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Rheological properties of long chain branched polyethylene melts at high shear rate

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ABSTRACT

Capillary extrusion experiments involving a number of polyethylenes with emphasis on assessing the effect of long chain branching (LCB) are performed. None of the metallocene catalyzed linear low density polyethylenes (mLLDPE) produced by Dow Chemicals, which are believed to have some level of LCB, show temperature dependence on the viscosity at the gross melt fracture regime. Furthermore, these materials do not show spurt or stick-slip flow, in contrast with most linear polyethylenes. LDPE and blends of LDPE with LLDPE having LCB also show the absence of stick-slip flow, but show temperature dependence on the viscosity. From these observations, we conclude that the stick-slip flow is very sensitive to the existence of LCB.

1. Introduction

In a polyethylene extrusion process, defects such as surface irregularities and melt fractures are not avoidable at high extrusion rates [1,2]. So far, many studies have been performed on this subject [3–10]. However, most studies focused on the rheological behaviors at relatively low shear rate regimes. Recently, we have been conducting capillary extrusion experiments with various metallocene catalyzed polyethylenes [8,10]. We observed very interesting rheological behaviors for these materials. In recent publications, we reported that the flow curves (shear stress vs. shear rate relationship) in the GMF regime for most metallocene catalyzed low density linear polyethylenes (mLLDPE) produced by Dow Chemicals do not show temperature or molecular weight dependency. For all of Dow Chemical's mLLDPEs, except one grade, the shear stress at the GMF regime maintained the same value even when the melting temperature was increased. Hereafter, we denote this abnormal rheological behavior as a flow curve coincidence. More interestingly, the shear stress at the GMF regime shows no molecular weight dependency when two PEs have similar octene comonomer content. It was revealed that the mLLDPEs produced by Dow Chemicals have a small degree of long chain branching (LCB) [10]. By rheological analysis, it was found that the mLLDPE that does not show the flow curve coincidence has the lowest degree of LCB. We also investigated the flow behaviors of a mLLDPE produced by ExxonMobile (poly(ethylene-*r*-hexene), trade name: Exact 3132), which is known to have no LCB [5]. This polymer shows no flow curve coincidence. From these observations, we speculated that there is a significant relevance between the LCB and the flow curve coincidence, which may be used to detect the degree of LCB in mLLDPEs.

To extend this concept, in the present work we perform capillary extrusion experiments with chromium catalyzed HDPE (which is believed to have very small amounts of LCB), a LDPE that has a larger amount of LCB, and two mLLDPEs (one has small amounts of LCB and the other has no LCB).

2. Experimental

2.1. Materials

Two metallocene-catalyzed linear low-density polyethylenes (mLLDPE), LDPE and HDPE, were investigated in this study. mLLDPE manufactured by Dow Chemicals (trade name: ENR7340) is a butene copolymer, and is believed to have a small degree of LCB due to the catalytic nature of the technology employed by Dow Chemical. mLLDPE manufactured by ExxonMobile (trade name: Exceed 3518) is a hexene copolymer, and is believed to contain no LCB due to the nature of ExxonMobile's Exxpol™ technology. HDPE is produced by a chromium catalyst used in the Phillips process. According to the manufacturer, this resin has a small portion of very high molecular weight (thus a very high molecular weight

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distribution), and its rheological properties show typical long chain branched characteristics, i.e. strain hardening and elevated zero shear viscosity. The relevant physical and molecular properties of these resins are tabulated in Table 1.

2.2. Apparatus and method

Capillary extrusion experiments with HDPE, LDPE, and two mLLDPE/LDPE blends were carried out using a piston-driven homemade capillary rheometer. The blends were prepared by melt mixing in a laboratory-scale twin screw extruder. The blend code, mLLDPE-C6/LDPE(95/5), indicates that the blend is composed of mLLDPE-C6 and LDPE with 95–5 wt% ratio. Temperature for the extrusion experiments was varied from 140 °C to 200 °C. The capillary die used was 0.54 mm in diameter and 9.3 mm in length. Details of the experiment and apparatus have been described elsewhere [8].

3. Results and discussions

Fig. 1 shows the flow curve (wall stress vs. apparent shear rate) of mLLDPE-C4-LCB. The filled symbols shown in Fig. 1 indicate the onset of GMF. The flow curve and melt fracture behavior of mLLDPE-C4-LCB are similar to those of Dow EG8100 (metallocene catalyzed poly(ethylene-*co*-octene) with 9.5 mol% octene), which has been widely investigated [8,9,12–14]. At low shear rate, the extrudate is smooth and transparent. As the shear rate is increased, visible sharkskin begins to appear on the extrudate surface. 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; otherwise referred as flow curve coincidence.

In previous studies [7,8,10], we investigated several mLLDPEs produced by Dow Chemicals and ExxonMobile. These two companies use different catalyst technologies, and as a consequence, they produce different skeleton structured mLLDPEs. Dow mLLDPEs are known to contain a small amount of LCBs [9,12,13] whereas ExxonMobile mLLDPEs do not (except a few grades) [5,15]. Flow curve coincidence was observed only in mLLDPEs having LCB (i.e. Dow mLLDPEs) whereas ExxonMobile mLLDPE does not show the flow curve coincidence.

The mLLDPE-C4-LCB investigated in this study is also synthesized by the same metallocene catalyst as used for octene-based mLLDPEs produced in Dow Chemicals. Therefore, it is most likely that the mLLDPE-C4-LCB has some degree of LCB. Rheological measurements such as the Dow rheology index and strain hardening behavior in transient extensional rheology also suggest that this resin contains some degree of LCB whereas mLLDPE-C6 (from ExxonMobile) does not. The flow curve coincidence is observed not only for the mLLDPE synthesized with octene comonomer but also for the mLLDPE synthesized with butene comonomer when the mLLDPE has LCB.

Table 1
Characteristics of polymers used in this study.

Code	Materials	Trade name	Supplier	PDI[a]	MFI[b] (dg/min)	LCB[c]
mLLDPE-C4-LCB	mLLDPE	ENR7340	Dow Chemicals	2.0	5.0	O
mLLDPE-C6	mLLDPE	Exceed3518	ExxonMobile	2.0	3.5	X
LDPE	LDPE	BF315	LG Chemicals	~8	1.0	O
Cr-HDPE	HDPE	TR147	Daerim Chemicals	>15	0.8	?

[a] Poly disperse index.

[b] Melt flow index.

[c] Existence of long chain branching of two mLLDPE was estimated by a rheological method suggested in the literature [11].

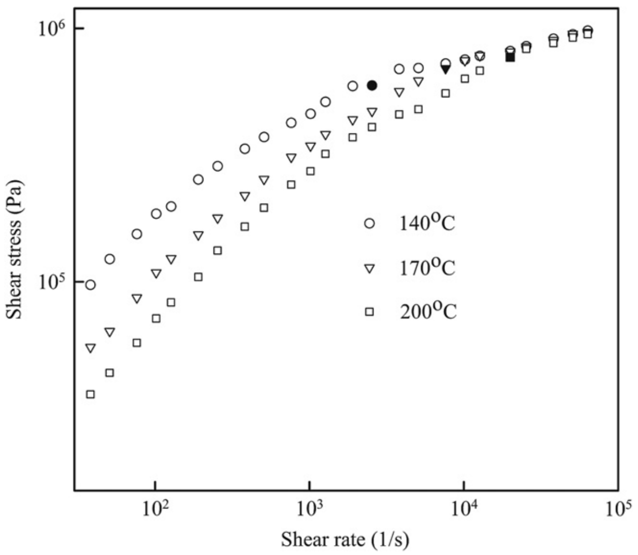

Fig. 1. Flow curves of mLLDPE-C4-LCB obtained at various temperatures. Filled symbols indicate onset of GMF.

A stick-slip or spurt flow regime accompanied by a typical flow curve discontinuity is not observed for mLLDPE-C4-LCB, unlike many linear PEs [1,2]. Flow curves of most linear polyethylenes reported in the literature show stick-slip behaviors. A few exceptions are the flow curves of Dow mLLDPEs and ExxonMobile Exact™ 0201, which also contains some level of LCB [5]. Because Dow mLLDPEs show flow curve coincidence and the absence of stick-slip flow, it is inferred that these two observations are relevant to the existence of LCB.

To investigate this issue in more detail, capillary extrusion experiments with LDPE, mLLDPE-C6, and their blends were carried out. Because LDPE contains many LCBs, these materials are expected to show flow curve coincidence and the absence of

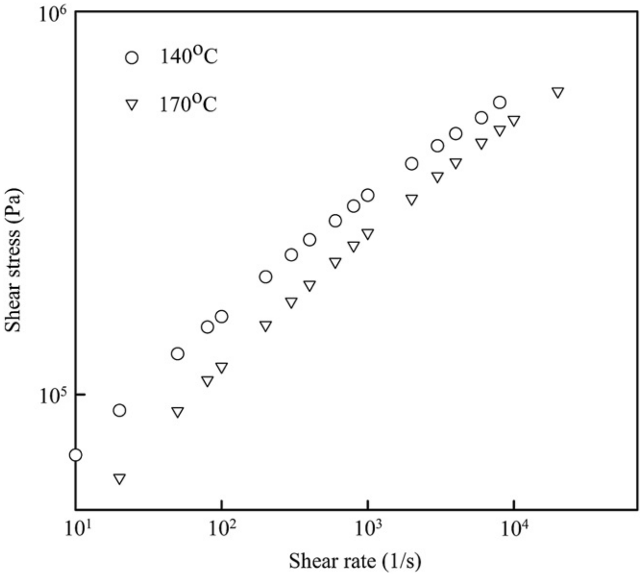

Fig. 2. Flow curves of LDPE obtained at two different temperatures.

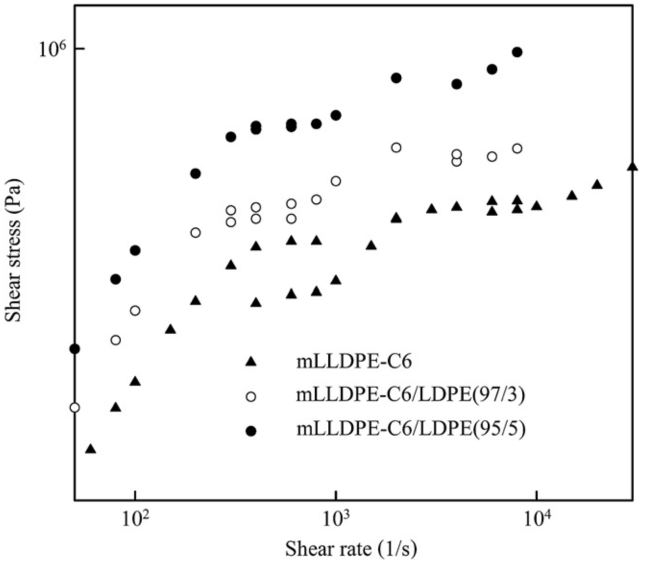

Fig. 3. Flow curves of mLLDPE-C6, mLLDPE-C6/LDPE(97/3) and mLLDPE-C6/LDPE(95/5) obtained at 140 °C. Shear stresses of mLLDPE-C6/LDPE(97/3) and mLLDPE-C6/LDPE(95/5) are shifted vertically by a factor of 1.3 and 1.7, respectively, to view the stick-slip region clearly. Shear stresses of mLLDPE-C6, mLLDPE-C6/LDPE(97/3), and mLLDPE-C6/LDPE(95/5) below the stick-slip region are almost identical.

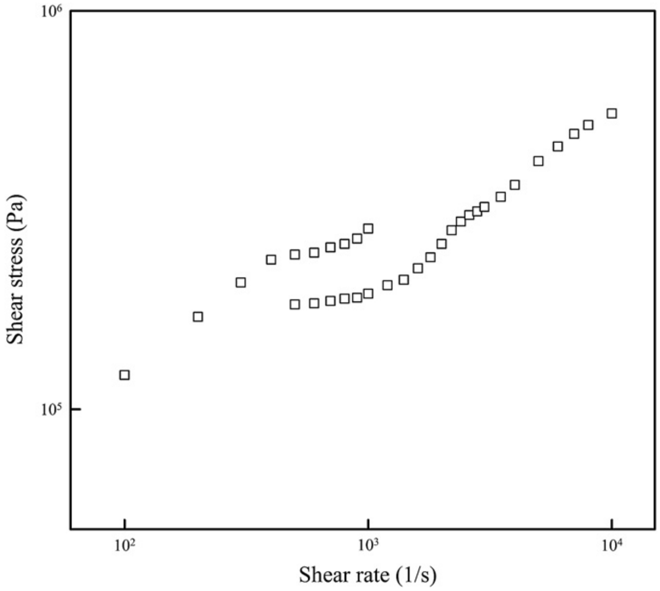

Fig. 4. Flow curve of Cr-HDPE obtained from a tungsten carbide die of $D = 0.76$ mm and $L = 25.6$ mm die at 170 °C.

stick-slip flow because these two phenomena are expected to be relevant to LCB.

Figs. 2 and 3 show the flow curves of LDPE, mLLDPE-C6, and blends of these polyethylenes. Contrary to our expectations, LDPE and its blends do not show flow curve coincidence (flow curves of the two blends obtained at 170 °C are not shown in Fig. 3 due to space considerations), but stick-slip flow is not observed, as expected.

All sparsely long chain branched mLLDPEs investigated in our group show the flow curve coincidence, but LDPE and LDPE/LLDPE blends do not show it despite of existence of LCB. Molecular weight distribution of metallocene catalyst PE is much narrower than that of Ziegler–Natta catalyst LDPE. The larger molecular weight distribution might be the cause of the fact that LDPE does not show the flow curve coincidence. In rheological methods for detection of the LCB reported in other studies, increase in LCB and molecular weight distribution have the same rheological consequences [16,17]. Therefore, reported method can be applied for the PEs having similar molecular weight distributions. Our effort to correlate the flow curve coincidence to the degree of LCB seems to have similar shortcoming.

Although more experimental evidence is needed, we presume that the flow curve coincidence is only valid for mLLDPE having LCB. Our previous effort to correlate the flow curve coincidence to the degree of LCB might be limited in sparsely long chain branched mLLDPE.

On the other hand, stick-slip flow is not observed in LDPE and its blends. Stick-slip or spurt flow accompanied by a typical flow curve discontinuity are observed at shear rates of 600–800 and 6000–8000 s^{-1} for mLLDPE-C6. Double data points at the same shear rate in the flow curves represent the stick-slip flow. The maximum and minimum values for the pressure oscillation are presented in the flow curves. The stick-slip flow almost disappears with the addition of only 3 wt% LDPE to mLLDPE-C6. The amplitude of the pressure oscillation is considerably decreased in the mLLDPE-C6/LDPE(97/3) blend. Upon the addition of 5% of LDPE, the stick-slip flow completely disappears. This is consistent with the observation by Delgadillo-Velazquez and Hatzikiriakos [18]. They observed that the amplitude of the pressure oscillation in stick-slip flow gradually decreases with increasing amounts of LDPE and finally disappears at higher concentration of LDPE. They presumed that this observation is relevant to the presence of LCB.

The stick-slip is a combined phenomenon of wall slip and compressibility. Pressure oscillation in the stick-slip flow is composed of an ascending and descending period. It is 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. It is most likely that the LCB promotes entanglement between the polymer chains, which consequently prohibits cohesive slip between the bulk polymer melts and polymer chains adhered to the die wall. According to many studies, slip in the stick-slip flow is caused by cohesive failure [19,20]. Therefore, as the degree of LCB increases, the level of slippage decreases, and finally the stick-slip flow is eliminated.

In this study, we found that polyethylene having some level of LCB does not have stick-slip flow. To the authors' knowledge, there has been no exception for this behavior (no stick slip flow for long chain branched PE) among all of studies on the polyethylene rheology found in the literatures. Few studies have addressed the absence of stick-slip flow for long chain branched PE. All HDPEs previously studied show stick-slip flow. mLLDPEs having some level of LCB do not show stick-slip flow [5,8–10].

The effect of LCB can be detected by extensional rheology or oscillatory rheology at very low frequency. However, these two experimental methods are not easily reproducible and are time-consuming. Moreover, a common problem associated with conventional rheological methods to detect LCB is that an increase of LCB and polydispersity has the same rheological consequences [16,17]. According to results reported in the literature [12,15], the degree of LCB of Dow mLLDPEs ranges from 0.1 to 1.0 × 10^4 carbons, which represents approximately one LCB per 3–30 molecules. The stick-slip flow regime is highly sensitive to the existence of such small amount of LCB.

This low degree of LCB can be detected by high shear rheology if our subsequent effort to correlate the absence of stick-slip flow to the degree of LCB for PE is successful.

Fig. 4 shows the flow curve of Cr-HDPE. According to the manufacturer, this resin has a small portion of very high molecular weight (thus, it has a very high molecular weight distribution), and its rheological properties show typical long chain branched characteristics, i.e. strain hardening and elevated zero shear viscosity, which are typical characteristics of HDPE produced by the Phillips process. There are debates over whether chromium catalyzed HDPE produced by the Phillips process has a small degree of LCB. Rheologists claim that Cr-HDPE contains LCB on the basis of its rheological properties [21,22]. On the other hand, catalytic chemists claim that the chromium catalyst polymerizes HDPE having no LCB due to the nature of the catalyst active sites [23]. They contend that the rheological behaviors of Cr-HDPE are similar with those of long chain branched PE due to the existence of a very high molecular-weight portion, not LCB. According to the findings reported in this study, Cr-HDPE investigated here has no LCB or an extremely small amount, since it shows stick-slip flow, although it shows strain hardening and elevated zero shear viscosity. This discrepancy is likely due to the presence of a very high molecular-weight portion, not LCB. This issue will be clarified in future work where we plan to introduce some LCB into HDPE by a chemical modification suggested in Refs. [24,25] and then measure the rheological properties of the thus obtained long chain branched HDPE.

In this study, the possibility that the absence of stick-slip flow can be used to detect the degree of LCB for PE has been demonstrated. In future work, we plan to study the stick-slip behavior of HDPEs having various degrees of LCB. More detailed discussions will be presented in our subsequent publication.

4. Conclusion

From capillary extrusion experiments with various polyethylenes, including sparsely long chain branched mLLDPE, LDPE, mLLDPE having no LCB, and HDPE, it was found that long chain branched PE having large molecular weight distribution does not show the flow curve coincidence whereas all long chain branched metallocene LLDPEs show the flow curve coincidence regardless of the comonomer incorporated. It was also found that the existence of LCB, even very small amounts, has a critical effect on the stick-slip flow behavior. Additional experiments with blends of LDPE and mLLDPE having no LCB show that the stick-slip flow behavior was observed for the PE having the LCB. However, the flow curve coincidence was observed only for the metallocene catalyzed LLDPE which has the LCB.

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