt flow and temperature-independent viscosity at the GMF regime) are very relevant to the existence of small amounts of LCB.

Finally, we investigated the effect of the LCB on melt fractures. Figure 7 shows critical shear stresses for the onsets of SMF the GMF as a function of the amount of mLLDPE-LCB in the blends. Critical shear stresses for the onsets of SMF the GMF are also summarized in Table II. It is observed that the critical shear stress for the onset of GMF increases with the degree of LCB. It is well known that extensional flow is dominant in the entrance region of a capillary rheometer due to accelerating flow in the contraction geometry (from the reservoir to the die land). When the extensional stress in the entrance region exceeds the melt strength of the polymer, the polymer melts actually fractures, causing GMF. It has been reported that the melt strength is increased as the degree of LCB increases due to increased chain entanglement.[6] Therefore, it is understandable that the GMF is delayed by an increase of the LCB degree. This is consistent with observations by Kim and Dealy.[28,29] On the contrary, the critical shear stress for the onset of SMF decreases with the degree of LCB. This is somewhat unexpected because SMF is also relevant to the melt strength of a polymer. SMF originates from the die exit where a reorganization of the velocity profile takes place (from zero in the die land to a "plug flow" in extrudates). This sudden increase of the velocity of the polymer melts

TABLE II
Critical Stress of SMF and GMF for the Blends Investigated in This Study

Materials	Critical stress for SMF (MPa)	Critical stress for GMF (MPa)
mLLDPE-LCB	0.33	0.66
mLLDPE-LCB/mLLDPE-no-LCP(8/2)	0.29	0.61
mLLDPE-LCB/mLLDPE-no-LCP(6/4)	0.31	0.59
mLLDPE-LCB/mLLDPE-no-LCP(5/5)	0.32	0.58
mLLDPE-LCB/mLLDPE-no-LCP(4/6)	0.34	0.54
mLLDPE-LCB/mLLDPE-no-LCP(2/8)	0.39	0.52
mLLDPE-no-LCP	0.41	0.43

induces high elongational flow at the surface of the extrudate. If the elongational stress exceeds the melt strength of the polymer, the surface of the extrudate fractures, causing SMF.

As both SMF and GMF are related to the melt strength, the effect of LCB on the two melt fractures was expected to be the same. There have been a few studies on the effect of LCB on SMF. To our knowledge, no study, however, has investigated SMF with samples having various degrees of LCB, except for a work by Wang et al.[14] The other studies only compared SMF behaviors for a linear PE and a one LCB PE. Furthermore, there is some controversy over the findings of existing works. Some studies reported that LCB delays SMF[16,17] whereas others did not observe this trend.[18–20] Wang et al. synthesized sparsely LCB PE with various degrees of LCB and investigated the SMF behaviors. They also argued that the SMF becomes severe as the degree of LCB increases. The degree of LCB for the PEs used in their study ranged from 0.22$\sim$ 0.44 per 10^4 carbons which is under the limit of the LCB degree that can be detected by SEC coupled with light scattering (typically below $1/10^4$ carbons.[20] Moreover, the effect of the degree of LCB on the onset of SMF was not as pronounced (σ_c for the onset of SMF = 140, 148, 138, 116, 107 MPa for LCB degree = 0.22, 0.35, 0.35, 0.40, 0.44 per 10^4 carbons). In our study, the effect of LCB on SMF is distinct.

At present, the reason for the increase in severity of SMF with the degree of LCB is not clear. Other physics may be involved in the mechanism of SMF rather than the extensional stress induced fracture mechanism proposed by Cogswell.[15] This study has, nevertheless, clearly shown that sparsely LCB increases the severity of SMF.

CONCLUSIONS

From capillary extrusion experiments with blends composed of sparsely long-chain-branched mLLDPE and mLLDPE without any LCBs, it is revealed that the existence of LCB has a critical effect on the stick-slip flow behavior and flow behavior at the GMF region. Stick-slip flow was not observed in the blends containing sparsely long-chain-branched mLLDPE. It was observed that GMF becomes weak as the degree of LCB increases. However, SMF becomes more severe with an increase of the degree of LCB, and this result is not in accordance with the majority of previous studies. Thus, we suggested that there may be another mechanism underlying SMF.

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