Rheological evidence for high-temperature phase transitions in melts of high-density polyethylene

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SUMMARY: Melts of commercial high-density polyethylene ($\bar{M}_w = 36-85 \times 10^3$) were subjected to the hydrodynamics of a Haake Rheocord blender at temperatures (T) spanning the normal processing range (190–260 °C), far beyond the disappearance of solid crystals at about 140 °C. Torque measurements revealed a peculiar dependence on T, including transitions at about 208 °C and 227 °C, and non-Arrhenius behavior above and below this range. Resemblances to liquid-crystal polymer phenomena are pointed out, and the impact on the melt processing industries is discussed.

General

Linear chains of methylene repeating units compose the commercial product high-density polyethylene (HDPE) and possess solid-state crystals that have a melting range of 135–140 °C. Despite its molecular simplicity, HDPE in the crystalline state exhibits numerous thermal transitions at temperatures below the melting point (T_m), such as those labeled the α, β, γ, γ' transitions[1]. At much higher temperatures ($T \gg T_m$), HDPE is by definition a melt and is usually thought to be amorphous, with molecules in the classical random coil form[2]. However, in recent years there have been several reports of structural order in the HDPE melts. For example, NMR data suggested[3] that even at 150 °C ($\approx T_m + 10°$) the volume fraction of ordered material in HDPE melts is about the same as the crystal fraction in the semi-crystalline solid state (about 50% amorphous) below T_m. Progress in understanding of the true condition of HDPE molecules in the liquid state has been somewhat diverted by the recent appearance of ultra-high molecular weight polyethylene (UHMWPE), also composed of linear chains but exhibiting numerous anomalies[4] for $T > T_m$. Among these are anisotropy persisting to temperatures above 300 °C and a tendency to fibrillate. These factors, as well as the extremely high average molecular weight ($\bar{M}$) which can reach 10^6, have made UHMWPE enormously difficult to process and its peculiar characteristics of uncertain relevance to the more processable ordinary HDPE and the character of possible HDPE melt ordering for $T > T_m$. Extrusion and molding for HDPE typically take place at 190°–240 °C for "low" molecular weight melts ($3 \times 10^4 < \bar{M} < 3 \times 10^5$). The importance of understanding HDPE at processing temperatures is highlighted by recent extrusion experiments[5] that unexpectedly found an abrupt drop in pressure (for constant flow rate) at 150 °C,

interpreted as due to a thermal/structural transition in the melt ordering at that temperature.

Theoretical support for substantial order in HDPE melts also exists now. Molecular dynamics simulations[6, 7] of chain conformational evolution in a non-flowing melt suggest that an "S"-shaped folded chain (not a random coil) is the natural state of the molecule at rest in the liquid ($T > T_m$), just as it is in the solid-state crystal when $T < T_m$. Ordering of this degree of regularity in polymeric fluids has previously been associated only with liquid crystal polymers (LCP), which are 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 melts, it would not be unreasonable to expect that HDPE melts might also possess several transitions far above T_m. This study was designed to explore the possibility that such high-temperature melt transitions exist, particularly in the range typical of PE melt processing.

Experimental part

Commercial molding-grade samples were obtained from six resin producers and characterized independently[8, 9] as to solid-state density (a measure of fractional crystallinity), molecular weight distribution (by gel permeation chromatography), melt index (inversely proportional to viscosity), and temperature-rising elution fractionation (to confirm that samples were free of branched components). Sample densities at 25 °C were similar (0.951 – 0.964 g/cm³), well within the HDPE range, but other features varied significantly: the weight-average molecular weight ($\bar{M}_w$) from 36 000 to 85 000 (far below UHMWPE levels), the breadth of molecular

weight distribution (characterized by $\overline{M}_w/\overline{M}_n$) from 3.3 to 5.9, and melt index from 0.49 to 40.2 g/10 min (190 °C). All samples contained normal anti-oxidant additives for protection from oxidative degradation at typical processing temperatures, the regime intended for study. For comparison, a commercial sample of atactic polystyrene (PS) was tested in an identical fashion; it, too, contained anti-oxidant. This polymer was selected as a reference because it has no solid-state crystals and is also known to be an amorphous melt in the temperature range explored here.

Because liquid-state mechanical properties of the polymer should be especially sensitive to morphological changes, rheological testing was desired. However, the determination of specific rheological properties was not the objective; rather, a rheological signal of thermal transitions was intended. It was therefore decided to use a melt-blending device (Haake Rheocord 90) and follow the torque as a function of melt temperature under standard testing conditions. In this blender, torque is generated by the resistance of the fluid in a heated mixing bowl to the rotation of two offset blades moving at constant angular speed. The flow field is complex, producing many shearing and extensional elements of the deformation rate tensor, and the torque is therefore a complex function of all elements of the stress tensor. However, any thermal transitions in the melt must have impact simultaneously on all rheological properties that contribute to the measured torque. Because this blender has very effective thermal mixing, near-isothermal conditions prevail throughout the polymer. Electrical heaters are embedded in heavy steel walls surrounding the bowl and controlled by computer to achieve a programmed rate of temperature change. Melt temperature, monitored by computer, is sensed by a thermocouple at the bowl bottom, contacting the melt directly.

The standard test procedure was to establish in the blender a starting condition at 160 °C with a rotor speed of 50 rev/min, load the bowl with 60 g of solid pellets, initiate a nitrogen flow through a plunger supported upon the pellets, to purge oxygen from the bowl, and then to compress the melting mass with a weight on the plunger. Torque stabilized in two minutes, but this 160 °C condition at 50 rpm was held for three minutes to break up any persistent residues of the melted solid crystals and assist their diffusion into a homogeneous state. Thereafter, heating was increased to achieve a linear ramp in the wall temperature from 160 to 260 °C at a rate of 5 °C/min, while rotor speed continued at 50 rpm. Torque ($\mathscr{T}$) and melt temperature (T) were sampled every six seconds, during the holding period and thereafter, producing more than 200 points for each $\mathscr{T}(T)$ curve.

The $\mathscr{T}(T)$ responses showed some minor differences among the six HDPE samples, though similar reproducible behavior was displayed by all. The two responses that differed the most widely are shown in Fig. 1 (melt A) and 2 (melt B). For ease of comparison, the PS melt behavior is superimposed on both figures. Clearly, the HDPE melts exhibit a complex series of transitions that occur at temperatures far beyond the disappearance of the solid-state crystals at about 140 °C. The PS behaves as expected, with the torque declining regularly with temperature in a fashion akin to the viscosity of most liquids. The PS behavior serves not only to highlight the anomalous HDPE performance, but also to demonstrate that the latter is not an artifact of the equipment or its operation or of oxidation.

The main distinguishing features of the HDPE behavior appear for all six samples (without any dependence on $\overline{M}$) in the temperature range of roughly 210 to 225 °C. However, other anomalies can be seen too. For example, for $T > 225$ °C, the $\mathscr{T}(T)$ 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 $200 °C > T > 160 °C$ the $\mathscr{T}(T)$ also
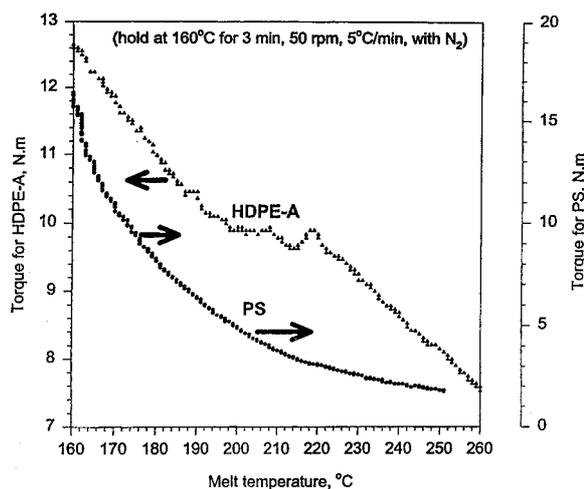

Fig. 1. Torque measurements in the blender for HDPE Sample A ($\overline{M}_w = 78\,030$; $\overline{M}_n = 16\,540$) over a 100 K-range, compared with the same for an atactic polystyrene sample (PS). Operational parameters are specified on the figure. Melt temperature was measured by a thermocouple in physical contact with the polymer
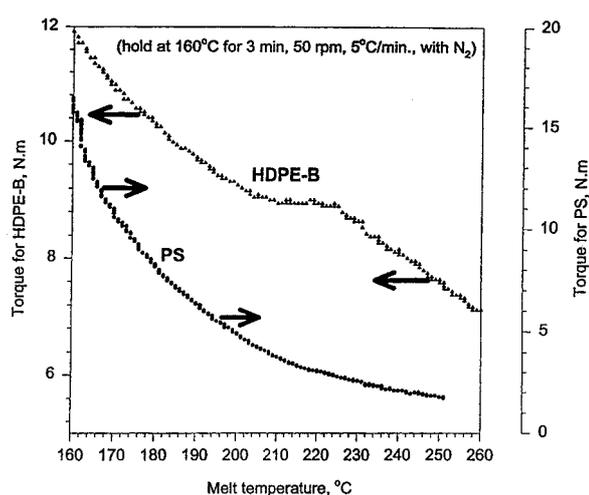

Fig. 2. Torque measurements in the blender for HDPE Sample B ($\overline{M}_w = 79\,690$; $\overline{M}_n = 17\,000$) over a 100 K-range. Commercial samples A (Fig. 1) and B were manufactured by different resin producers. Testing conditions were identical in obtaining the data in Fig. 1 and Fig. 2

descends in non-Arrhenius fashion (again, more linear), as is more evident for melt A in Fig. 1 than for melt B in Fig. 2. However, the most dramatic features are the midrange ones. The initial $\mathscr{T}(T)$ decrease in Fig. 2 ends at about 208 °C, moving into a plateau and a subsequent transition at 227 °C where the plateau ends. In Fig. 1, the initial decrease merges with a short plateau that terminates at 208 °C, followed by a sharp minimum at 215° and a major peak that subsides before the final decrease commences at about 227 °C. In Fig. 1, there is also considerable irregularity in the decline over 188–208 °C.

Variation of the parameters selected for the standard test (blade rotational speed, holding time at 160 °C, T-ramp speed, etc.) had only minor influences on the behavior seen in Fig. 1 and 2, without altering the major features cited above.

It is surprising that this rheological (and thermo/structural) behavior of HDPE seems to have escaped the notice of the HDPE processing industry, which has been operating in this temperature regime for many decades without reporting any such peculiar phenomena. In fact, there seems to be no report anywhere in the rheological or melt processing literature that addresses HDPE performance specifically in this range of temperature. The implications for commercial melt processing are profound, as will be described below.

It is important to identify the molecular origin of this behavior. An explanation in the earlier report[5] of a transition in HDPE ($\overline{M}_w = 2.8 \times 10^5$) extrusion performance at 150 °C invoked the concept of a liquid-crystal transition of some sort. The investigation of fibrillating UHMWPE melts also noted the similarity of the anisotropy in those materials to that of smectic liquid crystals[4]. A study of UHMWPE by Raman spectroscopy[10] demonstrated strong tendencies toward all-*trans* chain order in melts, consistent with liquid-crystal structures, and that study terminated at 208 °C (identical to the lower-T transition found here) without comment by the authors. At the higher-temperature end, acoustic measurements[11] have detected a change in sound velocity in HDPE melts at about 230 °C, again in agreement with our data but without molecular interpretation.

Our contention is that the 208 °C and 227 °C transitions we find in the $\mathscr{T}(T)$ data are rheological manifestations of liquid-crystal transitions that are characteristic of the methylene chain structure and not necessarily related to other exaggerated behavior displayed by UHMWPE that is usually interpreted as due to long relaxation times[10]. The transitions are thus independent of $\overline{M}$ and the number of entanglements per chain. Additional rheological support for the fundamental LCP interpretation of HDPE melts below 208 °C was recently presented by our laboratory[9], using these same six samples at 190 °C, with the finding that the $\overline{M}_w$-dependence of melt index implied that viscosity varied as $\overline{M}_w^{5.5}$ (as opposed to $\overline{M}_w^{3.4}$ for entangled amorphous melts such as PS), a result previously associated only with the LCP[12].

HDPE melts have previously been associated with other fluid mechanical anomalies, such as slip at solid boundaries[13] – e.g., in pressure-driven capillary die extrusion. This prompts one to question whether the behavior displayed in Fig. 1 and 2 could be attributed to some kind of slip or slip/stick flow. This possiblity must be rejected, however, since slip is known to correlate with the magnitude of the wall shear stress[13] (with onset at 0.1 MPa for HDPE). A given shear stress is achieved for polymers of different $\overline{M}_w$ and viscosities at different temperatures, unlike the case here where the same transitions at 208 and 227 °C were displayed by samples whose viscosities varied by a factor of approximately 100 in this temperature range. The possibility that oxidation-induced crosslinking could be producing these results was evaluated by cone-and-plate rheometry in an RMS800 (also under nitrogen). Measurements were made of the storage modulus (G') during a temperature sweep with $T(t)$ increasing with time, followed by a similar sweep with $T(t)$ decreasing, for the same sample. Exactly the same G' values were produced in the two sweeps, demonstrating that no sample degradation was occurring during exposure to these temperatures, which covered the same range used in the blender tests (e. g., Fig. 1 and Fig. 2).

In conclusion, we recommend that the PE processing industry re-examine its strategies for processing HDPE, particularly as to the temperatures employed for specific purposes. Such process scrutiny could lead to process re-design for the purpose of avoiding these thermal transitions in some cases, when various flow instabilities might otherwise be encountered, or possibly taking advantage of the transitions in other cases, in order to optimize product quality in the solid state by drawing on the tensile strength and orientation associated with the LCP.

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