Melt Flow Indexer Evidence of High-Temperature Transitions in Molten High-Density Polyethylenes

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ABSTRACT: A melt flow indexer (MFI) was used to investigate high-temperature transitions in melts of high-density polyethylene (HDPE). The MFI data were obtained in the range 190–230°C. These transitions were found in the MFI at about 210 and 225°C and reproduced in a Haake melt blender. Polystyrene was used in the blender experiment to demonstrate typical amorphous behavior. For HDPE melts, the MFI–temperature behavior and the torque–temperature data of the blender were found to be alternative images of the same anomalous temperature dependency in the range 210–225°C. Also, the Haake melt blender was able to reproduce the 150°C transition observed by Kolnaar and Keller in the extrusion of HDPE. Regardless of the simplicity of the MFI device, results are in agreement with our previous DSC findings. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1309–1313, 2004

Key words: polyethylene; transitions; melt flow indexer; molecular dynamics; melt

INTRODUCTION

Despite its molecular simplicity, high-density polyethylene (HDPE) in the crystalline state exhibits numerous thermal transitions at temperatures below the melting point T_m (135–140°C), such as those labeled as α-, β-, γ-, and γ'-transitions.[1] At temperatures $T \gg T_m$, HDPE is by definition a melt and is usually thought to be amorphous with molecules in the classic random coil conformation.[2]

However, in recent years there have been several reports of structural order in the HDPE melts. For example, NMR data[3,4] suggested substantial molecular order in the range 140–204°C. The importance of understanding HDPE at processing temperatures is highlighted by extrusion experiments[5–7] that unexpectedly found an abrupt drop in pressure at 150°C, interpreted as being attributable to a thermal/structural transition in the melt ordering at that temperature. Our measurements[8] of steady shear viscosity, $\eta(\dot{\gamma})$ and normal stress difference, $N_1(\dot{\gamma})$ for HDPE melts suggested the existence and persistence of molecular order at high temperatures (up to 240°C).

Theoretical support for substantial order in HDPE melts also exists from single-chain molecular dynamics simulations[9] that showed chain folding rather than random coil conformation. Ordering of this degree of regularity in polymeric fluids has previously been associated only with liquid crystal polymers, noted for their rigid-chain character, which differs enormously from the flexible HDPE chain.

In view of the fact that solid-state HDPE crystals exhibit such a large number of thermal transitions far below T_m, and that crystal-like order has been both measured and modeled in solids, it would not be unreasonable to expect that HDPE melts might also possess several transitions far above T_m. Our measurements[10] of torque ($\Im$) in a rotary blender as a function of measured melt temperature (T) showed evidence of transitions in HDPE melts at 208 and 227°C. Further, the $\Im(T)$ data are in agreement with our DSC findings.[10] These transitions must be seen in all instruments, regardless of the nature of flow fields. In view of the controversial nature of the appearance of transitions in PE, we must demonstrate its true existence by using as many instruments as possible. Therefore, we were encouraged to explore the possibility of detecting these high-temperature melt transitions in processing-like equipment, such as the melt flow indexer.

EXPERIMENTAL

Materials

Commercial HDPE samples were obtained from five resin producers and characterized independently as to solid-state density, molecular weight distribution (by

TABLE I
Characterization and Sources of Polymers

Type	Supplier	Code	Density (kg/m³)	Molecular weight			Branch content (CH₃/1000°C)	Melt flow index (g/10 min)
				$\overline{M_w}$	$\overline{M_n}$	$\overline{M_w}/\overline{M_n}$		
HDPE	Quantum	A	960	85,149	17,347	4.93	0	0.7
HDPE	Union Carbide	B	961	78,292	13,340	5.87	0	0.8
LDPE	Dow	C	923	95,114	17,849	5.33	N/A	0.28
HDPE	Phillips	D	964	78,031	16,545	4.73	0	0.65
HDPE	Solvay	E	960	79,689	16,970	4.70	0	0.7
HDPE	NOVA	F	957	137,000	28,000	4.89	<0.5	1.0

gel permeation chromatography), melt flow index (MI), temperature rising elution fractionation, and ^{13}C-NMR for branch content (thus verifying the absence of significant branching) in HDPE samples. Also, low-density polyethylene (LDPE) and polystyrene (PS) samples from Dow (Dow–Corning, Midland, MI) were used in this study. Characterization data of polyethylenes are given in Table I. All samples contained normal antioxidant (AO) additives for protection from oxidative degradation at typical processing temperatures, the regime intended for study.

Testing in the melt flow indexer (MFI)

The MFI is a simple device that resembles the capillary viscometer. This device is widely used in industry for molecular weight characterization. The MI is defined as the weight of polymer resin (in g/10 min) extruded through the capillary die of an MFI using a constant standard plunger force. Although the MI is usually defined at a temperature of 190°C, the MI was measured here in the temperature range of 190–235°C. A Kayeness 7053 MFI was used according to ASTM D-1238 (2.16 kg). Testing at temperatures higher than 235°C was not done to avoid oxidative degradation, given that the MFI does not have a system for nitrogen atmosphere. The oxidation temperature obtained in air for HDPE with "normal" AO using DSC is 235°C.[12] The reported MI is an average of three samples taken 3 min apart during a single piston descent. The weight of the three samples was approximately the same, suggesting the steadiness of the flow during this period of measurement, as verified for the same apparatus by Ghosh et al.[13] Measurements were taken at a temperature interval of 5°C for Sample A and 10°C for Samples B and C. Fresh loadings were used for each T.

Testing in the batch-melt blender

The investigation of the effect of temperature on the flow properties of HDPEs was extended to a more complicated flow field, the batch-melt blender. A Haake Rheocord 90 (close to isothermal; Haake, Bersdorff, Germany) was used to follow the torque as a function of melt temperature under standard testing conditions. The wall temperature was set to increase at a constant rate and the two thermocouples embedded in the heating blocks always showed the same reading. However, the melt temperature was measured by a separate thermocouple that was in direct contact with the melt. The measured melt temperature was always higher than the set temperature attributed to viscous heating. The standard test procedure was explained in an earlier publication.[10] In another test aimed at investigating the 150°C transition in HDPEs (Samples D, E, and F), the initial wall temperature was 135°C instead of the standard 160°C. The melt temperature was higher than 138°C resulting from viscous heating.

RESULTS AND DISCUSSION

The MI(T) behavior of Samples A, B, and C is shown in Figure 1. For Samples A and B, anomalies appeared in two ways: (1) the overall MI(T) behavior was distinctly non-Arrhenius in nature, suggesting that or-
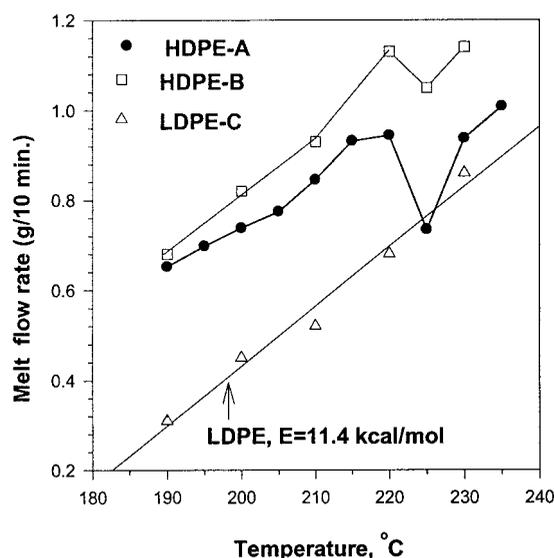

Figure 1 Melt flow index as a function of temperature for Samples A, B (HDPE), and C (LDPE).

dered molecular conformational states prevailed, as opposed to the disordered random coils[2] expected for high-T melts, and (2) transitions in the MI(T) appeared at about 210°C (T_1) and 225°C (T_2), where T_1 occurs at the shoulder of a maximum and T_2 at a minimum. Results for Sample A (circles) revealed a distinctive MI(T) behavior in the range 210°C < T < 230°C. The MI(T) curve displayed a flat upper plateau followed by a drop (increase of viscosity) with a minimum of MI at about 225°C and then an increase in MI. Sample B (squares) demonstrates a similar behavior. The main distinguishing features of the HDPE behavior appeared for the two samples in the temperature range of about 210 to 225°C. The MI data at 225°C were reproduced with another fresh sample. Also, our MI measurement for Samples A and B at 190°C reproduced the values reported by resin manufacturers. Torque measurements in the blender (discussed below) exhibited transitions at the same T_1 and T_2 values.

Further, to check the validity of our MI measurements, flow activation energy (ΔE) was estimated from MI data in the range 190–210°C only. We assumed the applicability of the Hagen–Poiseuille law for Newtonian flow in the MFI capillary, where the volumetric flow rate (Q), the pressure drop (ΔP), the tube radius (R), length (L), and fluid viscosity (η_0) are related by $Q = \pi R^4 \Delta P / 8\eta_0 L$. Because [(mass melt flow rate)$/\rho] = Q \propto 1/\eta_0 \propto e^{-\Delta E/RT}$, neglecting the small T-dependency of density $\rho(T)$, then an Arrhenius plot of log(MI$/\rho$) versus $1/T$ (K) would give the activation energy. The assumption of constant melt density in the temperature range 190–210°C is supported by the experimental observations.[14] Activation energies calculated from the melt flow rate data in the range of 190–210°C were 24.7 and 31.0 kJ/mol for Samples A and B, respectively. These values are in excellent, if not exact, agreement with theoretical predictions and experimental observations[15–17] that reported ΔE to be in the range 23.0–31.4 kJ/mol. This is in fact a support for the sensitivity of the MFI device regardless of its simplicity.

Moreover, the blender $\Im(T)$ responses showed similar reproducible behavior for the two HDPE samples. The $\Im(T)$ data for Sample A are shown in Figure 4 and those of Sample B are shown elsewhere.[11] For comparison, a commercial sample of atactic polystyrene (Dow Styron 666 D) was tested in an identical fashion (PS behavior, Fig. 2). The amorphous PS behavior serves not only to highlight the anomalous blender HDPE behavior, but also to demonstrate that the latter is not an artifact of the equipment or its operation or of oxidation. A separate degradation study that shows the stability of the linear molecule PE was published elsewhere.[18]

The main distinguishing features of the HDPE behavior appear for Sample A in the temperature range
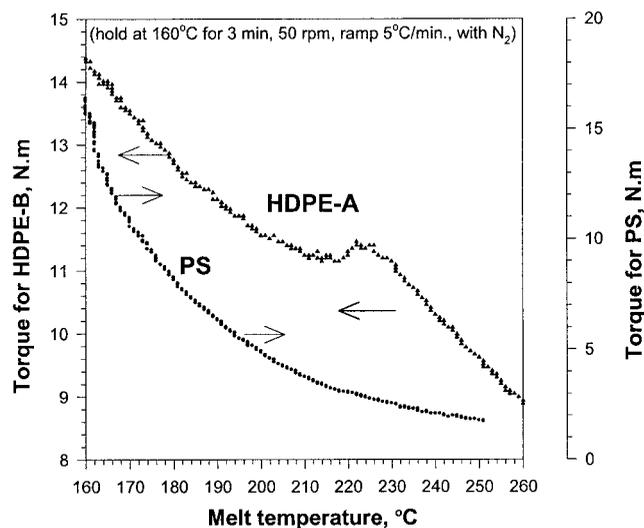
Figure 2 Evidence for phase transitions in HDPE melt, Sample A. The transitions are believed to occur at the base of the left-hand decreasing branch of the curves (208°C) and at the beginning of the right branch (220–227°C). The lower curve represents a melt of atactic polystyrene.

of roughly 208 to 225°C. Also, for T > 225°C, the $\Im(T)$ decrease is distinctly non-Arrhenius, being almost linear as far as 260°C. This suggests that the polymer chains remain ordered in some fashion and do not "melt" into the amorphous random coil conformation until T > 260°C, if at all. For 200° > T > 160°C the $\Im(T)$ also descends in non-Arrhenius fashion (again, more linear). However, the most dramatic features are those in the midrange. The initial $\Im(T)$ decrease in Figure 2 ends at about 208°C, moving into a plateau and a subsequent transition at about 225°C at which the plateau ends. This unique $\Im(T)$ behavior of HDPEs was reproduced in the presence of extra antioxidants.[8] Also, HDPEs from four different resin manufacturers reproduced this unique $\Im(T)$ behavior.[8,10]

The results obtained for Sample A in the two different rheological devices (with totally different flow fields) provided the same information, and presented the "distinctive" behavior at the same temperatures. Furthermore, Sample B displayed the same behavior. It is interesting to note that the torque maxima and MI minima both occur at T_2. A comparison of the decrease in MI shown in Figure 1 to the increase in $\Im$ data in Figure 2 reveals this interesting observation.

The above results may prompt us to question whether the behavior displayed in Figures 1 and 2 could be attributed to some kind of slip instability at the wall. This possibility must be rejected, however, because slip is known to correlate with the magnitude of the wall shear stress with the onset at 0.1 MPa for HDPE.[19] Moreover, flow instability in simple shear at low Re number has never been established.[20] Furthermore, a given shear stress is achieved for polymers of
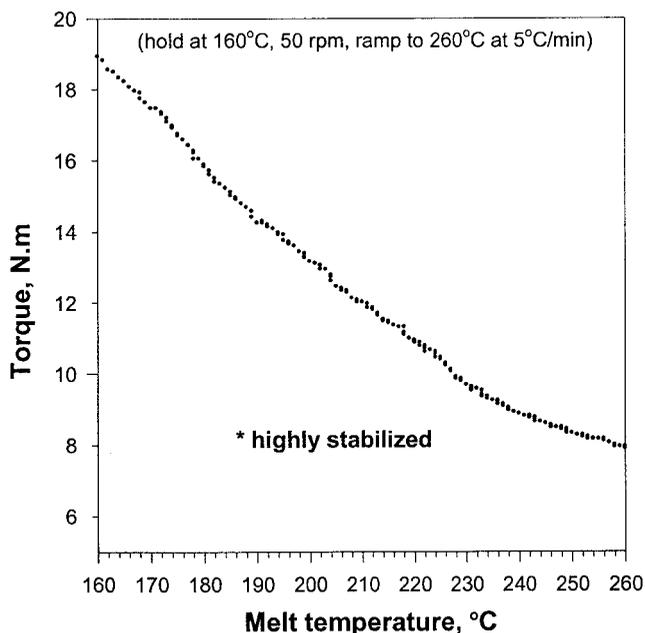
Figure 3 Torque as a function of temperature for Sample C (LDPE).

different $\overline{M_w}$ and viscosities at different temperatures, unlike the case here where the same transitions at 210 and 225°C were displayed by samples of different viscosities experiencing different kinds of stresses in different rheological equipment.

For the LDPE, both the MI (Fig. 1) and the torque measurements (Fig. 3) implied ease of flow above 210°C. Sample C did not show evidence of T_1 or strong T_2. Calculation of activation energy for Sample C using all of the MI data resulted in a value 47.7 kJ/mol that is similar to previous literature reports.[21] The LDPE showed a decrease in the torque and an increase in the MI at $T > 210$°C; however, the responses were not as strong as that of HDPEs, which is not a surprise for a branched polyethylene. Recently, one of the co-authors observed a strong influence for branching on the conformations of polyethylene.[22]

Additional rheological support for the molecular interpretation of high-T transitions in HDPE melts below 210°C was found in the work of Kolnaar and Keller,[5–7] who reported a transition in the interval 148–152°C (observed in the extrusion of HDPE). Here, in Figure 4 the torque measurement technique was capable of reproducing the 150°C transition. Three HDPEs (Samples D, E, and F) were selected for this study. All samples reproduced the distinct high-temperature behavior (T_1 and T_2), but here the attention was focused (Fig. 4) in the range 130–190°C. The three resins displayed a low-T maximum in the torque versus T curves (usually associated with crystal melting) at 138°C. For Sample F, the torque showed a significant decrease (from 36 to 20 N m^{-1}) in the temperature

window 148–152°C. Samples D and E showed similar behavior in the interval 146–150°C. The observed decrease in the torque (in a blender) reinforces the findings of Kolnaar and Keller on pressure drop (in extrusion, $M_w = 2.8 \times 10^5$) in the same temperature window. Furthermore, these observations suggest a weak dependency of the 150°C transition on M_w. Samples D and E (both with $M_w = 79,000$) have the same transition temperature, but sample F (with $M_w = 137,000$) has a transition 2°C higher than that of the others. Such a small difference in transition temperature for polymers having such a large difference in M_w indicates that the 150°C transition is essentially independent of molecular weight. It is surprising that there seems to be no report anywhere in the rheological or melt processing literature that addresses HDPE performance specifically in this range of temperature.

It is important to identify the molecular origin of this behavior. An explanation in the earlier reports of Keller's group[5–7] of a transition in HDPE extrusion at 150°C invoked the concept of a microstructural transition of some sort. A study of ultrahigh molecular weight polyethylenes (UHMWPE)[23] demonstrated strong tendencies toward an all-*trans* chain order in melts, consistent with molecular order, and that study terminated at 208°C (identical to the T_1 transition found here) without comment by the authors. At higher temperatures, acoustic measurements[25] detected a change in sound velocity in low-$\overline{M}$ linear PE melts at about 230°C, again in agreement with our T_2 data but presented without molecular interpretation.

Our contention is that the 210 and 225°C transitions we find in the MI(T) and $\Im(T)$ data for HDPE are
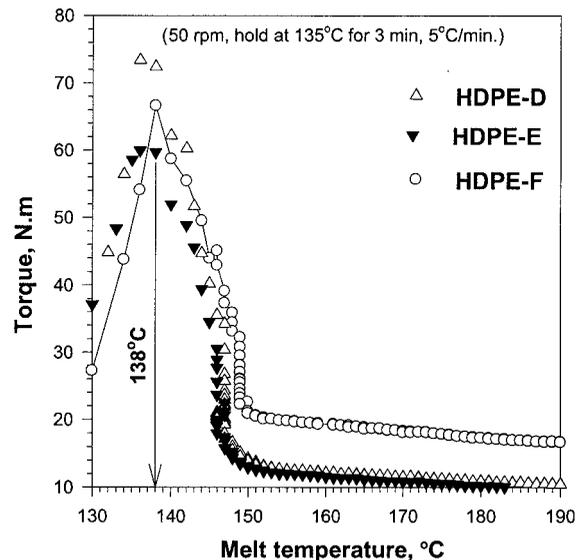

Figure 4 Torque–melt temperature behavior of HDPE Samples D, E, and F. The data show the ability of the melt blender to reproduce the 150°C transition reported by Keller and coworkers.[14]

rheological manifestations of molecular order that are characteristic of the methylene chain structure as also described in the most recent work by Kolnaar and Keller[7] and not necessarily related to other exaggerated behavior displayed by UHMWPE. The transitions are thus independent of $\bar{M}$ and the number of entanglements per chain.

The melt indexer was previously used to study shear-induced crystallization, as reported by Liang.[14] However, that study was at lower temperatures ($T < 200°C$) than the anomalous phenomena described in our work ($T > 200°C$) and therefore not relevant here. Moreover, the explanation for the T_1 and T_2 transitions cannot lie with flow-induced chain orientation because the blender flow is highly chaotic rather than orderly, and our earlier work[11] found T_1 and T_2 in the DSC where there is no flow at all. Thus, the present MI results are compatible with our previous results and our contention that the high-temperature transitions are fundamentally thermodynamic in origin.

CONCLUSIONS

In conclusion, the melt flow indexer presented new evidence of the existence of high-temperature transitions in HDPE at about 210 and 225°C. Measurements in the melt blender reflected the melt flow indexer data. Also, the melt blender reproduced the Kolnaar–Keller 150°C transition observed in the capillary extrusion of HDPE.[5–7,14] Molecular order in melts of HDPE seems to persist even beyond these high-temperature transitions. Two different rheological devices presented confirmation of the molecular order and microstructural high-temperature transitions in melts of HDPE at 210 and 225°C. The results of the simple MFI device are in agreement with our previous measurements obtained with much more sophisticated instruments.

References

1. Popli, R.; Glotin, M.; Madelkern, L.; Benson, R. S. J Polym Sci Polym Phys Ed 1984, 22, 407.
2. Flory, P. J. Principles of Polymer Chemistry; Cornell University Press: Ithaca, NY, 1953.
3. Bremner, T. J.; Rudin, A. J. Polym Sci Polym Phys Ed 1992, 30, 1247.
4. Kamel, I.; Charlesby, A. J Polym Sci Polym Phys Ed 1981, 19, 803.
5. Kolnaar, J. W. H.; Keller, A. Polymer 1994, 35, 3863.
6. Kolnaar, J. W. H.; Keller, A. Polymer 1995, 36, 821.
7. Kolnaar, J. W. H.; Keller, A. J Non-Newtonian Fluid Mech 1997, 69, 71.
8. Hussein, I. A.; Williams, M. C. J Non-Newtonian Fluid Mech 1999, 86, 105.
9. Kavassalis, T. A.; Sundararajan, P. R. Macromolecules 1993, 26, 4144.
10. Hussein, I. A.; Williams, M. C. Macromol Rapid Commun 1998, 19, 323.
11. Hussein, I. A.; Williams, M. C. Macromolecules 2000, 33, 520.
12. Hussein, I. A. Ph.D. Thesis, University of Alberta, Edmonton, Canada, 1999.
13. Ghosh, T.; Huang, J. C.; Williams, M. C. In: Proceedings of the XII International Congress on Rheology; Ait-Kadi, A.; et al., Eds.; Chemical Engineering Department, University of Laval: Quebec City, 1996; p. 85.
14. Liang, J. Z. Polym Test 2001, 20, 469.
15. Kauzmann, W.; Eyring, H. Am Chem Soc J 1940, 62, 3113.
16. Bersted, B. H. J Appl Polym Sci 1985, 30, 3751.
17. Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G. Encyclopedia of Polymer Science and Engineering, 2nd ed.; Wiley: New York, 1986; Vol. 6, p. 477.
18. Hussein, I. A.; Ho, K. G.; Karbashewski, S. E.; Williams, M. C. Polym Degrad Stab 2000, 68, 381.
19. Dealy, J. M.; Wissbrun, K. F. Melt Rheology and Its Role in Plastic Processing; Nelson: Ontario, Canada, 1990; p. 174.
20. Denn, M. M. In: Fluid Mechanical Issues in Polymer Processing; Samanta, et al., Eds.; Interdisciplinary Issues in Materials Processing and Manufacturing, Vol. 2; 1987; p. 587.
21. Sabia, R. J Appl Polym Sci 1964, 8, 1651.
22. Abu-Sharkh, B. F.; Hussein, I. A. Polymer 2002, 43, 6333.
23. Wunder, S. L.; Merajver, S. D. J Polym Sci Polym Phys Ed 1983, 21, 821.
24. Kruger, J. K. Solid State Commun 1979, 30, 43.